According to this assumption, as the antibonding character increases in a series of complexes, the rate of photochemical reaction increases, thus increasing the quantum yields or *vice versa*, *i.e.*, $d\Phi/dk_r > 0$.

The conditions under which the above assumption is valid can be derived using a differential analysis of eq 28. The total differential is

$$d\Phi = \frac{(k_n + k_l)dk_r - k_r(dk_n + dk_l)}{(k_r + k_n + k_l)^2} \qquad (29)$$

From eq 29, the change in quantum yield with respect to k_r will always be positive when

$$dk_r > \frac{k_r}{k_n + k_l}(dk_n + dk_l) \qquad (30)$$

Numerical values for $k_r/(k_n + k_l)$ can be calculated from eq 28. For example for cobalt(III)-ammine complexes, $\Phi = 0.05$ and $k_r/(k_n + k_l) = 0.053$; for rhodium(III)-ammine complexes, $\Phi = 0.5$ and $k_r/(k_n + k_l) = 1$. Thus, assuming the simplest connection between the rate and bonding models, it can be seen that the assumed neglect of other deactivation processes (k_n and k_l) does not put severe constraints on the applicability of our bonding model. It can also be seen that the bonding model will be most likely to fail when (1) the reaction quantum yields approach unity and (2) the changes in the sum of the rates of radiative and nonradiative processes are of the same order of magnitude and of the same sign as the change in the rate of reaction.

As another extreme, the correlation between the mixing parameter λ and the quantum yields of solvation could be interpreted totally in terms of changes in the per cent $d_{x^2-y^2}$ character causing changes in the rate of radiationless deactivation *via* vibrational deactivation in the *xy* plane. In our bonding model, the per cent $d_{x^2-y^2}$ character decreases as the per cent d_{z^2} character increases. A decreasing rate of radiationless deactivation can be associated with decreasing $d_{x^2-y^2}$ character if it is assumed that the σ-antibonding character in the *xy* plane is not great enough to cause photochemical reactions but instead is dissipated *via* ligand vibrations. This interpretation is consistent with the "strong coupling" scheme in the Englman-Jortner theory.[21,22] Because of the inverse relationship between the rate of nonradiative deactivation and the quantum yield in eq 28, decreasing $d_{x^2-y^2}$ character would result in an increase in the quantum yield.

Our preferred interpretation of our correlation between fractional excited-state composition and the quantum yield of solvation lies between the two extremes. Both the rates of reaction and the rates of radiationless deactivation are implicitly contained in the bonding model. Experimental determination of which of the rates is most important in affecting the quantum yields will probably be limited to those few systems where luminescence and photochemical reactions are observed under the same conditions. We wish to stress, however, that the ligand field bonding model is self-contained and, in principle, is capable of explaining all of the experimental observables. The rate model starts from a completely different point of view and uses completely different language. Any discussion of the bonding model in terms of rates, or *vice versa*, must rest on connective assumptions and must be considered an interpretation of one model in terms of the other. Because both models explain the same observables, explicit points of connection between them can be found.

Registry No. Cobalt, 7440-48-4; rhodium, 7440-16-6; iridium, 7439-88-5.

(21) R. Englman and J. Jortner, *Mol. Phys.*, 18, 145 (1970).
(22) D. J. Robbins and A. J. Thomson, *Mol. Phys.*, 25, 1103 (1973).

Contribution from the Evans Chemical Laboratory,
The Ohio State University, Columbus, Ohio 43210

Metal Ion Controlled Syntheses of Novel Five-Coordinate Zinc and Cadmium Complexes Containing a Helical Coordination Geometry and Their Template Reaction to Form Complexes of a Pentadentate Macrocyclic Ligand

