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The Metal-Ion Induced Rearrangement of 2-(2-Pyridyl)benzothiazoline

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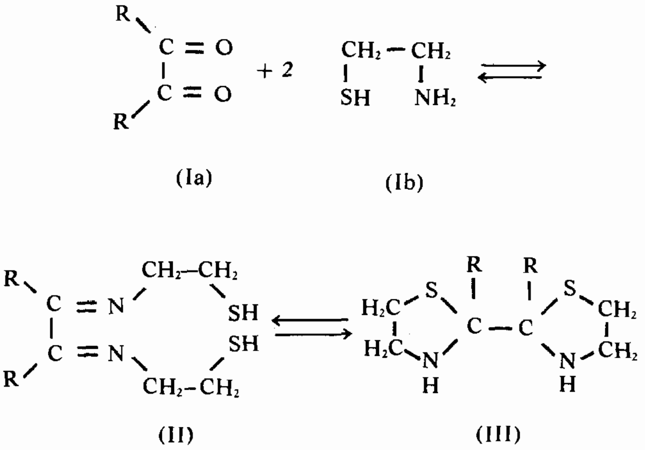
The reactions of a solution of 2-(2-pyridyl)benzothiazoline with various salts of zinc, cadmium, and mercury have been studied. In several cases rearrangement to the corresponding Schiff base, N-2-*mercaptophenyl·2′-pyridylmethyleneimine, was observed to occur and, in these cases, intensely coloured metal complexes of the Schiff base could be isolated. The factors influencing this metal-ion induced rearrangement are discussed.*

Introduction

Previously we have reported *S*-demethylation reactions of coordinated thioether ligands and also *S*-alkylation reactions of coordinated thiolo-ligands.[1-5] In this paper some examples of another type of reaction of a sulphur-containing chelate, namely the metal-ion induced rearrangement of an organic ligand, are discussed.

It has been established that condensation of a β-mercaptoamine with an aldehyde does not normally lead to isolation of the corresponding Schiff base but rather a thiazolidine (with a β-mercaptoalkylamine) or a benzothiazoline (with an *o*-aminobenzenethiol) or their oxidation products are obtained.[6-10] Busch and Thompson[11,12] have shown that alcoholic solutions of various α-diketones react with β-mercaptoethylamine in the presence of nickel ions to give a nickel complex of the corresponding doubly-deprotonated tetradentate Schiff base in good yield. It is interesting that repetition of these experiments in the absence of the metal ion yielded both the bis-thiazolidinyl (60-75%) and the impure Schiff base (*ca.* 10%). These authors concluded that the metal ion acts as a template which favours the formation of the Schiff base rather than the bis-thiazolidinyl. However, Freiser *et al.*[13] have shown that metal complexes of the Schiff base can also be prepared by reacting the metal ion directly with a solution of the bis-thiazolidinyl. Solutions of thiazolidines are known to give positive tests for the presence of free mercapto groups[14,15] and it has been suggested[13,16] that the bis-thiazolidinyl(III) exists in solution in equilibrium (Scheme I) with small amounts of both the Schiff base (II) and the initial reactants (Ia, b) and that the appropriate metal-ion sequesters the intermediate Schiff base from the equilibrium mixture.

Scheme I.



Condensation of *o*-aminobenzenethiol with α-diketones also yields in solution an analogous equilibrium mixture.[13,17,18,19] The conversion of the bis-benzothiazolinyl(V) to the tautomeric Schiff base (VI) is known to be influenced by firstly, the pH of the solution — basic conditions cause the equilibrium to favour formation of the Schiff base — and secondly, the presence of metal ions which bond strongly with the

