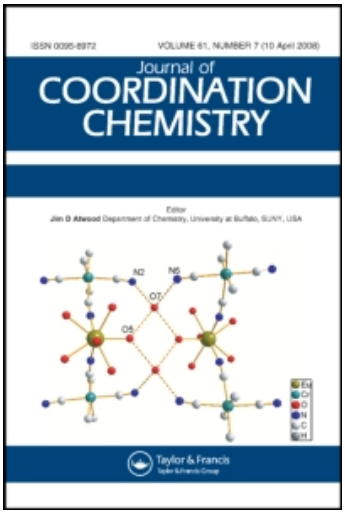

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Review: synthetically modified carbohydrates as ligands

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REVIEW: SYNTHETICALLY MODIFIED CARBOHYDRATES AS LIGANDS

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The coordinative properties of synthetically modified carbohydrates to metal cations are reviewed. Such metal complexes are distinct, owing to the structural diversity of the ligands and coordination modes. The influences of complex-formation conditions on chemical properties of modified carbohydrates, as well as on organic reactions (especially diastereoselective ones), are examined. In addition, this manuscript demonstrates the practical importance of the coordination interactions.

Keywords: Synthetic modification of carbohydrates; Sugar–metal complexes; Supramolecular structures; Diastereoselective reactions

INTRODUCTION

The coordination chemistry of carbohydrates has a long-standing history; natural carbohydrate complexation initially predominated. Development of boron carbohydrate complexes was covered by Böeseken [1] as far back as 1949 and by Ferrier [2]. Reeves [3] summarized his own data on a polarimetric study of cupramminium–glycoside complexes. A variety of anionic complexes of hydroxyacids and polyhydroxy compounds were reviewed by Sawyer [5]. Complexation between natural carbohydrates and s-metal cations was discussed by Rendleman [6], Cook and Bugg [7], Poonia and Bajaj [8], Angyal [9–12], Whitfield and coworkers [13], Alexeev and coworkers [14] and by Gyurcsik and Nagy [15]. Metal complexes of ascorbic acid were considered by Kriss and coworkers [16]. Verchère and coworkers [17] discussed carbohydrate-metal complexes in solution and the survey of Piarulli and Floriani [18] was mainly devoted to coordination of natural carbohydrates with d-metal cations (see also [13–15]). Metal complexes of synthetically modified carbohydrates were partly elucidated by Burger and Nagy [19] and by Alexeev and coworkers [20]. The main

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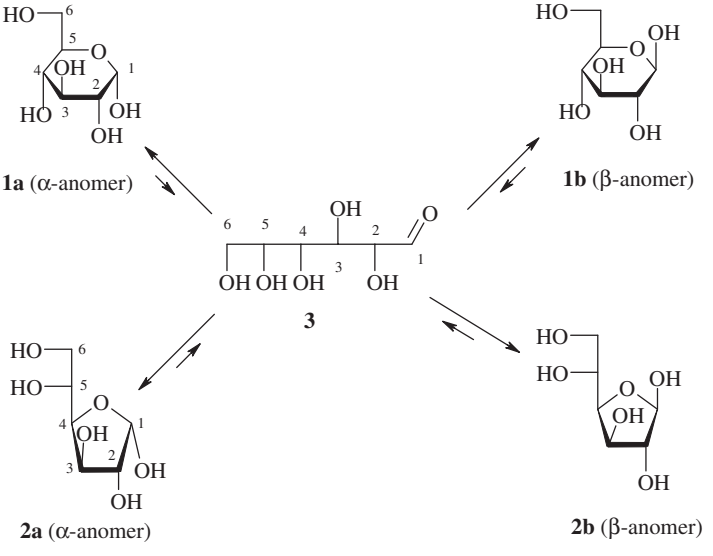
achievements of modern coordination chemistry of modified monosaccharides were collected by Zhdanov and Alexseev [21]. Yano's surveys [22,23] dealt with d-metal complexation of synthetic N-glycosides. Separate topics also discussed include carbohydrate metal chelates, by Alexeev and coworkers [24], carbohydrate complexes of platinum group metals, by Steinborn and Junicke [25], as well as metal complexes of synthetic 1,3,5-triamino-1,3,5-trideoxy-*cis*-inositol by Hegetschweiler [26]. The authors of the present paper seek to give a comprehensive account of this field.

Synthetic modification of natural carbohydrates means first of all the introduction of mainly achiral hydrophobic or coordinating fragments into a carbohydrate molecule resulting in hydrophobic and/or metal complexing carbohydrate derivatives, although this concept may be considerably broadened by transformations leading to carbohydrate surfactants and food additives [27–29]. Such a *modus operandi* essentially increases the variety of carbohydrate metal complexes including hydrophobic ones. These complexes as chiral substances by definition are the most significant catalysts and auxiliaries for obtaining diastereomerically pure pharmaceuticals in the future, taking into account the availability and photosynthetic reproducibility of carbohydrates on the global scale [28].

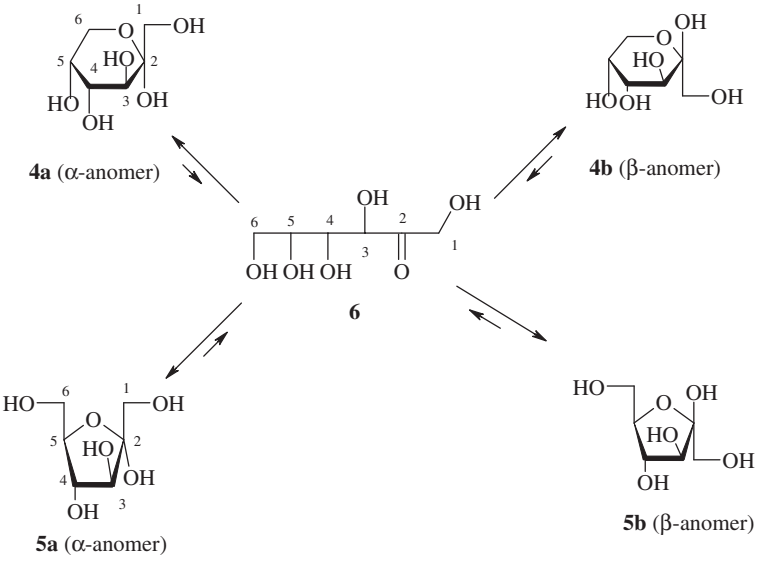
GENERAL TYPES OF SYNTHETICALLY MODIFIED MONOSACCHARIDES USED AS LIGANDS OR THEIR PRECURSORS

Aqueous solutions of natural monosaccharides contain some cyclic forms and one acyclic form due to ring–chain tautomerism [30]. For instance, the most abundant monosaccharide, D-glucose, exists as α-D-glucopyranose **1a**, β-D-glucopyranose **1b**, α-D-glucofuranose **2a** and β-D-glucofuranose **2b** interconverting through a minor acyclic aldehyde form **3**; the pyranose forms are highly predominant. Pairs **1a**,**b** and **2a**,**b** are anomers distinguished only by configuration at C(1).

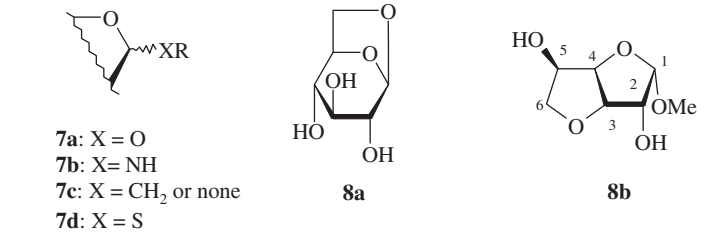


The primary modification methods are O-alkylation (mainly O-methylation) [31–33] and O-acylation (mainly O-acetylation) [32,33] of hydroxyl groups resulting in fixation of the cyclic forms and in their hydrophobization. Per-O-alkylation in superbase media is the most efficient [34,35].

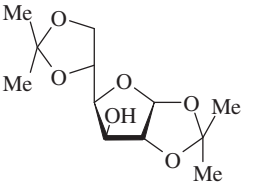
Monosaccharides possessing acyclic aldehyde forms are aldoses. Their keto analogues, ketoses, display similar ring–chain tautomerism [30], which in the case of the most abundant 2-ketose, D-fructose, may be represented as follows with pyranose **4a**,**b** and furanose **5a**,**b** anomeric pairs and acyclic keto form **6**.



Glycosides are distinctive sugar derivatives subdivided for aldoses into *O*-glycosides **7a** [31–33], *N*-glycosides **7b** [36,37], *C*-glycosides **7c** [38–41] and *S*-glycosides **7d** [42]. Anhydro derivatives such as **8a** and **8b** are inner *O*-glycosides [32,43] and inner ethers [32,44–46], respectively.



Diol groupings of monosaccharides may temporarily be blocked by acid-catalyzed interaction with some aldehydes or ketones with the formation of cyclic acetals and ketals, respectively (acetalated or ketalated derivatives) [47]. Thus D-glucose forms furanoid diketal **9** with acetone and pyranoid monoacetal **10** with benzaldehyde. These derivatives may be deblocked by acid hydrolysis.



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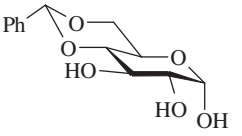
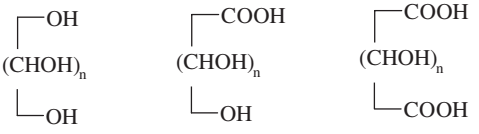


10

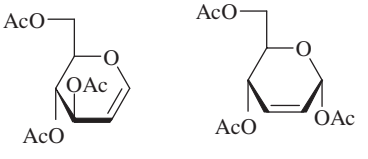
Aldehyde forms of type **3** and keto forms of type **6** are precursors of acyclic derivatives. Reduction and oxidation of the aldehyde group gives acyclic polyols **11** [32] and glyconic acids **12** [32], respectively. Oxidation of a primary hydroxyl group of the latter leads to glycaric acids **13** having two carboxylic groups.



11 **12** **13**

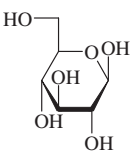
n = 2 - 4

Unsaturated monosaccharides with an endocyclic carbon–carbon double bond such as glucal **14** and its isomer **15** were obtained by α- or β-elimination reactions of appropriately functionalized monosaccharides [48,49] as the Wittig reaction is a source of numerous exocyclic ones [50].



14 **15**

Synthesis of amino sugars is possible by some methods [31,32] that include the introduction of an azido group by a nucleophilic substitution reaction of *O*-tosyl- or *O*-mesyl derivatives with the azide ion. Nucleophilic opening of an oxirane ring by the same ion is also used. The *O*-tosyl or *O*-mesyl groups may be substituted by hydrazine. Oximes of aldehyde forms of type **3** are also useful precursors of amino sugars. These transformations are followed by reduction. Opening of sugar oxiranes by ammonia is the only direct method for preparation of amino sugars. A more original approach includes the periodate oxidation of glycoside sugars **16** followed by interaction of the resulting dialdehyde **17** with deprotonated nitromethane. Each of the resulting diastereomeric nitroalcohols **18a**,**b** is formed depending on the reaction conditions, and can then be reduced by hydrogenation to the desired products **19a** or **19b**.



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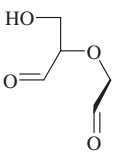

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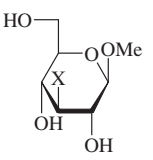
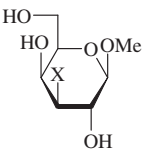
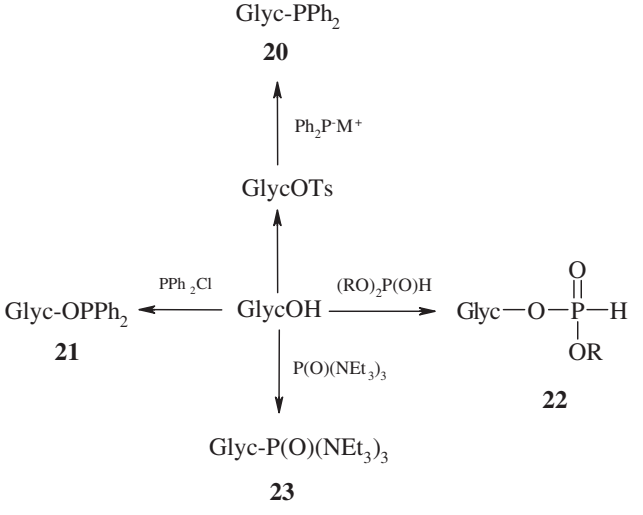


18a: X = NO_2
19a: X = NH_2



18b: X = NO_2
19b: X = NH_2

Phosphorus-containing sugar derivatives used as ligands are restricted to certain types. Sugar phosphines **20** were obtained [51] by O-tosylation of available hydroxyl groups followed by an organometallic synthesis. The interaction of diphenylchlorophosphine with a deprotonated hydroxyl group leads [52] to phosphinites **21**. Analogous reactions with secondary phosphates or amidophosphites gives sugar alkyl phosphates **22** [53] or amidophosphites **23** [54], respectively.

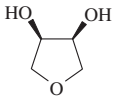


The approaches indicated may naturally be applied to oligo- and polysaccharides.

COMPLEXATION WITH s-METAL CATIONS

Oxygen-containing Ligands

Carbohydrates as polyhydroxy compounds are hard Lewis bases and prima facie should coordinate well with s-metal cations according to Pearson's 'Hard and Soft Acids and Bases' (HSAB) principle [55,56]. In fact, this is not the case since these interactions usually take place in aqueous solutions where water molecules strongly compete in coordination [14]. For this reason, such sugar complexes are known only in the solid state [6,8,14] with low concentrations in solution [9–12]. Methyl α-D-glucopyranoside, for instance, forms a 1 : 1 adduct with potassium hydrocarbonate [57] and 1,4-anhydroerythritol **24** forms L_2Na complexes (where L is the ligand) with sodium perchlorate [58] and iodide [59,60].



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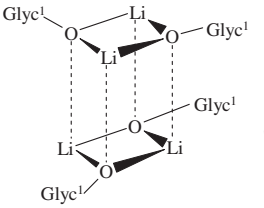

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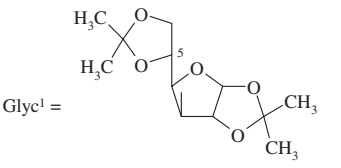
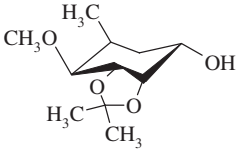


According to X-ray data, a distorted octahedron is present around the sodium ion. In the first case, it consists of two hydroxyl groups of the first ligand, the ring oxygen atom of the second ligand and three perchlorate oxygen atoms. In the second case, four hydroxyl groups of two ligands and ring oxygen atoms of two other ligands take part in coordination.

Lithium alcoholate **25** of the ketalated monosaccharide diacetone glucose **9** [61,62] presents a three-dimensional structure **26**. Another ketalated sugar **27** binds the sodium cation in acetone solution [60]. Methylated dianhydromannitol **28** possesses [63] an elevated affinity for the lithium cation, as anticipated from the HSAB principle with increased hydrophobicity of a ligand and a solvent.



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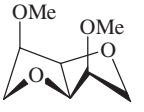

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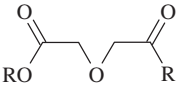
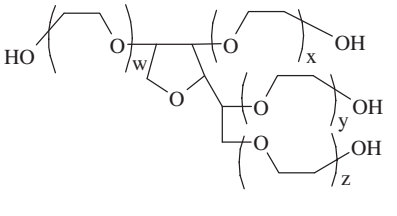
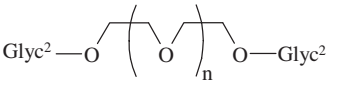


29

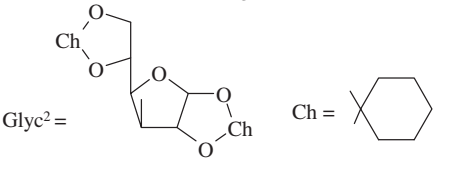
The affinity of compound **27** to s-metal cations increases considerably [60] when the methoxy group is changed to the fragment $-O(CH_2)_2OH$ and the affinity of compound **28** increases by changing the methoxy groups to the fragments $-O(CH_2)_2OEt$ and $-O(CH_2)_2O(CH_2)_2OEt$ [63]. The resulting products are acyclic analogues of crown ethers, podands [64]. The podands **29** (where R are the moieties of per-*O*-acetylated monosaccharides) are excellent complexones for s-metal cations [65], probably due to additional participation of carbohydrate fragments in coordination. The ionophoretic properties of the known sugar detergent, Polysorbate-80 (compound **30**) in relation to the Na^+, K^+, NH_4^+ and Ca^{2+} cations, have been reported [66].



30
w + x + y + z = 20

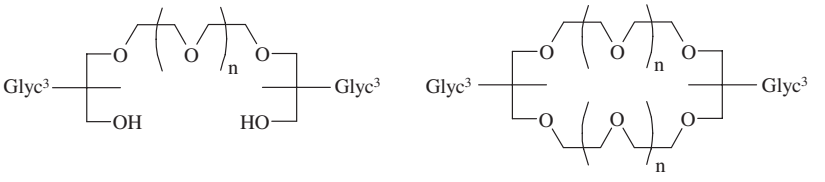


31
n = 1 - 13



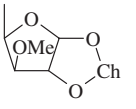
The simplest and most effective approach to the synthesis of sugar podands is by interaction of a monohydroxy ketalated monosaccharide such as dicyclohexylideneglucose deprotonated under the conditions of phase-transfer catalysis (PTC) [67,68], with oligoethylene glycol ditosylates. The podands **31** are formed in quantitative yields and show good complexing activity in relation to Na^+ and K^+ cations (qualitative tests).

A regiomeric mixture of the podands **32** was formed together with regiomeric crown ethers (corands) **33** by interaction of 1,2-*O*-cyclohexylidene-3-*O*-methyl-α-D-glucofuranose with oligoethylene glycol ditosylates under PTC conditions [67,69,70].



32 **33**

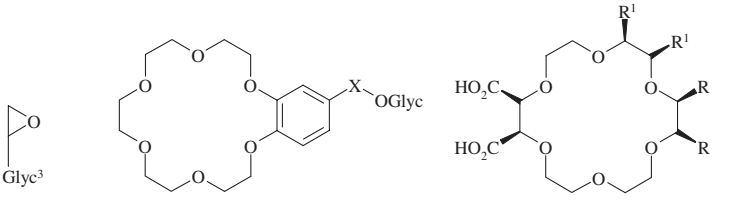
n = 0 - 3; Glyc³ =



Another approach to the synthesis of sugar podands by opening of carbohydrate oxyrane **34** with oligoethylene glycols deprotonated under PTC conditions proved to be unsuccessful [71] owing to competition between mono- and bis-nucleophilic opening with the formation of complex reaction mixtures.

Numerous carbohydrate corands have been synthesized, usually as chiral hosts to resolve racemates of enantiomeric guests [72,73]. However, their use as complexons for s-metal cations is known. Thus, corands **35** (Glyc is the acetalated or acetylated monosaccharide) were synthesized [74] with the hope that sugar moieties would offer additional sites for coordination; with some exceptions that was not the case.

Nevertheless, many sugar corands demonstrate participation of the carbohydrate fragment in coordination. For example, derivatives of tartaric acid **36** showed high affinity for Na^+, K^+, Tl^+, Ca^{2+} and Ba^{2+} cations, probably by additional coordination of the cation in a cavity of the corand with the carboxyl group [75]. (Tartaric acids as glycaric acids of tetroses must be considered as natural carbohydrate derivatives [33,76]).



