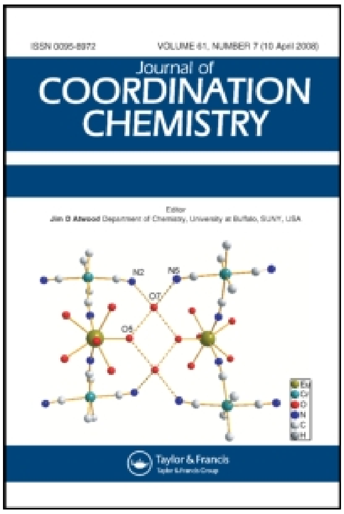

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2′-DEOXYADENOSINE ADDUCTS WITH 3d METAL PERCHLORATES*

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Adducts of 2′-deoxyadenosine (L) with 3d metal perchlorates were synthesized by refluxing mixtures of ligand and metal salt in triethyl orthoformate-ethanol. Solid complexes of the following types were obtained: ($X = ClO_4$): $M_2L_3X_6.4H_2O$ (M = Cr, Fe), $M_2L_3X_4.4H_2O$ (M = Mn, Co, Ni, Zn), $FeL_2X_2.2H_2O$ and $Cu_2L_3X_4$. The Cu(II) complex is magnetically subnormal and appears to be a dimer of the type $\{O_3ClOCuL_3CuOClO_3\}(ClO_4)_2$, involving a triple bridge of N1,N7-bound L ligands. The rest of the new complexes exhibit normal ambient temperature magnetic moments and were characterized as linear chainlike polymers comprising a singlebridged $\text{-(}M\text{-}L\text{)-}_n$ backbone, terminal unidentate L, $-OClO_3$ and aqua ligands and ionic perchlorate. Bridging L is also N1,N7-bound in the latter adducts, while the terminal L ligands present bind most probably *via* N7.

Keywords: 2′-deoxyadenosine, first row complexes, perchlorates, synthesis

INTRODUCTION

Earlier work in these laboratories has dealt with the syntheses and characterization of 3d metal complexes of adenine (adH),[2,3] adenosine (ado)[4] and their *N*(1)-oxides.[5,6] Recently we became interested in extending our work to include the corresponding complexes of 2′-deoxyadenosine (dado; L; I) and synthesized a series of adducts of this ligand with 3d metal perchlorates,[1] which are the subject of the present paper. L has been found to function as terminal unidentate N7-bound in bis(acetylacetonato)(nitrito)(dado)Co(III).[7] Neutral ado or dado most commonly function as N-ligands, binding *via* one or more ring nitrogens. N7 is favoured over N1 to function as the binding site of terminal ado in its transition metal complexes,[8,9] owing to the steric influence of the exocyclic NH_2 group at C6.[8] Binding of ado or dado *via* N3 is prevented by the steric hindrance introduced by the sugar residue at N9.[4,10] N1 and N7 are the likely binding sites of bridging bidentate ado or dado; in fact, bridging bidentate 9-methyladenine (mad) reportedly binds *via* N1,N7.[11] The exocyclic primary amino group at C6 does not have the tendency to function as an N-ligand in neutral ado or dado complexes.[12] However, when this amino group is monodeprotonated, it becomes one of the preferred binding sites, as, for instance, in the cases of anionic adenine or adenosine *N*(1)-oxide ligands, which

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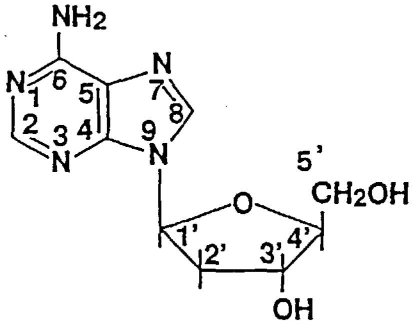
function as strong O1,N6-bound chelating agents.[5,6,13] Ado was also found to act as a bidentate O,O-chelating ligand, binding through the O2′ and O3′ hydroxyl oxygens of the ribose fragment in its bis(pyridine)osmate(VI) ester.[14] This type of chelation is not applicable to the 2′-deoxyribose fragment of dado, in which the O2′ oxygen is absent. For some of the ado adducts with metal perchlorates we previously studied, the evidence favoured participation of N1, N7 and one ribose oxygen (O2′ or O3′) in coordination.[4] Regarding the ribose and 2′-deoxyribose sugars, the former is a stronger ligand, readily acting as an O2′, O3′-bound chelator.[12] while the latter may also function as a chelating agent in the 2′-deoxyribofuranose form, binding *via* the ether ring and alcohol(O5′) oxygens,[15] *i.e.*, sites that would be sterically prevented from binding in the 2′-deoxyribose fragment of dado.



