Metal-ion Control in the Synthesis of Schiff Base Complexes

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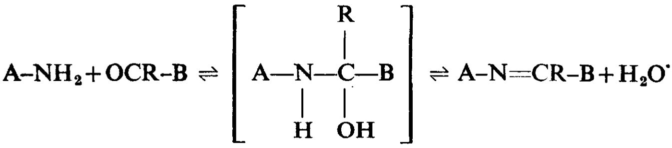
1 Introduction

Throughout the years, Schiff bases have played a central role as chelating ligands for a large variety of metal ions. Both the syntheses and properties of Schiff base complexes are very often intimately related to the associated metal ion and it is this aspect which is given emphasis in the following discussion. Apart from the obvious implications for synthetic co-ordination chemistry, aspects of the topic are of relevance to those whose interests include organic synthesis in the presence of metal ions, areas of metal-ion catalysis, and biochemical reactions involving Schiff bases.

Two excellent reviews of Schiff base complexes appeared in 1960[1] and 1966.[2] The first of these stressed the chemistry of inner complexes whereas the latter dealt in detail with the chemistry of salicylaldimines, β-ketoamines, and closely related ligands. A text concerned primarily with the stereochemistry of Schiff base complexes, as well as aspects of behaviour of such complexes in solution, has also been published.[3]

2 Synthetic Methods

A. Direct Ligand Synthesis Followed by Complexation.—The preparation and isolation of the free Schiff base ligand followed by complexation with a metal ion has traditionally been the most common method for preparation of metal complexes. The reaction sequence is given below where A and B are organic moieties, which may or may not contain other atoms capable of donation to the metal, and R is alkyl, aryl, or hydrogen.



$$\text{A–NH}_2+\text{OCR–B} \rightleftharpoons \left[\text{A}-\underset{\text{H}}{\text{N}}-\overset{\text{R}}{\underset{\text{OH}}{\text{C}}}-\text{B}\right] \rightleftharpoons \text{A–N=CR–B}+\text{H}_2\text{O}$$

$$\text{A–N=CR–B}+\text{M}^{n+} \rightleftharpoons [\text{M(A–N=CR–B)}]^{n+}$$

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[1] B. O. West, *Rev. Pure Appl. Chem.* (*Australia*), 1960, **10**, 207.

[2] R. H. Holm, G. W. Everett, and A. Chakravorty, *Progr. Inorg. Chem.*, 1966, **7**, 83.

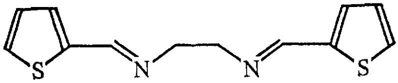
[3] B. O. West, 'The Chemistry of Co-ordination Compounds of Schiff Bases', in 'New Pathways in Inorganic Chemistry', eds. E. A. V. Ebsworth, A. G. Maddock, and A. G. Sharpe, Cambridge University Press, 1968.

The isolation of the free Schiff base before reaction with a metal ion has certain inherent advantages compared with the *in situ* preparations discussed in following sections. The reactants used to prepare Schiff bases are often excellent co-ordination agents themselves. Hence, a small excess of one or other of these reactants may lead to product contamination if not removed before the Schiff base is complexed with a metal ion. In the direct type of ligand synthesis discussed here the removal of such impurities is usually possible using normal purification techniques. Characterisation of the free ligand enables a comparative study to be made of its physico-chemical properties with those of the corresponding metal complexes. In this manner, the elucidation of the nature of the latter may be facilitated.

B. Synthesis *in situ*.—In this class of synthesis the formation of the Schiff base occurs in the presence of the metal ion to give the corresponding metal complex directly.

If the presence of a metal ion promotes the formation of a Schiff base (as its metal complex) then a metal-ion template effect is said to be operating. For the formation, *in situ*, of Schiff base complexes two template effects have been recognised.[4] When the role of the metal ion is to organise and orientate the reacting species such that the required product forms in higher yield then this amounts to a sterically directed kinetic mechanism and has been named the kinetic template effect. If, however, the metal ion removes the Schiff base from an equilibrium (for example, with its components) by complexation, and thus promotes its formation in high yield, then a thermodynamic template effect is in operation.