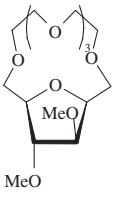
34 **35** **36**

X = -CH_2-,

R, R^1 = H, CO_2H

The corand **37** forms [77] extremely stable complexes with Group IA cations owing to participation of the sugar fragment in coordination. On the contrary, the coordinative activity in corand **38** decreased [78] on account of the conformational rigidity of the sugar fragment. The last phenomenon is probably characteristic [72] of the majority of

sugar corands. The usual coordination of corand **38** (R = H) with $NaBPh_4$ is supplemented with coordination of O(1) of the neighboring ligand [79]. In the complex of corand **39** with KI, the K^+ cation is disposed in a mean plane formed by the corand oxygen atoms; the distance $K^+ \cdots O$ is close to the distance in the complex 18-crown-6 · KSCN [80]. The cation K^+ occupies the same position in the complex of **39** with KSCN [81].



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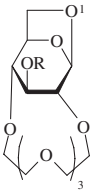
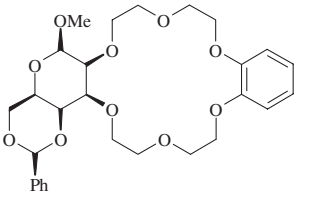


38

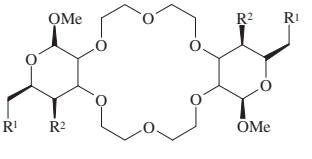
R = H, Ac



39

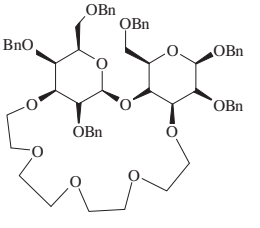
The corands **40** with two cyclic sugar fragments are excellent complexones for calcium picrate [82] with activity exceeding that of dibenzo-18-crown-6.

A series of corands having two and four cyclic sugar fragments (e.g. the compounds **41** and **42**, respectively) have been obtained [83,84] from the disaccharide lactose; compounds **41** and **42** coordinate Group IA cations with association constants K_a of approximately $10^3\,M^{-1}$. Interestingly, the derivative of an initial compound, the podand **43**, forms [84] a Li^+ complex of the same stability. The stability of the complexes is lower than that of common corands owing to the conformational rigidity of the lactose corands [84].

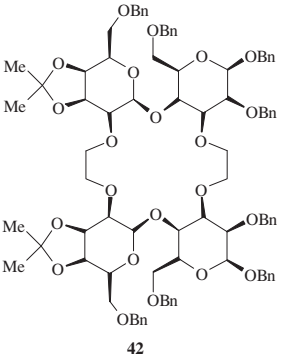


40

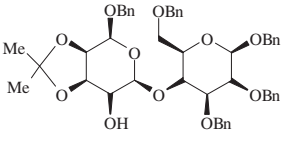
R^1, R^2 = OH, OAc



41



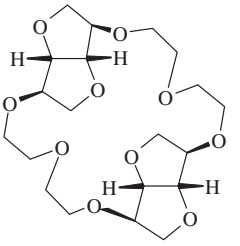
42



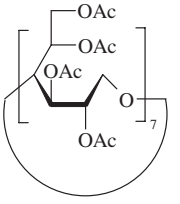
43

Bn = CH_2Ph

Besides the above 18-crown-6 sugar corands, a synthesis of the 30-crown-10 derivative **44** has been reported [85] starting from dianhydro-D-mannitol. Corand **44** coordinated alkali metal cations with participation of sugar oxygen atoms in the coordination as effectively as corands **40**–**42**. The most stable complexes (corand **44**) formed with K^+ ($K_a = 120 \times 10^3\ M^{-1}$) and with Rb^+ ($K_a = 160 \times 10^3\ M^{-1}$) [85].



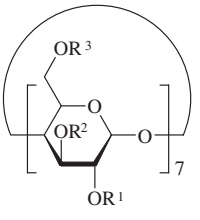
44



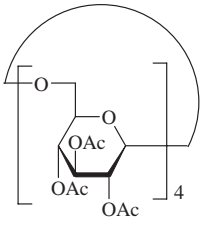
45

A chiral macrocycle **45** obtained [86] from β-cyclodextrin (βCD) selectively binds the Li^+ cation ($K_a = 82 \times 10^3\ M^{-1}$) like the standard 14-crown-4 and 15-crown-5 although having no corand structure.

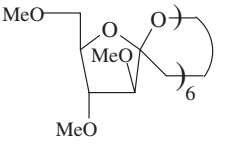
Unlike cyclic oligosaccharides, cyclodextrins, whose capacity for coordination of s-metal cations is limited [14], have *O*-protected derivatives that are excellent complexones for these ions.



46



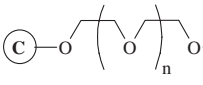
47



48

Thus, per-*O*-acetylated βCD (**46**: $R^1 = R^2 = R^3 = Ac$) and per-*O*-phenylcarbomoylated βCD (**46**: $R^1 = R^2 = R^3 = CONHPh$) bind s-metal salts having lipophylic anions in organic solvents [87]. Mixed-substituted βCDs [88] (**46**: $R^1 = R^2 = Ac$, $R^3 = –OSO_2\text{-}\alpha\text{-}C_{10}H_7$; $R^1 = R^2 = H$, $R^3 = –OSO_2\text{-}\alpha\text{-}C_{10}H_7$) are stronger complexons for s-metal cations than common corands. For example, the mixed-substituted βCD [89,90] (**46**: $R^1 = R^3 = C_5H_{11}$, $R^2 = Ac$) binds Na^+, K^+, Rb^+ and Cs^+ cations better than dibenzo-18-crown-6 although being less specific. Cyclogentiotetraose per-*O*-acetate **47** coordinates [91,92] the Group IA cations as effectively as per-*O*-methylated cycloinulotetraose **48**, which form [93] the most stable complex with Ba^{2+}.

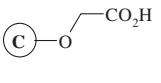
Considerable s-metal complexation is noted [94] for the products of interaction of cellulose with oligo- and polyethyleneglycol ditosylates in a superbase medium; a proposed structure of these compounds is represented by formula **49** (where © is a fragment of a cellulose molecule).



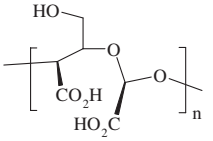
49

n = 2, 3, ~ 17;

R = H, Ts, C

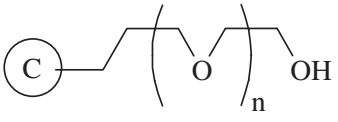


50



51

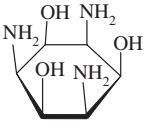
Measurements of the equivalent conductivity $\wedge$ of aqueous solution of Li, Na, K and Cs salts of carboxymethylcellulose **50** showed [95] a decrease of $\wedge$ with increasing polymer concentration in each case up to deviations from the Manning theory [96] of polyelectrolytes. These deviations testify to an additional binding of the counterions by neighboring carboxyl or hydroxyl groups. 2,3-Dicarboxy derivatives **51** of starch and amylose bind strongly to calcium ions [97]. Oxyethylcellulose **52** possesses [98] podand activity conditioned by ethyleneglycol groups.



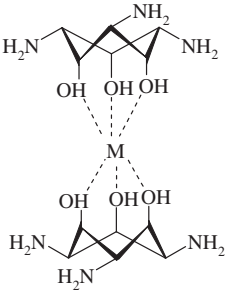
52: n = 1, 2

Nitrogen-containing Ligands

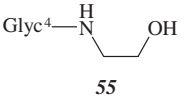
Rather simple carbohydrate structures called pseudo-podands [99] were proved to be wonderful complexons for s-metal cations. Thus, synthetic 1,3,5-triamino-1,3,5-trideoxy-*cis*-inositol **53** which is a classic complexone for d-metal cations forms [100] stable ionic complexes **54** with the Group IIA metal cations. Two ligands in chair conformation are coordinated with a hard metal ion through axial hydroxyl groups according to the second Angyal rule [14] and to the HSAB principle [55,56].



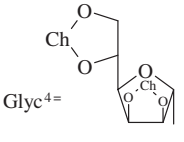
53



54: M = Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}

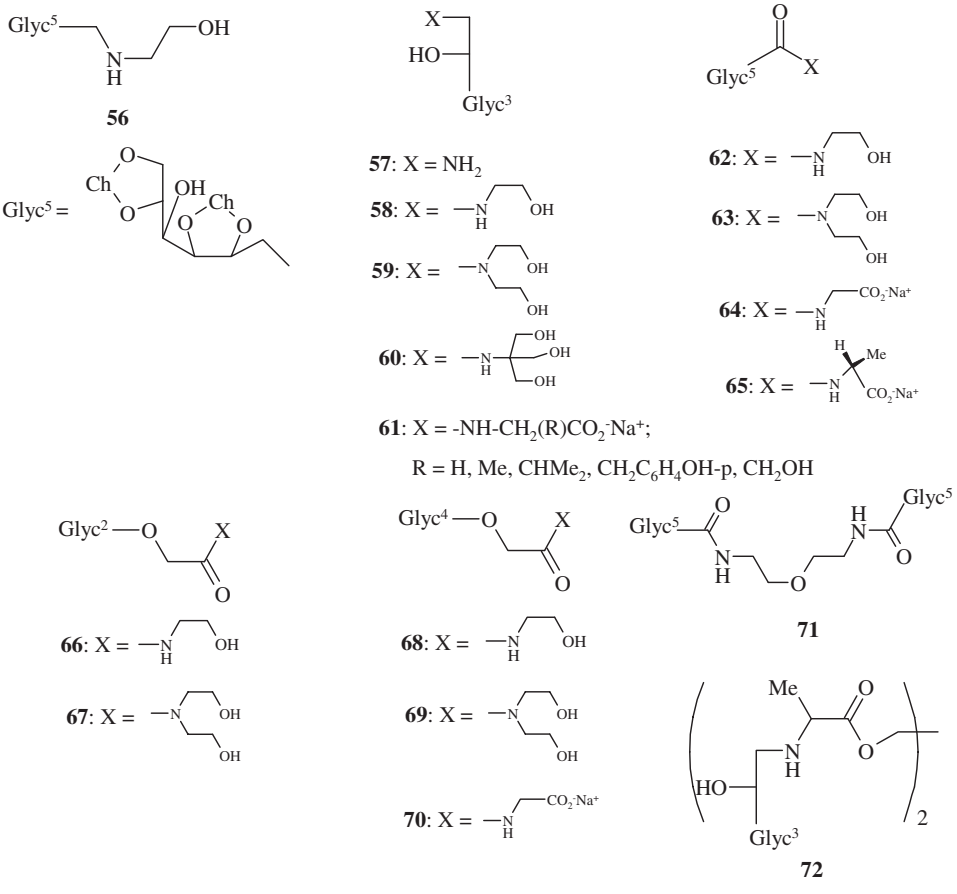


55



The amino derivatives **55**, **56** [101], **57**–**59** [102], **60** [103,104], **61** [105,106] and amido derivatives **62**–**70** [107] also proved to be pseudo-podands (qualitative tests).

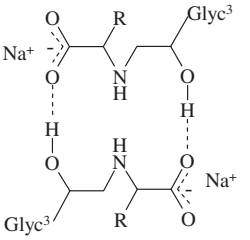
Carbohydrate aza-podands **71** [107] and **72** [108] with good s-metal complexing properties were also reported.



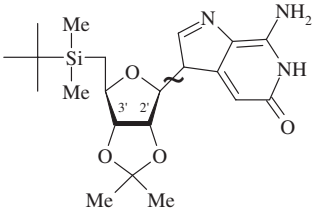
N-Glycosylaminocarboxylates **61** [105,106] are interesting pseudo-podands. Their podand activity is explained [108,109] by the formation of dimers **73** in non-polar solvents. An illustration of the formation of a cavity compound by aggregation of non-cavity molecules is the behavior of the ketalated *N*-glycoside of guanidine **74**. In non-polar media it is the tetramer **75** [110–112] forming stable complexes L_8M (two tetramers per alkali metal atom) with K^+ and Cs^+ ions. The coordination probably takes place through the carbonyl oxygen atoms [111]. Additionally, high selectivity for Cs^+ was found [112]. The structure of a carbohydrate moiety is an important factor since the replacement of the 2′,3′-*O*-isopropylidene protecting group by the *O*-acetyl groups prevents formation of an aggregate of type **75**.

Carbohydrate aza-corands **76** possess [113] approximately equal affinity to Na^+ and K^+ cations ($\lg K_a = 4$–6 in $CDCl_3$). The aza-corands **77**, **78** [102] were also reported.

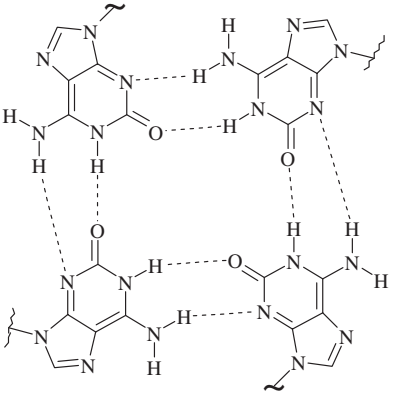
The more complex system **79** [114] starting from the disaccharide tregalose binds Group IA metal cations in a sequence $Cs^+ > K^+ > Na^+$ and forms more stable complexes with Ca^{2+} and Ba^{2+}.



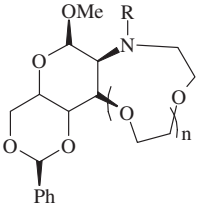
73



74

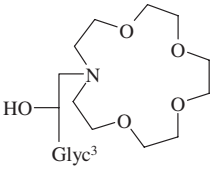


75

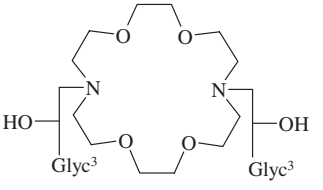


76

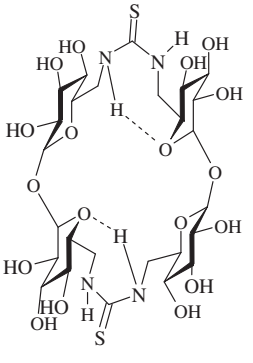
R = H, Et; n = 3, 4



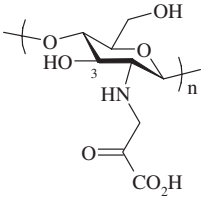
77



78



79



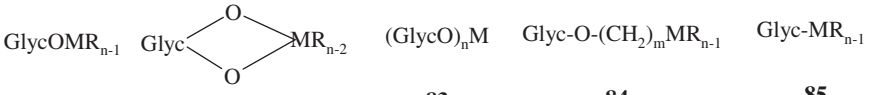
80

N-Carboxymethylchitozan **80** is a polymeric synthetically modified nitrogen-containing derivative which produces [115] complexes with Group IIA metal cations by participation of the cavity formed by the *N*-carboxymethyl group and the hydroxyl group to at C(3) of the neighboring monomeric unit.

COMPLEXATION WITH p-METAL CATIONS

Oxygen-containing Ligands

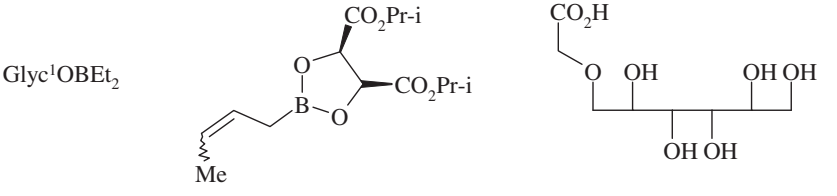
This area is represented by esters of the respective oxoacids **81**–**83**, ethers **84**, and organometallic compounds **85**, although most of the compounds also contain organometallic groups. On the other hand they may be regarded as coordination compounds, owing to the presence of neighboring oxygen atoms able to provide additional coordination with a metal atom (*vide infra*).



81 **82** **83** **84** **85**

R = Me, Et, n-Bu, Ph; n = 3, 4; m = 1, 2

From boron complexes only a series of boron esters of ketalated sugars of type **86** [116] and tartrate esters modified by crotyl boronates of type **87** [117,118] have been reported. The comparatively available 1-*O*-carboxymethyl-D-galactitol **88** (not gulitol as reported in [119]) binds [119] the Al^{3+} cation in unknown fashion.



86 **87** **88**

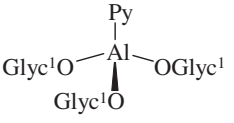
Complex **89** of diacetoneglucose with Al(III) is interesting [120] with three carbohydrate ligands and the metal atom forming a trigonal pyramid; the ligands rotate freely in solution and in the crystalline form of the compound. The aluminium atom is chirotopic but not stereogenic (see [121] for these terms).

In organotin complexes **90** [116,122] the C-Sn bond is removed from the ketalated carbohydrate moiety.

The synthesis of compounds **91**–**94** [123] demonstrates the structural variability of this type of compound. In the diketal **95a** [124], the organometallic moiety is removed from the carbohydrate fragment.

Stannylene carbohydrate acetals such as **96a**,**b**, used [125–127] in synthetic chemistry of carbohydrates for temporary blocking of vicinal hydroxyl groups [125,128], form

dimers such as **97**. Such ability to associate is peculiar to many organotin compounds [129]. The *trans* isomer **97** [C(1) and C(4) carbon atoms of two ligands are in *trans* positions] is formed [128] if the axial and equatorial oxygen atoms are close to the stannylene group as in the α anomer **96a**. In the case of neighboring diequatorial oxygen atoms as in the β anomer **96b** a mixture of *cis* and *trans* dimers is formed [128]. In another stereochemical situation, as the compound **98**, a trimer is formed [128]. The formation of a pentamer from compound **99** was also reported [125,128]. The Sn(II) and Sn(IV) halides form coordination compounds of type **100** through free hydroxyl groups [127].



89

$Glyc^1OSnR_3$

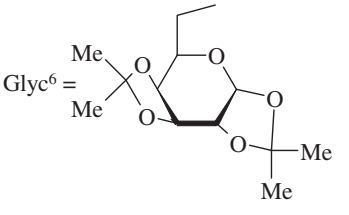
90

R = Ph, Me

$Ph_nSn(CH_2OGlyc^6)_{4-n}$

91

n = 1 - 3



$Bu_3SnCH_2OGlyc^4$

92

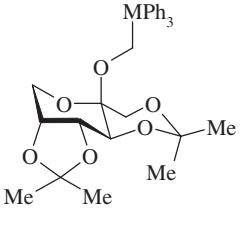
$IPh_nSn(CH_2OGlyc^4)_{3-n}$

93

n = 0 - 2

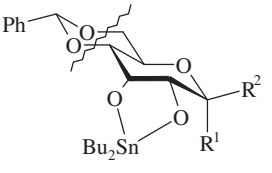
$IPh_nMe_{2-n}Sn(CH_2OGlyc^6)$

94



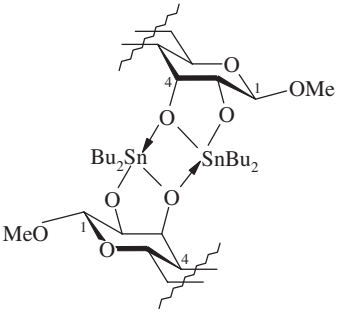
95a-c

M = Sn (a), Si (b), Pb (c)

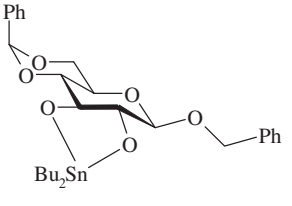


96a,b

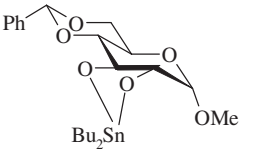
R^1 = OMe, R^2 = H (a);
R^1 = H, R^2 = OBn (b)



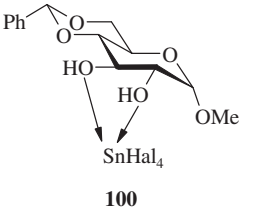
97



98

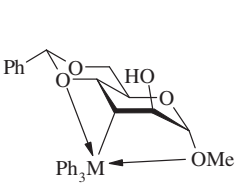


99



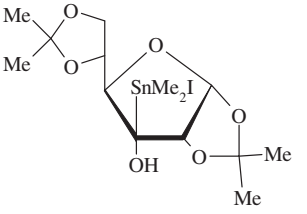
100

For those tin-containing compounds where the organotin fragment is connected directly to the carbohydrate fragment [130,131] an intramolecular coordination occurs which can be illustrated by the coordination of the tin atom in compound **101a** with the glycosidic and nearest acetal oxygen atoms. The decomposition of organotin complex **102** forming the simple dimer **103** in aqueous ethanol has been reported [132].

