plain the observation of an apparent lower activation energy for "enantiomerization" in the last two of these compounds[9,22] that is observed for the cis–trans isomerization. A set of unsplit or weakly split M_3 or M_4 processes will give statistical isomers in one step, but will equilibrate the two A sites (*i.e.*, racemize in M_3) in half a step, so that the apparent rates can differ by a factor of 2. However, further studies are required on these systems to ascertain if there is really any stereospecific character to justify such an interpretation.

The experiments of Pignolet, Lewis, and Holm[7] on $\mathrm{Fe(Me,Ph(dtc))_2(tfd)}$, where tfd = $-\mathrm{S[C_2(CF_3)_2]S}-$, can also be interpreted as either of the split-mode processes M_3' or M_4'. Similar to the case of the tris chelates discussed above the HTP could be speculatively associated with an intramolecular rearrangement of split modes M_3'' or M_4'' as an alternative to the C–N bond rotation.

In concluding this section we would note that the present discussion has been limited to a consideration of the modes of rearrangement and to the explicit rearrangement within the modes; individual mechanisms that can produce the various stereochemistries have not been considered at all. The problem of analyzing mechanisms is highly complex as can be seen by the discussion of Holm and coworkers[8] for some mechanisms in M_3' alone. Without extensive further research we could clearly not do justice to the various conceivable mechanisms for the remaining modes. Such an analysis we leave for a future study after which one might be able to make a comparison of the energetics for the most favorable mechanisms which give rise to other stereochemistries for different metal atoms and different types of substituents.

4. Conclusions

We have demonstrated here the different modes of rearrangement which an octahedral complex can undergo. The theory has been applied to the special case of tris-chelate complexes and has permitted a complete analysis of the recent experimental results. It would have been most convenient were all octahedral molecules to undergo intramolecular rearrangements according to the same preferred mode or modes, such that the variation in metal atoms or ligands would not significantly change the *ordering* of the energetics of the different preferred pathways which give the stereochemistry of each of the modes. Unfortunately there is no reason to expect that such would be the case, and a comparison of the results of section 3 with those for H_2ML_4 complexes[10] which rearrange according to a split M_1 mode—although, as mentioned above, these authors are unable to distinguish between *two* stereochemically different arrangements—provides a counter example to such an argument. In the present article we have provided a framework within which all experiments can be analyzed without concern that possible types of processes have been overlooked.

For those who believe in the efficacy of nonempirical or semiempirical molecular calculations it would be a worthwhile task to search the multidimensional configuration space for some six-coordinate complex, or even a metal hexahydride. The unbelievably many possible pathways might be effectively reduced without much loss of information by starting off the rearrangement along the direction of the various different permutations corresponding to any given mode. It is in this sense that the different permutations can serve as aids in visualizing the actual mechanism which gives the rearrangement. It should not be forgotten, of course, that the mechanism may well go through an intermediate or transition state which makes more than one mode possible. The limiting case of this would give all isomers in equal probability and would be a complete scrambler of all relative configurations.

Acknowledgments.—This research has been supported in part by the Office of Naval Research, the National Science Foundation, and the North Atlantic Treaty Organization.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
BOWDOIN COLLEGE, BRUNSWICK, MAINE 04011

Complexes of Bridged Diphosphinothioyl Chelates[1]

BY DAVID A. WHEATLAND,* CHARLES H. CLAPP, AND RICHARD W. WALDRON

Received February 24, 1972

A series of bridged diphosphinothioyl bidentate ligands has been synthesized and several have been found to form stable complexes with a number of "class b" metal halides. The infrared spectra indicate that the ligands form six-membered ring chelates by coordination *via* both thiophosphoryl donor sites. The sulfur-bridged ligands undergo cleavage to yield phosphorodithioate complexes.