L. F. LINDOY and DARYLE H. BUSCH*[1]

Received March 18, 1974 AIC40186P

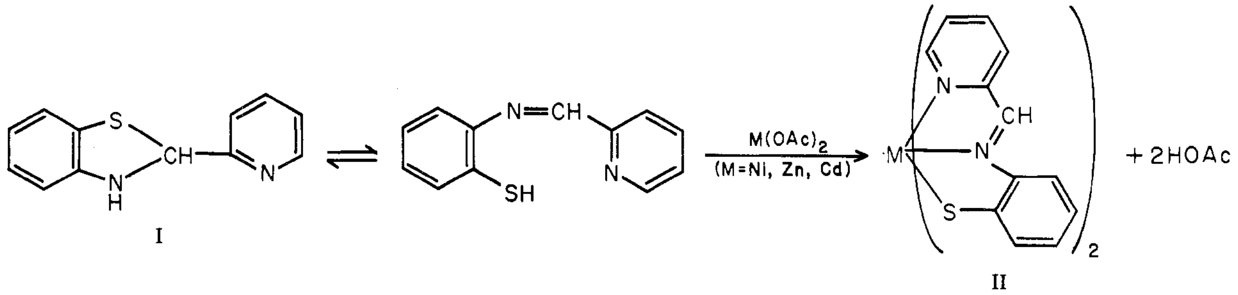
Zinc and cadmium ions induce rearrangement of 2,6-bis(2-methyl-2-benzothiazolinyl)pyridine under basic conditions producing complexes of the deprotonated tautomeric Schiff base. The complexes are five-coordinate and the coordinated Schiff base is present in a novel helical configuration. Zinc and cadmium complexes of this ligand, 2,6-bis[1-methyl-2-(2-thiolophenyl)-2-azaethene]pyridine, readily react with methyl iodide to yield complexes of the corresponding S,S′-dimethylated ligand, which contain two coordinated iodide ions and appear to be seven-coordinate. The corresponding reactions with a bifunctional alkyl halide, α,α′-dibromo-*o*-xylene or 1,4-diiodobutane, result in a number of ring-closing S-alkylation reactions. Shorter chain difunctional alkylating agents fail to span the sulfur-sulfur distances and ring closure does not occur.

Introduction

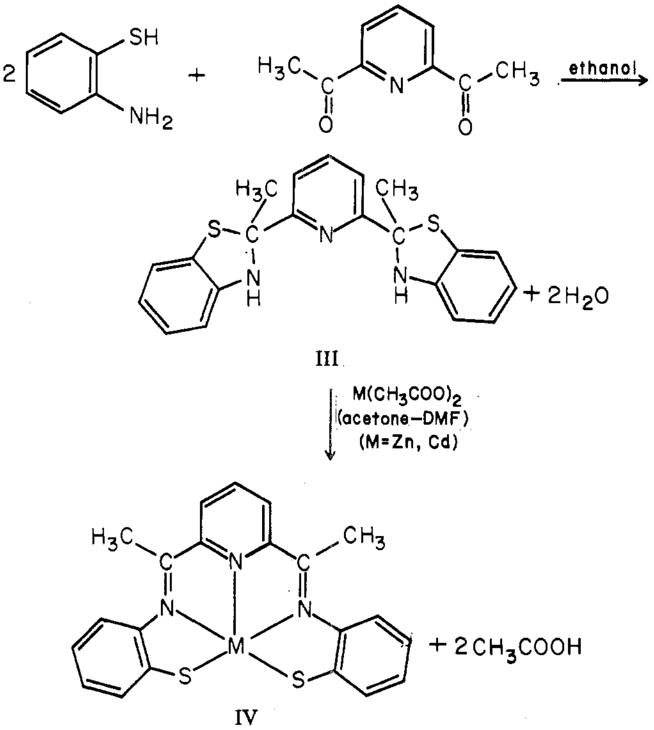
Condensation of an aldehyde or a ketone with 2-aminobenzenethiol does not normally lead to the isolation of the corresponding Schiff base but rather the main product is usually a benzothiazoline.[2,3] Nevertheless, in solution, the benzothiazoline may exist in equilibrium with its tautomeric Schiff base. Such is the case for 2-(2′-pyridyl)benzothiazoline (I) which is obtained by condensation, in alcohol, of 2-

(1) To whom correspondence should be addressed.
(2) L. F. Lindoy, *Coord. Chem. Rev.*, 4, 41 (1969).
(3) D. H. Busch, *Rec. Chem. Progr.*, 25, 107 (1964).

Scheme I



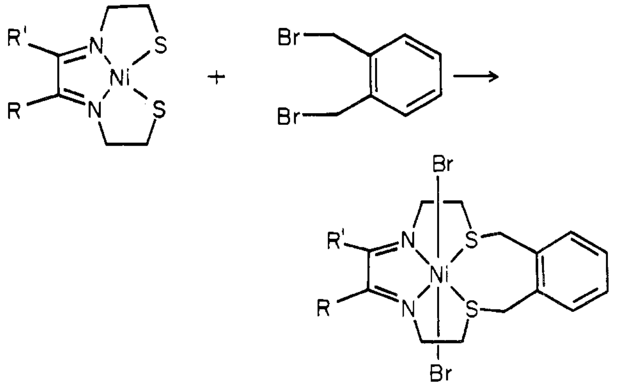
Scheme II



aminobenzenethiol and 2-pyridinecarboxaldehyde.[4,5] Reaction of zinc or cadmium acetates with a solution of I leads to precipitation of dark red Schiff base complexes of type II.[4] It has been postulated that in each of these reactions, the metal ion sequesters the Schiff base form of the ligand from the equilibrium mixture[2,3] (Scheme I). There are a number of other reports of benzothiazolines,[6-8] as well as of their aliphatic counterparts thiazolidines,[3,6] undergoing metal ion induced rearrangements in the presence of certain metal salts.