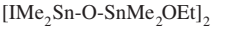


101 a-c

M = Sn (a), Si (b), Pb (c)



102



103

For other p-metals, only complexes **95b**,**c** and **101b**,**c** are known [124]. Binding of lead(II) and copper(II) ions to starch and amylose 2,3-dicarboxy derivatives has also been reported [133].

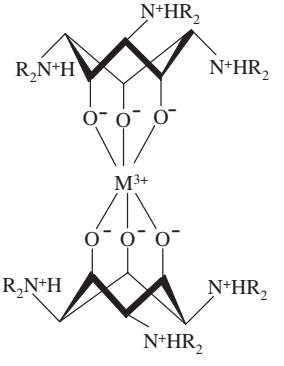
NITROGEN-CONTAINING LIGANDS

In this series complex formation using the synthetic ligand **53** was mainly studied. The Al(III) complex **104** was reported [134] which contains deprotonated hydroxyl and protonated amino groups. The Ga^{3+} ion forms [134] complex **105** of the mixed type; Tl^{3+} is coordinated [134] only through axial amino groups (complex **106**). The association constants for these complexes are high [134]: $\lg \beta_2$ is 18.8 and 27.5 for complexes **104** and **105**, respectively. Taking into account an increase of softness in the series Al^{3+}, Ga^{3+}, In^{3+} and Tl^{3+}, complex formation of ligand **53** corresponds to the HSAB principle [55,56]. The *N*-dimethyl derivative of ligand **53** (compound **107**) forms [135] complexes **108** with M^{3+} only through coordination with deprotonated hydroxyl groups; dimethylamino groups are protonated. Six-coordinated oxygen atoms and six NH groups are organized in a hydrophilic pocket and twelve methyl groups are arranged in a hydrophobic pocket filled by twelve water molecules. Complexes with Ge^{4+} and Sn^{4+} have an analogous structure [135]. Such coordination is probably caused by the tendency of the bulky protonated dimethylamino groups to adopt the equatorial orientation.

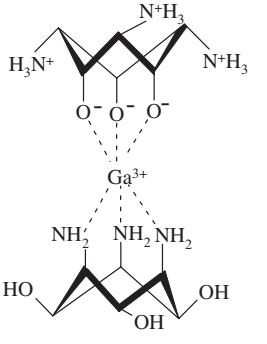
Complex formation of ligand **53** with Pb^{2+} and Bi^{3+} ions takes place [136] *via* a more complicated route. In the first case a monoligand bridge, trinuclear complex **109**, is formed [136] in which three lead atoms and three oxygen atoms form a six-membered cycle possessing a chair conformation. In the case of Bi^{3+} the formation of a bisligand bridge, trinuclear complex **110**, with a sandwich structure was established [136].

Unlike the cyclic nitrogen-containing ligand **53**, complex formation with the acyclic *N*-methyl derivative, glucamine **111**, probably occurs in a more complicated form.

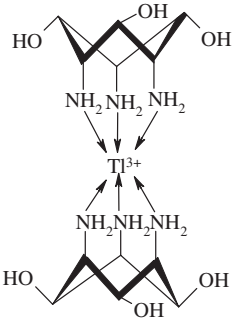
Some complexes [137], formed by interaction of ligand **111** with the Pb^{2+} cation, were found in aqueous solutions; their structures depend on the metal : ligand ratio. These complexes (**112** and its derivatives) are products of partial or full protonation of nitrogen and bridge oxygen atoms.



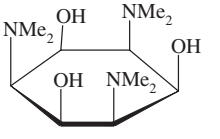
104:R = H, M = Al;
108: R = Me, M = Al, Ga, In



105



106



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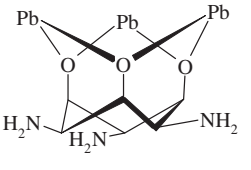
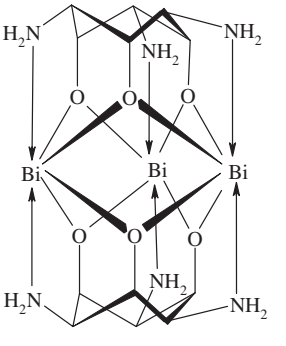
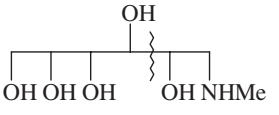


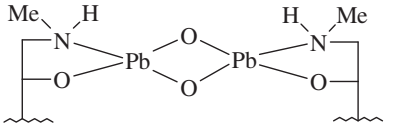
109



110



111

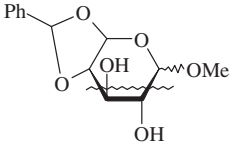


112

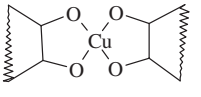
COMPLEXATION WITH d- AND f-METAL CATIONS

Oxygen-containing Ligands

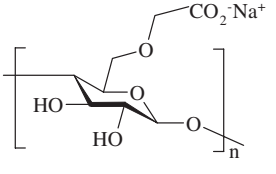
The d-metal cations are widely represented. Thus, copper bis-chelates **114** were obtained by selective O-alkylation and O-acylation of the *O*-glycoside **113** (α- and β-anomers) [138].



113

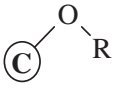


114



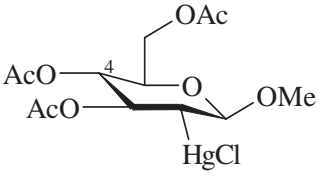
115

The *O*-carboxymethyl derivative **88** coordinates actively not only with the copper(II) cation, but also with a series of other d-cations (Fe^{3+}, Co^{2+}, Ni^{2+} and Mn^{2+}) [119]. The interaction of the polymer analogue sodium carboxymethylcellulose (SCMC) **115** with Zn(II) [139] and Cd(II) [140] is purely electrostatic. Cellulose unsaturated ethers **116** coordinate poorly with heavy metal salts; this fact was explained [141] by steric hindrances in the environment of the polymeric molecule. Good results were obtained [141] only using propargylcellulose with $AgNO_3$, $HgCl_2$ and $AlCl_3$. Unsaturated esters of cellulose such as methacrylates (**116**: R = –C(O)C(CH$_3$)=CH$_2$) [142], cinnamates (**116**: R = –C(O)CH=CHPh) [143] and oleates (**116**: R = –C(O)(CH$_2$)$_2$CH=CH(CH$_2$)$_7$CH$_3$) [143] bind Hg(II), evidently through mercuration of the C=C bond. The formed organomercury compounds should be considered as metal complexes due to a possibility of intra- and/or intermolecular coordination of the mercury atom with neighboring donor sites [such coordination is possible, e.g. in compound **116a** between the mercury atom and *O*-acetyl at C(4)] [144].



116

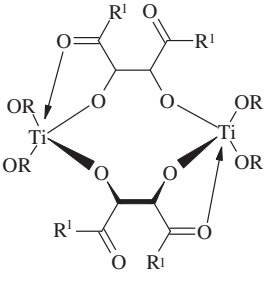
R = 1-naphthyl, 2-pyridine, crotyl, propargyl, etc.



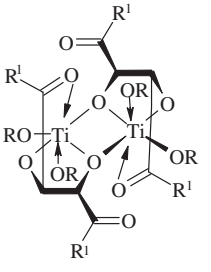
116 a

Complexes of sugar oxygen derivatives with the Group IIIB d-metal cations were not found in the literature. For the Group IVB metals Ti(IV) complexes are represented especially extensively, undoubtedly related to their wide use in modern organic synthesis. Thus, for example, sugar Ti(IV) complexes are among the best enantioselective catalysts [144–148] as well as chiral nucleophilic agents [149,150].

The Ti(IV) complexes of D- and L-tartaric acid derivatives are very attractive owing to their key role in highly effective enantioselective epoxidation of allyl alcohols according to Sharpless [145–147]. These complexes have not been obtained in crystalline form and consequently their structures have not been resolved by X-ray diffraction. However, according to their NMR spectra in solution and structural data for their structural analogues, either dimeric structures (cyclic **117** [145–147,151] or bridge **118** [147,151, 152]) were possible. The last one is preferable especially as titanium complexes of tartaric acid amides possess [149,152] precisely such a structure (**118**: $R^1 = NHCH_2Ph$) in the solid state.



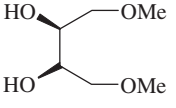
117



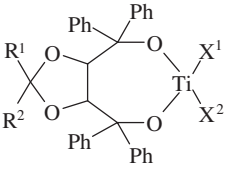
118

R = i-Pr; R^1 = O-i-Pr, $NHCH_2Ph$

However, other researchers have shown [153,154] that the structures of Sharpless catalysts in solution are diverse. Complexes of tartaric acid derivatives mostly possess the structure of cyclic dimers such as **117**, while bridge structures are characteristic for complexes of sugar diols such as **119** [163,154].



119



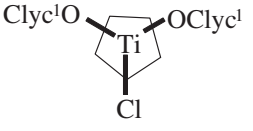
120

R^1 = H, Me; R^2 = H, Ph, t-Bu;
X^1 = Me; X^2 = i-Pr

Ti(IV) complexes of other tartaric acid derivatives may have [155] a dimeric bridge structure **118** with participation of the third sugar ligand (instead of OR at neighboring titanium atoms) as well as tri- and even tetrameric structures [88]. Such a situation explains why epoxidation products with one enantiomer of tartaric acid derivative

but starting with different Ti(IV) complexes in the preparation of a catalyst have opposite configurations [156]. A series of titanium complexes of general structure **120** has been successfully used as nucleophilic reagents in some enentioselective transformations [148–150] (see section Organic Reactions Modulated by Complexation).

According to X-ray diffraction data a stable product of a cyclopentadienyl Ti(IV) complex with diacetone glucose $Glyc^1$-OH possesses structure **121**. Owing to a partial double Ti–O bond, rotation of the sugar ligands is hindered; this is reflected in NMR spectra especially at −200°C (see ref. [157]). In complex **121** the chlorine atom is easily exchanged for alkyls. Thus, a stable complex with the allyl substituent was obtained [158] and successfully used for enantioselective interaction with a carbonyl group [158,159].



121

$M(OGlyc^1)_4$

122: M = Ti
123: M = Zr
124: M = Hf

$M(OGlyc^1)_4Py_2$

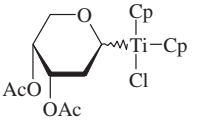
125: M = Ti
126: M = Zr
127: M = Hf

Free rotation of sugar ligands was observed [120] in complexes **122**–**124** and their pyridine adducts **125**–**127**. According to X-ray diffraction data [120] a pseudo-octahedral coordination with *cis* pyridine ligands is realized in **126**.

The interaction of $TiCl_4$ and *cis*- or *trans*-1,2-diacetylcyclohexane (model compound) [160], per-*O*-acetates [161,162] and per-*O*-benzoates [162] of aldoses has been reported, with the formation of complexes of various composition and with preferential coordination of the metal atom to the carbonyl of the *O*-acyl group and sometimes to the ring oxygen atoms.

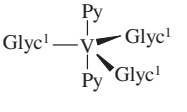
Complexes of type **128** were used [163] to obtain variously protected glycols with an organometallic moiety as a nucleofuge group.

In a series of Group VB metals only complex formation with diacetoneglucose was studied [164–166]. In complex **129** [164–166] the sugar ligands are in a fixed position owing to shortened multiple V–O bonds forming an asymmetric propeller with the Λ configuration [164,166]. Unusual complexes $[V(OGlyc^1)_6M_3]$ (M = Li, Na) were obtained by interaction of $V(OGlyc^1)_3$ with lithium or sodium alcoholates of diacetoneglucose of type **25** [164–166]. According to X-ray diffraction data of the lithium derivative the sugar ligands in these complexes create a solvate type of environment for Li^+ ions forming structure **130**, each Li^+ ion is additionally bound with the oxygen atom at C(5) of the sugar ligand [164–166]. Analogous complexes with Ti and Cr instead of V have also been obtained [165,166].

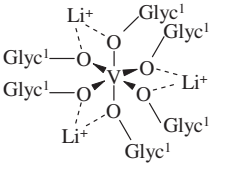


128

Cp - cyclopentadienyl

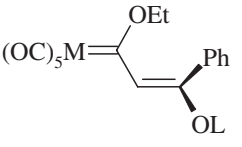


129



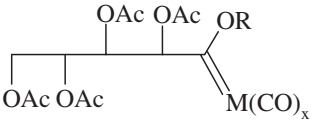
130

The Group VIB d-metals are mainly represented by carbene complexes. Such complexes, **131**, have been synthesized in which the ketalated carbohydrate moiety is in the β position to the carbene carbon atom [167]. In carbene complexes **132** and **133** the carbohydrate moiety is joined directly to the carbene carbon atom [168]. The existence of peroxo complexes of aldonic and aldaric sugar acids (complexes **134** and **135**, respectively) should be noted [169].



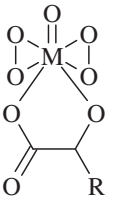
131

M = Cr, W
L = Glyc[1] etc.

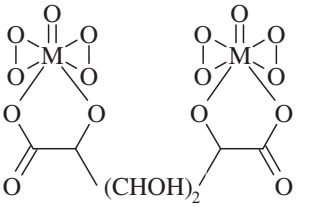


132: M = Cr, Mo, W; X = 5

133: M = Fe; x = 4
R = Me, Et

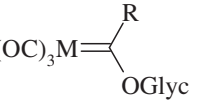


134: R = $(CHOH)_3CH_2OH$



135

M = W(VI), Mo(VI)



136

R = Ph, PhMe-p
M = Mn, Re

Analogous carbene complexes **136** have been prepared [170] with a series of Group VIIB d-metals. The interaction in solution of 1,6-anhydrohexopyranoses of type **8a** with Mn^{2+}, Mn^{4+} and Mn^{6+} cations was studied [171]. The coordination is tridentate in all cases; complexes with *ax*, *eq*, *ax* orientation of three neighboring hydroxyl groups are the most stable (the first Angyal rule [14]). Organometallic complexes **137** were used [172] for synthesis of exotic *C*-glycosides. Manganese complex **138** was obtained [166] by interaction of $MnCl_2$ with the lithium alcoholate **25**. Based on $M(OGlyc^1)_2$ (M = Mn, Fe), derivatives with participation of phenanthroline (complexes **139**) and mesitylene (complexes **140**) have been obtained [173].

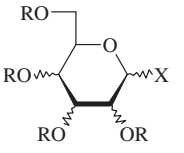
Finally, Group VIII metal complexes will be discussed. Iron complex **141** (analogous to **137**) is very stable and may be distilled [174]. However, the structurally related complex **142** proved to be unstable [175].

The π-complexes **143** exist as two diastereomers having the iron-carbonyl group above or below the ring plane [176].

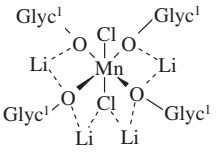
μ^3-Carbyne clusters of type **144** were suggested [177] as biologically active compounds and molecular sensors.

Double deprotonated vicinal diols reacting in aqueous basic solution with the complex *trans*-$[en_2CoCl_2]Cl$ (en – ethylenediamine) form Co(III) complexes of type **145** [178] with mostly Λ or Δ configuration depending on the configuration of the ligand. In the case of a ligand with two vicinal diol groupings the coordination took place only

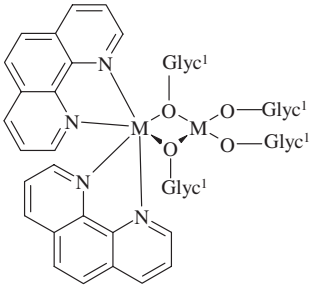
through one of them, i.e., regioselectively. Co(III) complexes of aldonic acids have similar structures with participation of the carboxylato group in coordination [179].



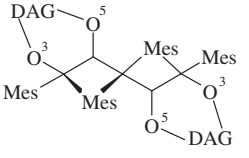
137: R = Ac; X = $Mn(CO)_5$



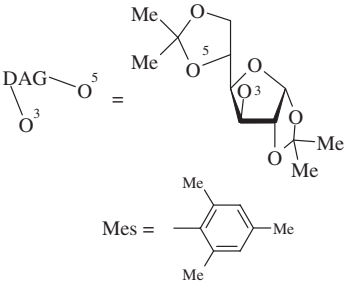
138

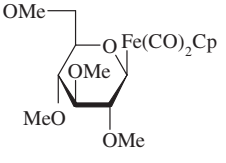


139
M = Mn, Fe

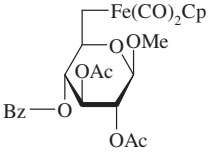


140
M = Mn, Fe

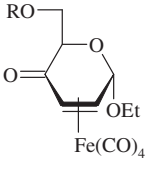




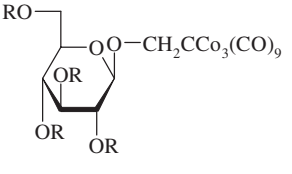
141



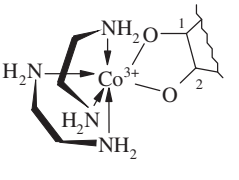
142



143
R = H, Ts

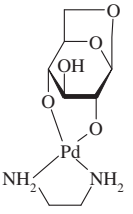


144



145

The ethylenediamine dihydroxo palladium(II) readily forms [180] similar complexes such as **146** with the diol grouping. The intermediate complexes **147** were isolated [181,182] in the processes of *C*-hetaryl glycoside synthesis from pyranoid glycols in the presence of palladium complexes.



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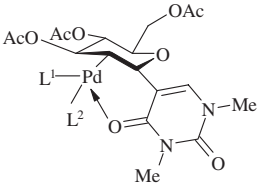
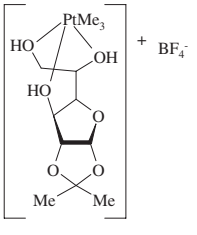


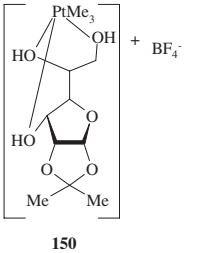
147

L^1, L^2 = Cl, PPh_3, $AsPh_3$

The platinum complex $[PtMe_3(Me_2CO)]^+BF_4^-$ (**148**) proved to be a useful reagent for obtaining diverse sugar complexes [25] owing to its ability to coordinate oxygen sites. Three hydroxyl groups are most preferred as in complexes **149** [183] and **150** [184]. Coordination of the hydroxyl group at C(3) with opposite configuration is conditioned by the conformational flexibility of a furanose ring [76]. Ring oxygen may also participate in coordination in the presence of only two coordinated hydroxyl groups as in complex **151** [183] as well as the ketal oxygen atom (complex **152** [183]). However, the diacetonemannose **153** does not react with complex **148** in spite of the presence of both these possibilities [184] since favorable stereochemistry of coordinating sites is necessary. An acyl group may also be coordinated as in complex **154** [185]. The unusual ruthenium complex **155** is noteworthy [186].