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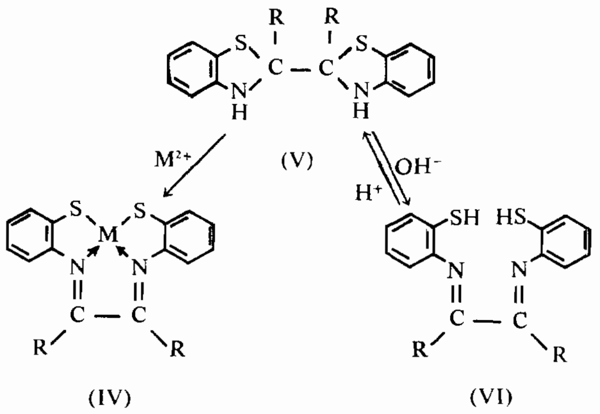
(1) L. F. Lindoy, S. E. Livingstone, and T. N. Lockyer, *Austral. J. Chem.*, *19*, 1391 (1966).
(2) L. F. Lindoy, S. E. Livingstone and T. N. Lockyer, *Nature*, *211*, 519 (1966).
(3) L. F. Lindoy, S. E. Livingstone and T. N. Lockyer, *Austral. J. Chem.*, *20*, 471 (1967).
(4) S. E. Livingstone and T. N. Lockyer, *Inorg. Nucl. Letters*, *3*, 35 (1967).
(5) L. F. Lindoy, S. E. Livingstone and T. N. Lockyer, *Inorg. Chem.*, *6*, 652 (1967).
(6) M. T. Bogert and B. Naiman, *J. Amer. Chem. Soc.*, *57*, 1529 (1935).
(7) M. Claasz, *Ber.*, *49*, 1141 (1916).
(8) S. Ratner and H. T. Clarke, *J. Amer. Chem. Soc.*, *59*, 200 (1937).
(9) F. J. Kreipa, V. Mature, J. J. Finn, J. G. McClarnon and F. Lombardo, *J. Amer. Chem. Soc.*, *73*, 1155 (1951).
(10) R. C. Elderfield and E. C. McClenachan, *J. Amer. Chem. Soc.*, *82*, 1982 (1960).
(11) M. C. Thompson and D. H. Busch, *J. Amer. Chem. Soc.*, *84*, 1762 (1962).
(12) M. C. Thompson and D. H. Busch, *J. Amer. Chem. Soc.*, *86*, 213 (1964).
(13) H. Jadamus, Q. Fernando and H. Freiser, *Inorg. Chem.*, *3*, 928 (1964).
(14) G. Hease and G. Ludwig, *Ann.*, *632*, 158 (1960).
(15) M. P. Schubert, *J. Biol. Chem.*, *114*, 341 (1936).
(16) D. H. Busch, *Record of Chem. Progr.*, *25*, 107 (1964).
(17) H. Jadamus, Q. Fernando and H. Freiser, *J. Amer. Chem. Soc.*, *86*, 3056 (1964).
(18) E. Bayer, *Angew. Chem.*, *73*, 659 (1961).
(19) E. Bayer, *Angew. Chem.*, (Internat. Edit.), *3*, 325 (1964).

Schiff base also favour its formation. The rates of formation, in dimethylformamide, of the zinc(II) and cadmium(II) complexes of (VI, R = H) have been studied spectrophotometrically.[13,17] The rate determining step in the formation of the zinc complex is probably the conversion of (VI, R = H) to the Schiff base tautomer, whereas with cadmium the reaction has been shown to proceed via a direct attack on the benzothiazoline by the metal-ion and thus the course of the reaction depends upon the particular metal-ion involved. In the latter case it is possible that the metal ion causes a direct cleavage of the $-S-CH<$ bond of the benzothiazoline ring and, if this is the case, the mechanism of this cleavage could well be similar to that previously postulated[5] for the *S*-dealkylation of certain thioethers in the presence of metal ions.

Complexes of (VI; R = H or CH_3) with a number of metal-ions have so far been reported.[13,17,18,19] The reactions are summarised in Scheme II. The analogous metal-ion catalysed rearrangement of 2,2′-bisbenzoxazoline has also been studied.[19,20]

Scheme II.

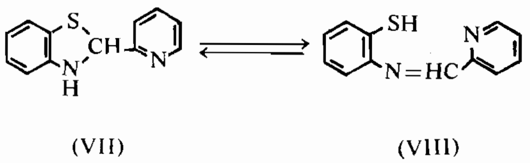


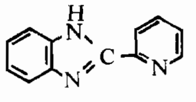
Charles and Freiser[21] have shown that the direct condensation of *o*-aminobenzenethiol with salicylaldehyde results in formation of 2-(2-hydroxyphenyl)-benzothiazoline. The yellow crystals obtained were characterized by elemental analysis, infrared and ultraviolet spectral measurements, and a molecular weight determination. In contrast, Muto[22] has claimed that when this condensation occurs in alcohol, the corresponding Schiff base is obtained in the solid state and not the benzothiazoline.

Results and Discussion

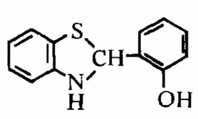
Condensation of *o*-aminobenzenethiol with pyridine-2-aldehyde in alcohol yields a cream crystalline product and reaction of this product with molybdenum(III) has been reported to result in the formation of a metal complex of the corresponding Schiff base.[23] On the basis of this complex and by analogy with the work of Muto, the organic condensation product was considered to be the Schiff base (VIII). However, subsequently we have reinvestigated this organic product and, although in solution it undoubtedly exists as an equilibrium mixture of the Schiff base, *N*-2-mercaptophenyl-2-pyridylmethyleneimine (VIII) and 2-(2-pyridyl)benzothiazoline (VII), the infrared spectrum of the solid contains no band which can be assigned to the S-H stretching mode of the Schiff base form ($\nu_{(S-H)}$ for *o*-aminobenzenethiol occurs at 2540 cm^{-1}).[24] The spectrum displays a band of medium intensity at 3185 cm^{-1} with a shoulder at 3170 cm^{-1}; these bands are assigned to $\nu_{(NH)}$ of the benzothiazoline form. For comparison the N-H stretching modes occur at 3040 cm^{-1} and 3030 cm^{-1} for 2-(2-pyridyl)benzimidazole (IX)[25] and at 3200 cm^{-1} for 2-(2-hydroxyphenyl)benzothiazoline (X).[21]

Scheme III.