On the basis of the results of this earlier work, it has been possible in the present investigation to adapt the general reaction to the synthesis of unusual zinc and cadmium complexes of a new Schiff base pentadentate ligand (Scheme II, structure IV). This ligand is stabilized by complex formation and cannot be isolated free of its associated metal ion.

Previous studies[5,9-13] have demonstrated that terminal thiolo groups in metal complexes usually retain sufficient of their nucleophilic character to react with alkyl halides and produce the corresponding coordinated thioether complexes. Kinetic studies[1,7] indicate that the sulfur atoms remain coordinated during such S-alkylation reactions. By the use of suitable difunctional alkyl halides it has been found possible to use this reaction to bridge sulfur donors which occupy mutually cis positions in a square-planar coordination geometry.[2,14-16] In fact, the early studies that clearly demonstrated the coordination template effect used the reaction of α,α′-dibromo-*o*-xylene with the nickel complexes of quadridentate Schiff bases derived from the condensation of α-diketones with 2-aminoethanethiol (eq 1).[15]



(1)

In the work reported here S-alkylation of the coordinated thiolo groups in a number of helical complexes (IV) of a pentadentate ligand[17] has been performed such that unusual zinc and cadmium products are obtained.

Experimental Section

2,6-Diacetylpyridine (Aldrich Chemical Co.) was recrystallized before use; all other chemicals were reagent grade and were used as supplied. Infrared spectra were obtained with a Perkin-Elmer Model 337 spectrophotometer using Nujol or halocarbon mulls. Conductances were determined by means of an Industrial Instruments Inc. conductivity bridge using a cell with platinized electrodes. The mass

---

(4) L. F. Lindoy and S. E. Livingstone, *Inorg. Chim. Acta,* **1**, 365 (1967).

(5) L. F. Lindoy and S. E. Livingstone, *Inorg. Chem.,* **7**, 1149 (1968); *Inorg. Chim. Acta,* **2**, 166 (1968).

(6) H. Jadamus, Q. Fernando, and H. Freiser, *Inorg. Chem.,* **3**, 928 (1964).

(7) H. Jadamus, Q. Fernando, and H. Freiser, *J. Amer. Chem. Soc.,* **86**, 3056 (1964); E. I. Stiefel, J. H. Waters, E. Billig, and H. B. Gray, *ibid.,* **87**, 3016 (1965).

(8) E. Bayer, *Angew. Chem.,* **73**, 659 (1961); *Angew. Chem., Int. Ed. Engl.,* **3**, 325 (1964); E. Bayer and E. Breitmaier, *Chem. Ber.,* **101**, 1579 (1968).

(9) D. H. Busch, J. A. Burke, D. C. Jicha, M. C. Thompson, and M. L. Morris, *Advan. Chem. Ser.,* No. 37, 125 (1963).

(10) D. H. Busch, D. C. Jicha, M. C. Thompson, J. W. Wrathhall, and E. Blinn, *J. Amer. Chem. Soc.,* **86**, 3642 (1964).

(11) E. L. Blinn and D. H. Busch, *J. Amer. Chem. Soc.,* **90**, 4280 (1968).

(12) N. J. Rose, C. A. Root, and D. H. Busch, *Inorg. Chem.,* **6**, 1431 (1967).

(13) L. F. Lindoy, S. E. Livingstone, and T. N. Lockyer, *Inorg. Chem.,* **6**, 652 (1967).

(14) E. L. Blinn and D. H. Busch, *Inorg. Chem.,* **7**, 820 (1968).

(15) M. C. Thompson and D. H. Busch, *J. Amer. Chem. Soc.,* **86**, 3651 (1964).

(16) M. S. Elder, G. M. Prinz, P. Thornton, and D. H. Busch, *Inorg. Chem.,* **7**, 2426 (1968).

(17) L. F. Lindoy, D. H. Busch, and V. Goedken, *J. Chem. Soc., Chem. Commun.,* 683 (1972).

spectra were obtained on a MS-9 mass spectrometer. Elemental analyses were performed by the Galbraith Analytical Laboratory. The ^1H nmr spectrum was recorded on a JEOL Minimar 100-MHz spectrometer (TMS as internal standard). Molecular weights were determined in chloroform using a Mechrolab Model 301A vapor pressure osmometer.

2,6-Bis(2-methyl-2-benzothiazolinyl)pyridine. To 2,6-diacetylpyridine (6.6 g) in methanol (15 ml) was added 2-aminobenzenethiol (10.0 g). The solution was refluxed under nitrogen for 20 min and then let stand at 0°. The product separated as a yellow oil. Excess methanol was decanted off and the oil was triturated with petroleum ether. Attempts to induce the freshly prepared oil to crystallize were unsuccessful and it was used for the preparation of the metal complexes without further purification. On standing in a refrigerator for several months, a sample of the oil was observed to solidify to a yellow solid. The infrared spectrum of this crude product indicated that it was the required bis(benzothiazoline).