149



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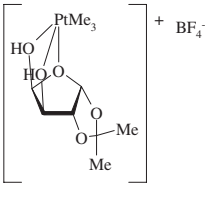

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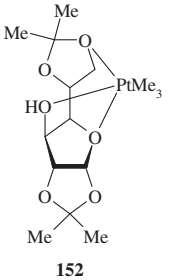

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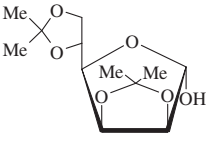

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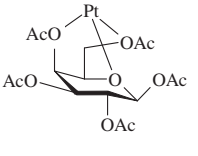

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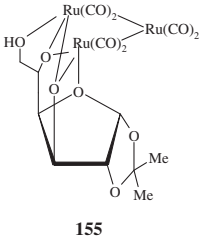

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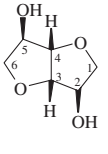
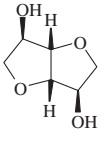
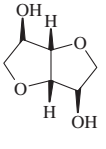


156a



156b



156c

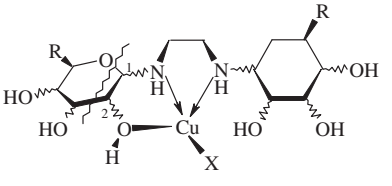
Unlike d-metals, f-metals are not popular objects for the study of complexation with the ligands. Complexes of f-metals were investigated in solutions by NMR spectroscopy using shift-reagents. Tridentate coordination of a lanthanide cation similar to that taking place in manganese complexes [171] was found [187] in 1,6-anhydro-β-D-hexoses (such as **8a**). Bidentate coordination between ring and hydroxylic oxygen atoms in dianhydrohexitols **156a–c** is determined [188] by the disposition of oxygen atoms on the fragment, –O–C–C–OH being most favorable for fragments having the *erythro* configuration, *viz*., –O(1)–C(4)–C(5)–OH in **156a** as well as –O(1)–C(4)–C(5)–OH and –O(6)–C(3)–C(2)–OH in **156b**.

Nitrogen-containing Ligands

The predominance of *N*-containing d-metal complexes in modern coordination chemistry [189,190] is also peculiar to carbohydrate coordination chemistry. Owing to the magnitude of reported data on this theme, a further subdivision according to types of nitrogen-containing sugar derivatives is required.

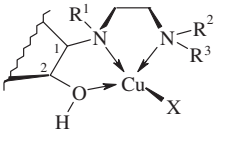
N-Glycosides and Related Compounds

N-Glycosides **7b** of amino acids ($R = CHR^1CO_2H$) are well known. Their metal complexes with Mg(II), Ca(II), Co(II), Cu(II) and Zn(II) were isolated [191] by interaction of aldoses with amino acids in basic media in the presence of metal salts, although the structures of these complexes have not been investigated. This template idea was the basis of an important investigation by Japanese workers [22,23] on the interaction of aldoses and ketoses with metal complexes of ethylenediamine (en) or its derivatives. Bis-ligand complexes **157** and mono-ligand complexes **158a**,**b** were thus obtained [192] with en or *N*,*N*′- and *N*,*N*-dimethylethylenediamine, respectively, where one sugar ligand is coordinated through the *N*-glycoside secondary amino group at C(1) and the hydroxyl group at C(2). The second sugar ligand is coordinated through the amino group in complexes **157**. Complexes **157** and **158a**,**b** have square planar geometry typical for copper(II).



157

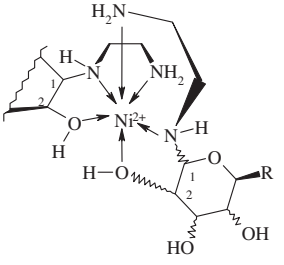
R = H, CH_2OH; X = Cl, Br



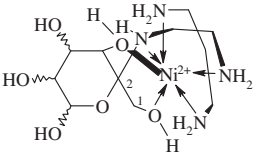
158a: $R^1 = R^2 = Me$; $R^3 = H$

158b: $R^1 = H$; $R^2 = R^3 = Me$

The interaction of nickel(II) and cobalt(II) tris(en) with monosaccharides is a more fruitful approach [22]. In the case of Ni(II), the bis(carbohydrate) complexes **159** of aldoses and monocarbohydrate complexes **160** of ketoses with octahedral configuration are formed [22,193,194]. In the first case, the coordination is similar to that in copper complexes **157** and **158a**,**b**; in the case of ketoses, the primary hydroxyl group at C(1) participates in coordination. Complexes **159** may be distinguished [195] by mass spectrometry. The structures of complexes formed in the case of aldoses and trimethylenediamine are similar [196,197] to those of complexes **159**.

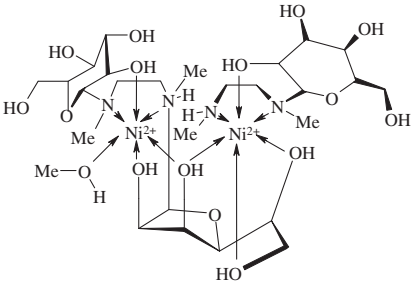


159: R = H, CH_2OH



160

However, when en is changed to its *N*,*N*′-dimethyl derivative, an unusual dinuclear complex **161** is formed [22,197,198] with D-mannose, in which one carbohydrate ligand possesses the rare furanose form. By changing D-mannose to D-glucose, complex **161** and its analogues, in which one or two pyranose ligands are D-glucose, were obtained under the same conditions [198]. This indicates that complex formation in this case is accompanied by the Lobry de Bruyn–Alberda van Ekenstein transformation [199] (analogous cases were noted earlier). Complexes **162** analogous to complexes **159** were formed [22,200] with β-alanine.



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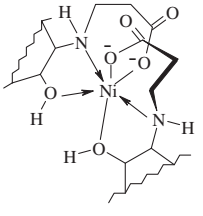
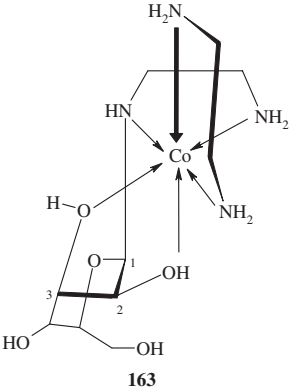
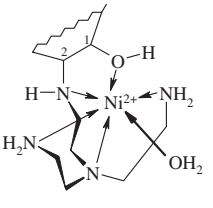


162

In the case of Co^{3+} and aldoses, three donor centers in the carbohydrate ligand take part [22,201,202] in coordination, *viz*., glycosidic imino group and hydroxyl groups at C(2) and C(3), which promotes a distortion of the chair ligand conformation in complexes of type **163**.

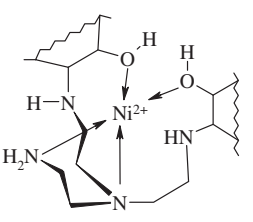


163

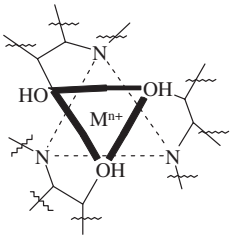


164

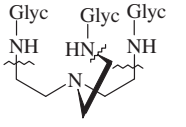
In the case of structurally more complicated tris(2-aminoethyl)amine (tren), D-glucose forms [22,203] the mono-carbohydrate complex **164**; reaction with D-mannose leads to the bis-carbohydrate ligand complex **165** [22,23,203]. Tris-carbohydrate ligand complexes of type **166** with Ni^{2+} [22,23,204] and Co^{2+} [22,23,205] using *N*-glycosides **167** were also obtained.



165



166

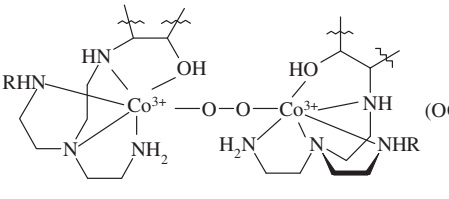


167

Metal complexes **159**–**164** possess a definite anomeric configuration (α or β), conformation of five-membered metal cycles (λ or δ), and helical configuration (Λ or Δ) [206,207] that is undoubtedly conditioned by chiral induction of the carbohydrate ligands to metal centers. Unprecedented reversible chiral inversion around the metal center (Δ ⇄ Λ) was observed in complexes **166** (M=Co^{3+}) when inorganic counterions were exchanged [205,208].

Synthesis of the bridging double-charged complexes **168** based on D-glucose or maltose is another notable achievement of Yano's research group [209,210]. When exposed to air a solution of the D-glucose complex reversibly binds O_2 after irradiation [209].

A similar approach, i.e., the interaction of metal complexes with glycosylamines, was successfully used for the preparation of complexes **169** and **170** from very popular protected D-galactosamine **171** and the alkynylcarbone complexes **172** with the ratio **169** : **170** being 3 : 2 [211].



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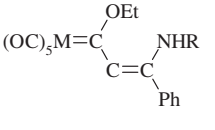

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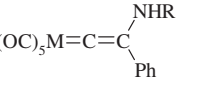

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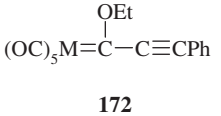
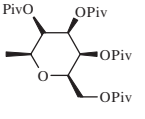
171



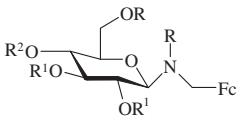
172

M = Cr, W

R =

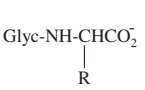


N-Ferrocenylglycosylamines **173** were obtained in a similar way [212] as redox antennae for monitoring structure and function in biological systems.



173

R = H, CH_2Fc;
R^1 = H, Ac;
R^2 = H, galactosyl;
Fc = ferrocenyl



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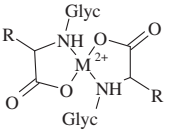

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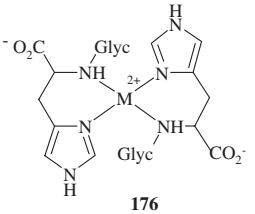
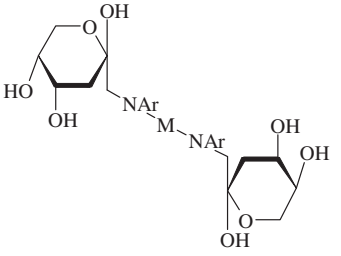


176

M = Pt, Pd;
R = H, Me, CH_2OH, CH(OH)Me, CH_2NH_2, $(CH_2)CO_2Na$,

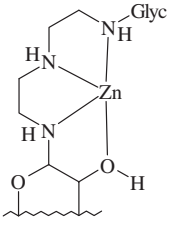
Glyc is α-D-glucopyranosyl or β-D-N-fructopyranosyl

Amino acid salt *N*-glucosides **174** obtained [213] by interaction of D-glucose with α-aminoacid salts react with complex salts $M^1{}_2[M^2Cl_4]$ (M^1 = Na, K; M_2 = Pt, Pd) forming ordinary chelates **175** via normal *N*,*O*-coordination [25,213]. However, *N*,*N*-coordination was realized with the histidine derivative [25,213] as structure **176** together with the ordinary structure **175** (competitive coordination [189]). When D-glucose reacts with free amino acids (glycine, β-alanine) the Amadori rearrangement [214] leads finally to chelates **175** containing β-D-fructopyranosyl instead of α-D-glucopyranosyl [25,213]. The Amadori product prepared from D-glucose and *p*-toluidine affords [25,215] complexes **177** with monodentate *N*-coordinated ligands.



177

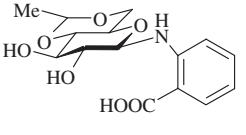
M = Pd, Pt; Ar = C_6H_4Me-p



178

Amino glycosides obtained from D-glucopyranose, D-galactopyranose, D-allopyranose or L-fucopyranose and diethylenetriamine readily form zinc complexes **178** together with other products [216].

Salts of the carboxyl-containing acetalated *N*-glucoside **179** were proved to be coordination compounds [217] with additional coordination of sugar hydroxyls for Na, K, Mg, Ca, Ba and of the imino group for Cd and Hg.



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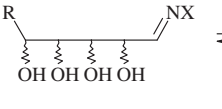
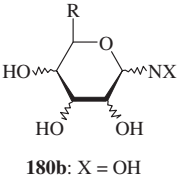


180a: X = OH
181a: X = NHC(S)Ph



180b: X = OH
181b: X = NHC(S)Ph

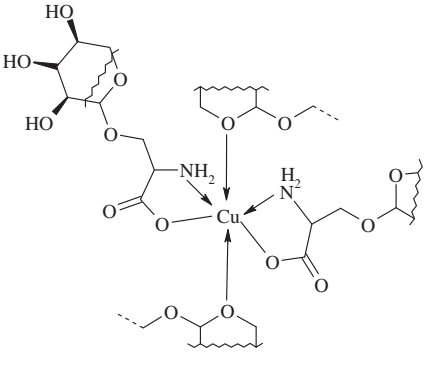
R = H, CH_2OH

Aldoximes (in the acyclic **180a** and cyclic **180b** forms or their mixture, depending on the character of the initial aldose [214]) form [218] stable coordination compounds ML and ML_2 of unknown structure with Cu^{2+}, Co^{2+}, Ni^{2+} and Fe^{3+}. The complexes of a series of heavy metal ions including Cu^{2+} and Ag^{+} were obtained [219] with aldose thiobenzhydrazides **181a**,**b**; their composition and structure are unknown. Thus the readily available ligands **180a**–**181b** are essentially *tabula rasa* of carbohydrate coordination chemistry until now.

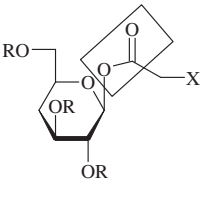
O- and C-substituted Carbohydrates with Nitrogen-containing Substituents

Copper complex **182** of *O*-(β-D-xylopyranose)-L-serine contains [220] Cu(II) in a distorted octahedral configuration caused by four carbohydrate ligands.

Complex formation [221] of *O*-glucopyranosyl glycine esters **183a** and partially (**183b**) or fully (**183c**) substituted derivatives with Fe(III) is a typical example of the simplification of structure of a complex with a decrease in the number of donor centers in the ligand (complexes **184a**, **184b** and **184c**, respectively); the Fe(III) in these complexes is coordinated through carboxyl oxygen atoms (they are framed in the structures **183a**–**c**).

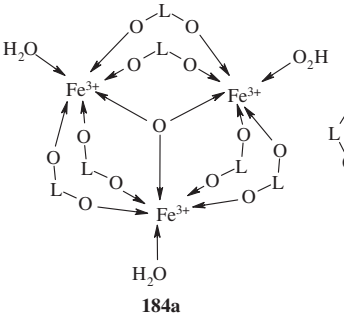


182

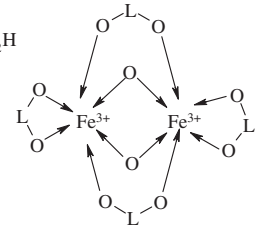


183a-c = (O-L-O)

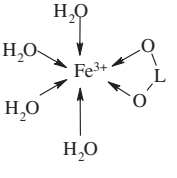
R = H, X = $NH_2^+CF_3CO_2^-$ (a);
R = Ac, X = $NH_2^+CF_3CO_2^-$ (b);
R = Ac, X = NHC(O)O-t-Bu



184a

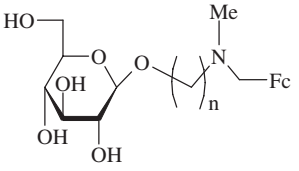


184b



184c

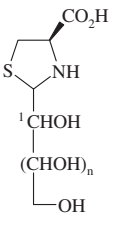
Ferrocenyl-containing *O*-glucosides **185** have been obtained [222] as water-soluble analogues of ferrocenylmethylamine, whose platinum(II) complex showed antitumor activity.



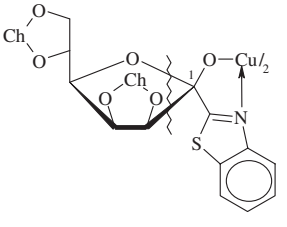
185

n = 2, 3, 5

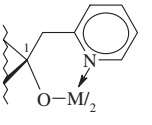
Metal complex formation [223–225] of 2-(polyhydroxyalkyl)thiazolidine-4-carboxylic acids **186** (products of interaction of L-cysteine with aldoses) is determined by the nature of a metal ion. The cation Cu^{2+} is coordinated [223] to amino and carboxylic groups, as well as in other α-amino acids (compare complexes **175** and **215**); Zn^{2+} is bound [224] through the above donor centers and through the hydroxyl group at C(2) of the carbohydrate moiety; Pd^{2+} is coordinated through the nitrogen and sulfur atoms [223]. ML_2 complexes are formed in all cases. The magnitude of the complex formation constant depends on the configuration of C(1) in the polyhydroxy chain [223].



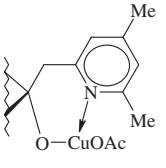
186: n = 2, 3



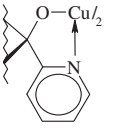
187



188: M = Cu (a), Ni (b), Co (c)



189



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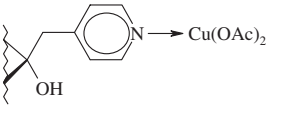


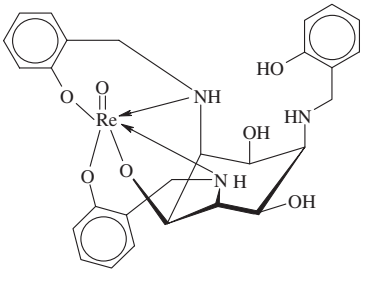
191

The *C*-hetarylmonosaccharide metal complexes **187**–**191** [226–228] were obtained in high yields by direct electrochemical synthesis (electrolysis of methanol solutions of ligands, using a corresponding sacrificial metal anode and platinum cathode) [227,228]. (There is a review [229] on this topic.) The stability of chelates **187**–**190** is probably caused by increased acidity of the glycosidic hydroxyl group at C(1) in the corresponding ligands [230].

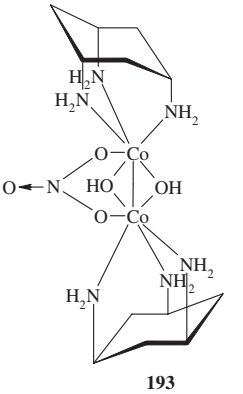
Aminosugars and their Derivatives

The synthetic complexone **53** gives complexes of type **106** [231,232] with Cu(II), Zn(II) and Co(II) as well as complexes of type **105** with Fe(III) and Cr(III) [114]. Thus, this compound forms complexes of type **54** or **104** with hard cations, complexes of type **106** with soft cations and complexes of type **105** with intermediate cations representing

ideally organized (preorganized) groupings of three axial hydroxyl or amino groups [114,232]. Lanthanide complexes $[Ln_3L_2H_6]^{3+}$ with obvious coordination through deprotonated axial hydroxyl groups have also been obtained [233]. In the case of *N*-methylated derivative **101** the Fe^{3+} cation coordinates through axial hydroxyl groups forming a complex of type **108** [132,234]. A similar situation is realized [235] in the complex of Co^{2+} with a triacetamido derivative of complexone **53**. Its 2-hydroxybenzylamido derivative and rhenium(V) form [236] complex **192** with mixed (through N and O) non-symmetric coordination. An analogue of **53**, all-*cis*-1,3,5-triaminocyclohexane gave [235] an unusual dinuclear Co(II) complex **193** with participation of a counterion, as well as the heteroleptic complex **194** with *cis*-inositol [235].