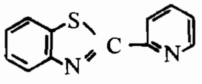




(IX)



(X)



(XI)

Oxidation of a warm alcoholic solution of the present ligand leads to the predicted conversion to 2-(2-pyridyl)-benzothiazole (XI) which has been reported by several investigators.[26-29] The infrared spectrum of this oxidised product shows the absence of the N-H stretch found in the spectrum of its precursor. Thus, in the solid state, the non-oxidized ligand exists completely or virtually completely in the benzothiazoline form (VII). Apparently, in the formation of the molybdenum complex, the metal ion effects the rearrangement of the 2-(2-pyridyl)benzothiazoline in an analogous manner to the metal-ion induced rearrangements discussed in the Introduction.

Reaction of a solution of excess 2-(2-pyridyl)benzothiazoline (i.e. $C_{12}H_{10}N_2S$) with zinc or cadmium acetates yields reddish-black crystalline complexes of the type $M(C_{12}H_9N_2S)_2$. The cadmium complex can also be isolated from a solution in which the formation of the ligand from pyridine-2-aldehyde and *o*-aminobenzenethiol is allowed to occur in the presence of the cadmium acetate. The conductivities of these and

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(20) E. Bayer and G. Schenk, *Ber.*, *93*, 1184 (1960).
(21) R. G. Charles and H. Freiser, *J. Org. Chem.*, *18*, 422 (1953).
(22) Y. Muto, *Bull. Chem., Soc. Japan*, *33*, 1242 (1960).
(23) L. F. Lindoy, S. E. Livingstone and T. N. Lockyer, *Austral. J. Chem.*, *18*, 1549 (1965).
(24) Cyanamid New Product Bulletin, Collective Volume II, American Cyanamid Company, New York, p. 67 (1950).
(25) T. R. Harkins, J. L. Walter, O. E. Harris and H. Freiser, *J. Amer. Chem. Soc.*, *78*, 260 (1956).
(26) B. L. Bastic and M. V. Piletic, *Glasnik. Hem. Drustva. Beograd*, *28*, 149 (1963).
(27) H. Saikachi and T. Hisano, *Chem. Pharm. Bull.*, *7*, 716 (1959).
(28) P. E. Miller, G. L. Oliver, J. R. Dann and J. W. Gates, *J. Org. Chem.*, *22*, 664 (1957).
(29) B. Emmert and M. Groll, *Ber.*, *86*, 208 (1953)

other compounds reported in this paper are listed in Table I.

Table I. Zinc, Cadmium and Mercury Complexes

Compound	Colour	Λ_{2000} in $MeNO_2$ at 25°
$Zn(C_{12}H_9N_2S)_2$	reddish-black	3.3 (mho)
$Cd(C_{12}H_9N_2S)_2$	reddish-black	3.6
$Zn(C_{12}H_9N_2S)(CH_3COO)$	maroon	0.7
$Cd(C_{12}H_9N_2S)(CH_3COO)$	yellow	i
$Zn(C_{12}H_9N_2S)Cl$	yellow	i
$Cd(C_{12}H_9N_2S)Cl$	yellow	i
$Hg(C_{12}H_9N_2S)_2$	yellow	1.2
$Zn(C_{12}H_9N_2S)_2.NiCl_2.H_2O$	brown	i
$Hg(C_{12}H_9N_2S)_2.CuCl_2.H_2O$	brown	i

i = insoluble.

The previously reported metal complexes of the Schiff bases (II and VI) are all intensely coloured, *e.g.* the complexes (IV, R = CH_3; M = Zn, Cd) are reddish-orange and the complexes (IV, R = H; M = Zn, Cd) are bluish-black.[13,17] The intense colour of our compounds suggests that the metal-ion induced rearrangement has occurred. In addition, treatment of a solution of 2-(2-pyridyl)benzothiazoline in alcohol with alkali or sodium ethoxide also favours conversion to the Schiff base with the concomitant development of a bright reddish-orange colour, which, however, is not as intense as that of the zinc and cadmium complexes. This result is in accord with the observation of Bayer[19] that rearrangement to the Schiff base form is favoured by alkaline conditions.

The absorption spectrum of a solution ($10^{-3}M$) of 2-(2-pyridyl)benzothiazoline in alcohol and the spectra after the addition of firstly, a small excess, and secondly, a large excess of sodium are given in Figure 1. It is seen that in the absence of sodium the spectrum consists of an absorption of small intensity (ε, 52) at 350 mμ with a «tail» which extends well into the visible region. It is apparent that the band at 350 mμ is essentially due to an absorption by the benzothiazoline form of the ligand. The addition of base is accompanied by the formation of a much more intense band in the visible region; this band is postulated to be due to absorption by the sodium salt of the rearranged (Schiff base) form of the ligand. It is interesting that the addition of a large excess of sodium leads to an increase in intensity and an apparent shift to longer wavelengths of this band in the visible region. This indicates that even in the presence of *ca.* 2.5 mole equivalents of sodium, there is apparently only partial conversion to the Schiff base form.