2,6-Bis[1-methyl-2-(2-thiolophenyl)-2-azaethene]pyridinezinc(II) Hemihydrate. To zinc acetate dihydrate (1.4 g) in a hot acetone (90-ml)–DMF (10 ml) solvent mixture was added the oil (2.4 g) from the above preparation in acetone (5 ml). The bright red solution which resulted was let cool and the red crystalline product which formed was filtered off, washed with acetone, and dried over P_2O_5 *in vacuo*; yield 2.0 g. *Anal.* Calcd for $Zn(C_{21}H_{17}N_3S_2)\cdot{}^1/_2H_2O$: C, 56.1; H, 4.0; N, 9.3; Zn, 14.5. Found: C, 56.3; H, 4.0; N, 9.2; Zn, 14.4.

The infrared spectrum of this product contained a small broad absorption at ~3500 cm^{-1} which is due to the ν(OH) mode of the water molecule. This small amount of water was reproducibly present in the products from several preparations. It is not removed on heating the complex at 110° for 12 hr.

2,6-Bis[1-methyl-2-(2-thiolophenyl)-2-azaethene]pyridinecadmium(II). To cadmium acetate (5.3 g) in a hot acetone (300 ml)–DMF (300 ml) solvent mixture was added the crude bis(benzothiazoline) (7.6 g) in acetone (50 ml). A bright red coloration appeared and orange-red crystals deposited. After the solution had cooled, the product was filtered off, washed with acetone, and dried *in vacuo* over P_2O_5. Dried in this manner the compound contained acetone. *Anal.* Calcd for $Cd(C_{21}H_{17}N_3S_2)\cdot{}^1/_2C_3H_6O$: C, 52.3; Cd, 21.7; H, 3.9; N, 8.1. Found: C, 52.1; Cd, 21.7; H, 4.0; N, 8.2.

The infrared spectrum of this product contains a medium-intensity absorption at 1705 cm^{-1} and a weak absorption at 1680 cm^{-1} resulting from the ν(C=O) mode of acetone. On heating this product *in vacuo* to constant weight at 175°, the acetone is lost (loss in weight 5.5%; calcd loss for $^1/_2$ acetone 5.6%) and the infrared spectrum no longer contains carbonyl stretching absorptions. *Anal.* Calcd for $Cd(C_{21}H_{17}N_3S_2)$: C, 51.7; H, 3.5; N, 8.6. Found: C, 51.5; H, 3.5; N, 8.6.

Diiodo{*S,S'*-dimethyl-2,6-bis[1-methyl-2-(2-thiolophenyl)-2-azaethene]pyridine}zinc(II), $Zn(P\text{-}Me_2)I_2$. $Zn(P)\cdot{}^1/_2H_2O$ (1.0 g) was partially dissolved in acetone (170 ml) containing iodide (2.5 g). The mixture was heated at the reflux for 40 min. The solution was then cooled and the yellow product was filtered, washed with acetone, and dried over P_2O_5 *in vacuo*; yield 1.4 g. *Anal.* Calcd for $Zn(C_{23}H_{23}N_3S_2)I_2$: C, 38.1; H, 3.2; I, 35.0; N, 5.8; Zn, 9.0. Found: C, 37.9; H, 3.1; I, 35.3; N, 5.8; Zn, 9.2.

Diiodo{*S,S'*-(1,4-butyl)-2,6-bis[1-methyl-2-(2-thiolophenyl)-2-azaethene]pyridine}zinc(II), $Zn(P\text{-}Bu)I_2$. $Zn(P)\cdot{}^1/_2H_2O$ (1.3 g) was suspended in acetone (250 ml) containing 1,4-diiodobutane (1.24 g). The suspension was then stirred and heated at reflux temperature for 20 hr. The solution, which contained a small amount of yellow precipitate, was then concentrated to 50 ml and allowed to stand at room temperature. The yellow product (1.2 g) that formed was isolated, washed with alcohol, and then recrystallized from acetone. It was dried *in vacuo* at 60° and then over P_2O_5; yield 0.8 g. *Anal.* Calcd for $Zn(C_{25}H_{25}N_3S_2)I_2$: C, 40.0; H, 3.4; I, 33.8; N, 5.6; S, 8.7; Zn, 8.5. Found: C, 40.1; H, 3.4; I, 33.9; N, 5.6; S, 8.6; Zn, 8.6.