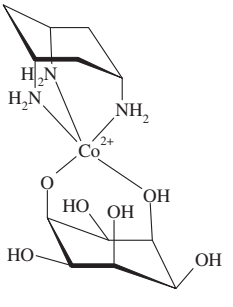


192



193

A specific feature of the synthetic aminotriols **195** and aminotetrols **196** is [237] formation of dinuclear copper(II) complexes of type **197** whose stability depends on the chirality of carbon atoms C(2) and C(3). Interaction of D-glucosamine **198a**, D-mannosamine **198b** and D-galactosamine **198c** with $Ni^{II}en_3$ leads to formation [22,238] of complexes of type **159** {NH_2 instead of OH at C(2)}. An analogous complex of **198a** and Zn(II) was also reported [239].



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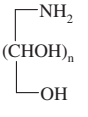
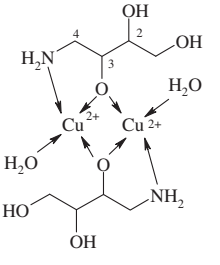


195: n = 2

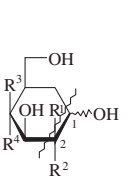
196: n = 3

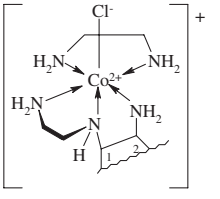


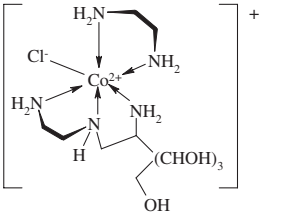
197

D-Glucosamine **198a** forms [240] cobalt complexes of type **145** [NH_2 instead of OH at C(2)] with complexes $[Co(NH_3)_3]^{3+}$, $[Co(en)_2]^{2+}$ and $[Co(phen)_2]^{2+}$ (where phen is *o*-phenanthroline), i.e., a simple ligand exchange takes place; the Δ diastereomer predominates (in the last two cases). Under the same conditions but using another treatment of the reaction mixture the interaction of D-glucosamine **198a** with $[Co(en)_2]Cl_2$

gave [241] eight complexes, which were characterized by X-ray diffraction. Among them complexes **199** and **200** are obviously primary. In other complexes, D-mannosamine **198b**, 1-deoxyfructopyranosyl- and 1-deoxyfructofuranosylamine take part as ligands, i.e., primary complex formation is accompanied not only by the Lobry de Bryin–Alberda van Ekenstein transformation [140] but also by the Amadori rearrangement [214]. All complexes possess Δ or Λ configuration. The oxidation product of D-glucosamine **198a**, D-glucosaminic acid **201**, forms [242,243] stable complexes with Cu(II), Zn(II), Cd(II), Hg(II), Pb(II), Fe(II), Co(II) and Ni(II) similar to natural α-aminoacids.





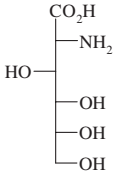


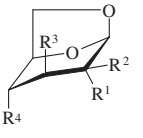
198: $R^1 = R^3 = H$, $R^2 = NH_2$, $R^4 = OH$ (a);
$R^1 = NH_2$, $R^2 = R^3 = H$, $R^4 = OH$ (b);
$R^1 = R^4 = H$, $R^2 = NH_2$, $R^3 = OH$ (c)

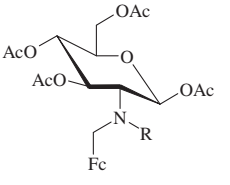
199

200

The aminodeoxyderivatives **202a**–**d**, i.e., aminosugars with a fixed $^1C_4$ conformation of the pyranose ring in contrast to the usual $^4C_1$ conformation behave very interestingly [244,245] forming complexes CuL, CuL_2, $Cu(L\text{-}H)_2$ and $Cu(L\text{-}2H)_2$ (one and two hydroxyl groups of a ligand are deprotonated, respectively) with copper(II) salts. The stability of the formed complexes is decreased in comparison with copper complexes of the usual aminosugars, from hindrance of additional coordination of the metal ion with non-chelate hydroxyl groups owing to the conformational rigidity of the pyranose ring. Based on aminosugars **202a** and **202c** with the vicinal position of the aminogroup in relation to the 1,3-dioxolane ring, the binuclear complexes Cu_2L_4 were isolated [244].







201

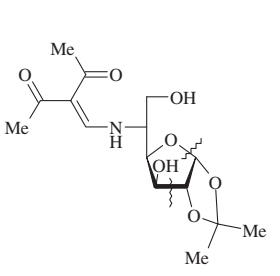
202: $R^1 = NH_2$, $R^2 = H$, $R^3 = R^4 = OH$ (a);
$R^1 = R^4 = OH$, $R^2 = H$, $R^3 = NH_2$ (b);
$R^1 = R^3 = OH$, $R^2 = H$, $R^4 = NH_2$ (c);
$R^1 = H$, $R^2 = NH_2$, $R^3 = R^4 = OH$ (d)

203: R = H,CH_2Fc

Sugar ferrocenyl derivatives **203** together with non-nitrogen analogues have been obtained [246] as potential drugs and catalysts.

Interaction of a primary furanosyl amine with 3-ethoxymethylene-2,4-pentanedione led [247] to an oxoenamine ligand **204** which gave two copper complexes, one of which had a dinuclear structure **205** according to X-ray diffraction investigations. An analogous pyranoside ligand gave a trinuclear copper(II) complex from insertion

of copper acetate monomer in a dinuclear compound similar to **205** [247]. This work shows both the possibility of enlargement of the coordination capability of the primary amino group and the influence of a sugar moiety on the structure of a complex.



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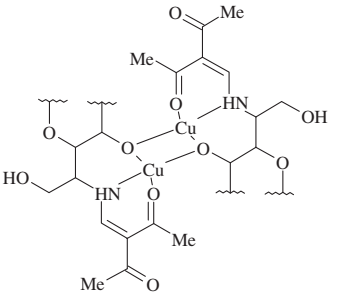

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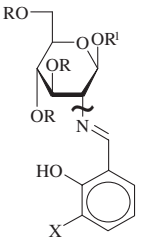
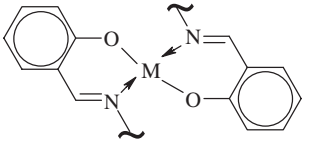
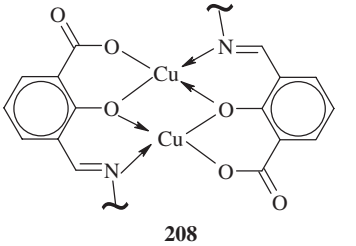


206: R = Ac, R^1 = Me, X = H (a);
R = R^1 = X = H (b);
R = Ac, R^1 = Me, X = CO_2H (c)

The formation of Schiff bases as useful ligands is a better known mode of derivatization of primary amines. The pioneering work of Adam and Hall [248,249] dealt with Schiff bases **206a**–**c** of acetylated D-glucosamine which gave metal complexes **207** as normal bis-chelates; a carboxyl derivative **206c** gave a dinuclear bridge complex **208** with Cu(II) [249]. In the case of unprotected D-glucosamine **198a**, monochelates with Ni(II) and VO(II) were also formed [250].

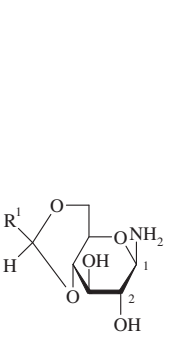


207: M = Cu(II), Zn(II), Co(II), VO(II)

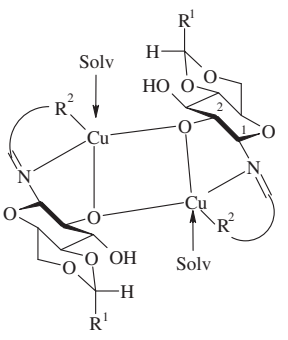


208

Schiff bases obtained from acetalated glucosylamines **209** gave [251] dinuclear 3D copper(II) complexes **210** with participation of the hydroxyl group at C(2) in complexation. The Cu(II) exhibits square-pyramidal geometry with solvent occuping an axial position. An unusual tetranuclear copper(II) complex **211** obtained from a Schiff base **212** with a cyclic polyol chain has similar characteristics of copper(II) [252]. Hydroxyls at C(3) or C(4) play the role of the solvent molecules in the preceding case. Complex **211** has a central core formed by an eight-membered $[Cu_4L_4]$ ring in a boat-like conformation. The phenyl rings and the polyol chains alternately project from the core in all directions, imparting a globular shape to the molecule. Structures **210** and **211** are additionally stabilized by intramolecular hydrogen bonds between sugar hydroxyls [251,252]. The examples cited show a strong dependence of the sugar Schiff-base complex structure on the structure of the sugar ligand.

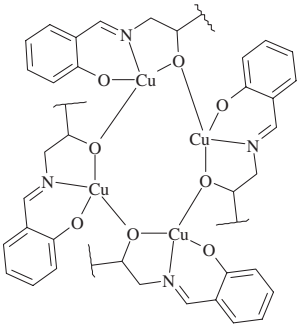


209

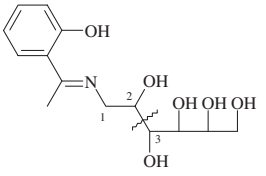


210

$R^1 = CH_3$, $CH_3CH_2CH_2$-; R^2 - salicylaldehyde or 1-hydroxy-2-naphthaldehyde rest;
Solv = MeOH, Py, DMSO

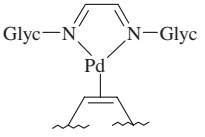


211



212

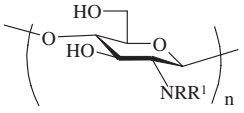
Interesting mixed-ligand complexes **213** of zero-valent palladium have been prepared [253] from bis-azomethines.



213

Glyc = per-O-acetyl-β-D-glucopyranoside;

= E-dimethyl fumarate, E-fumarodonitrile and maleic anhydride

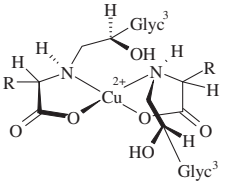


214: R = R^1 = H (a);
R = $-CH_2CO_2^-$, R^1 = H (b);
R = R^1 = -C(S)S- (c);
80: R = CH_2COOH, R^1 = H

The only nitrogen-containing polysaccharide, chitozan **214a**, obtained by N-deacetylation of the biopolymer chitin was the object of several investigations as a ligand together with its derivatives. The chitozan **214a** absorbs many d-metal cations including uranyl [254]. A Schiff base of chitozan was reduced to an amine [255]. Both derivatives proved to be excellent complexones of Cu^{2+} [255]. Chitozan glyoxylate was used [256] for preparing a Schiff base, *N*-(carboxymethylene)chitozan, which, when transformed into salt **214b** of a carboxymethyl derivative **80**, absorbed many metal

ions [256]. The respective acid **80** possesses the same properties [257]. Chitozan dithiocarbamate **214c** coordinates the Cu^{2+} cation in a 1 : 1 ratio respective to a monomeric unit [258].

Complex formation [67,259,260] of *N*-glycosylaminocarboxylate **61** [105,106] with Cu(II), Co(II) and Ni(II) has been studied in detail. On the basis of UV and circular dichroism spectroscopy as well as magnetochemical data, the Cu(II) complexes possess a bis-chelate structure **215**, while in Ni(II) and Co(II) complexes additional coordination through the hydroxyl group at C(5) takes place forming structure **216** (structures with the D-configuration of α-amino acid fragments of a ligand are pictured).



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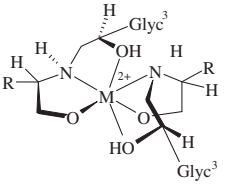
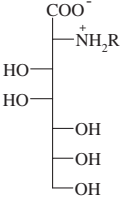


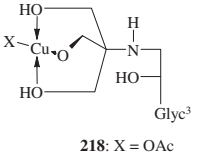
216: M = Ni, Co



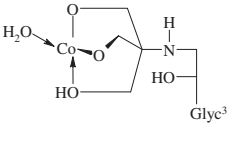
217

Complexes of synthetic α-amino acid derivatives **217** with Zn(II) or Cu(II) have [261] a 1 : 2 metal-to-ligand ratio, and octahedral coordination occurs through the nitrogen atom of the amino group and oxygen atoms of the bridging carboxyl group.

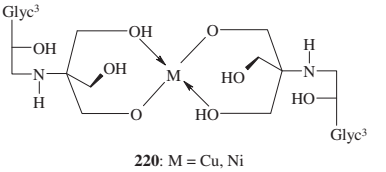
Coordination of ligand **60** depends on the basicity of the medium [104]. The monoligand complexes **218** and **219** with corresponding metal acetates are formed in basic medium and bis-carbohydrate complexes **220** are formed in neutral medium.



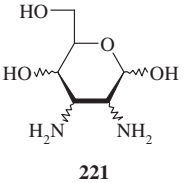
218: X = OAc



219



220: M = Cu, Ni

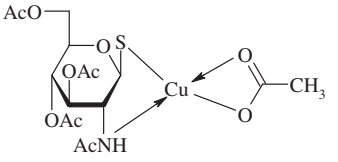


221

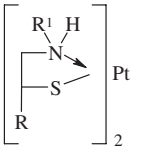
For the synthetic diaminosugars **221** formation of planar *bis*-carbohydrate complexes NiL_2 is typical [262]; monocarbohydrate complexes $PtLCl_2$ have also been reported [263]. Both amino groups are coordinated in the examined complexes.

Other Nitrogen-containing Sugars

Coordination compounds of thioaminosugars with proposed structures **222** [264] and **223** [265] have been reported.

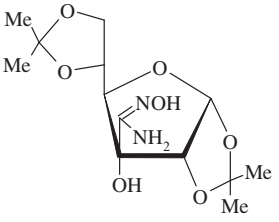


222

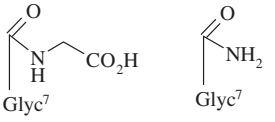


223: R - acetalated sugar moiety; R^1 = n-Pr, n-Bu

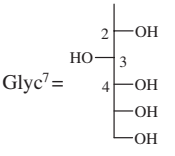
The platinum(II) complex with the amidoxime derivative **224**, similar to known platinum blue complexes, is formed only in the presence of oxidants, in particular molecular oxygen from air, and is paramagnetic (its structure is unknown) [266].



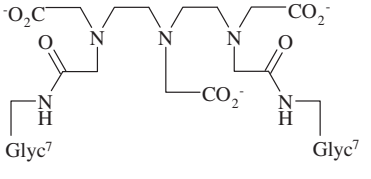
224



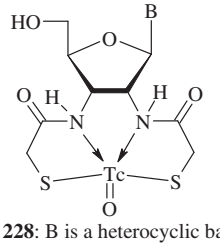
225 **226**



Complex formation of *N*-gluconylglycine **225** with Cu(II) at physiological pH is an extremely complicated process [267] with participation of deprotonated amide and neighboring hydroxyl groups. As a result, the mononuclear CuL and CuL_2 and dinuclear M_2L_2 complexes are formed. Gd(III) and Mn(II) coordination with D-glucosamide derivatives **226** takes place [268] through neighboring hydroxyl groups at C(2), C(3) and C(4) in *ax-eq-ax* orientation, i.e., according to the first Angyal rule [14]. On the contrary, the Nd^{3+} ion in the amide complexone **227** is coordinated only through the nitrogen-containing fragment [269].

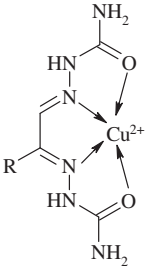


227

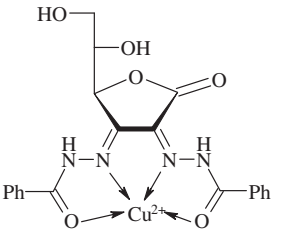


228: B is a heterocyclic base

The technetium(IV) complex **228** with synthetic nucleoside thiodiamide has been described [270]. Copper complexes of aldose carbamoylosazones and substituted dihydrazones of dehydroascorbic acid with proposed structures **229** [271] and **230** [272], respectively, have been obtained.



229: R is an acyclic sugar moiety



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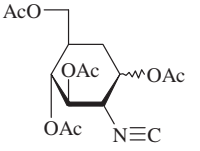
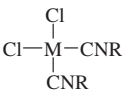
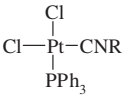


231 (CNR)

Various complexes **232**–**237** were synthesized starting from carbohydrate isocyanide **231**; complexes **233** and **235** can add isocyanide ligands, as well as amines and alcohols, forming carbene complexes of type **238** [273].



232: M = Pd, Pt



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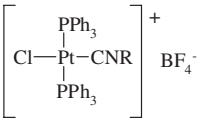

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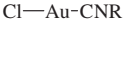

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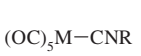
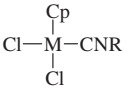
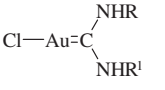


236a: M = Cr, W

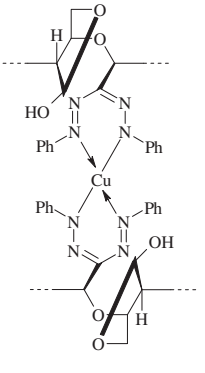


237: M = Rh, Ir



238: R - is a sugar moiety; R^1 = t-Bu, Ph

The formazanes of the products of periodate oxidation of polysaccharides readily form [274] stable polymeric complexes of type **239** with heavy metal salts.



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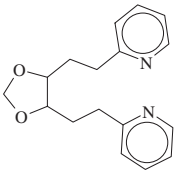

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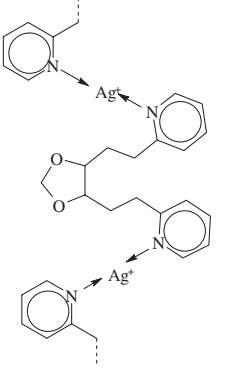
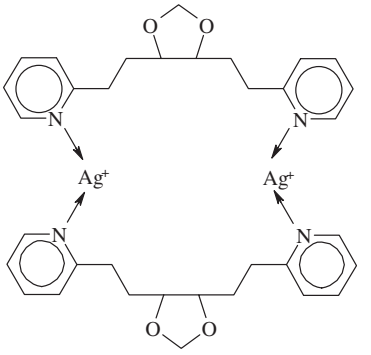


241

The tartaric acid derivative **240** possesses unusual complexing properties. As a result of its reaction with silver triflate, the polymeric complex **241** was isolated [275] in helical form; the derivative **240** of D-tartaric acid forms a right helix and the derivative of L-tartaric acid forms a left helix. The products are representatives of supramolecular

polymeric complexes, helicates [276]. Derivative **240** of the racemic acid gave in this case the cyclic dimer **242** [275].

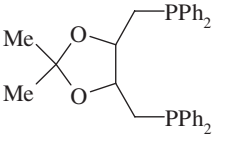


242

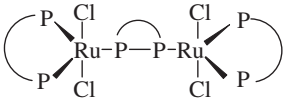
COMPLEXATION OF d-METAL CATIONS WITH PHOSPHORUS-, SULFUR- AND SELENIUM-CONTAINING CARBOHYDRATE DERIVATIVES

Wilkinson's discovery of chlorotris(triphenylphosphine)rhodium(I) as an efficient catalyst of homogenous low-temperature and low-pressure hydrogenation reactions [277] was followed by numerous publications devoted to molecular design and application of such catalysts including enantioselective ones. A chiral pool of catalysts is, in particular represented by sugar phosphines **20**, phosphinites **21**, alkyl phosphates **22** and amidophosphites **23** (see section General Types of Synthetically Modified Monosaccharides Used as Ligands or their Precursors), whose syntheses have been developed [278–282] for such a reaction. The respective complexes are obtained as a rule *in situ* with the exception of some examples described here.