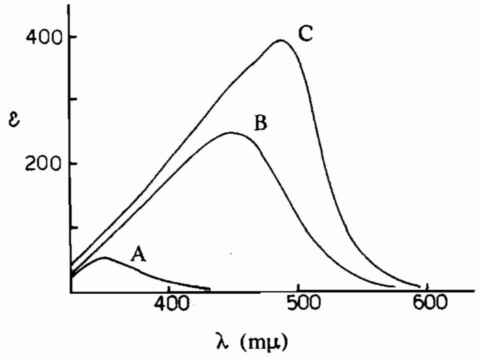


Figure 1. Absorption spectrum of 2-(2-pyridyl)benzothiazoline. (A) In alcohol. (B) in alcohol containing 2.5 mole equivalents of sodium. (C) In alcohol containing 17 mole equivalents of sodium.

The unusual colour of the zinc and cadmium complexes suggests that this ligand may have an application as a colorimetric reagent for these ions, each of which are known to play an important role in many biological systems.[30] The absorption spectra of these two compounds in dimethylformamide are given in Figure 2 and are somewhat similar to the reported spectra of (IV; M = Zn, Cd; R = H or CH_3) in dimethylformamide.[13] The solid state reflectance spectra of these two compounds also exhibit broad absorption bands with a maximum at ~500 mμ.

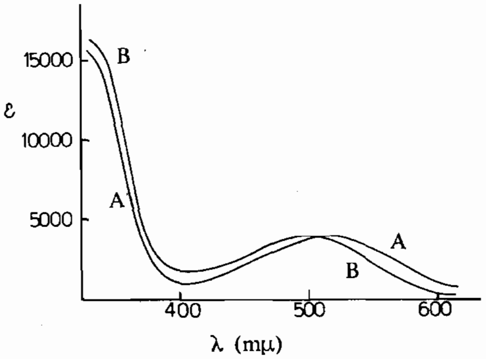
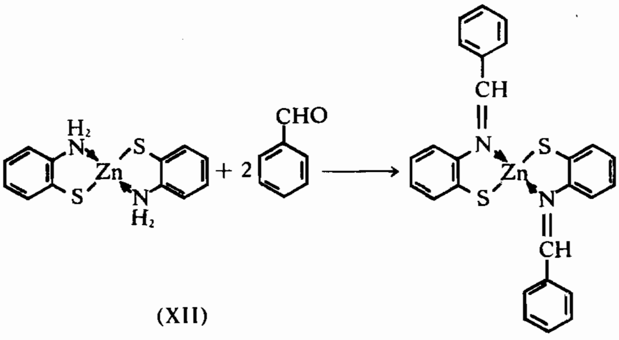


Figure 2. Absorption spectra in dimethylformamide. (A) $Zn(C_{12}H_9N_2S)_2$. (B) $Cd(C_{12}H_9N_2S)_2$.

In 1935 Bogert and Naiman[6] reported the reaction of bis-*o*-aminobenzenethiolozinc(II) with refluxing benzaldehyde (Scheme IV). Condensation occurred to yield the corresponding Schiff base complex (XIII) as reddish-orange crystals.

Scheme IV.



(XII)

(XIII)

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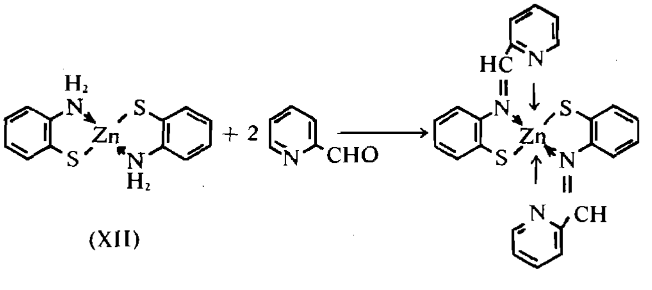
[30] B. L. Vallee and J. E. Coleman, «Metal Coordination and Enzyme Action», ch. 6 in *Comprehensive Biochemistry, 12,* 165 (1964), (Eds. M. Florkin and E. H. Stotz).