Even though *in situ* preparations proceed without isolation of the metal-free Schiff base, the latter can sometimes be obtained by a ligand exchange reaction involving replacement of the Schiff base by a strong co-ordinating ligand such as the cyanide ion. Nevertheless, this may not be possible, for the ligand is frequently unstable towards hydrolysis in the absence of a co-ordinated metal ion. This is so even though co-ordination of an imine function is expected to increase that function's ease of hydrolysis. Any drain of electron density from the -HC=N- linkage towards a positive metal will tend to make the imine carbon more susceptible to nucleophilic attack and thus aid hydrolytic cleavage. Indeed, such is the case for the bidentate ligand (1) which is more readily hydrolysed



(1)

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[4] D. H. Busch, *Rec. Chem. Progr.*, 1964, **25**, 107; L. F. Lindoy and D. H. Busch, 'Metal Complexes of Macrocyclic Ligands', in 'Preparative Inorganic Reactions', ed. W. L. Jolly, Wiley-Interscience, New York, 1971, Vol. 6, in the press.

when co-ordinated.[5] Nevertheless, the above-mentioned effect is often overshadowed by other effects which result from co-ordination of the imine nitrogen to a metal ion. It is appropriate to consider here these other roles that the metal ion may play in the stabilisation or destabilisation of a co-ordinated Schiff base since these will also influence, in varying degrees, the success or failure of a particular *in situ* synthetic procedure.

If the metal ion has filled orbitals suitable for back donation to π-acceptor orbitals on the imine then this will help reduce the effective positive charge on the imine carbon and make it less susceptible to hydrolysis. In addition, the electron density associated with such a π-bond may shield, to some degree, the imine carbon from an attacking nucleophile. Condensation of methylamine with glyoxal in the presence of iron(II) leads to isolation of a purple spin-paired complex (2):[6]

$$6CH_3{\cdot}NH_2 + 3OHC{\cdot}CHO + Fe^{2+} \rightarrow [Fe(H_3C{\cdot}N{=}CH{\cdot}CH{=}N{\cdot}CH_3)_3]^{2+} + 6H_2O$$

(2)

The co-ordinated Schiff base is remarkably stable towards hydrolysis even in solutions of low pH. It is not possible to isolate the ligand in the absence of the metal ion but, rather, polymeric products are obtained. The thermodynamic stability of this type of complex is also unusually high. The strong chelating ability of ligands containing an α-di-imine linkage has long been recognised[7] and has been rationalised, in part, by postulating $d\pi$–$p\pi$ bonding from the metal to the ligand. The delocalised nature of the π-electron system in each chelate ring of the iron(II) complex (2) has been discussed recently and there has been evidence presented for the existence of a ring current.[8] Thus, the rings appear to have some aromatic character and it seems clear that the stability of the Schiff base ligand in this type of chelate owes much to its participation in π-bond formation.

Reaction of salicylaldehyde with glycine in the presence of copper ion also leads to formation of the corresponding Schiff base complex even at low pH where the free ligand is hydrolysed.[9] Once again special considerations apply. A major influence in this case is undoubtedly the tridentate nature of the ligand formed which, because of the increased chelate effect on co-ordination, will result in metal complexes having enhanced thermodynamic stability. It appears that this greater overall stability is more than sufficient to counteract the effect of electron withdrawal from the imine linkage.

Reaction of 1,3-diaminopropane with various α-dicarbonyl compounds in

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[5] G. L. Eichhorn and J. C. Bailar, *J. Amer. Chem. Soc.*, 1953, **75**, 2905; G. L. Eichhorn and I. M. Trachtenberg, *ibid.*, 1954, **76**, 5183; R. K. Y. Ho and S. E. Livingstone, *Austral. J. Chem.* 1965, **18**, 659.

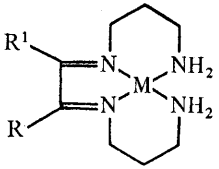
[6] P. Krumholz, *J. Amer. Chem. Soc.*, 1953, **75**, 2163.

[7] L. F. Lindoy and S. E. Livingstone, *Co-ordination Chem. Rev.*, 1967, **2**, 173.

[8] T. Ito and N. Tanaka, *J. Inorg. Nuclear Chem.*, 1970, **32**, 155.