The most popular sugar diphosphine ligand is derivative **243** of D- or L-tartaric acid, DIOP, which gave the complex compounds [283] $H_4Ru_4(CO)_8[(-)\text{-DIOP}]_2$ and $Ru(CO)_{28}$ $[(-)\text{-DIOP}]_3$ as well as the complex [284,285] with proposed structure **244** (one of the possible structures). The rhodium complex of the ligand in solution has the structure [(DIOP)RhCl] [286].

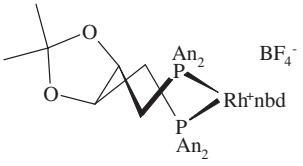


243- DIOP = (P⌒P)

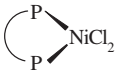


244

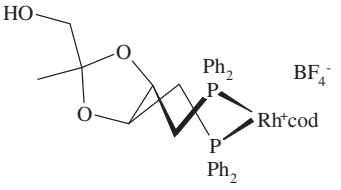
The rhodium complex **245** [287] of the anisyl analogue of DIOP and nickel(II) DIOP complex **246** [288] were also reported together with the hydroxyDIOP complex **247** [289].



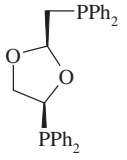
245: An = C_6H_4OMe-o; nbd = norbornadiene



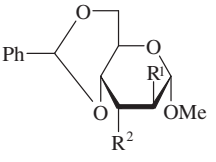
246



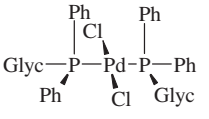
247: cod = 1,5-cyclooctadiene



248 - DIOXOP



249: $R^1 = PPh_2$, $R^2 = OH$ (a); $R^1 = OH$, $R^2 = PPh_2$ (b)

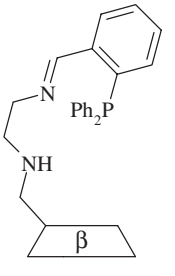


250: Glyc is carbohydrate moiety of the ligand **249b**

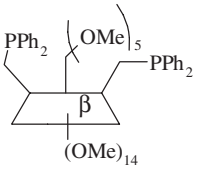
Another known diphosphine ligand is the derivative of 1,6-anhydro-D-glucose, DIOXOP **248**, whose complex $[(DIOXOP)Rh^+cod]ClO_4^-$ [290,291] probably has a coordination unit similar to **245**.

A series of metal complexes was obtained on the basis of monophosphine ligands, e.g., compounds **249a**,**b**. Complex **250** was formed [292] as a result of interaction of the phosphine **249b** with $[PdCl_2(MeCN)_2]$. Also, a series of gold(I) coordination compounds of general formula [AuLX], where L = **249a**,**b**, X = Cl, pyridine-2-thiol, 2-mercaptobenzimidazole [293] or 1-*H*-pyrimidine-2-thione, 3,5-dimethyl-1-*H*-pyrimidine-2-thione, was isolated [294].

In the cyclodextrine series this type of ligand is represented by phosphine derivatives **251** [295] and **252** [296] together with the respective complexes $[MCl(L^1)]Cl$, $[Pd(\eta^3\text{-}C_3H_5)(L^1)]Cl$ (L^1=**251**) [195], $[PtCl_2L^2]$ and $[Rh(cod)(L^2)]BF_4$ (L^2=**252**) [296].

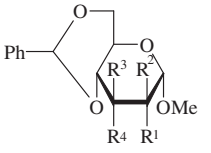


251

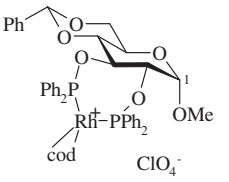


252

Synthetically more available sugar diphosphinites of the type **253a**,**b** are useful chiral ligands for construction of chiroselective catalysts. The chelates $[LRh^+cod]ClO_4^-$ (L = **253a**,**b**) [297] with structures of the type **254** (L = **253a**) [298] and analogous complexes [299–302] with deblocked ligands bearing varying substituents at the glycosydic center C(1) and with the same configuration are also known.

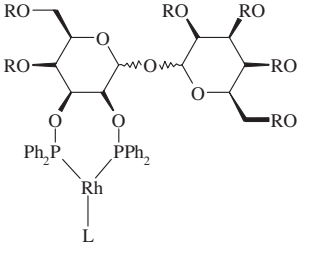


253: $R^1 = R^3 = OPPh_2$, $R^2 = R^4 = H$ (a);
$R^1 = R^3 = H$, $R^2 = R^4 = OPPh_2$ (b)

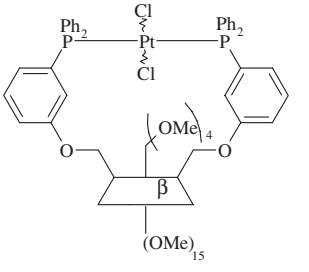


254

Disaccharide diphosphinite complexes **255**, prepared from α,α- or β,β-tregalose, were used to catalyze chiroselective hydrogenation reactions (*ee* up to 99%) [303–306].



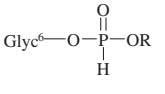
255: L = cod, nbd; R = H, Me



256

Cyclodextrine complex mixture **256** was successfully separated [307] into *cis*- and *trans*-isomers.

Metal complexes of sugar phosphites have also been studied. Thus, using the hydrophosphites **257** and **258** as ligands (they exist as two diastereomers at the phosphorus atom) the complexes L_2PdCl_2 (L = **257**) were obtained [308,309] which have structure **259** [310] and (η^3-C_3H_5)PdLCl (L = **258**), respectively. Similar coordination compounds are also formed from cyclophosphites **260a**,**b** (mixture of diastereomers at the phosphorus atom) [311].



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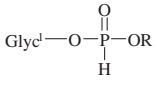
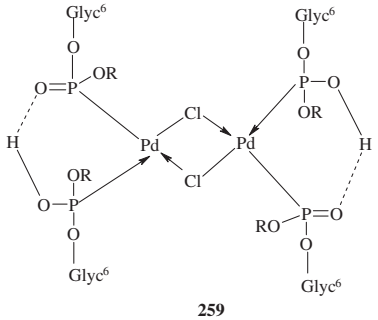
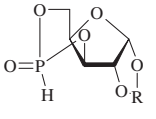


258

R = Et, Pr, i-Pr



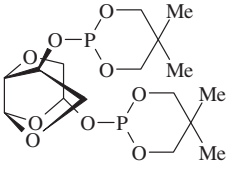
259



260: R = i-Pr (a), Ch (b)

Treating the phosphate $(Glyc^1O)_3P$ with Cu(CO)Cl, the tetramer $\{CuCl[P(OGlyc^1)_3]\}_4$ with a cubic structure was formed [312]. The derivative of 1,4 : 3,6-dianhydro-D-mannitol, dicycliphosphite **261**, reacted with $Pt(cod)Cl_2$ to give [282,313] the complex L_2PtCl_2 (L = **261**).

Complex formation with bicyclophosphites **262**–**265a**,**b** has been studied in detail. The complexes [LCuX] (L = **262** [314], **264** [315] and **265a**,**b** [316,317], X=Br, I) exist as tetramers of type **266** [318] in the solid state. Rhodium complexes [LRh(acac)] (acac = acetylacetone, L = **263** [317,319], **264** [315] and **265a**,**b** [316,320]) are represented by structure **267** [320]. A complex $[(\eta^3\text{-}C_3H_5)PdLCl]$ (L = **265**) was also isolated [316].



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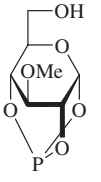

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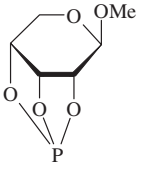

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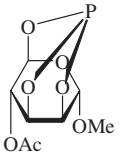

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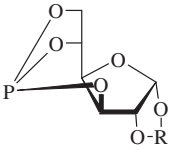
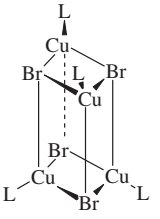
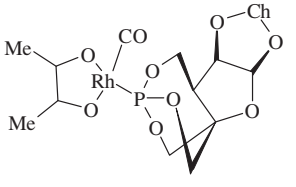


265: R = i-Pr (a), Ch (b), $CHCCl_3$ (c)



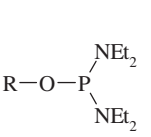
266



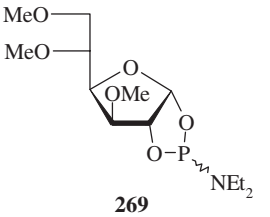
267

In a pentacarbonyl complex $LCr(CO)_5$ (L = **265a**), the chromium atom is surrounded [318] by a distorted octahedron formed by five carbonyl groups and one sugar ligand coordinated through the phosphorus atom. In L_2PtCl_2 (L = **265a**,**c**) the sugar ligands are *cis* [318].

Sugar amidophosphites are also included in the research on coordination interactions. Complexes $(\eta^3\text{-}C_3H_5)Pd(L)Cl$ and $L_2Rh(CO)Cl$ [321], where L is a diamidophosphite of type **268** (the structures of the complexes were not determined), and $[LCuBr_2]$ [322] of cycloamidophosphite **269** (mixture of diastereomers at the phosphorus atom), in which the ligand is coordinated through the phosphorus atom, have been reported in addition to platinum(II) complexes [323].

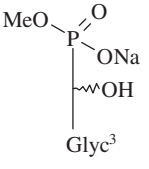


268: R is an acetylated sugar moiety

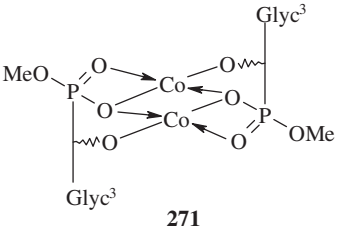


269

Sugar phosphorus(V) compounds are poorly studied as ligands. Only synthesis of the cobalt(II) complex of phosphonate **270** was reported [324] which probably has dimeric structure **271**.



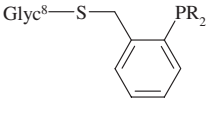
270



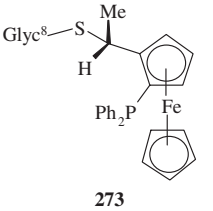
271

Additional information on platinum-group complexes with phosphorus-containing sugars can be found in a review [25].

Chiral sugar ligands **272** and **273** containing phosphorus and sulfur atoms as donor centers became the source of interesting structural and catalytic π-allyl complexes. Ligands **272** afforded complexes of the type **274** [325]; complex **275** was obtained [326] from the ferrocenyl derivative **273**.



272: R = Ph, Ch



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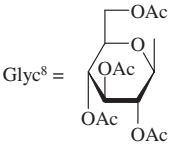

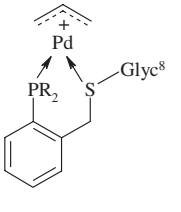

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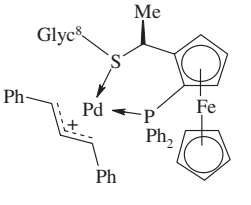
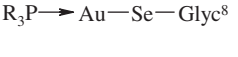
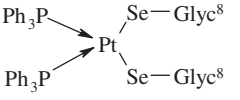


275

Per-*O*-acetylated selenoglucose $Glyc^8SeH$ forms [327] various metal complexes **276**–**280** (one of three possible stereomers, differing in the orientation of the carbohydrate fragments, is presented in the last case).



276: R = Me, Et, Ph



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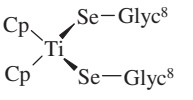

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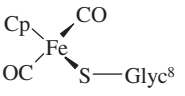

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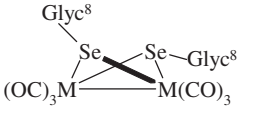
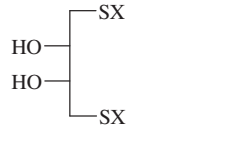
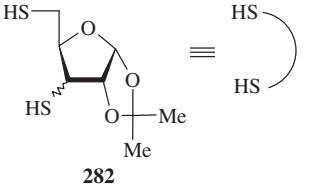


280: M = Fe, Ru

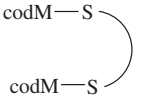
Little information on metal complexes of sugar dithiols is available. Dithiol **281a** forms [328] a mixed complex **281b** of gold(I). Dithiols **282** form [329] analogous complexes **283**. Thioethers **284** behave similarly giving complexes **285** [330]. Synthetically available sugar dithione **286a** reacts with $K_2[PtCl_4]$ to produce complex **286b** [331].



281: X = H (a), $AuPEt_3$ (b)

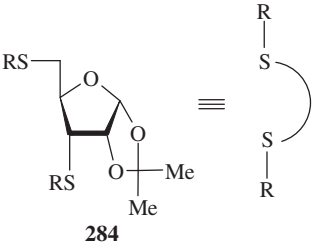


282

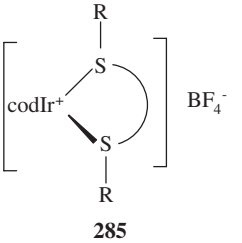


283

M = Rh(I), Rh(II)
Ir(III), Ir(IV)



284



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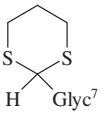
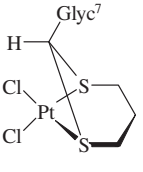
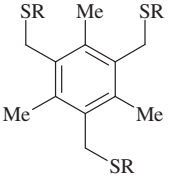


286a



286b



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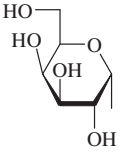
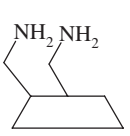
R = 

The first report [332] on the preparation of an $Au_{55}L_4$ cluster (L = **287**) possibly means the advent of sugar coordination nanochemistry.

COMPLEXATION OF d-METAL CATIONS WITH SYNTHETICALLY MODIFIED CYCLODEXTRINS HAVING *N*-CONTAINING MOIETIES

Cyclodextrins are usually not good complexones of metal ions since they bind both cations and anions [14]. Blocking their hydroxyls by alkyl or acyl groups makes them good complexones of s-metal cations (see section Oxygen-containing Ligands). As in the case of carbohydrates, the binding properties of cyclodextrins may be considerably improved by introduction of chelators, mainly the most spread nitrogen-containing ones [333]. This topic required separate consideration.

Interaction of K_2PtCl_4 with 6A,6B-diamino-6A,6B-dideoxy-β-cyclodextrin (CD) **288** produced [334] the complex $PtLCl_2$ in which the platinum is square-planar with two chlorine atoms and two *cis*-amino groups of the ligand. Mono-(6-β-aminoethylamino-6-deoxy)-β-CD **289** was coordinated [335] with the copper complex of the clay mineral montmorillonite with intercalation of the ligand molecules into interlayer areas.



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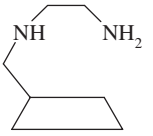

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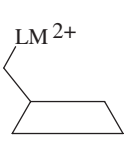
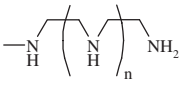
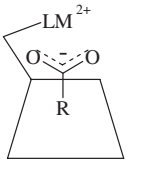


290: L =

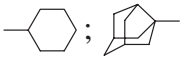


n = 1, 2; M = Cu, Zn, Mg

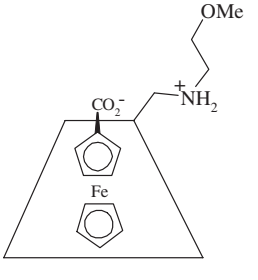
A series of reported data in this area is determined by the ''multirecognition'' concept [336], providing additional stabilization of inclusion complexes with cyclodextrins by the introduction of polar groups into host and guest molecules. Besides the main hydrophobic cavity–guest interaction, additional polar interactions appear. Thus, metal complexes **290** in the modified β-cyclodextrins form [336] inclusion complexes **291** with increased stability due to the double recognition with an additional coordination interaction. An analogous situation takes place in complex **292** [337].



291: R =



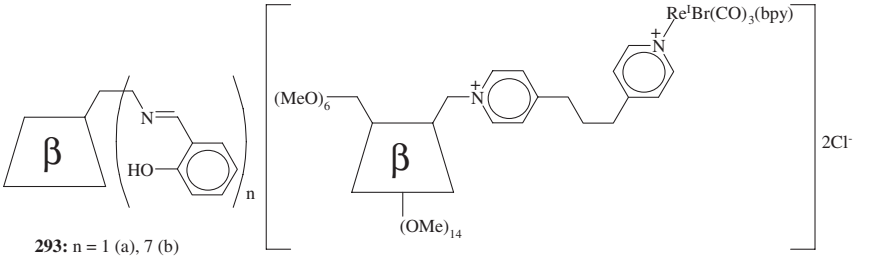
etc.



292

Complex formation of cyclodextrins bearing Schiff-base moieties such as **293a** and **293b** with Cu^{2+} and UO_2^{2+} has been studied [338]. Ligand **293a** formed the chelate

L_2Cu with Cu(II), while compound **293b** leads to chelates LCu_2 in methanol and LCu_3 in the solid phase. On the other hand, UO_2^{2+} in solution formed the chelate $[L(UO_2^{2+})_2]$ with **293a**; **293b** formed the chelate $[LUO_2^{2+}]$.

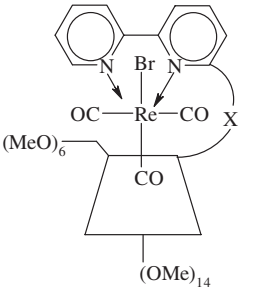


293: n = 1 (a), 7 (b)

294

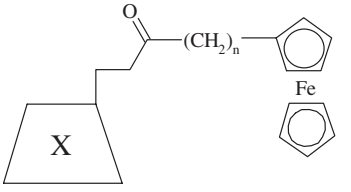
bpy = α,α'-bipyridyl

Similar cyclodextrins (CDs) modified by *bpy* fragments were obtained [339–341] to study energy and electronic interaction between the photoactive fragment and a guest, incapsulated in the cavity of CD on photo-excitation. Thus, luminescence of complex **294** [339], in which the coordination center is far from the cavity of the CD, was cancelled by adding *N*,*N*-diethylaniline, probably by electron transfer from the incapsulated guest to the coordination center, which is permitted by the length of the spacer. In complex **295** [340], the coordination center is over the CD cavity; the complex exists as four equilibrated diastereomers, caused by different orientations of ligands of the metal center relative to the upper plane of the CD molecule. The photophysical and electrochemical properties of similar complexes **296** and **297** with longer spacers were studied in detail [341].



295: X = none

296: X = -CH_2OCH_2-

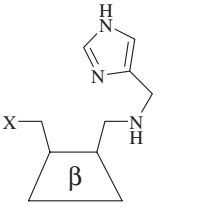


297: X = β-CD, n = 0 (a);
X = β-CD, n = 3 (b);
X = γ-CD, n = 3 (c)

The role of spacer length in complexes of this type follows from the data reported [342], showing that, in complexes **297a**–**c**, the ferrocenyl moiety is included in the CD cavity, i.e., there is no necessity for a longer spacer ($n = 3$).

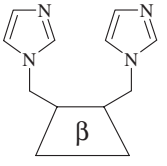
The copper complex of histamino-β-CD **298** possesses an interesting peculiarity [343–346] to distinguish enantiomers of aromatic α-amino acids by preferential incapsulation of their D-enantiomers. Other metal cations enhanced (Ni^{2+}), weakened (Co^{2+}) or annihilated (Zn^{2+}) this effect [346]. Similar properties are probably characteristic

of many other metal complexes of chemically modified cyclodextrins. Thus, metal complexes of 6A-deoxy-6A-hydroxyethylamino-β-CD may also recognize enantiomers of amino acids, especially the Ni(II) complex [347]. Complex formation of dihistamino-β-CD **299** with Cu(II) was studied [348] for simulation of superoxide dismutase (SOD) action. Five main copper complexes were characterized, in which the copper ion is coordinated through four nitrogen atoms of histamine moieties and can be distinguished from each other by the grade of ligand protonation and position of histamine moieties in them. Three of these complexes showed SOD activity, only one order of magnitude below the activity of the native enzyme. Strong incapsulation of polar cyclohexane derivatives by the zinc complex of bisimidazolyl-β-CD **300** has been described in detail [349]. This incapsulation is mainly hydrophobic with polar and coordination contributions.