dado

I

EXPERIMENTAL

The synthetic procedure employed was as follows: 1 mmol hydrated metal perchlorate was dissolved in 50 cm^3 of a 7:3 (v/v) mixture of triethyl orthoformate (teof)–ethanol and the resulting solution stirred at 50°C for 2 h. Then, 2 mmol dado were added and the mixture boiled under reflux for 4–5 days. The mixture was allowed to cool, and the precipitate formed collected by gravity filtration, washed with ethanol and stored *in vacuo* over anhydrous calcium chloride. The new complexes isolated are generally adducts of neutral dado, involving 3:2 ligand to metal molar ratios in all but one case, as shown by the analytical data (Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.) given in Table I. The sole exception is the Fe(II) complex, which involves a 2:1 dado to Fe ratio. Only the new Cu(II) complex is anhydrous, while the rest of the adducts contain two molecules of water per metal ion. Teof is obviously not an effective dehydrating agent[16] for this particular synthetic method. The complexes are generally insoluble in all common organic solvents. Infrared spectra (Table II) were recorded in KBr discs (4000–500 cm^{-1}) and Nujol mulls between high density polyethylene windows (700–200 cm^{-1}), in conjunction with a Perkin-Elmer 621 spectrophotometer. Solid-state (Nujol mull) electronic spectra and ambient temperature (300°K) magnetic susceptibility measurements (Table III) were obtained by methods described elsewhere.[17]

TABLE I
Analytical data for the new dado (L) complexes.[a]

Complex	Colour	Yield%	C%	H%	N%	M%	Cl%
$Cr_2L_3(ClO_4)_6.4H_2O$	Pale grey	19	23.92 (23.60)	2.95 (3.10)	14.11 (13.76)	6.70 (6.81)	14.18 (13.93)
$Mn_2L_3(ClO_4)_4.4H_2O$	Greyish	69	27.31 (27.02)	3.52 (3.55)	16.07 (15.76)	7.93 (8.24)	10.62 (10.63)
$FeL_2(ClO_4)_2.2H_2O$	Taupe	28	30.67 (30.26)	2.77 (3.01)	17.97 (17.65)	6.85 (7.04)	9.22 (8.93)
$Fe_2L_3(ClO_4)_6.4H_2O$	Beige	24	23.54 (23.49)	3.25 (3.09)	13.89 (13.69)	7.44 (7.28)	13.62 (13.86)
$Co_2L_3(ClO_4)_4.4H_2O$	Brick red	26	27.13 (26.86)	3.74 (3.53)	15.92 (15.66)	8.47 (8.79)	10.30 (10.57)
$Ni_2L_3(ClO_4)_4.4H_2O$	Yellow green	60	26.65 (26.87)	3.41 (3.53)	15.88 (15.67)	8.82 (8.76)	10.39 (10.57)
$Cu_2L_3(ClO_4)_4$	Violet	46	28.28 (28.23)	3.17 (3.08)	16.63 (16.46)	10.12 (9.95)	11.32 (11.11)
$Zn_2L_3(ClO_4)_4.4H_2O$	Pale peach	40	26.34 (26.65)	3.67 (3.50)	15.80 (15.54)	9.85 (9.67)	10.21 (10.49)

[a] Found%, with calcd% in parentheses.

RESULTS AND DISCUSSION

Dado behaved in a similar manner as ado,[4] forming exclusively adducts with the metal perchlorates studied. In contrast, adenosine *N*(1)-oxide (adoNO) yielded complexes involving anionic adoNO ligands, monodeprotonated at the exocyclic amino group at C6.[6] This difference in behaviour between dado or ado and adoNO is due to the decrease of pK_a for NH_2 deprotonation from 16.7[12] to 12.86[18] upon *N*-oxidation of ado. The stoicheiometries of the new M(III) (Cr, Fe) adducts of dado are analogous to those of the corresponding M(III) perchlorate adducts with ado,[4] involving 3:2 dado to metal molar ratios and two aqua ligands per metal ion. In contrast, whereas ado afforded 1:1 adducts with all the M(II) perchlorates (Mn, Fe, Co, Ni, Cu, Zn),[4] the new dado adducts with these salts involve either 3:2 (Mn, Co, Ni, Cu, Zn) or 2:1 (Fe) ligand to metal ratios, as already mentioned.