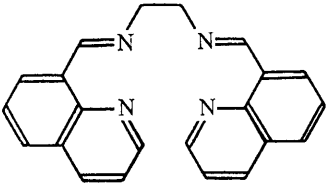
[9] G. L. Eichhorn and M. D. Marchand, *J. Amer. Chem. Soc.*, 1956, **78**, 2688; L. J. Nunez and G. L. Eichhorn, *ibid.*, 1962, **84**, 901.

the presence of nickel or copper ions leads to the formation of complexes of type (3).[10] The ligands in such complexes cannot be isolated in the absence of a metal ion. The stability of these complexes can be considered to reflect the enhanced chelate effect arising from the quadridentate nature of the ligands. In addition, the complexes all contain co-ordinated α-di-imine linkages. Although stable in neutral conditions the complexes are, nevertheless, still fairly susceptible to both acid and base hydrolysis.



(3)

There is evidence that the ease of solvolysis of an imine function is influenced by the degree of steric strain introduced into the Schiff base ligand on co-ordination. Attempts to prepare a number of metal complexes of the quadridentate ligand (4) formed by reaction of quinoline-8-aldehyde and ethylenediamine (in 2:1 mole ratio) led to isolation of two types of complex.[11] The condensations were carried out *in situ* and, for a particular transition metal ion, complexes of either the quadridentate (4) or the tridentate (5) were obtained. It was only for Ni^{II} that complexes of both ligands were isolated. Molecular models indicate that when the quadridentate (4) is co-ordinated around a square-plane, steric clashes occur between the hydrogen atoms in the 2-positions of the respective quinoline rings. Twists of the quadridentate ligand at its imine functions (because of steric clashes) would distort these linkages and make π-overlap less effective. Hence the linkages in such a complex would be expected to be fairly susceptible to hydrolytic cleavage. Parallel reactions using quinoline-8-aldehyde and *o*-phenylenediamine have been investigated. Because of the greater rigidity of the



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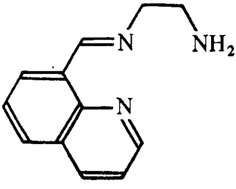

(5)

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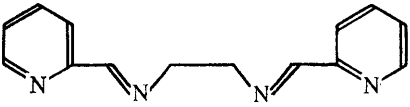
[10] L. T. Taylor, N. J. Rose, and D. H. Busch, *Inorg. Chem.*, 1968, **7**, 785; C. Pelizzi, *Inorg. Nuclear Chem. Letters*, 1970, **6**, 249.
[11] J. Dekkers and H. A. Goodwin, *Austral. J. Chem.*, 1966, **19**, 2241.

backbone in the quadridentate ligand derived from *o*-phenylenediamine, the imine linkages would be expected to be particularly strained on co-ordination of the ligand. As might be predicted, no complexes containing this ligand intact have been isolated.

It should be mentioned that an alternate mechanism could also be operating in these systems. The metal ion may simply sequester the ligand which forms the most stable complex from competing equilibria in the reaction solution. That is, a thermodynamic template effect may occur.

Steric influences need not result in complete solvolytic cleavage of a Schiff base linkage. Attempts to prepare a copper complex of *NN'*-bis-(2-pyridylmethylene)-ethane-1,2-diamine (6) in alcohol led to partial ligand solvolysis and a complex of the ligand (7) was isolated in which an alcohol molecule had added across one of the imine linkages.[12]



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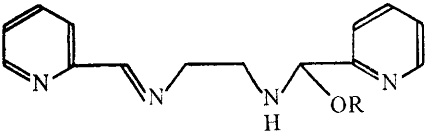

(7)

The increased flexibility of (7) enables alleviation of the steric clashes that would occur on co-ordination of its more rigid di-imine precursor. Related examples of additions to strained co-ordinated imine functions in other metal complexes are known.[13]

The most common procedure for *in situ* syntheses is to add the metal ion during or shortly after the mixing of the Schiff base reactants. However, it is sometimes possible to co-ordinate one of the components of the Schiff base first before performing the condensation. Generally, it is not desirable to use a co-ordinated amine for such a reaction since co-ordination severely impairs the nucleophilic character of the nitrogen. Indeed, for most reactions of this type that do occur there is little evidence that the amine remains co-ordinated during the condensation. One reaction of this type is illustrated in Scheme 1 and in this case it has been suggested that the heterocyclic nitrogen of the pyridine-2-