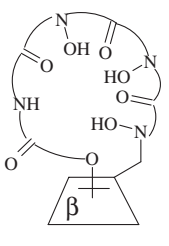
298: X = OH

299: X =



300

Synthetic siderophore **301** [350] is unique, since the Boc protecting group of the coordinating fragment is intramolecularly incapsulated by the β-CD cavity forming a cyclic structure. Structurally more complicated cyclodextrin siderophore **302** formed [357] a highly stable complex with Fe(III) ($K_{stab} \sim 10^{39}$), in which the metal cation is coordinated through three vicinal diol aromatic groupings and becomes an anion Fe^{3-}. Siderophore **302** also formed [351] the complex with Al(III), with *n*-nitrophenolate simultaneously included in the cavity of per-*O*-methylated α-CD.



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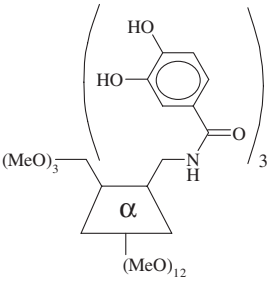

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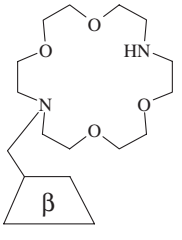
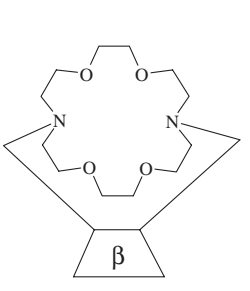


303

Cyclodextrin azacorand **303**, as a receptor with two recognition sites, formed [352] very stable inclusion complexes with *p*-nitrophenolates, in which the cation is incapsulated by the corand fragment and the anion by the cyclodextrin fragment. The complex of compound **303** with Eu(III) possesses [353,354] chemosensor properties, since

the fluorescence of Eu(III) is enhanced when a benzene molecule enters into the CD-fragment cavity. Such a phenomenon is not observed in complex **304** with a more rigid structure [354,355]; the structurally harder complex **305** was proved to be [356] an excellent chemosensor for naphthalene and tetramethylbenzene. Complex **306** of cyclodextrin cyclen with Co(III) showed a 900-fold enhancement [357] of the hydrolysis of esters in comparison with the initial ligand.



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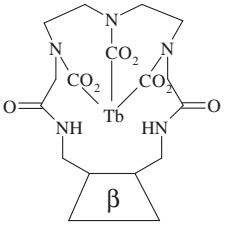

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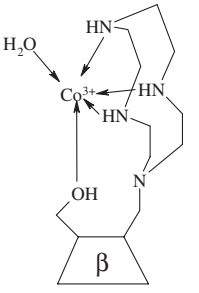
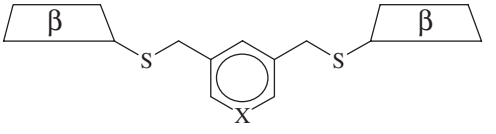


306

For simulation of photosynthesis, the zinc complex of porphyrin-cyclodextrin with the porphyrin fragment as a donor and incapsulated benzoquinone as an acceptor was obtained [358]. As models for ferredoxin, the cyclodextrin cluster of type $[Fe_4S_4(SR)_4]^{2-}$, where R is the β-CD moiety, was synthesized [359,360], together with structurally more complicated clusters of the analogous type [360], which, unlike easily hydrolyzed ferredoxin, are stable in water for many hours.

Modifications with two linked CD molecules are less common. Examples are compounds **307a**,**b**, which are capable [361] of incapsulating a series of bulky metal complexes (metal porphyrins, metal cyclams, other metallated macrocycles). The corresponding inclusion complexes possessed unusually high (ca. 10^6–10^8) stability constants.



307: X = N (a), CH (b)

A dimer containing two β-CD moieties, connected by two en fragments, incapsulated [362] cyclopentadienyltricarbonylmanganese.

PRACTICAL ASPECTS OF SYNTHETICALLY MODIFIED CARBOHYDRATE COMPLEXATION

Modulation of Chemical Properties of Sugars by Complexation

Chemically active complexes of mercury salts with acetohalogenoses are formed as intermediates [363] in the Helferich's preparation of *O*-glycosides. As a result,

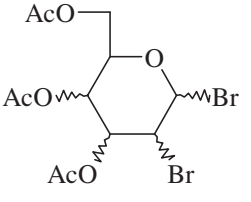
their subsequent interaction with alcohols is facilitated. Analogous complexes were observed in the synthesis of acetohalogenoses by treatment of sugar per-*O*-acetates with titanium tetrachloride [160–162,364] as well as in the preparation of triacetyllevoglucosan from 1,2,3,4-tetra-*O*-acetyl-β-D-glucopyranose in the presence of tin tetrachloride [365]. Oxidation of *O*-alkyl glycosides with chromium trioxide forming *O*-formyl glycosides also includes [366] intermediate complex formation at C(1).

Coordination of synthetically modified carbohydrates is sometimes accompanied by ligand rearrangement. Thus, the Beckmann rearrangement in the presence of d-metal salts [367] was also observed [368] on complexation of ketalated aldoximes with Cu(II). *C*-Glycosylbenzothiazolines (products of condensation of aldoses with *o*-aminobenzenethiol) were easily transformed [369] into the corresponding *N*-glycosides in the presence of mercury salts. For some unsaturated sugars the complexation is accompanied by carbocycle formation [370,371]. The complex formation was also successfully used [96,98,372–378] for preparation of *C*-derivatives of sugars, including intermediates **137** [172] and **143** [176], as well as for obtaining diastereomerically pure tricyclic compounds [379] from carbohydrate templates.

Formation of π-complexes of unsaturated monosaccharides with Hg(II) or Pd(II) led to hydration [380], allyl rearrangement of glycols [381], synthesis of their *C*-derivatives [382], as well as oxyglycol formation from *O*-alkylated or acetalated aldoses with free glycosidic hydroxyl groups [383].

MoO_4^{2-} ions catalyze not only epimerization of aldoses with intermediate formation of substrate metal complexes [14], but also stereoselective hydroxylation of glycols [384,385], oxidative destruction of deoxynitroaldites [386,387] and phenylhydrazones of aldoses [388–390] forming aldoses containing one fewer carbon atoms than the substrates. These reactions were used for preparation of rare sugars [384–390]. Hydrolysis of an *O*-hetaryl glycoside is accelerated ca. 10^5–10^6 times in the presence of Cu(II), Ni(II) or Co(II) salts [391].

Transformations of dibromine derivatives **308** into 2-deoxyglyconic acids **309** in the presence of lead(II) hydroxide (the Danilov–Gakhokidze reaction [392]), as well as similar reactions of protected aldoses with free hydroxyl groups at C(1) and C(2) [393,394], sulfonates of aldoses [395,396] and ketoses [397], and 1-chloroketoses [398,399], are carried out [400,401] supposedly *via* the intermediate coordination of the reagent through substrate hydroxyl groups.



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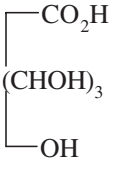
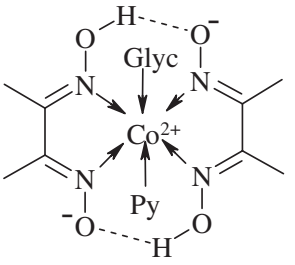


309

C-Glycosylcobaloximes **310** were used [402–406] to synthesize monosaccharide *C*-derivatives; this is a new approach to lengthening the carbon skeleton in monosaccharides. The reaction is based on the transformation of complex **310** into a sugar radical under irradiation by homolytic destruction of the C–Co bond [402].

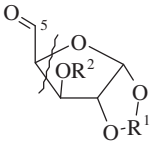


310: Glyc is O-acetylated or acetylated monosaccharide
Py is pyridine

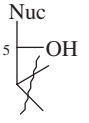
Use of the blocking function of metal complex formation with modified monosaccharides was the basis of effective regioselective O-acylation and O-alkylation of partially protected sugars. To carry it out, copper complexes of type **114** [70, 407–410], mercury(II) [410,411] and tin(IV) complexes of type **96a**,**b** [65,412–415] were employed and allowed also syntheses of oligosaccharides [416,417]. Coordination of a carbohydrate lactone with a Grignard reagent (deprotonator of a hydroxyl group) provides [418] its selective O-mesylation. Regioselective O-alkylation of an acetalated *O*-methyl glycoside in DMSO in the presence of $Ba(OH)_2$ and BaO [419] is probably also caused by intermediate complex formation. O-Alkylation of diacetone-D-mannose (compound of the type $Glyc^4OH$) leads, in general, to β-anomers. In the presence of a crown ether binding Na^+ cations, the α-anomers were mostly formed [420]. This was explained by intermediate coordination of Na^+ ion through four acetal oxygen atoms and a deprotonated β hydroxyl group at C(1). In the first case, i.e., the β-anomer of diacetone-D-mannose is a pseudo-podand (see section Nitrogen-containing Ligands). The pseudo-podand properties of dicyclohexylidene-D-mannose $Glyc^4OH$ have been further confirmed experimentally [421].

The coordinative properties of carbohydrate aldehydic forms promote stereoselective reactions with organometallic reagents under chelate control [281,422–426]. Thus, as a result of the interaction of aldehydic forms **311a**–**c** with Grignard reagents, epimers **312** with the L-configuration at C(5) predominate [423,424]. This was explained [423,424] by formation of intermediate **313**, in which the attack of the nucleophile on the carbonyl group is facilitated from the side opposite to the position of OR^2. This proposal was confirmed [424] by a decrease of stereoselectivity in the series **311c**, **311b**, **311a**. However, the Reformatsky reaction with analogous aldehydic forms **311d**,**e** proceeded [427] with preponderant formation of the (D)-C(5)-epimer **314**, as well as the Ivanov reaction [428].

The results obtained are probably conditioned [428,429] by another direction of the coordination of aldehydic forms with these organometallic reagents. An alternative explanation [99] supposes non-chelate control of the reaction with conformation of the substrate, in which the carbonyl group and hydrogen atom at C(4) are in the same plane resulted in the same direction of reagent's attack as in **313**. The above situation is caused by charge delocalization of type **315** in the Ivanov and Reformatsky reagents and, as a consequence, by a lower stability of complex **313**.



311: R^1 = i-Pr, R^2 = H (a);
R^1 = i-Pr, R^2 = Me (b);
R^1 = i-Pr, R^2 = CH_2Ph (c);
R^1 = Ch, R^2 = Me (d);
R^1 = Ch, R^2 = CH_2Ph (e)



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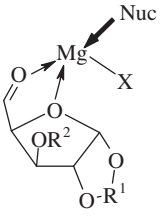
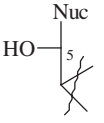
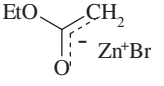


313

Nuc = Me, Ph; X = Cl, Br

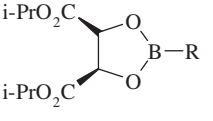


314: Nuc = CH_2CO_2Et, $CH(Ar)CO_2H$

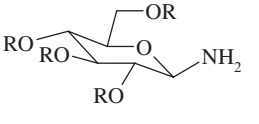


315

Other examples of stereoselective carbohydrate reactions under chelate control are those that use titanates of type **121** as promoters in aldol-like reactions [430–433], C-allylation of *O*-alkylated *O*-glycosides with allyltrimethylsilane in the presence of titanium tetrachloride [434] and Diels–Alder reactions with unsaturated esters of substituted monosaccharides in the presence of $TiCl_4$ [433,435]. Carbohydrate organoborane reagents of type **316** react with aldehydes also under chelate control [436–439], as well as the addition of organoaluminium reagents to α,β-unsaturated acetals of amides of tartaric acids [440]. The following processes are also chelate-controlled stereoselective carbohydrate reactions: stereoselective reduction of dithioacetals of carbohydrate ketenes with lithium alumodeuteride [441], nucleophilic addition of organometallic reagents to aldehydic forms [442], and as C-alkylation of aldehydic forms with phenolates [443].



316: R =



317: R = Me, Et, i-Bu, CH_2Ph,

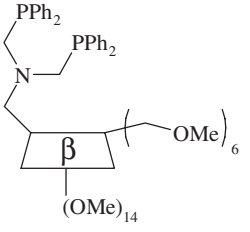
Stereoselective transformations of glycopyranosyl amines of type **317**, including the Strecker reaction [433,444–446], the Ugi reaction [433,446–449] and similar processes [433,450–452], take place in the presence of zinc chloride probably under chelate control [443,444,450,451].

Organic Reactions Modulated by Complexation

For these reactions, the fact that modified carbohydrates are diastereomerically pure chiral compounds is taken into account. Thus, d-metal complexes of types **117**, **118**,

244, **250**, **254** are widely used both after preliminary isolation and *in situ* during homogeneous enantioselective catalysis of such reactions as hydrogenation [298,300, 453–460], hydroformylation [208,456,461,462], epoxidation by Sharpless [79,80,463], hydrocarbonylation [456,458,464,465], hydrosilylation [456,458,465], interaction of organometallic reagents with alkyl halides (coupling reactions) [456,466], and isomerization of functionalized olefins [280,456]. Enantiomeric excesses (*ee*) in the majority of reactions are higher than 80%, reaching 100% in hydrogenation. However, many of these catalysts are too expensive for industrial application, so the search for cheaper catalysts is important. Sugar phosphinites also proved to be excellent catalysts for asymmetric hydrogenation [468–470] as well as asymmetric allylic alkylation [471]. Catalysts with C_2 symmetry are the most effective [472].

Rhodium complexes of modified β-cyclodextrins **318** and **319** are [473] highly substrate-selective supramolecular catalysts for hydrogenation and hydroformylation processes.



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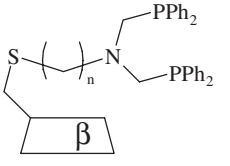


319: n = 2 - 4

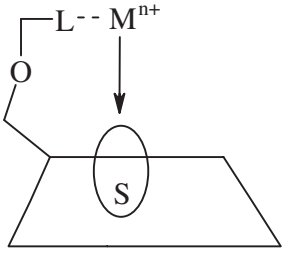
Rhodium complexes of mono- and disaccharide phosphinites such as **253a**,**b** have shown [474] high enantioselective catalytic activity in hydrocyanation of vinylarenes with *ee*s up to 85%. The same metal complex of a phosphinite cellulose derivative catalyzes hydrogenation with *ee*s of only 28% [475]. An analogous complex of DIOP (**243**) suspended on polystyrene as an achiral carrier was very efficient in the enantioselective hydrosilylation of ketones [475]. Using the rhodium complex of a co-polymer of oxyethylated methacrylate and *p*-styrene-DIOP, hydrogenation of prochiral precursors of aminoacids led to the same *ee* and the same absolute configurations of the products as homogeneous rhodium complexes with DIOP. Insertion of an additional chiral center into this complex has little influence on the *ee* [475].

Phase-transfer catalysis (PTC) [476], which is widely used in organic chemistry, has become popular in carbohydrate synthesis [34,477]; many carbohydrate s-metal complexones are excellent catalysts for PTC, including enantioselective ones. In addition to the pseudo-podand Glyc^{4}OH, PTC activity is typical for penta-O-benzyl-D-glucose [478] and aza-pseudo-podands **56–60**, **62**, **66–68** [99,421]. Among carbohydrate podands, such catalysts are the tetrapodand **30** [479], octapodands from sucrose [480], and ethyleneoxide polymers of sucrose [481]. Regiomeric mixtures **32**, **33** and podands **31**, however, showed weak PTC activity [99,421].

The diastereomeric purity of carbohydrate s-metal complexones allows their use as enantioselective phase transfer catalysts. Indeed, the pseudopodands **56** and **74** in PTC-borohydride reduction of prochiral ketone (acetophenone) showed *ee*s of 17 and 14% for coronands **94** and **95**, 48 and 20%, respectively [382]. Carbohydrate

corands based on enantiomerically pure tartaric acids were in this case weak enantioselective PT catalysts [383].

When PTC Michael addition was performed in the presence of corands based on D-tartaric acid [484], monosaccharides [485], and disaccharides [83,84], *ee*s of 16–70% were registered. Metal complexes of modified CDs, combining the properties of a metal complex and a phase-transfer agent with capacity for molecular recognition, are [486,487] effective supramolecular PT catalysts for hydroxylation of aromatic compounds and Wacker oxidation (transformation of terminal olefins into terminal ketones). Such catalysts provide simultaneous complexation of the substrate with both the metal center and the hydrophobic cavity of the CD (double recognition) according to the following scheme:



L is a ligand (pyrocatechol, en, polyethylene oxide);
S is a substrate

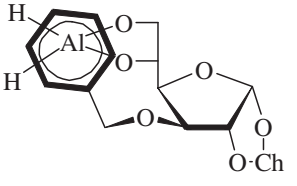
Scheme 1

Copper complexes of ligands similar to **204** are efficient catalysts in catechol oxidation [488].

An outstanding achievement in the area of practical enantioselective homogeneous catalysis by metal complexes of modified carbohydrates was the epoxidation of allyl alcohols by Sharpless [78–81] with very high (60–98%) *ee*, which allowed, in particular, a total synthesis of D- and L-hexoses [489,490]. Polymer Sharpless catalysts are also known, giving, however, reduced (up to 60%) *ee*s [491]. Enantioselective epoxidation was also carried out [492,493] in the presence of metal-porphyrin catalysts with protected monosaccharide fragments on the molecule periphery.

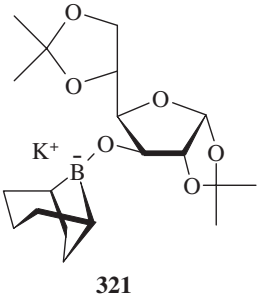
Titanium complexes of type **120** (so-called Ti-TADDOLates) proved to be not only chiral nucleophilic reagents in stereoselective organometallic reactions [148–150] but also stereoselective catalysts of Diels–Alder reactions [494–496] with *ee*s up to 92% as well as in dialkylzinc addition to aldehydes [497] with *ee*s up to 99%. Polymer-supported ligands and metal complexes of this type have been used in asymmetric hydrogenation and hydroformylation [498] as well as Diels–Alder reactions [499,500]. Much attention has been paid to the synthesis of dendrimeric Ti-TADDOLates as recoverable catalysts having outstanding catalytic activity [501–503]. Immobilization of chiral transition metal complexes on ordered mesoporous and microporous molecular sieves as inorganic matrices was also studied intensively to obtain recoverable stereoselective catalysts with enhanced mechanical and thermal stability [504].

Intensive studies have been carried out on applications of equimolar and higher quantities of metal complexes of modified carbohydrates in enantioselective organic syntheses. Ketalated monosaccharides were used for reduction by $LiAlH_4$ of prochiral ketones [505–508], ketoximes [508,509], Schiff bases [510,511], β-allyl alcohols [512], and acetylenic alcohols [513] with *ee*s 3–80%. 3-*O*-benzyl-1,2-*O*-cyclohexylidene-α-D-glucofuranose was found to be the best chiral additive. Formation of complex **320**, providing enantiodifferentiation [507], was demonstrated [506], indicating the possible formation of metal complexes with other chiral additives. Use of 1,4 : 3,6-dianhydro-D-mannitol and 1,3 : 4,6-di-*O*-benzylidene-D-mannitol as chiral additives gave a very low (1.5–4%) *ee* [514], but symmetric branched-chain ketalated alditols increased it a little [515].