The infrared spectra of ado and dado are fairly similar insofar the absorptions corresponding to the adenine fragment are concerned.[19] Some differences are observed at 1200-800 cm^{-1}, where vibrations associated with the sugar residues occur.[19-21] The band assignments for the IR spectrum of dado were made on the basis of previously reported assignments for this nucleoside,[19-21] as well as adenine,[2,3,22,23] ado[4,24-27] adenosine 5'-monophosphate.[28] and low-frequency IR studies of various nucleobases and nucleosides.[29] Free dado shows three maxima at 3500–3050 cm^{-1}, at 3390 (νOH,2'-deoxyribose), and at 3275 and 3067 (νNH_2). The only water-free new complex (M = Cu(II)) exhibits the following bands in the same region: 3425s, 3330s, 3160s, 3055m. The spectra of the remaining complexes exhibit a very strong and broad νOH (aqua) band at 3370–3330 cm^{-1},[30] which masks most of the above ligand absorptions. Table II gives the relevant IR spectral bands of dado and its new adducts at 1750–200 cm^{-1}. The δNH_2 mode, which appears at 1672 cm^{-1} in free dado,[19] is generally split into two components in the spectra of the

TABLE II

Pertinent infrared data for the new dado metal complexes (cm^{-1}).

dado[a]	M = Cr^{3+}	M = Mn^{2+}	M = Fe^{2+}	M = Fe^{3+}	M = Co^{2+}	M = Ni^{2+}	M = Cu^{2+}	M = Zn^{2+}	Band assignment
1672vs	1722w, 1660vs	1719w, 1661vs	1717w, 1662vs	1711w, 1661vs	1721w, 1657vs	1721w, 1658vs	1705w, 1653vs	1720w, 1659vs	δNH_2
1612s, 1574s	1637s, 1616s	1636s, 1620s	1637s, 1622ms	1636s, 1620ms	1640s, 1601ms	1640s, 1610s	1610s, 1584m	1640s, 1603s	
1515w, 1473w	1602m, 1575m	1590s, 1566s	1600m, 1577m	1603m, 1580m	1570ms, 1559m	1579s, 1560w	1560w, 1518w	1568m, 1554m	δHOH + $\nu C{=}C$ +
1447w, 1418w	1558w, 1543w	1554ms, 1530w	1561w, 1540w	1559w, 1538w	1520m, 1497w	1535s, 1521s	1454m, 1406m	1530w, 1520vw	
1366w, 1339m	1490w, 1470m	1512w, 1495w	1520vw, 1484w	1513m, 1492w	1463w, 1440m	1505s, 1497w	1343w, 1316m	1492w, 1463w	$\nu C{=}N$ + ring vibr.
1324m, 1300s	1438m, 1403m	1440s, 1397s	1445m, 1426w	1471m, 1440m	1400m, 1351m	1440s, 1398s		1448w, 1402m	
	1380w, 1350w	1342s, 1319m	1400m, 1383w	1400m, 1376w	1335m	1343s, 1330s		1357w, 1300w	
	1317w	1302mw	1341w, 1319w	1348w, 1315w		1317m,sh			
1264w, 1233w	1277w, 1220w	1267w, 1220w	1275vw, 1219w	1280vw, 1220w	1276vw, 1221w	1265w, 1222m	1257w, 1218m	1278w, 1220mw	
1209m, 1180w	1175w	1174w	1170w,sh	1172w,sh	1177w,sh	1177w,sh	1175w,sh	1180w,sh	$\nu C{-}NH_2$ + $\nu C{-}N$ +
1158w, 1123w									
1099s, 1054s					1102vvs,sh				$\nu C{-}O$ + ring vibr. +[b]
1028m, 1006m	1026w	1019w,sh	1023w,sh	1020w,sh	1024w,sh	1018w	1026w,sh	1024w,sh	ρNH_2
	1145s, 1113	1140s, 1110	1141s, 1115	1144s, 1116	1141s, 1120	1142s, 1108	1137s, 1107	1141s, 1088	$\nu_3(ClO_4)$
	vvs, 1090vvs	vvs, 1082vvs	vvs, 1082vvs	vvs, 1088vvs	vvs, 1084vvs	vvs, 1084vvs	vvs, 1090vvs	vvs, 1088vvs	
	932w	927w	925w	934w	927w	924w	930w	931w	$\nu_1(ClO_4)$
	639m, 626m	640m, 624m	637m, 622m	641m, 623m	636m, 624m	638m, 621m	640m, 622m	637m, 621m	$\nu_4(ClO_4)$
	611mw	608mw	610mw	613mw	611mw	608mw	606mw	609mw	
639m, 596m	598w, 572vw	588w, 575w	585w, 573w	600w, 571vw	643w,sh, 590w	643w,sh, 590w	590w,sh, 570w	641w,sh, 579w	
569w, 533w	543w, 511w	541w, 502w	540w, 502w	545w, 513w	570w, 539w	572w, 539w	530vw, 446w	550w, 504w	
500m, 450w,sh	458w,sh, 421w	427vw, 390vw	450w, 420w	460w,sh, 420w	462vw, 437vw	448w, 425vw	422vw, 400vw	458w, 442vw	νdado at
419w, 390vw	390vw, 375vw	367w,b, 331w	393vw, 363w	385vw, 370vw	424w, 392vw	396vw, 365w,b	380w, 333w	411w, 368w	
377vw, 348vw	270vw, 243vw	268vw	331w, 269vw	273vw, 245vw	367w,b, 331w	330w, 266vw	270vw, 238vw	351w, 332w	650–200 cm^{-1}
335w, 300w	224mw,b			224mw,b	265vw		222mw,b	266vw, 247w,sh	
266w, 241w									
225w,b									
	475w,sh	470w	473w,sh	478w,sh	483w	472w	475w	473w	$\nu_2(ClO_4)$
	500mw	403mw	404mw	495mw	411mw	415mw		399mw	$\nu M{-}O$ (aqua)
	339w	301w	303w	333w	306w	309w	346w	299w	$\nu M{-}O$ ($OClO_3$)
	295w	241w, 220mw	244w, 222mw	287w	247w, 225mw	251w, 230mw	314w, 298w	238w, 219w	$\nu M{-}N$