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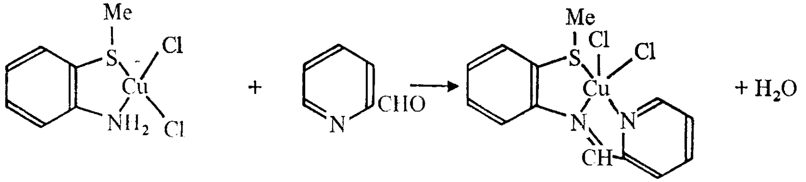
[12] C. M. Harris and E. D. McKenzie, *J. Chem. Soc.* (*A*), 1969, 746; B. F. Hoskins and F. D. Whillans, *J. Chem. Soc.* (*A*), 1970, 123.

[13] D. H. Busch and J. C. Bailar, *J. Amer. Chem. Soc.*, 1956, **8**, 1137; L. T. Taylor, F. L. Urbach, and D. H. Busch, *ibid.*, 1969, **91**, 1072; V. Katovic, L. T. Taylor, and D. H. Busch, *ibid.*, 1969, **91**, 2122.



Scheme 1

aldehyde may first effect amine (or ligand) displacement prior to Schiff base condensation.[14] After reaction, co-ordination of the resulting tridentate ligand would yield the required metal complex. Other similar condensations involving co-ordinated amines and pyridine-2-aldehyde as reactants have been reported.[14,15]

Related to the reactions just discussed is the reaction of salicylaldehyde with an aqueous solution of tetrakis(ethylenediamine)-μ-dichlorodinickel(II) chloride in the presence of a few drops of pyridine.[16,17] From the solution the nickel complex of the quadridentate Schiff base from salicylaldehyde (2 mol) and ethylenediamine (1 mol) has been isolated in near quantitative yield. The general procedure has been extended to the preparation of a range of other similar complexes. A mechanism involving reaction of the co-ordinated amine has been postulated; however, it seems that a reaction sequence involving displacement of the amine groups by pyridine prior to the occurrence of Schiff base condensation is also in harmony with the experimental observations.

Condensations using co-ordinated aldehydes or ketones as reactants have been performed and in fact it was Schiff[18] who first used a reaction of this type to prepare bis(salicylaldimino)copper complexes. Polarisation of the carbonyl group on co-ordination to a positive metal ion will result in the carbonyl-carbon becoming more susceptible to nucleophilic attack by the lone pair of the amine. However, a carbonyl oxygen is usually a very poor donor towards most metal ions and thus, in solution, it is generally readily displaced from the co-ordination sphere by solvent molecules. Nevertheless, if the carbonyl-containing moiety contains another donor atom which enables the formation of a strong chelate ring then this will aid the carbonyl to remain co-ordinated in solution and Schiff-base condensation will be facilitated. Many such reactions involving co-ordinated salicylaldehyde have been performed[2] and a typical example[19] is illustrated in Scheme 2. Hence in planning a synthesis of this type, the choice of a metal ion is important as it should bind the carbonyl-containing

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[14] L. F. Lindoy and S. E. Livingstone; *Inorg. Chim. Acta,* 1967, **1,** 365; *Inorg. Chem.,* 1968, **7,** 1149.

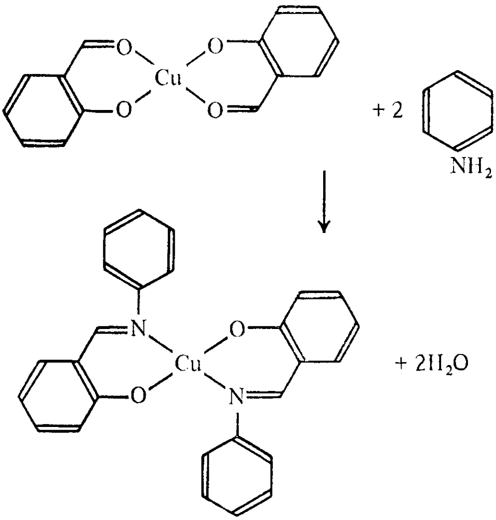
[15] B. Kirson and S. Yariv, *Bull. Soc. chim. France,* 1964, 2969; 1965, 149.