Introduction

There has been considerable interest in studying metal complexes with bidentate chelating ligands containing donor thiophosphoryl groups. Tetraalkyldiphosphine disulfides have been reported to form five-membered chelate ring complexes with a variety of metals.[2-8] Complexes with anionic "imidodiphos-

---

[1] Financial support from the Petroleum Research Fund, administered by the American Chemical Society under Grant No. 1363-G3, is gratefully acknowledged.

(2) D. W. Meek and P. Nicpon, *J. Amer. Chem. Soc.*, **87**, 4951 (1965).

(3) H. Teichmann, *Angew. Chem.*, **77**, 809 (1965).

(4) K. Baker and G. W. A. Fowles, *J. Less-Common Metals*, **8**, 47 (1965).

(5) M. Arshad, A. Beg, and K. S. Hussain, *Chem. Ind. (London)*, 1181 (1966).

(6) M. Arshad, A. Beg, and S. H. Khawaja, *Spectrochim. Acta, Part A*, **24**, 1031 (1968).

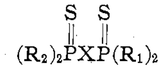
(7) V. W. Hieber and K. Kaiser, *Z. Anorg. Allg. Chem.*, **358**, 271 (1968).

(8) V. W. Hieber and K. Kaiser, *ibid.*, **362**, 169 (1968).

phinates"[9-14] or "methinodiphosphinates"[15] have been studied in which the chelate forms six-membered rings.[9-15]

There is only one report[16] of complexes with neutral bidentate thiophosphoryl chelates capable of forming six-membered rings. Consequently, it was of interest to see if other complexes of this type could be prepared and studied.

We have recently synthesized a series of neutral chelates of type **1**, where $R_1 = R_2 = CH_3$, $X = O$, S;



$$(R_2)_2\overset{\overset{S}{\|}}{P}X\overset{\overset{S}{\|}}{P}(R_1)_2$$

1

$R_1 = R_2 = C_6H_5$, $X = CH_2$, O, S; $R_1 = CH_3$, $R_2 = C_6H_5$, $X = CH_2$, O, S. This large group of potential chelating ligands capable of forming six-membered ring complexes is well suited for the study of the effects of variation of the terminal substituents R_1 and R_2 as well as the variation of the bridging group X. This communication deals with the synthesis of many of the type **1** chelates and their complexes with "class b"[17] metals.

Experimental Section

Caution! The organophosphorus compounds described below are probably toxic anticholinesterase agents and should be handled with care.

Materials.—Chlorodiphenylphosphine and diphenyldithiophosphinic acid were purchased from Aldrich Chemical Co. Thiophosphoryl chloride and bis(diphenylphosphino)methane were obtained from Alfa Inorganics, Inc., and Strem Chemicals, respectively. Benzene, tetrahydrofuran, and low-boiling petroleum ether (bp 30–60°) were dried over sodium. All other chemicals used were commercial reagent grade.

The following compounds were prepared according to literature procedures: tetramethyldiphosphine disulfide,[18] bromodimethylphosphine sulfide,[19] chlorodiphenylphosphine sulfide,[20] methyldiphenylphosphine sulfide,[21] bis(diphenylphosphinothioyl)methane, $[(C_6H_5)_2P(S)]_2CH_2$ (BPM),[22] and bis(diphenylphosphinothioyl) sulfide, $[(C_6H_5)_2P(S)]_2S$ (BPS).[23]

Preparation of Diphenylphosphinothioyldimethylphosphinothioylmethane, $(C_6H_5)_2P(S)CH_2P(S)(CH_3)_2$ (PMM).—In a procedure similar to that of Seyferth, *et al.*,[24] a solution of phenyllithium (0.41 mol) prepared from bromobenzene and lithium metal in tetrahydrofuran was added with stirring and cooling in ice to diphenylmethylphosphine sulfide (64 g, 0.41 mol) in 450 ml of dry ether. When all the phenyllithium was added, the resulting mixture was stirred at 30° for 5 hr. The solution was cooled in ice and dimethylbromophosphine sulfide (67 g, 0.41 mol) in 100 ml of dry ether was added dropwise with stirring. When the addition was complete, the mixture was stirred for 1 hr. After hydrolysis with water the ether layer was decanted off and the ether was removed on a rotatory evaporator. Volatile byproducts were removed by vacuum distillation at 180° (*ca.* 1 mm). The crude oil residue was sublimed at 200° (*ca.* 0.5 mm) and white crystals of the desired product were obtained. The product was recrystallized twice from ethanol; yield 10.3 g (12%); mp 147–148°. *Anal.* Calcd for $C_{15}H_{15}P_2S_2$: C, 55.51; H, 5.59. Found: C, 55.30; H, 5.66.