Diiodo{*S,S'*-(*o*-xylyl)-2,6-bis[1-methyl-2-(2-thiolophenyl)-2-azaethene]pyridine}zinc(II), $Zn(P\text{-}xyl)Br_2$. $Zn(P)\cdot{}^1/_2H_2O$ (1.5 g) was suspended in warm acetone (200 ml) containing α,α'-dibromo-*o*-xylene (1.2 g). The warm solution was stirred for 2.5 hr and then allowed to cool. The yellow product which formed was washed with acetone. When the compound was dried over P_2O_5 *in vacuo*, the infrared spectrum of the product indicated that it contained a small amount of acetone. This was removed by further drying *in vacuo* at 175° for 20 hr; yield 2.5 g. *Anal.* Calcd for $Zn(C_{29}H_{25}N_3S_2)Br_2$: C, 49.4; H, 3.6; N, 6.0. Found: C, 49.4; H, 3.6; N, 6.0.

Diiodo{*S,S'*-dimethyl-2,6-bis[1 methyl-2-(2-thiolophenyl)-2-azaethene]pyridine}cadmium(II), $Cd(P\text{-}Me_2)I_2$. $Cd(P)\cdot{}^1/_2$(acetone) was suspended in acetone (150 ml) containing methyl iodide (0.8 g). The suspension was stirred at room temperature for 100 hr (in a sealed flask). The bright yellow product was filtered, washed with acetone, and dried over P_2O_5 *in vacuo*; yield 0.5 g. *Anal.* Calcd for $Cd(C_{23}H_{23}N_3S_2)I_2$: C, 35.8; H, 3.0; Cd, 14.6; N, 5.4. Found: C, 36.3; H, 3.0; Cd, 14.7; N, 5.8.

Dibromo{*S,S'*-(*o*-xylyl)-2,6-bis[1-methyl-2-(2-thiolophenyl)-2-azaethene]pyridine}cadmium(II), $Cd(P\text{-}xyl)Br_2$. $Cd(P)\cdot{}^1/_2$(acetone) (1.00 g) was suspended in hot acetone (200 ml) containing α,α'-dibromo-*o*-xylene (0.51 g). The suspension was heated at the reflux temperature for 16 hr. The solution was then concentrated to 100 ml and allowed to cool. The yellow product that formed was isolated and washed with acetone. As with the analogous zinc compound, this product contained a small amount of acetone which was removed by drying at 175° *in vacuo* for 20 hr; yield 1.35 g. *Anal.* Calcd for $Cd(C_{29}H_{25}N_3S_2)Br_2$: C, 46.3; H, 3.3; N, 5.6. Found: C, 46.3; H, 3.3; N, 5.6.

Results and Discussion

Helical Complexes of the Linear Polydentate Ligand. Reaction of 2,6-diacetylpyridine in alcohol with 2-aminobenzenethiol in a 1:2 mole ratio yields a yellow product whose infrared spectrum shows no absorptions which can be assigned to ν(C=O) or ν(S–H) modes. The absence of such absorptions together with the presence of a single amine stretching mode of medium intensity at 3350 cm^{-1} is in accord with the product being the expected bis(benzothiazoline) (III, Scheme II). This product reacts with zinc acetate or cadmium acetate in a dimethylformamide–acetone solvent mixture to yield bright red solutions from which red crystals of the respective metal complexes deposit. Basic conditions were chosen for the reaction since previous work[4,5] has indicated that such conditions should favor the conversion of III to its tautomeric Schiff base, a fact that has been confirmed by an X-ray structure determination on the zinc complex.[17,18]

Both complexes are nonelectrolytes in nitromethane and nitrobenzene and their infrared spectra do not contain bands which can be attributed to amine or carbonyl stretching modes. However, the spectra do show absorptions at 1625, 1585, and 1570 cm^{-1} for the zinc complex and at 1630, 1615, 1580, and 1570 cm^{-1} for the cadmium complex and these absorptions can be ascribed to imine and aromatic ring vibrations.

Comparison of the spectra and properties of the above complexes with those of the complexes[4] of type II indicates that both zinc and cadmium ions promote the rearrangement of III so that the respective metal complexes (IV) of the tautomeric Schiff base ligand are produced (Scheme II). Under similar conditions the corresponding product from the condensation of 2-aminophenol and 2,6-diacetylpyridine also yields orange zinc and cadmium complexes but these are of more complicated stoichiometry than the simple 1:1 metal to ligand complexes obtained from IV.[19] The linear-chain ligand in the latter complexes is potentially pentadentate and hence is a new example of this relatively uncommon ligand type.[20,21] The coordination number of 5 is reasonably common for both zinc[22] and cadmium[23] ions. Owing to the low solubilities of each of the complexes, their molecular weights could not be determined using vapor pressure osmometry. However, the mass spectra of the compounds show no peaks at *e/m* values greater than those of the respective parent ions and thus the complexes are monomeric under the conditions used to obtain the spectra while their

---

(18) V. L. Goedken, and G. G. Christoph, *Inorg. Chem.*, 12, 2316 (1973).