[16] E. J. Olszewski and D. F. Martin, *J. Inorg. Nuclear Chem.,* 1964, **26,** 1577.

[17] E. J. Olszewski, L. J. Boucher, R. W. Oehmke, J. C. Bailar, and D. F. Martin, *Inorg. Chem.,* 1963, **2,** 661.

[18] H. Schiff, *Annalen,* 1869, **150,** 193.

[19] E. J. Olszewski and D. F. Martin, *J. Inorg. Nuclear Chem.,* 1965, **27,** 345.



Scheme 2

moiety as strongly as possible in order to aid nucleophilic attack by the amine. For salicylaldehyde, which contains two oxygen donors, the use of a metal ion having substantial *a*-class character is thus a logical choice.

C. Metal-ion Induced Rearrangements.—Many 2-hydroxy or 2-thiol amines react with aldehydes or ketones to yield not Schiff bases but heterocyclic compounds.[20] The chief product from the reaction of biacetyl and 2-thiolethylamine in a 1:2 mole ratio is the dithiazolidine (8).[21,22] Similarly, 2-thiolaniline yields the corresponding dibenzothiazoline (9).[23,24] Nevertheless, in solution, it has been shown that both products exist in equilibrium with their respective tautomeric Schiff bases (10) and (11). Addition of a number of metal ions to a solution of (8) or (9) results in isolation of high yields of intensely coloured metal complexes of the corresponding dianionic forms of (10) and (11).[22-26]

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[20] M. Claasz, *Chem. Ber.*, 1916, **49**, 1141; M. T. Bogert and A. Stull, *J. Amer. Chem. Soc.*, 1925, **47**, 3078; S. Ratner and H. T. Clarke, *J. Amer. Chem. Soc.*, 1937, **59**, 200; F. J. Kreysa, V. Maturi, J. J. Finn, J. G. McClarnon, and F. Lombardo, *J. Amer. Chem. Soc.*, 1951, **73**, 1155; F. J. Goetz, *J. Heterocyclic Chem.*, 1967, **4**, 80; *ibid.*, 1968, **5**, 509; E. Uhlemann and V. Pohl, *Z. Chem.*, 1969, **9**, 385.

[21] H. Jadamus, Q. Fernando, and H. Freiser, *Inorg. Chem.*, 1964, **3**, 928.

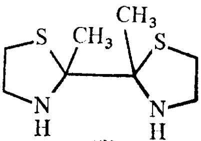
[22] M. C. Thompson and D. H. Busch, *J. Amer. Chem. Soc.*, 1962, **84**, 1762; *ibid.*, 1964, **86**, 213.

[23] H. Jadamus, Q. Fernando, and H. Freiser, *J. Amer. Chem. Soc.*, 1964, **86**, 3056.

[24] E. Bayer and E. Breitmaier, *Chem. Ber.*, 1968, **101**, 1579.

[25] L. F. Lindoy *Co-ordination Chem. Rev.*, 1969, **4**, 41.

[26] E. I. Stiefel, J. H. Water, E. Billig, and H. B. Gray, *J. Amer. Chem. Soc.*, 1965, **87**, 3016; F. Lalor, M. F. Hawthorne, A. H. Maki, K Darlington, A Davison, H. B. Gray, Z. Dori, and E. I. Stiefel, *J. Amer. Chem. Soc.*, 1967, **89**, 2278; M. S. Elder, G. M. Prinz, P. Thornton, and D. H. Busch, *Inorg. Chem.*, 1968, **7**, 2426.



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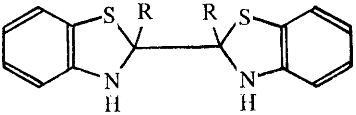

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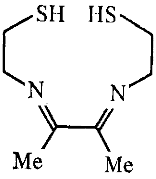

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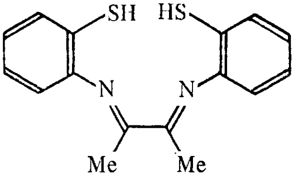

(11)

It has been postulated that the metal ion sequesters the Schiff base form from the equilibrium and hence thermodynamic template effects appear to operate in these reactions. Provided that the metal complex produced is only slightly dissociated in solution or that it precipitates from the solution then its formation in high yield will occur. Analogous studies on the metal-ion induced rearrangement of 2-(2-pyridyl)benzothiazoline have also been carried out.[14,27] Once again, competing equilibria are involved and the isolation of the required product depends upon a number of factors, including the pH of the solution, the nature of the solvent, and the relative solubilities of the species present. Basic conditions favour formation of the Schiff base tautomer.