Preparation of Bis(dimethylphosphinothioyl) Oxide, $[(CH_3)_2P(S)]_2O$ (BMO).—In a procedure similar to that of Kuchen and coworkers,[25] a solution of bromodimethylphosphine sulfide (13.0 g, 0.075 mol) in 60 ml of benzene was added to a suspension of silver oxide (8.7 g, 0.038 mol) in 100 ml of benzene. The reaction mixture was heated to 60° during the addition and heated to reflux when the addition was complete. After 2 hr of reflux, the gray reaction mixture was cooled, silver bromide and excess silver oxide were filtered off, and the filtrate was concentrated in a rotatory evaporator. The material that solidified upon cooling was dissolved in 25 ml of acetone and crystallized by adding 75 ml of hexane and cooling at −18°. The product was recrystallized from 2-propanol; yield 3.9 g (52%); mp 109.5–110.5°. *Anal.* Calcd for $C_4H_{12}OP_2S_2$: C, 23.75; H, 5.98; S, 31.55. Found: C, 23.64; H, 6.06; S, 31.98.

Preparation of Bis(diphenylphosphinothioyl) Oxide, $[(C_6H_5)_2P(S)]_2O$ (BPO).—This compound was obtained as a by-product when chlorodiphenylphosphine sulfide (12 g, 0.048 mol) was added to 40 ml of 3 *M* NaOH at 70° in the synthesis of diphenylphosphinothioic acid.[26] The mixture was heated for 4 hr and a white solid formed and was filtered off. This material when recrystallized from toluene–ethanol was identified as BPO by its infrared spectrum and by its melting point, 198–200° (lit.[27] mp 196.5–197.5°); yield 4.3 g.

Preparation of Diphenylphosphinothioyldimethylphosphinothioyl Oxide, $(C_6H_5)_2P(S)OP(S)(CH_3)_2$ (PMO).—The aqueous filtrate from the preceding hydrolysis reaction was acidified with HCl and the diphenylphosphinothionic acid that precipitated was extracted with three 100-ml portions of benzene. Ammonia was bubbled through this solution for 30 min and the resulting milky solution concentrated on a rotatory evaporator. The dried product, ammonium diphenylphosphinothioate, was used without further purification; yield 5.2 g (43%); dec pt *ca.* 160°. Acidification of a small sample of this material with subsequent recrystallization from toluene yielded diphenylphosphinothionic acid, mp 140–141° (lit.[26] mp 140–143°). A solution of bromodimethylphosphine sulfide (3.4 g, 0.0187 mol) in 50 ml of dry tetrahydrofuran was added to a solution of the ammonium salt (4.7 g, 0.0187 mol) in 50 ml of dry tetrahydrofuran. A white precipitate (NH_4Br) began to appear almost immediately. The mixture was stirred for 1 hr at 25°, filtered, and concentrated on a rotatory evaporator. Crystallization was achieved with the addition of 2-propanol and cooling at −18°. The product was recrystallized from 2-propanol; yield 1.8 g (31%); mp 80–81°. *Anal.* Calcd for $C_{14}H_{16}OP_2S_2$: C, 51.52; H, 4.94. Found: C, 51.77; H, 4.94.