(19) L. F. Lindoy and H. C. Lipp, unpublished work.

(20) H. A. Goodwin in "Chelating Agents and Metal Chelates," F. P. Dwyer and D. P. Mellor, Ed., Academic Press, New York, N. Y., 1964, Chapter 4.

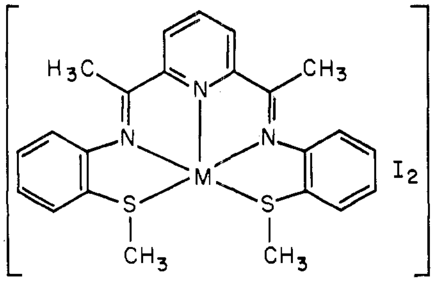
(21) F. Lions, *Rev. Pure Appl. Chem.*, 19, 177 (1969).

monomeric character in solution can only be assumed.

From the structural study[17,18] the terminal sulfur donors are nonbridging in the solid state and the complex is five-coordinate with all metal donor contacts within normal bonding distances. The linear-chain ligand wraps around the metal so that the donors are regularly spaced around one coil of a helix. In this arrangement there is an approximate C_2 axis passing through the zinc(II) atom and the nitrogen of the pyridine moiety. If one considers the relative positions of the donor atoms, then they can be considered to describe a very distorted trigonal-bipyramidal arrangement around the central zinc ion. Nevertheless, the overall ligand geometry resembles one coil of a tightly coiled spring. Although no structural data are available, it seems likely that the corresponding red cadmium complex also contains the ligand in an analogous helical arrangement.

It is becoming increasingly apparent that many metalloenzymes (including zinc metalloenzymes) contain unusual coordination environments at their active sites.[24,25] It has been proposed that such unusual geometries are a consequence of the particular steric requirements of the surrounding enzyme structure and for several such enzymes there is evidence that the unusual stereochemical arrangement about the metal is in fact essential to the enzyme's activity. The structure of the present zinc complex amply illustrates the manner in which the steric and other requirements of a particular polydentate ligand can yield a coordination geometry of a type not found in zinc complexes of simpler ligands.

Template Reactions and Their Products. Reaction of the red zinc or cadmium complexes of type IV in acetone with excess methyl iodide yields yellow products whose elemental analyses correspond to S-methylated products of type V.

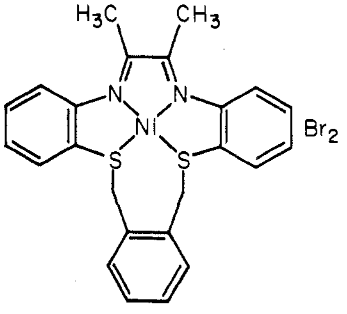


V [M(P-Me$_2$)I$_2$]; M = Zn, Cd

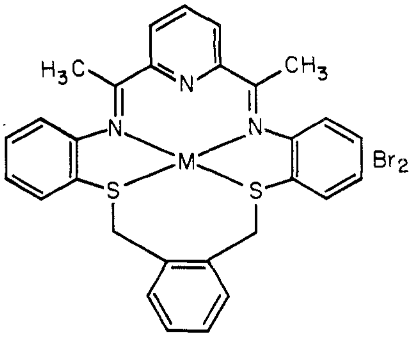
Conductance studies (see Table I) indicate that the complexes are nonelectrolytes in nitrobenzene. In the more ionizing solvent nitromethane both complexes are slightly dissociated but the conductance values are still considerably below the value expected for a 1:1 electrolyte.

As expected, the infrared spectra of these compounds in the imine stretching region (see Table I) are quite similar to the spectra of their thiolo complex precursors and contain no absorptions which can be assigned to free amine or carbonyl groups. The imine linkings thus remain intact during the S-alkylation reactions. Because of their low solubilities, no molecular weight determinations nor nmr studies were performed on the products.

As discussed in the Introduction, ring-closing reactions are sometimes possible when difunctional alkyl halides are treated with complexes containing thiolo donors in adjacent positions in the coordination sphere. It has been shown previously[16] that reaction of the nickel complex of the Schiff base derived from condensation of 2-aminobenzenethiol and biacetyl (in a 2:1 molar ratio) with α,α'-dibromo-*o*-xylene yields the macrocyclic derivative VI. Since the dithiolo precursor of VI is structurally related to complexes of type IV, it seemed possible that the latter might also undergo similar S-alkylation reactions to yield products of type VII [abbreviated M(P-xyl)Br$_2$]. Few pentadentate macrocyclic ligands have been reported previously[26-28] although a larger number of open-chain pentadentate ligands are known.[20] Reaction of α,α'-dibromo-*o*-xylene with both the red zinc and cadmium complexes IV yielded yellow products whose elemental analysis and physical properties (see later) are in accord with a cyclic structure of type VII. The use of this difunctional alkylating agent was particularly appropriate because the crystal structure[17,18] of the helical zinc complex precursor confirms that a four-carbon chain is required to produce a strain-free bridge (3.83 Å) between sulfur atoms.