Rearrangements of the type discussed above are not restricted to sulphur heterocycles. Oxygen compounds such as 2,2′-bisbenzoxazoline (12) also undergo metal-ion induced rearrangements to yield complexes of the corresponding tautomeric Schiff bases.[28–30] Scheme 3 illustrates one such reaction sequence.[29]

Condensation of 1,1,1-tris(aminomethyl)ethane with pyridine-2-aldehyde does not yield the corresponding Schiff base (13) but rather a cyclic product of structure (14: R = CH_3) is formed.[31] Previously, the condensation product from tris(aminomethyl)methane and pyridine-2-aldehyde had been assigned the structure (13; R = H)[32] since this product reacts with ferrous ion to give permanganate-coloured compounds of the type Fe(ligand)X_2,$n$$H_2O$ whose properties are typical of complexes containing the characteristic tris-α-di-imineiron(II) chromophore. Indeed, reaction of (14; R = CH_3) with ferrous ion

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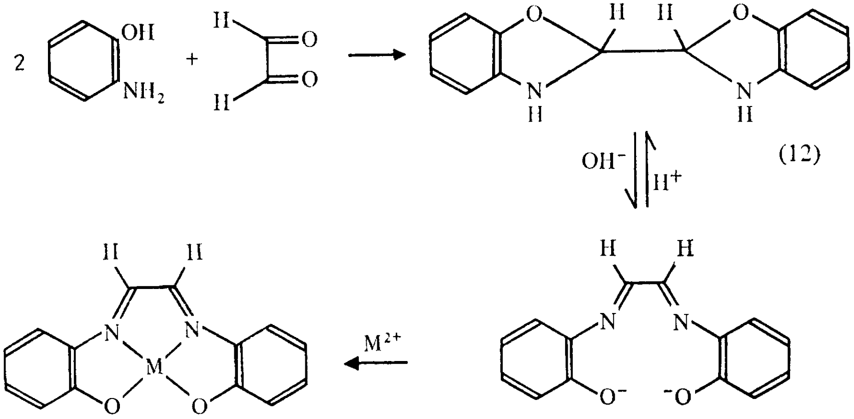
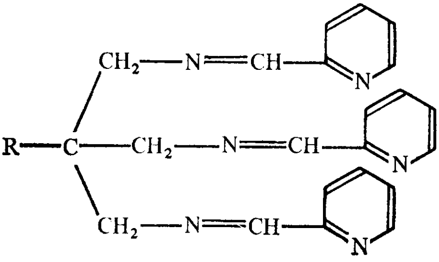
[27] L. F. Lindoy and S. E. Livingstone, *Inorg. Chim. Acta.*, 1968, **2**, 119.
[28] E. Bayer and G. Schenk, *Ber.*, 1960, **93**, 1184.
[29] E. Bayer, *Angew. Chem. Internat. Edn.*, 1964, **3**, 325.
[30] I. Murase, *Bull. Chem. Soc. Japan*, 1960, **33**, 607.
[31] D. A. Durham, F. A. Hart, and D. Shaw, *J. Inorg. Nuclear Chem.* 1967, **29**, 509.
[32] F. P. Dwyer, N. S. Gill, E. C. Gyarfas, and F. Lions, *J. Amer. Chem., Soc.*, 1957, **79**, 1269.