We have repeated this reaction by adding the benzaldehyde to a suspension of the zinc complex (XII) in hot alcohol. The solution was then heated for several hours; however, only a small yield of reddish-orange crystals could be isolated from the reaction mixture. On the other hand, substitution of pyridine-2-aldehyde for benzaldehyde in the above reaction results in complete reaction within 25 min. and the reddish-black crystalline compound, $Zn(C_{12}H_9N_2S)_2$, is obtained in 85% yield. Comparison of the infrared spectrum of this compound with that of the compound obtained from the reaction of zinc acetate with a solution of 2-(2-pyridyl)benzothiazoline indicates that these two products are identical. The much darker colour of this compound compared to the colour of (XIII) suggests, *a priori,* that the difference between these two compounds is greater than would normally be expected for replacement, in the zinc chelate of the Schiff base ligand (VIII), of the pyridine ring by a phenyl ring. It seems likely that in the case of the pyridine-containing chelate that the two heterocyclic nitrogen donors are coordinated to give the zinc atom an octahedral stereochemistry (Scheme V). It is known that zinc readily forms complexes in which the coordination number is greater than four.[31] The intense colour of (XIV) is undoubtedly related to the fact that all atoms in the ligand are in conjugation and hence considerable electron delocalization can occur. It is pointed out that the ligand in this chelate incorporates the α-diimine structure $-N=C-C=N-$ found in many ligands which bind strongly to metal ions; the coordination chemistry of bidentates containing this structure has recently been reviewed.[32]

Scheme V.



(XII)

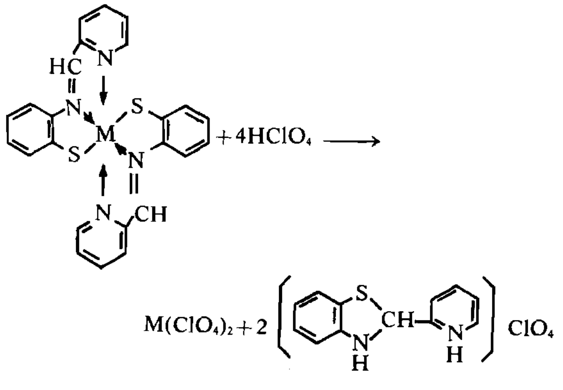
(XIV)

The infrared spectrum of (XII) shows strong absorption at 3225 cm^{-1} and 3030 cm^{-1}; these bands are assigned to the stretching modes of the coordinated amine. In *o*-aminobenzenethiol these occur at 3470 cm^{-1} and 3370 cm^{-1},[24] and it is known that coordination normally leads to a shift of the N-H stretching vibration to lower frequencies.[3] The spectrum of (XII) also shows a band of strong intensity at 1535 cm^{-1} which is assigned to the (N-H) deformation mode. In the infrared spectrum of (XIV) each of these strong N-H absorptions has disappeared, confirming that the Schiff base condensation has occurred.

It has been suggested[16,33] that there is little evidence to indicate that amine ligands will undergo Schiff base condensation reactions whilst coordinated. If this is the case then the rate of reaction of benzaldehyde with (XII) must be dependent on an equilibrium between the free ligand (or free amine groups) and the zinc complex in the reaction mixture. The very much faster rate of reaction with pyridine-2-aldehyde could be the result of a larger concentration of free ligand (or amine groups) in the solution owing to displacement being effected by the pyridine-2-aldehyde; however, the possibility of other less obvious mechanisms cannot be discounted. The presence of heterocyclic bases has been reported to catalyse Schiff base type condensations of aldheydes or ketones to metal chelates of amine ligands.[34,35] A solution of (XIV) in dimethylformamide reacts with nickel chloride in alcohol to yield the paramagnetic brown crystalline complex, $Zn(C_{12}H_9N_2S)_2 \cdot NiCl_2 \cdot H_2O$. The infrared spectrum of this complex shows a broad weak absorption at 3400 cm^{-1} which is due to the O-H stretching mode of the water molecule. In view of the fact that many complexes of thiolo-ligands are polymeric with bridging sulphur atoms,[36] a thiolo-bridged structure for this compound seems likely; however, in the absence of confirmatory data, it is inappropriate to postulate further concerning the nature of this complex.

The reddish-black complexes, $M(C_{12}H_9N_2S)_2$ (M = Zn, Cd), dissolve in dilute perchloric acid to yield yellow solutions. Concentration of these solutions yields, in each case, the yellow perchlorate salt of 2-(2-pyridyl)benzothiazoline and ligand displacement, as illustrated in Scheme VI, appears to have occurred.

Scheme VI.



The behaviour of a solution of (VII) with excess of zinc acetate and cadmium acetate, respectively, is interesting. Zinc acetate yields the maroon complex $Zn(C_{12}H_9N_2S)(CH_3COO)$, in which the ligand has apparently rearranged to the Schiff base form. The analogous reaction using cadmium acetate yields a bright red solution from which a yellow compound is deposited. The composition of this compound is $Cd(C_{12}H_9N_2S)(CH_3COO)$ and its yellow colour indicates

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(31) G. E. Batley and D. P. Graddon, *Austral. J. Chem., 20,* 877 (1967), and references therein.

(32) L. F. Lindoy and S. E. Livingstone, *Coord. Chem. Revs., 2,* 173 (1967).