[a] For free dado band assignments see text. [b] The very strong $\nu_3(ClO_4)$ bands mask the ligand absorptions at 1160–1030 cm^{-1}.

TABLE III

Solid-state (Nujol mull) electronic spectra and magnetic susceptibilities at 300°K of the new dado metal complexes.

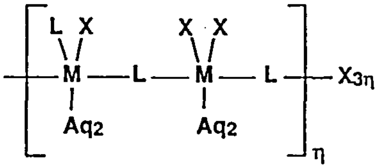
M	λmax,nm[a]	$10^6\chi_A^{cor}$, cgsu[b]	μeff, μB
Cr^{3+}	<200vvs, 218vvs, 244vs, 269vs,b, 306s,sh, 353s, 395s, 422ms, 450ms, 488m,sh, 535m,sh, 569m, 630w, 690w,sh	5989	3.81
Mn^{2+}	<200vvs, 215vvs, 241vs, 272vs,b, 313s,sh, 351s, 429s, 496w,vb	14,765	5.97
Fe^{2+}	198vvs, 214vvs, 239vs, 270vs,b 309s,sh, 355s, 813mw,b, 1160w,vb	10,842	5.12
Fe^{3+}	<200vvs, 218vvs, 243vs, 275vs,b, 311s,sh, 352s, 414s, 530w,sh	14,911	6.00
Co^{2+}	198vvs, 213vvs, 245vs, 274vs,b, 308s,sh, 354s, 480s,sh, 507s, 523s,sh, 1165w,b	9797	4.87
Ni^{2+}	<200vvs, 212vvs, 240vs, 269vs,b, 307s,sh, 354s, 424s, 630mw, 725mw,b, 970w, 1165w,b	4402	3.15
Cu^{2+}	197vvs, 213vvs, 240vs, 268vs,b 307s,sh, 352s, 552s,b, 677ms,sh, 732m,sh	1013	1.56
Zn^{2+}	<200vvs, 217vvs, 238vs, 272vs,b, 309s,sh, 351s, 383m,sh	Diamagnetic	