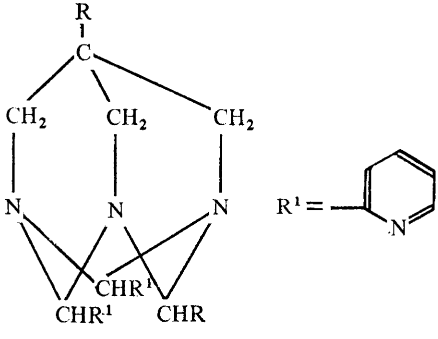
(12)

(M = Cu, UO_2, Ni, *etc.*)

Scheme 3



(13)

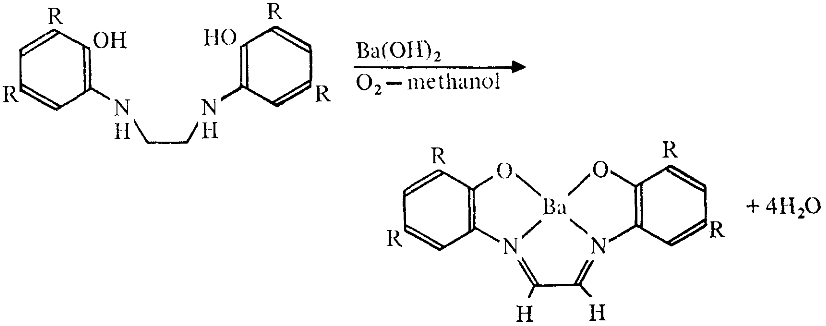


(14)

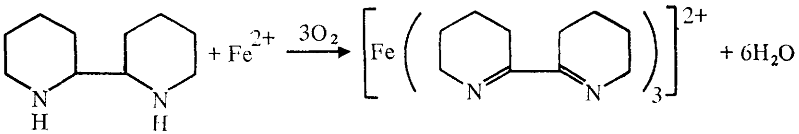
in methanol–water at 60 °C also leads to the formation of a similar purple complex. It is apparent that in both of these cases the metal-ion induced rearrangement of the cyclic product (14) to the corresponding α-di-imine Schiff base occurs. The Schiff base form is much more suitable than its precursor for chelation with iron(II). In contrast, lanthanide ions do not promote the rearrangement of (14; R = CH_3) but form instead complexes of this cyclic compound. Once again it seems that the driving force for the rearrangement reaction in the presence of iron(II) is the formation of very stable spin-paired complexes. Apparently there is insufficient stabilisation on reaction with lanthanides to promote a similar rearrangement. Thermodynamic factors thus appear to control the course of the reaction.

D. Oxidation of Co-ordinated Secondary Amines.—Another route that is sometimes used to prepare Schiff bases is oxidative dehydrogenation of the corresponding secondary amines. This may be effected in the presence of suitable metal ions such that a Schiff base complex is obtained directly. Two such reactions are illustrated in Schemes 4[33] and 5.[6]

The use of redox reactions for generating imine linkages *in situ* provides a reaction type of great versatility since there is available a wide range of chemical



Scheme 4



Scheme 5

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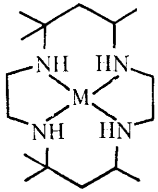
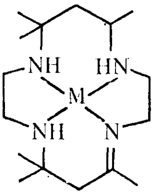
[33] F. Lober and K. Ley, G.P. 1,104,552 (*Chem. Abs.*, 1962, **56**, 5887a).

oxidising agents whose mode of action will very often depend upon the reaction conditions as well as on the particular metal ion present. Electrochemical oxidations are also possible. By the choice of suitable conditions, selective redox reactions can sometimes be used to produce a series of closely related complexes which differ only in their degree of unsaturation. The choice of conditions for such reactions is at the present largely empirical since very little is known about the role of the metal ion in reactions of this type. However, it is apparent from the limited studies[33–35] that have been made that the metal ion can influence both the ease with which a reaction occurs as well as the structure of the redox product.

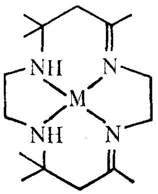
One system that has been investigated in a little detail is the production of macrocyclic complexes containing from zero to four imine linkages (15)—(19).[35] The starting complex for all these products is the di-imine (17), first prepared by Curtis by *in situ* methods.[35]



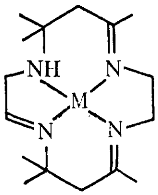
(15)



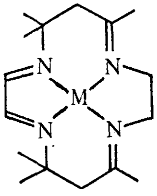
(16)



(17)



(18)



(19)