(33) D. St. C. Black and E. Markham, *Revs. Pure and Appl. Chem., 15,* 109 (1965).

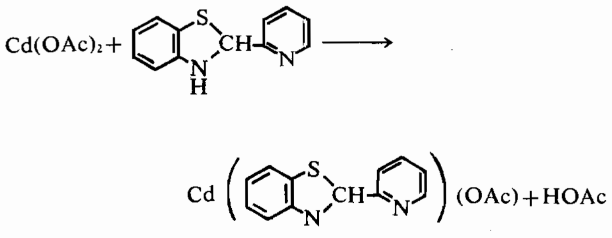
(34) E. J. Olszewski and D. F. Martin, *J. Inorg. Nucl. Chem., 26,* 1577 (1964).

(35) N. F. Curtis, *J. Chem. Soc.,* 4409 (1960).

(36) S. E. Livingstone, *Quart. Revs., 19,* 386 (1965).

that the benzothiazoline has not rearranged to the Schiff base. Nevertheless the red colour of the reaction solution indicates that some rearrangement to the Schiff base tautomer occurs in solution. It is postulated that the yellow cadmium compound contains the deprotonated form of the benzothiazoline and the reaction is illustrated in Scheme VII.

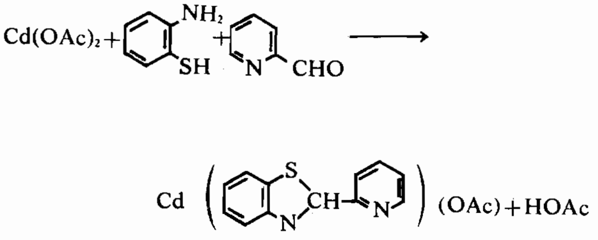
Scheme VII.



(XV)

The structure of the yellow compound (XV) is presumably polymeric but its low solubility in common organic solvents precluded the possibility of a molecular weight determination. It is significant that (XV) is also obtained when an alcohol solution of cadmium acetate is allowed to react *in situ* with pyridine-2-aldehyde and *o*-aminobenzenethiol (Scheme VIII).

Scheme VIII.



(XV)

The reactions of zinc and cadmium chlorides with solutions of (VII) have also been investigated. It might be expected that the less basic conditions arising from the substitution of chloride ions for acetate ions may favour the coordination of the benzothiazoline form of the ligand and in agreement with this both metal chlorides form yellow complexes of the type M-$(C_{12}H_9N_2S)Cl$ which are apparently analogous to the yellow cadmium acetate complex (XV) and probably exist as dimers or polymers. The tendency of the benzothiazoline group to lose a proton when coordinated parallels the behaviour of the ligand 2-(2-pyridyl)benzimidazole (IX) in which the imino hydrogen of the imidazole group has been shown to become more acidic after coordination[37] and in fact it is possible to prepare bis[2-(2-pyridyl-benzimidazolato]-nickel(II) which contains the deprotonated form of (IX).[38] Other related cases of the deprotonation of ligands on coordination are known.[32]

The yellow complexes, $M(C_{12}H_9N_2S)X$ (M = Cd, X = CH_3COO, Cl; M = Zn, X = Cl), are soluble in their corresponding dilute acids to yield yellow solutions and if excess sodium hydroxide solution is then added quickly, a bright red precipitate is produced in each case. The slow addition of alkali produces initially a yellow product, which is probably the original complex, and this is followed by the deposition of the red complex as the solution becomes more alkaline. The red cadmium chloride complex was found to have essentially the same composition as that of the yellow starting material and probably contains the ligand in the Schiff base form. It was not possible to obtain a pure sample of this red complex, as attempts at recrystallization led to a discharge of the red colouration.

It is emphasized that the isolation of complexes of the ligand both in its deprotonated benzothiazoline form and in its Schiff base form is probably influenced by other factors such as the solvent used and the relative solubilities of the products.

A solution of (VII) reacts with mercuric acetate to yield the complex $Hg(C_{12}H_9N_2S)_2$. The yellow colour of this compound indicates that the ligand is still in the benzothiazoline form, yet it is significant that it crystallizes from an orange solution. This complex reacts with copper chloride to yield the brown crystalline mixed-metal complex, $Hg(C_{12}H_9N_2S)_2 \cdot CuCl_2 \cdot H_2O$ and the room-temperature moment of the copper ion in this compound (χ'_M, 1550; $\mu = 1.83$ B.M.), confirms that the copper is in the bivalent state.

The reactions of 2-(2-pyridyl)benzothiazole (XI) with zinc(II), cadmium(II), mercury(II), and other metal ions have been investigated and other rearrangements of 2-(2-pyridyl)benzothiazoline (VII) induced by transition metal ions have been observed.[39] These results will be reported in due course.