320

Reduction of prochiral ketones with sodium borohydride in the presence of analogous ketalated monosaccharides [516–519] or dianhydroalditols [519,520] proceeds with moderate to high *ee* (83%). Analogous reaction of complexes of C-acylated ferrocenes and CD with sodium borohydride under the same conditions gave analogous results ($ee \leq 84\%$) [521]. However, the best *ee* (up to 100%) were obtained [522–525] in the case of chiral organoborane **321**.



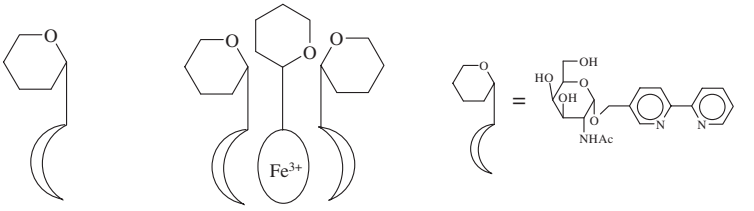
321

Other stereodifferentiating reactions with chiral monosaccharide additives have been also studied. Derivatives of D- and L-tartaric acids gave only moderate *ee*s (up to 40%) in the case of addition of butyllithium to aldehydes, even at 10-fold excess of the additive [526]. Titanium complexes of ligands of type **120** were used [81–83,527–529] as nucleophilic reagents of enantioselective addition to the carbonyl group with moderate *ee*. Diastereoselective Diels–Alder reactions were promoted by these complexes with *ee*s 44–92% [530,531]. Osmium tetraoxide, coordinated with chiral diamines from L-tartaric acid, oxidized olefins diastereoselectively with *ee*s 34–90% [532]. The C-allylation product (exchange of Cl to allyl) of complex **121** reacts with aldehydes, giving *ee*s 85–93% [91].

Among other applications of metal complexes of modified carbohydrates, not related to their chirality, the use of the palladium complex of chitozan **214a** as a hydrogenation catalyst [533], the cluster $[Pt_{15}(CO)_{30}]$, connected with the anionite based on sephadex, as a water-soluble hydrogenation catalyst for soft reduction of biomolecules [534], and initiation of vinyl polymerization by copper complexes of chitozan [535] and its glycol derivative [536] should all be noted.

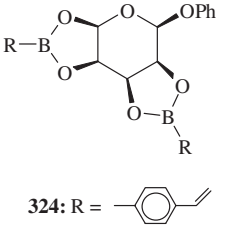
Mimics of Biological Structures by Complexation

The role of metal complexes of modified carbohydrates in biomimetic chemistry is considerable. The simplest case is the self-assembly of biostructures by binding three ligand **322** molecules into complex **323** owing to interaction with Fe(III) [537].

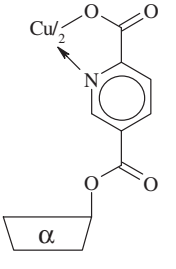


322 **323**

An unusual approach for modelling enzymes and antibodies (molecular imprinting) consists [538,539] in a radical-initiated polymerization of diboronates of type **324** with a large quantity of an achiral bifunctional cross-linking agent. The polymer formed is then treated with water; the boronate protecting groups are eliminated by hydrolysis; the resulting free sugar is washed away from the copolymer, forming chiral cavities within it. Such a polymer resolves the racemate of *O*-phenylmannopyranoside. Inserting analogous fragments into [60]-fullerene forms chiral cavities on its surface [540].



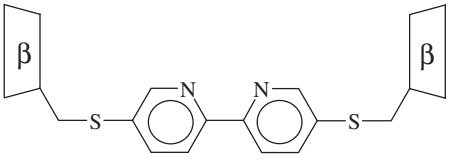
324: R =



325

However, in the majority of investigations on biostructure modelling, cyclodextrins modified with chelators are used. These compounds are synthetic siderophores [350,351] and ferredoxins [359,360] (see section Complexation of d-Metal Cations with Synthetically Modified Cyclodextrins having *N*-containing Moieties), as well as enzyme models (synzymes), designed for multiple recognition [336,349,541–545] (Scheme 1). Metal complex **325** was the first synzyme capable of hydrolyzing *n*-nitrophenylacetate four times faster than a non-catalytic process. Changing Cu(II)

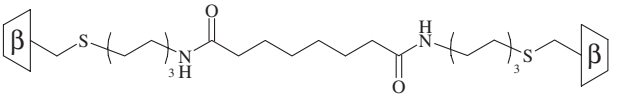
for Ni(II) and introduction of the second chelator (pyridinecarboxaldoxime), increased the hydrolysis rate 10^3 times [544–546]. Higher acceleration (10^4 times) was registered [544,547,548] in the case of the copper complex of dimer **326**; the La(III) complex of this compound [549] is a catalyst in the hydrolysis of phosphate groups (model of ribonucleases). The zinc complex of compound **207** ($n = 1$, M = Zn) possesses analogous activity [549,550]. Superoxidedismutase activity was observed in the case of copper complexes of derivatives **288** [551], **298** [344,552] and **300** [348].



326

The zinc complex of bis(histamino)-β-CD **299** incapsulates and hydrates carbon dioxide, i.e., it mimics carbonic anhydrase [541,553,554]. The aluminum complex of pyridoxal grafted to β-CD mimics tryptophan synthase [554,555]. The Fe(III) complex with bis(6-*O*-carbonylbenzenesulphonyl)-β-CD shows oxidoreductase activity [556]. Cobalamin, grafted on β-CD, carried out [557] a radical rupture of a substrate incapsulated in the β-CD cavity, thus imitating the first step of the transfer of alkyl groups *in vivo*.

Using modified CD other biostructures can be also modelled. Thus, the zinc complex of porphyrin linked to β-CD carries out electron transfer from the porphyrin fragment to incapsulated benzoquinone imitating one of the steps of photosynthesis [358]. CDs modified by long coordinative fragments can serve as artificial ionic channels, for example **327** (which transports Co^{2+} and Cu^{2+} with a rate higher than the standard 18-azacrown-*N*-6 [558]) and **328** [559] (channel of the ''bouquet'' type [276]).



327

328

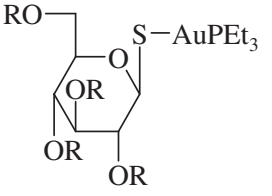
The heme molecule, attached to α-CD, binds oxygen reversibly in aqueous medium [560,561].

Use of Metal Complexes in Medicine

In continuation of the synthesis and application of low-toxicity anticancer platinum complexes, a series of Pt(II) complexes with diaminosugars of type **221** was prepared [262,562]; these compounds possess high antitumor activity. At present, a cancer

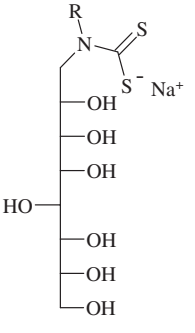
therapy is being developed based on irradiation generated by the capture of thermal neutrons by various nuclides; among them, a non-radioactive ^{10}B is especially effective. To obtain compounds capable of being inserted into tumors, in particular, the products of addition of decaborane to thiosugars were synthesized [563].

In chryzotherapy of rheumatoid polyarthritis gold-containing complexes are used [564,565], auropofin **329a** and solganol **329b**.

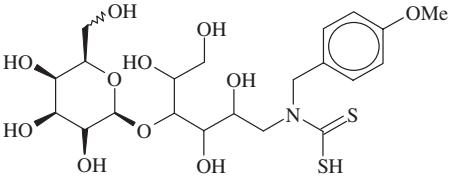


329: R = Ac (a), H (b)

Cd(II) is effectively removed from the organism with ligands **330** [566] and **331** [567].

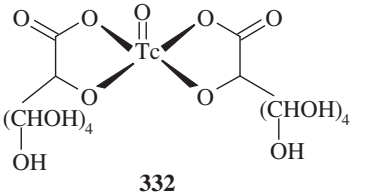


330: R = Me, Et



331

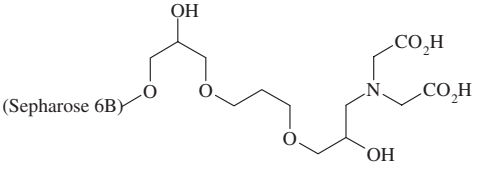
A technetium complex with proposed structure **332** is used [568] for imaging kidney and brain damage and to assess renal and brain perfusion.



332

Also, the use of paramagnetic metal complexes of modified polysaccharides as contrast agents for magnetic resonance imaging for decrease of spin relaxation T_1 and T_2 of water protons in tissues should be noted. The first contrast agents [569] of such a type were complexes of polymer **333** with Cu(II), Mn(II), Fe(III) and Gd(III), which are better than metal complexes of similarly derivatized polystyrene. Mn(II) and Gd(III) complexes with the following ligands were offered [570]: hydroxypropylstarch, dextran, inulin,

carboxymethyldextran, dextran-phosphate, ficoll (copolymer of sucrose and epichlorohydrin), aminoethyldextran, carboxymethylcellulose, as well as the above polysaccharides after grafting with strong chelators of the type of ethylenediaminepentaacetic acid. All are considerably better than low-molecular analogues, but worse than corresponding complexes with proteins [570]. A biodegradable contrast agent [Gd(III) with diethylenetriaminepentaacetic acid, grafted on starch, cross-linked with epichlorohydrin] was reported [571]. Other good contrast agents are [572] Gd(III) complexes with *N*-[2-bis(carboxymethyl)aminoethyl]-*N*-[2-bis(carboxymethyl)amino-(2-benzyl)ethyl]-glycine and 10-[*N*-(2-aminoethyl)carbamoyl]methyl-α,α′,α″-trimethyl- 1,4,7,10-tetraazacyclodecane-1,4,7-triacetic acid, grafted to dialdehydostarch and dialdehydoamylose. As model compounds for understanding the functions of polysaccharides in these contrast agents, Nd(III) with low-molecular analogues **227** and **334** were synthesized [269].



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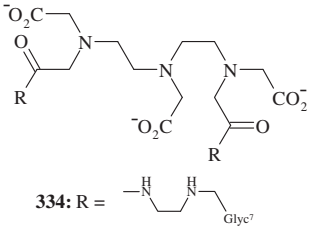


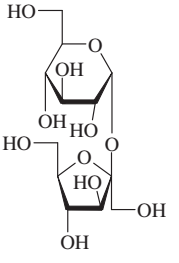
Miscellaneous

Complex formation of modified carbohydrates with shift-reagents (lanthanide chelates) is one popular method of conformational analysis of sugars by NMR spectroscopy [573–581]. Organotin(IV) complexes of type **90** are herbicides, bactericides, fungicides, algicides, and ascaricides [65]. Less toxic derivatives R_2SnX_2 (X is a sugar moiety) are [65] antitumor and antileishmaniosis remedies.

Earlier (see section Complexation of d-Metal Cations with Synthetically Modified Cyclodextrins having *N*-containing Moieties), we noted the chemosensor properties of lanthanide complexes with nitrogen-containing modified CD of type **294** [339], **303** [353,354] and **305** [356]. In relation to this theme, the review [582] on chemosensors for aromatic hydrocarbons [of the type Eu(III) complexes with ligands **303** and **304**] and work [583] on further study of complex **305** have been reported. γ-CD modified with dansyldiethylenetriamine after addition of such guests as adamantancarboxylic acid shows [584] a strong increase of fluorescence in the presence of Cu(II). The β-CD simultaneously modified with fluorophore (dansyl group) and another fragment (the acyclic ionophore antibiotic monensin, which forms a macrocycle when it binds Na^+) was first synthesized [585]. Adding guests like adamantan-1-ol decreases the intensity of fluorescence owing to displacement of the dansyl group from the CD cavity; adding Na^+ intensifies this phenomenon. Dy(III) complexes with CD, modified with diethylenetriaminotetraacetic acid, were suggested [586] as probes for elucidating optical purity of chiral compounds by NMR spectroscopy.

A series of polymer chelators for binding heavy metal ions was synthesized from sucrose **335**, the cheapest crystalline organic compound [587]. Initially some hydroxyl groups are esterified with methacrylate derivatives; radical polymerization of the

products leads to polymers **336**. Derivatization of these polymers with low-molecular chelators gives final polymer hydrogels [481]. The polymeric chelators **337** [481,588], **338** [481,588,589], **339** [481,588], **340** [481,590], and **341** [481,591] have been obtained in this way. The polymeric chelate **342** [481,592] catalyzes the photolysis of water with visible light, remaining active after eight days of irradiation, while the usual systems only work for up to 40 h.



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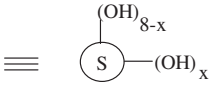
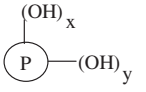
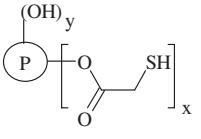
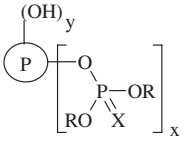




336



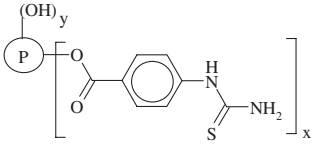
337: x ~ 3.8



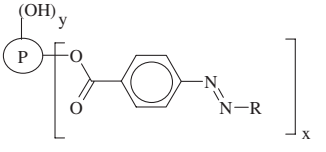
338: x ~ 2.5;

X = O, R = Et, n-Bu, Ph,  ,  ;

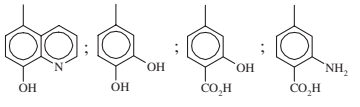
X = S, R = Et

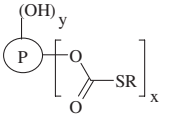


339: x ~ 3.8



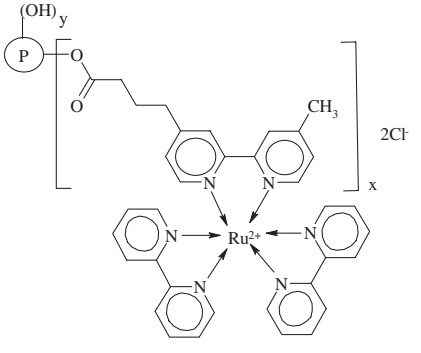
340: x ~ 2;

R = 



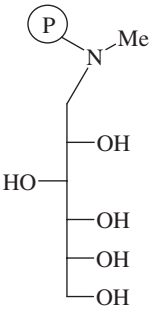
341: x ~ 2

R = H, Ph,  , 

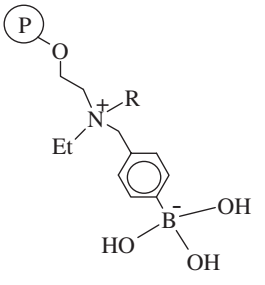


342

The polymer **343** was used to eliminate boric acid from carbohydrate solutions [593]. Chromatography on a cationic resin in the La(III) form is a good technique for separation of 1-deoxy-1-nitropolyols [594]. Polymers **344** preferentially absorb *cis*-diol compounds and have successfully been used [595] for chromatographic separation of polyols, carbohydrates, nucleosides, and nucleotides. Ti(IV) complexes with xanthates of cellulose or starch have been suggested [596] for the extraction of uranium from sea water.



343: (P) is polystyrene



344: (P) is dextran, cellulose, diethylaminoethylsephadex

Chemical modification of cellulose is a favourite approach to the preparation of various cheap polymeric complexones for heavy metal ions. This technique was used [76] to prepare cinnamates and oleates of cellulose, whose mercurated derivatives showed [76] a high stability to putrescence and satisfactory antimicrobial properties. Mercuration of 1-allyloxypropyl derivative of cellulose gave a product, successfully used [597] for the chromatographic purification of γ-globulin. A hydroxamic acid derivative of cellulose [598,599] binds Fe(III) specifically. Cellulose with imidodiacetate groups binds Ni(II) and Cu(II) [600]. Celluloses with fragments of nitriloacetic acid, thiourea, and cysteine were obtained [601] to absorb traces of heavy metal ions. Cellulose with 2,2′-diaminoethylamino groups accomplishes the same function in the presence of considerable amounts of alkali and alkali-earth metal ions [602]. Fragments of *N*-carboxyalkyl(aryl)aminotriazole [603] and corand [604] were also grafted to cellulose. Some anionic resin based on cellulose are capable of exchanging their anions for BH_4^-, CrO_7^{2-}, and MX_2 [M = Cu(II), Ni(II)], giving redox polymers [605]. Hydrazone and formazane groupings, covalently fixed to the chromatographic paper, lead to chromogenic analytical reagents for metal-indicator express-tests [606–610]. For obtaining polymeric complexones, SCMC (**115**), to which the 5-amido-8-hydroxyquinoline [611], hydrazide [612], and *N*-(1,3,4-triazol)amide [613] groupings are grafted, is also used. A cobalt complex of diethylaminoethylsephadex with grafted tetrasulfonylphthalocyanine groups catalyzes oxidation of thiols [614].

Among other polymeric carbohydrate complexones, CDs grafted to synthetic polymers should be mentioned: these compounds serve to extract heavy metal salts from aqueous solutions [615]. Chitin and the product of its basic hydrolysis (chitozan **214a**) have been repeatedly suggested [254,616–621] for the extraction of uranyl [254], Pd(II), Cu(II), Fe(II), Sb(III), Cr(III), Zn(II) [616,618,621], Cd(II), Pb(II) [617,618], Hg(II) [618–620], Ag(I) [619], and Cs(I) [616] ions from sea and waste water.

N-Carboxymethylchitozan (**80**) binds alkaline earth [115] and heavy (Ni^{2+}, Co^{2+}, Pb^{2+}) [255] metal ions well.

CONCLUSIONS

Numerous chemically modified carbohydrates have become possible available by the application of a series of modern synthetic methods to carbohydrate synthesis, including 20% of nominal organic reactions [622]. Simultaneously, the coordination chemistry of these derivatives has been developed.

Unlike the coordination chemistry of natural carbohydrates [14], realized in aqueous solutions, the coordination chemistry of modified carbohydrates is frequently the chemistry of metal complexes in non-aqueous solutions, since chemical modification of natural carbohydrates considerably increases their hydrophobicity.

Chemical modification of carbohydrates inevitably results in an increase in the number and variety of diastereomerically pure carbohydrate ligands; thus diastereomerically pure complexes may be obtained. In a number of cases this hope has been realized, and the formed complexes serve further as effective catalysts for diastereoselective processes. An honorable place in this line belongs to rhodium complexes of phosphorus-containing carbohydrates (see section Complexation of d-metal Cations with Phosphorus-, Sulfur- and Selenium-containing Carbohydrate Derivatives), whose discovery and application are the most important achievement of the research area examined in the present review. Sharpless research (see section Oxygen-containing Ligands) was granted the Nobel Prize 2001 [623]. This area of application for carbohydrate metal complexes is especially attractive for the future preparation of diastereomerically pure synthetic drugs owing to the constant availability of natural carbohydrates as chiral raw materials through photosynthesis. The chemistry of modified carbohydrate complexes of platinum-group metals has also developed extensively [25].

Results on the metal complexation of carbohydrate cavity compounds (podands and corands) (see section Complexation with s-metal Cations) as well as of cyclodextrins substituted by nitrogen-containing chelators (see section Complexation of d-Metal Cations with Synthetically Modified Cyclodextrins having *N*-containing Moieties) mean the advent of supramolecular coordination chemistry of carbohydrates resulting in simulation of biological structures. Metal complexation of unsaturated carbohydrates is in many respects *terra incognita* and its research is marked by many unexpected discoveries.

Coordination chemistry of synthetically modified carbohydrates enters the 21st century as a rapidly developing area of knowledge, equipped with effective techniques of structural analysis and perspectives in both theoretical and practical aspects.

Acknowledgments

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