The tetra-amine (15) is produced by reaction of (17) with a variety of reducing agents, such as hydrogen over platinum catalyst, sodium borohydride, or nickel–aluminium alloy in basic solution. It can also be produced by cathodic reduction. Oxidation of (17) with nitric acid yields the tetraimine (19). A redox pathway involving the formation of nickel(III) intermediates has been postulated for this and similar oxidations.[35] The formation of such an intermediate may explain

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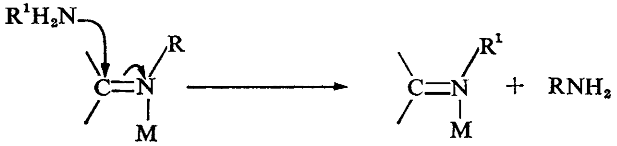
[34] E. G. Vassian and R. K. Murmann, *Inorg. Chem.*, 1967, **6**, 2043.
[35] N. F. Curtis, *Co-ordination Chem. Rev.*, 1968, **3**, 3.

the observation that the induced unsaturation almost always occurs adjacent to a co-ordinated secondary amine such that a co-ordinated imine function is produced. Careful treatment of the oxidised compound (19) with mild reducing agents has led to isolation of the remaining members of the series, namely (16) and (18).[35]

It is perhaps significant that attempts to oxidise the cobalt(III) analogue of (17) were unsuccessful.[36] This failure may reflect the reluctance of Co^{IV} reaction intermediates to form since cobalt(IV) compounds are extremely rare.

E. Amine Exchange Reactions.—The formation of new Schiff base complexes by amine exchange reactions performed on existing Schiff base complexes has been used synthetically in a few instances[16,19,37–40] and is related to the well-known transamination reactions of biological systems. The general reaction can be illustrated thus:



Bis-salicylaldimino-[19,37,38] and, to a lesser extent, bis-β-ketoimino-metal complexes[16,39] have both been used as starting materials for such reactions. The reactions may proceed by an initial attack of the exchanging amine on the electron-deficient carbon of the polarised imine linkage and appear to be equilibrium-controlled. The exchanging amine is usually reacted in considerable excess and indeed has even been employed as the reaction solvent.[37]

From a study of a number of exchange reactions in chloroform using a three-fold excess of reacting amine, it was concluded that a high yield of product is only obtained when the reacting amine is significantly more basic than the displaced amine.[19]

F. Metal Exchange Reactions.—There are a few reports of Schiff base complexes containing a labile metal ion being used for metal exchange reactions.[4,41,42] Chiefly complexes of salicylaldimines or β-ketoimines have been employed for such reactions.[41,42] An advantage of metal exchange as a synthetic method is

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[36] K. E. Barefield, Ph.D. Thesis, The Ohio State University, 1969.

[37] Y. Muto, *Nippon Kagaku Zasshi*, 1955, **76**, 252 (*Chem. Abs.*, 1957, **51**, 17559f).

[38] H. S. Verter and A. E. Frost, *J. Amer. Chem. Soc.*, 1960, **82**, 85.

[39] D. F. Martin, *Adv. Chem. Series*, 1963, **37**, 192.

[40] Y. Muto, *Bull. Chem. Soc. Japan*, 1960, **33**, 1242.

[41] A. W. Struss and D. F. Martin, *J. Inorg. Nuclear Chem.*, 1963, **25**, 1409 and references therein.

[42] R. J. Cozens, K. S. Murray, and B. O. West, *Austral. J. Chem.*, 1970, **23**, 683.

that it often tends to minimise side reactions that may be troublesome in other procedures.[41]

The exchange reactions of various *N*-substituted salicylaldimine thallium(I) complexes well illustrate this type of synthesis.[42] Such reactions have been used to prepare a range of Schiff base complexes in high yield. A typical reaction is:

$$\mathrm{CuCl_2 + Tl_2\,(salen) \xrightarrow[65\,°C]{MeOH} Cu(salen) + 2TlCl}\ (\text{yield } 85\%)$$

where H_2salen = *NN'*-ethylenebis(salicylaldimine).

The method has been extended to the preparation of little-studied Schiff base chelates of the second- and third-row transition elements which are often difficult to obtain by other routes.[42] The increasing emphasis given to the study of such complexes will almost certainly lead to metal exchange becoming more popular as a synthetic method in the future.