Experimental Section

All complexes were washed with alcohol and dried *in vacuo* over phosphorus pentoxide. Analyses for carbon, hydrogen, and nitrogen were carried out by Dr. E. Challen of the Microanalytical Laboratory, University of New South Wales. Analyses for sulphur were carried out by the Australian Microanalytical Service, Melbourne.

2-(2-Pyridyl)benzothiazoline. This compound was prepared as previously reported.[23]* (Found: C, 67.3; H, 4.8; N, 12.7; S, 15.0. Calc. for $C_{12}H_{10}N_2S$: C, 67.3; H, 4.7; N, 13.1; S, 15.0%). The m.p. of different batches varied between 85° and 99°. The m.p. of any particular product also varied with the age of sample and the rate of heating. These variations could be due to (i) the occurrence of a small amount of oxidation of the 2-(2-pyridyl)benzothiazoline to 2-(2-pyridyl)benzothiazole—a similar variation in m.p. of 2-(2-hydroxyphenyl)benzothiazoline has been observed[21] and is considered to be due to oxidation—and/or (ii) the concurrent formation of small, varying amounts of the tautomeric Schiff base (VIII). A similar mixture

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(37) T. R. Harkins and H. Freiser, *J. Amer. Chem. Soc.*, *78*, 1143 (1956).

(38) B. Chiswell, F. Lions and B. S. Morris, *Inorg. Chem.*, 3, 110 (1964).

(39) L. F. Lindoy and S. E. Livingstone, unpublished results.

(*) In this reference the compound is named as the tautomeric Schiff base, *N*-2-mercaptophenylene-2′-pyridylmethyleneimine.

of products was obtained from the condensation of β-mercaptoethylamine with α-diketones.[11,12]

2-(2-Pyridyl)benzothiazole. This compound was prepared by a modification of the method of Miller *et al.*[28] who used oxidation of an aqueous solution of 2-(2-pyridyl)benzothiazoline hydrochloride with ferric chloride.

In the present work this compound was prepared by passing air through a warm solution of 2-(2-pyridyl)-benzothiazoline (19.0 g) in alcohol (400 ml) for 30 hr. After concentration of the solution, the product formed as cream crystals; yield 13.5 g; m.p. 133.5° (lit.[28] 133-133.5°). (Found: C, 67.9; H, 3.8; N, 12.9. Calc. for $C_{12}H_8N_2S$: C, 67.9; H, 3.8; N, 13.2%).

Bis(N-*2-thiolophenyl-2'-pyridylmethyleneimine*)-*zinc*(*II*). Zinc acetate dihydrate (0.2 g) in hot alcohol (10 ml) was added to 2-(2-pyridyl)benzothiazoline (0.8 g) in hot alcohol (25 ml). The dark red solution was warmed, then allowed to cool, whereupon reddish-black crystals of the *complex* formed; yield 0.2 g. (Found: C, 58.3; H, 3.7; N, 10.9; S, 12.4. $C_{24}H_{18}N_4S_2Zn$ requires C, 58.5; H, 3.7; N, 11.4; S, 13.0%).

This compound was also prepared by condensing pyridine-2-aldehyde (6 ml) directly with a suspension of bis(*o*-aminobenzenethiolo)zinc(II) (2.3 g) in ethanol (35 ml). The suspension was warmed for 25 min and by this time the product had formed as reddish-black crystals; yield 3.0 g. (Found: C, 58.7; H, 3.8; N, 11.1%).

Nickel Chloride Adduct. Nickel chloride hexahydrate (0.12 g) in hot alcohol (20 ml) was added to a solution of the zinc complex (0.5 g) in hot dimethylformamide (85 ml). The brown solution was let stand at 0° for several days. The *adduct* formed as brown crystals; yield 0.25 g. (Found: C, 45.5; H, 3.5; N, 8.3; Ni, 9.0. $C_{24}H_{18}N_4S_2Zn.NiCl_2.H_2O$ requires C, 45.1; H, 3.15; N, 8.8; Ni, 9.2%).

Bis(N-*2-thiolophenyl-2'-pyridylmethyleneimine*)-*cadmium*(*II*). Cadmium acetate dihydrate (0.3 g) in hot alcohol (30 ml) was added to 2-(2-pyridyl)benzothiazoline (0.8 g) in hot alcohol (20 ml). Reddish-black crystals of the *complex* were deposited from the deep red solution; yield 0.7 g. (Found: C, 53.8; H, 3.5; Cd, 21.3; N, 10.4. $C_{24}H_{18}CdN_4S_2$ requires C, 53.5; H, 3.4; Cd, 20.85; N, 10.4; S, 11.9%).

This compound was reprepared as above except that the formation of the ligand (0.8 g) from pyridine-2-aldehyde and *o*-aminobenzenethiol was carried out in the presence of the cadmium acetate dihydrate (0.3 g) in hot alcohol (50 ml); yield 0.7 g. (Found: C, 53.4; H, 3.4; N, 9.9; S, 11.7%).