VI



VII; M = Zn, Cd

On S-alkylation, the helical configuration of the ligand may partially collapse toward a planar configuration. Such a change may result from the removal of the formal negative charges on the sulfur atoms. Molecular models indicate that

---

(22) D. P. Graddon and D. G. Weedon, *Aust. J. Chem.*, 17, 607 (1964); J. S. Stephens, and C. Calvo, *Can. J. Chem.*, 45, 2303 (1967); D. P. Madden and S. M. Nelson, *J. Chem. Soc.*, 2342 (1968); M. Di Vaira and P. L. Oriolo, *Acta Crystallogr., Sect. B*, 24, 1269 (1968); P. C. Jain, E. C. Lingafelter, and P. Paoletti, *J. Amer. Chem. Soc.*, 90, 519 (1968); R. L. Belford, N. D. Chasteen, M. A. Hitchman, P. K. Hon, C. E. Pfluger, and I. C. Paul, *Inorg. Chem.*, 8, 1312 (1969); F. Bigoli, A. Tiripicchio, and M. Tiripicchio Camellini, *Chem. Commun.*, 120 (1970).

(23) E. Coates, B. Rigg, B. Saville, and D. Skelton, *J. Chem. Soc.*, 5613 (1965); A. Domenicano, L. Torelli, A. Vaciago, and L. Zambonelli, *J. Chem. Soc. A*, 1350 (1968); E. A. Shugam and V. M. Agne, *Sov. Phys.–Crystallogr.*, 13, 197 (1968); E. P. Epstein and I. Bernal, *J. Chem. Soc. A*, 3628 (1971).

(24) B. L. Vallee and R. J. P. Williams, *Proc. Nat. Acad. Sci. U. S.*, 59, 498 (1968); *Chem. Brit.*, 399 (1968).

(25) R. J. P. Williams, *R.I.C. (Roy. Inst. Chem.) Rev.*, 1, 13 (1968).

(26) S. M. Nelson, P. Bryan, and D. H. Busch, *Chem. Commun.*, 641 (1966); S. M. Nelson and D. H. Busch, *Inorg. Chem.*, 8, 1859 (1969).

(27) V. Katovic, L. T. Taylor, and D. H. Busch, *J. Amer. Chem. Soc.*, 91, 2122 (1969).

(28) D. St. C. Black and I. A. McLean, *Inorg. Nucl. Chem. Lett*, 6, 675 (1970).

Table I. Selected Infrared Data and Molar Conductance Data for the Macrocyclic Complexes

Compd	Infrared data,[a] ν(C=N) and aromatic ring vib, cm^{-1}	Conductance data,[b,c] ohm^{-1} cm^2 mol^{-1} In nitrobenzene	Conductance data,[b,c] ohm^{-1} cm^2 mol^{-1} In nitromethane
$Zn(P\text{-}2Me)I_2$	1640 s, 1600 sh, 1585 s, 1560 w	~0	22.4
$Zn(P\text{-}Bu)I_2$	1640 sh, 1630 s, 1595 sh, 1585 s, 1565 w	9.2	101.9
$Zn(P\text{-}xyl)Br_2$	1650 s, 1640 s, 1590 s, 1580 s, 1560 w	*d*	*d*
$Cd(P\text{-}2Me)I_2$	1635 s, 1625 s, 1580 s, 1560 m	2.4	17.1
$Cd(P\text{-}xyl)Br_2$	1645 s, 1590 m, 1580 s, 1560 w	*d*	*d*

[a] Key: s, strong; m, medium; w, weak; sh, shoulder. [b] At 25°. Values reported for 1:1 and 2:1 electrolytes in nitromethane are 80–95 and 160–190, respectively: T. D. DuBois and D. W. Meek, *Inorg. Chem.*, 8, 146 (1969). [c] Concentration ~1×10^{-3} *M*. [d] Not sufficiently soluble.

if the cyclic ligand does adopt such a configuration, a four-carbon bridge would be of ideal length to span sulfur donors. In accord with this observation, all attempts to perform bridging reactions using difunctional alkyl halides containing only two-carbon or three-carbon aliphatic bridges were unsuccessful. In such cases, mixtures of yellow products were obtained which could not be satisfactorily purified. These products could well be polymeric. In contrast, the red zinc complex smoothly reacts with 1,4-diiodobutane to yield a product which has the expected elemental analysis for the zinc complex of the corresponding macrocyclic ligand [abbreviated $Zn(P\text{-}Bu)I_2$].