Preparation of Bis(dimethylphosphinothioyl) Sulfide, $[(CH_3)_2P(S)]_2S$ (BMS).—The reaction of crude sodium dimethylphosphinodithioate[28] with bromodimethylphosphine sulfide yielded BMO presumably because of water contamination in the sodium salt. Anhydrous ammonium dimethylphosphinodithioate was prepared in 79% yield by acidification of the sodium salt, extraction of the dithiophosphinic acid with benzene, and precipitation of the ammonium salt by treatment with ammonia. A solution of bromodimethylphosphine sulfide (13.8 g, 0.08 mol) in 75 ml of dry tetrahydrofuran was added to a suspension of ammonium dimethylphosphinodithioate (10.5 g, 0.074 mol) in 300 ml of dry tetrahydrofuran. The mixture was stirred for 1 hr at 55°, refluxed for 1 hr, cooled, and filtered. The filtrate was concentrated on the rotatory evaporator and crystallization was achieved by addition of petroleum ether and cooling at −18°. The crude product was collected and redissolved in methylene chloride. The solution was washed with water and dried over anhydrous Na_2SO_4, and petroleum ether was added. The

---

[9] A. Schmidpeter, R. Bohm, and H. Groeger, *Angew. Chem.*, **76**, 860 (1964).

[10] A. Schmidpeter and H. Groeger, *Z. Anorg. Allg. Chem.*, **345**, 106 (1966).

[11] A. Schmidpeter and J. Ebeling, *Chem. Ber.*, **101**, 815 (1968).

[12] M. R. Churchill, J. Cooke, and J. Wormald, *J. Amer. Chem. Soc.*, **91**, 6518 (1969).

[13] M. R. Churchill and J. Wormald, *Chem. Commun.*, 703 (1970).

[14] A. Davison and E. S. Switkes, *Inorg. Chem.*, **10**, 837 (1971).

[15] A. Davison and D. L. Reger, *ibid.*, **10**, 1967 (1971).

[16] D. Brown, J. Hill, and C. E. F. Rickard, *J. Less-Common Metals*, **20**, 57 (1970).

[17] S. Ahrland, J. Chatt, and N. R. Davies, *Quart. Rev., Chem. Soc.*, **12**, 265 (1958).

[18] H. Reinhardt, D. Bianchi, and D. Molle, *Chem. Ber.*, **90**, 1656 (1957).

[19] R. Colln, German Patent 1,054,453 (1959); *Chem. Abstr.*, **55**, 6375*b* (1961).

[20] I. B. Johns and H. R. DiPietro, *J. Org. Chem.*, **29**, 1970 (1964).

[21] D. Seyferth and D. E. Welch, *J. Organometal. Chem.*, **2**, 1 (1964).

[22] D. J. Peterson, *ibid.*, **8**, 199 (1967).

[23] T. R. Hopkins and P. W. Vogel, *J. Amer. Chem. Soc.*, **78**, 4447 (1956).

[24] D. Seyferth, D. E. Welch, and J. K. Heeren, *ibid.*, **86**, 1100 (1964).

[25] W. Kuchen, J. Metten, and H. Buchwald, *Chem. Ber.*, **95**, 1703 (1962).

[26] W. A. Higgins, P. W. Vogel, and W. G. Craig, *J. Amer. Chem. Soc.*, **77**, 1864 (1955).

[27] L. Maier, *Helv. Chim. Acta*, **47**, 1448 (1964).

[28] Prepared in 58% yield by the method of W. Kuchen, K. Strolenburg, and J. Metten, *Chem. Ber.*, **96**, 1733 (1963).