Bis(o-*aminobenzenethiolo*)*zinc*(*II*). The preparation of this compound has been previously reported.[40] (Found: C, 45.8; H, 3.9; N, 8.5. Calc. for $C_{12}H_{12}N_2S_2Zn$: C, 45.9; H, 3.9; N, 8.9%).

Acetato (N-*2-thiolophenyl-2'-pyridylmethyleneimine*)*zinc*(*II*). 2-(2-Pyridyl)benzothiazoline (0.4 g) in hot alcohol (10 ml) was added to zinc acetate dihydrate (0.4 g) in hot alcohol (30 ml). A maroon crystalline *compound* separated from the dark red solution; yield 0.5 g. (Found: C, 50.2; H, 3.6; N, 8.7; Zn, 18.9. $C_{14}H_{12}N_2O_2SZn$ requires C, 49.8; H, 3.6; N, 8.3; Zn, 19.4%).

Acetato (N-*2-thiolophenyl-2'-pyridylmethyleneimine*)*cadmium*(*II*). 2-(2-Pyridyl)benzothiazoline (1.0 g) in hot alcohol (25 ml) was added to cadmium acetate dihydrate (2.0 g) in hot alcohol (100 ml). A yellow precipitate of the *complex* formed from the red solution; yield 1.4 g. (Found: C, 44.1; H, 3.4; N, 7.0. $C_{14}H_{12}CdN_2O_2$ requires C, 43.7; H, 3.1; N, 7.3%). This compound was prepared again as above except that the formation of the ligand was allowed to occur in the presence of cadmium acetate; yield 1.6 g. (Found: C, 43.3; H, 3.2%).

Chloro[*2-(2-pyridyl)benzothiazolinato*]*zinc*(*II*). 2-(2-Pyridyl)benzothiazoline (0.4 g) in hot alcohol (10 ml) was added to zinc chloride (0.3 g) in hot alcohol. The red solution was warmed, then allowed to cool, whereupon the yellow *complex* was deposited; yield 0.2 g. (Found: C, 45.9; H, 3.1; N, 8.9; S, 10.0. $C_{12}H_9ClN_2SZn$ requires C, 45.9; H, 2.9; N, 8.9; S, 10.2%).

Chloro[*2-(2-pyridyl)benzothiazolinato*] *cadmium*(*II*). 2-(2-Pyridyl)benzothiazoline (0.6 g) in hot alcohol (20 ml) was added to cadmium chloride 2.5 hydrate (0.3 g) in alcohol (50 ml). A yellow precipitate of the *complex* formed; yield 0.4 g. (Found: C, 39.9· H, 2.5; Cl, 9.7; N, 7.8. $C_{12}H_9CdClN_2S$ requires C, 39.9; H, 2.5; Cl, 9.8; N, 7.8%).

Bis[*2-(2-pyridyl)benzothiazolinato*]*mercury*(*II*). Mercuric acetate (0.3 g) in hot alcohol (10 ml) was added to 2-(2-pyridyl)benzothiazoline (0.8 g) in hot alcohol (25 ml). On standing, the orange solution yielded yellow crystals of the *complex*. (Found: C, 46.0; H, 3.1; N, 8.6; S, 10.2. $C_{24}H_{18}HgN_4S_2$ requires C, 46.0; H, 2.9; N, 8.9; S, 10.2%).

Copper Chloride Adduct. Copper chloride dihydrate (0.08 g) in hot acetone (40 ml) was added to a solution of the yellow mercury complex (0.30 g) in hot acetone (200 ml). The brownish-purple solution was let stand (under nitrogen) for several days. The *adduct* formed as brown needles; yield 0.25 g. (Found: C, 36.7, 37.4; H, 2.8, 2.6; Cu, 7.2; N, 7.6, 7.2. $C_{24}H_{18}HgN_4S_2.CuCl_2.H_2O$ requires C, 37.0; H, 2.6; Cu, 8.2; N, 7.2%).

Reaction of Perchloric acid with Bis[*2-(2-pyridyl)-benzothiazolinato*]*zinc*(*II*). Bis[2-(2-pyridyl)benzothiazolinato]zinc(II) (0.5 g) was dissolved in hot 2% perchloric acid (40 ml). The solution was let stand and yellow crystals of the perchlorate salt of the ligand formed; yield 0.5 g. (Found: C, 46.7; H, 3.8; N, 9.2. $C_{12}H_{10}N_2S.HClO_4$ requires C, 45.8; H, 3.5; N, 8.9%).

Reaction of Perchloric acid with Bis[*2-(2-pyridyl)-benzothiazolinato*]*cadmium*(*II*). By a similar procedure to that described above bis[2-(2-pyridyl)benzothiazolinato]cadmium(II) also yielded yellow crystals of the perchlorate salt of the ligand; yield 0.2 g.

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(40) E. J. Olszewski and M. J. Albinak, *J. Inorg. Nucl. Chem.*, *27*, 1431 (1965).