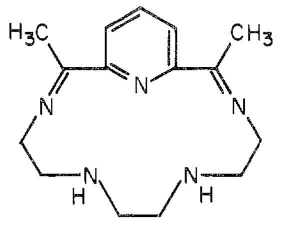
Unfortunately, neither complex containing the *o*-xylyl bridge was sufficiently soluble for solution studies; however, it was possible to perform conductance measurements on the other alkylated complexes (see Table I). In nitrobenzene all the products are essentially nonelectrolytes whereas in the more ionizing solvent nitromethane a greater degree of dissociation occurs. Nevertheless, these data suggest that the complexes are nonionic in the solid state. In keeping with its nonionic nature, the complex $Zn(P\text{-}Bu)I_2$ is moderately soluble in chloroform to yield a yellow solution, and molecular weight determinations were made by osmometry over a range of concentrations in this solvent. The values obtained decreased smoothly from 838 at a concentration of 1.43×10^{-2} *M* to ~735 at a concentration of 0.44×10^{-2} *M*. The expected monomeric value is 751 and hence it appears that, at higher concentrations, slight concentration-dependent association occurs in this solvent. Nevertheless, the limiting value at lower concentrations indicates the presence of discrete monomeric species.

The nmr spectrum of this complex in chloroform showed resonances resulting from the four-carbon methylene bridge protons as a complex multiplet centered at 1.56 ppm (downfield from TMS); the resonance from the methyl groups attached to each of the imine carbons appeared at 2.65 ppm as a singlet and the aromatic protons as two complex multiplets centered at 7.50 and 8.44 ppm, respectively.

From the evidence just discussed it appears very likely that the alkylated products are seven-coordinate. Recently, both the seven-coordinate complex[29] $Zn(py)_3(NO_3)_2$ and the eight-coordinate complex ion[30] $[Zn(NO_3)_4]^{2-}$ have been reported and their structures investigated by X-ray diffraction. The seven-coordinate complex contains a twofold axis of symmetry which passes through the zinc ion and one pyridine ring; the nitrate groups are equivalent and bidentate. The eight-coordinate complex contains bidentate nitrate groups and the overall geometry is dodecahedral. It is perhaps of significance to the present work that cadmium also forms a complex of the type $Cd(py)_3(NO_3)_2$.[31]

It is instructive to consider the possible geometries of the alkylated complexes prepared in the present work. As mentioned previously, the tendency to form a helical geometry of the type found in the thiolo precursors should be reduced somewhat on removal of the formal negative charges on the sulfur atoms by alkylation. In addition, if the organic ligand maintained the helical configuration in the alkylated products, then molecular models indicate that serious steric clashes will occur between the ligand and the halide ions if the latter tend to coordinate to the central metal along the spiral axis. For these reasons it is thought likely that the pentadentate ligands in the alkylated complexes will adopt a somewhat flatter geometry than the dithiolo ligand does in the helical precursors. The coordination geometry of the former complexes will thus approach a pentagonal bipyramid in which the organic ligand coordinates around a distorted pentagonal plane and the halide ions occupy axial points.

The proposed distorted pentagonal-bipyramidal structure for the above complexes is related to the known[32] structure of the complex cation in $[Fe(MAC)(NCS)_2]ClO_4$ [where MAC = VIII]. In this pentagonal-bipyramidal complex the five nitrogens of the ligand and the metal ion lie in the equatorial plane whereas the thiocyanate groups are in axial positions.



VIII

Acknowledgment. This investigation was supported by U. S. Public Health Service Grant GM-10040 from the National Institute of General Medical Sciences.

Registry No. Zn(P), 52019-98-4; Cd(P), 52154-44-6; $Zn(P\text{-}Me_2)I_2$, 52022-21-6; $Zn(P\text{-}Bu)I_2$, 52022-22-7; $Zn(P\text{-}xyl)Br_2$, 51933-90-5; $Cd(P\text{-}Me_2)I_2$, 51933-91-6; $Cd(P\text{-}xyl)Br_2$, 51933-92-7; 1,4-diiodobutane, 628-21-7; α,α'-dibromo-*o*-xylene, 91-13-4.

---

(29) A. F. Cameron, D. W. Taylor, and R. H. Nuttall, *Chem. Commun.*, 129 (1971).

(30) J. Drummond and J. S. Wood, *J. Chem. Soc. A*, 226 (1970).

(31) T. J. Ouellette and H. M. Haendler, *Inorg. Chem.*, 8, 1777 (1969).

(32) E. B. Fleischer and S. Hawkinson, *J. Amer. Chem. Soc.*, 89, 720 (1967).