[a] UV spectrum of dado from the literature, λ, nm (ε):[45,46] at pH 7.9: maxima 188.5 (20,600), 195 (18,100), 207.5 (21,000), 259.5 (14,900); minimum 226.3 (2,200). [b] χ_A is the magnetic susceptibility per metal atom.

complexes (a weak band at 1725–1705 and a very strong absorption at 1663–1652 cm^{-1}). The former band is suggestive of H-bonding between NH_2 and ClO_4^-,[6,22,23] while the latter shows relatively small shifts toward lower wavenumbers and is not indicative of participation of the N6 nitrogen in coordination.[2–6,22,23,28] Use of adenine ring nitrogens in coordination is suggested by more significant shifts and occasional splittings of the νC=C, νC=N and ring vibrations of the adenine fragment of dado, upon metal complex formation.[2–6,22–24] The νC–O (2'-deoxyribose) + νC–N ligand bands at 1150–1040 cm^{-1},[22,27,28] are masked by the very strong triply split $\nu_3(ClO_4)$ absorption bands in this region, in the spectra of the complexes. The $\nu_4(ClO_4)$ mode also appears as a triplet, while both ν_1 and $\nu_2(ClO_4)$ are IR-active. These features favour the invariable presence of both ionic ClO_4^- and unidentate coordinated $-OClO_3$ ligands in the new complexes.[31,32] The ρNH_2 mode of dado appears as a shoulder at 1026–1018 cm^{-1} in the spectra of the complexes.[23] Tentative metal-ligand band assignments were based on our previous studies of adH, ado and their *N*(1)-oxide complexes,[2–6] as well as assignments for 3d metal complexes with perchlorato[33] and aqua[30,34] ligands. These assignments favour coordination number four for the Cu(II) adduct and six for the remaining complexes.[2–6,30,33,34] Regarding the possibility of participation of hydroxyl oxygens of the 2'-deoxyribose residue of dado in binding, no IR evidence was found in its favour.[4]

The ambient temperature magnetic moment of the Cu(II) complex (1.56 μB) is clearly subnormal.[2,5] Several dimeric Cu(II) complexes involving quadruple or triple bridges of bidentate nucleobase ligands or their derivatives and characterized by room temperature magnetic moments of 1.5–1.7 μB have been reported in the literature.[2,5,35–40] The remaining paramagnetic new complexes exhibit normal room temperature magnetic moments (Table III) for high-spin $3d^3$–$3d^8$ compounds.[41] The normal ambient temperature paramagnetism of these adducts does not preclude the linear single-bridged polymeric structures proposed for these compounds later in the text. In fact, linear polymeric 3d metal (II) (Co, Ni, Cu) complexes with single purine bridges between adjacent metal ions were found to exhibit normal ambient temperature magnetic moments, showing evidence favouring magnetic exchange interactions at temperatures below 110°K.[42] Single-bridged Cu(II) polymeric complexes with diazines or diazoles show similar trends.[43,44] The $\pi \rightarrow \pi^*$ transitions of dado[45,46] undergo shifts toward lower energies and occasional splittings upon metal complex formation (200–280 nm region). The $n \rightarrow \pi^*$ transition of the ligand appears as a shoulder at 306–313 nm in the UV spectra of the new complexes[47] (Table III). The paramagnetic complexes exhibit strong metal-to-ligand charge-transfer absorption,[48] originating in the UV and trailing off into the visible region. The interaction of dado with $Cr(OH_2)_6{}^{3+}$ in aqueous media has been studied by UV-visible spectroscopy.[49] The d–d transition spectrum of the new Cr(III) adduct has its most intense maxima in the same regions,[49] but is characterized by clearcut splittings of the bands into several components, owing to its low-symmetry hexacoordinated configuration:[50] ${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ 395, 422, 450, 488; $\rightarrow {}^4T_{2g}(F)$ 535, 569, 630, 690 nm (Dq = 1650 cm^{-1}). The corresponding spectra of the Fe(II), Co(II) and Ni(II) complexes are also compatible with low-symmetry hexacoordinated configurations,[50–52] *viz*, M = Fe: ${}^5T_{2g} \rightarrow {}^5E_g$ 813, 1160 nm (Dq = 1014 cm^{-1}); M = Co: ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ 480; $\rightarrow {}^4A_{2g}(F)$ 507, 523; $\rightarrow {}^4T_{2g}(F)$ 1165 nm; M = Ni: ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ 424; $\rightarrow {}^3T_{1g}(F)$ 630, 725; $\rightarrow {}^3T_{2g}(F)$ 970, 1165 nm (Dq = 937 cm^{-1}). The calculated Dq values (for a pure O_h symmetry) are consistent with FeN_3O_3 or mixed MN_3O_3 and MN_2O_4 (M = Cr^{3+}, Ni^{2+}) chromophores[42,52,53] (*vide infra*). The Cu(II) complex shows d–d transition maxima at 552, 677 and 732 nm, and probably involves a severely flattened tetrahedral symmetry (D_{2d}), and a CuN_3O absorbing species[5,24,52,54] (essentially tetrahedral Cu(II) complexes with nucleobases and nucleosides exhibit their strongest d–d transition band at 750–900 nm[24,52–56]).

