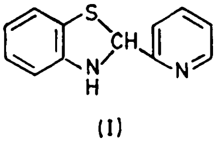
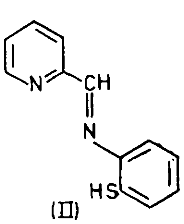
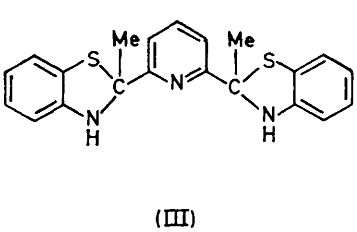
Helical Co-ordination: Five-co-ordinate Zinc and Cadmium Complexes Formed by Metal-ion-induced Ligand Reactions

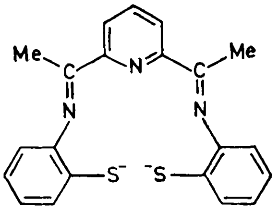
By L. F. Lindoy and D. H. Busch*
(*Chemistry Department, Ohio State University, Columbus, Ohio* 43210)
and V. Goedken
(*Chemistry Department, The University of Chicago, Chicago, Illinois* 60637)

Summary Metal-ion-induced rearrangement of 2,6-bis-(2-methyl-2-benzothiazolinyl)pyridine yields five-co-ordinate zinc and cadmium complexes of the corresponding Schiff base; the *X*-ray structure of the zinc complex shows that the co-ordinated ligand has a novel helical configuration.


(I)


(II)


(III)


(IV)

Condensation of 2-aminobenzenethiol and pyridine-2-carboxaldehyde is known to yield 2-(2-pyridyl)benzothiazoline (I).[1] In solution, certain metal salts induce a rearrangement of (I) to the tautomeric Schiff base (II) which may be obtained in the deprotonated form as its corresponding metal complex. Zinc and cadmium acetates yield dark red bis-ligand Schiff base complexes.[1].

Condensation of 2,6-diacetylpyridine with 2-aminobenzenethiol in a 1:2 molar ratio yields a yellow product whose infra-red spectrum shows no ν (C=O) or ν (S–H) absorptions but contains a ν (N–H) mode of medium intensity at 3350 cm^{-1}. Physical measurements confirm that this product is the bis-benzothiazoline (III). Reaction of (III) with zinc or cadmium acetates in dimethylformamide–acetone yields red crystals of the respective products. Both compounds are non-electrolytes in nitromethane. Their i.r. spectra show no amine or carbonyl stretching modes and both spectra show multiplets at *ca.* 1600 cm^{-1} which are attributable to imine and aromatic ring vibrations. Comparison of the properties of these complexes with those of (II) indicate that the former also contain the ligand in its Schiff base form (IV). The mass spectra of the complexes show no peaks at *m*/*e* values greater than the respective parent ions. Reaction of these complexes with methyl iodide results in *S*-alkylation to produce the corresponding thioether derivatives. The success of these reactions strongly suggests that the complexes contain non-bridging thiol groups since such groups do not usually retain sufficient nucleophilic character to undergo alkylation when they are bridging two positive metal ions.[2]

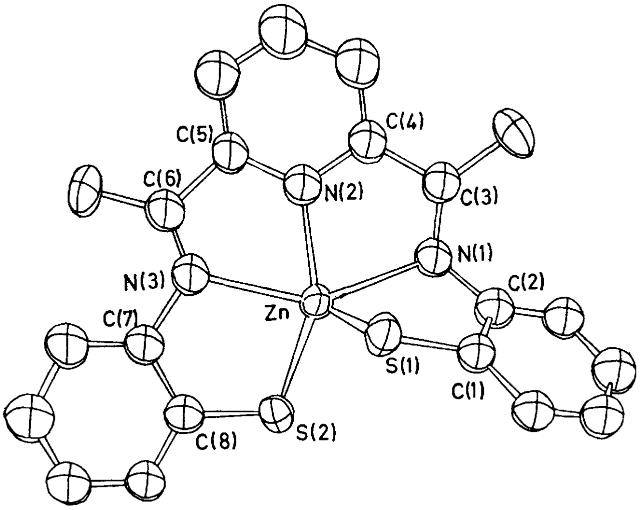


FIGURE. *Selected distances* (Å) *and angles* (°) *are:* Zn–S(1) 2·34; Zn–S(2) 2·33; Zn–N(1) 2·17; Zn–N(3) 2·21; Zn–N(2) 2·12; N(1)–C(3) 1·27; N(3)–C(6) 1·26; S(1)–S(2) 3·83; ∠ S(1)–Zn–N(1) 81·1; S(2)–Zn–N(3) 79·7; S(1)–Zn–N(2) 124·1; S(2)–Zn–N(2) 125·5°; N(1)–Zn–N(2) 73·2°; N–(3)Zn–N(2) 72·4°.

An *X*-ray structural determination of the zinc complex was carried out. It formed red monoclinic crystals from nitromethane: $a = 9{\cdot}268(8)$, $b = 13{\cdot}174(13)$, $c = 8{\cdot}172(7)$, $\cos\beta = -\ 0{\cdot}2588(7)$, space group $P2_1$, $Z = 2$. Intensities of 1769 unique observable reflections were collected using a Picker automated diffractometer. The structure was refined to R 0·05 and is illustrated in the Figure.

The complex is five-co-ordinate with all metal donor contacts within normal bonding distances. Despite the complete conjugation of the ligand it is not flat but has a helical twist. The space group ($P2_1$) contains no mirror planes and since there is only one independent molecule per unit cell, each crystal of the compound is optically active, containing only a single enantiomorphic form. This complex provides the first example of a linear chain polydentate co-ordinating in a helical geometry.

(*Received*, 10*th April* 1972; *Com.* 598.)

---

[1] L. F. Lindoy and S. E. Livingstone, *Inorg. Chim. Acta*, 1967, **1**, 365.

[2] D. H. Busch, D. C. Jicha, M. C. Thompson, J. W. Wrathall, and E. Blinn, *J. Amer. Chem. Soc.*, 1964, **86**, 3642; L. F. Lindoy, *Co-ordination Chem. Rev.*, 1969, **4**, 41.