The evidence presented, combined with the insolubility of the new complexes in organic media and the pronounced tendency of purine derivatives to function as bidentate bridging ligands,[57] favours bi- or polynuclear configurations for the adducts reported herein. The new magnetically subnormal Cu(II) complex is most probably a dimer of type $\{(O_3ClO)CuL_3Cu(OClO_3)\}(ClO_4)_2$, involving three bidentate bridging N1,N7-bound ligands between the two Cu^{2+} ions.[2,5,35–40] A number of magnetically subnormal Cu(II) dimeric complexes with four bidentate bridging N3,N9-bound adH or hypoxanthine ligands have been characterized by crystal structure determinations.[36–38] In the case of dado, N9 is blocked by the 2′-deoxyribose residue, whilst the participation of N3 in binding (N3,N7-binding of bridging hypoxanthine has been demonstrated[58]) is sterically prevented,[4,10] as already mentioned. Hence, coordination of bidentate dado *via* ring nitrogens can occur only through N1 and N7.[4,11] The remaining complexes are most likely linear chainlike polymers with single bridges of N1,N7-bound dado. Their probable structural types are analogous to those proposed for the Cr(III) and Fe(III) perchlorate adducts with ado,[4] involving, with the exception of the new Fe(II) complex, alternating MN_3O_3 and MN_2O_4 absorbing species, as shown in (II) (M = Cr(III), Fe(III)) and III (M = Mn(II), Co(II), Ni(II), Zn(II)) (X = coordinated $-OClO_3$ or ionic ClO_4^-; Aq = $-OH_2$ ligand). The Fe(II) adduct is represented by the simpler structural type IV. Regarding the terminal unidentate dado ligands in structural types II–IV, use of N7 rather than N1 as their binding site is considered as most probable in view of the conclusions of recent studies, which established that N7 is slightly favoured to act as the binding site of terminal 9-substituted adenines,[8,9] especially in hexacoordinated metal complexes.[59] Finally, the fact that no evidence pointing to participation of hydroxyl oxygens of the 2'-deoxyribose residue was found is not surprising (ado adducts with Fe(II) and Zn(II) perchlorates were previously characterized as involving bridging ado ligands binding via N1, N7 and either O'2 or O'3[4]). In fact, whereas both ado and dado form similar ring N-bound complexes with $CuCl_2$ in dimethyl sulfoxide,[60] interactions of both these nucleosides with aqueous solutions of trichlorodiethylenetriaminecobalt(III) at pH 8–11 (adjusted by NaOH addition) revealed that ado forms complexes, binding *via* hydroxyl oxygens of its ribose residue, while dado does not yield a complex under these conditions.[61]



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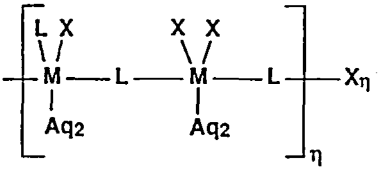
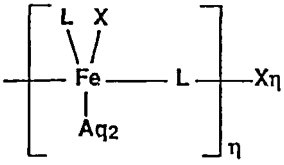


III



IV

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