TABLE I

CONDUCTANCE AND ANALYTICAL DATA FOR THE BRIDGED DIPHOSPHINOTHIOYL COMPLEXES

Complex	Color	Λ_M,[a] cm²/ohm mol	Yield, %	Analyses, % C Calcd	C Found	H Calcd	H Found
Cd(PMM)Br_2	Colorless	[b]	86	30.19	30.18	3.04	3.13
Hg(PMM)Br_2	Colorless	[b]	92	26.13	26.52	2.65	2.74
Pd(PMM)Cl_2	Red-brown	5.2	72	35.91	36.30	3.62	3.59
Pt(PMM)Cl_2	Colorless	15.4	71	30.50	30.33	3.07	2.98
Hg(BPM)Br_2	Colorless	[b]	89	37.12	37.30	2.74	2.67
Pd(BPM)Cl_2	Red-brown	7.6	77	47.98	47.92	3.54	3.59
Pt(BPM)Cl_2	Colorless	17.2	65	42.02	42.25	3.10	3.09
Cd(BMO)Br_2	Colorless	28.3	62	10.12	9.92	2.53	2.51
Hg(BMO)Br_2	Colorless	25.9	85	8.54	8.34	2.15	2.07
[Cu(BMO)$_2$][CuBr_2]	Colorless	160[c]	40	13.90	13.84	3.50	3.34

[a] Molar conductance on approximately 5×10^{-4} *M* solutions of dimethylformamide at 25°. Values reported for 1:1 and 2:1 electrolytes in dimethylformamide are 70–90 and 140–150, respectively.[33] [b] Insoluble. [c] On an approximately 5×10^{-4} *M* solution of acetonitrile at 25°. Values reported for 1:1 and 2:1 electrolytes in acetonitrile are 135–155 and 250–310, respectively.[33]

mixture was cooled overnight and the product crystallized as colorless needles; yield 11.1 g (69%); mp 100–101° (lit.[29] mp 91°). *Anal.* Calcd for $C_4H_{12}P_2S_3$: C, 22.01; H, 5.48. Found: C, 21.76; H, 5.48.

Preparation of Diphenylphosphinothioyldimethylphosphinothioyl Sulfide, $(C_6H_5)_2P(S)SP(S)(CH_3)_2$ (PMS).—A solution of bromodimethylphosphine sulfide (12.4 g, 0.072 mol) in 25 ml of dry tetrahydrofuran was added dropwise to a solution of ammonium diphenylphosphinodithioate (19.2 g, 0.072 mol)[30] in 300 ml of dry tetrahydrofuran at 35°. The reaction mixture was stirred for 45 min and filtered and the filtrate was concentrated on the rotatory evaporator. Hexane was added and the solution was cooled overnight at −18°. The white crystalline product was collected and recrystallized in the same manner used in the preceding preparation; yield 17.1 g (70%); mp 85.5–86°. *Anal.* Calcd for $C_{14}H_{16}P_2S_3$: C, 49.10; H, 4.71. Found: C, 49.25; H, 4.83.

Complexes of Methylene-Bridged Ligands.—In a typical preparation, PMM (1.0 g, 3 mmol) in 20 ml of absolute ethanol was added to a stirred solution of 3 mmol of the appropriate metal halide in 25 ml of absolute ethanol. The complexes usually precipitated immediately or after several minutes. The mixtures were stirred for several more minutes, filtered, washed with absolute ethanol, and dried *in vacuo*. Preparation of complexes with BPM were carried out in analogous fashion except that a few milliliters of acetone was used to aid the solution of the ligand in ethanol. Copper(II) bromide did react with both ligands, apparently resulting in the reduction of Cu(II) to Cu(I) with the precipitation of complexes that analyzed poorly for $[Cu^I(chelate)_2][Cu^IBr_2]$ (chelate = BPM, PMM). No complexes of either ligand were obtained from reactions with anhydrous halides of nickel(II), zinc(II), and cobalt(II). The complexes are insoluble in all common solvents except dimethylformamide in which they are slightly soluble. The properties and analytical data for the methylene-bridged complexes are summarized in Table I.

Complexes of Oxygen-Bridged Ligands.—In a typical preparation, BMO (202 mg, 1 mmol) in 25 ml of absolute ethanol was added to a stirred solution of 1 mmol of the appropriate metal halide in 15 ml of absolute ethanol. The precipitate which formed after several minutes was stirred a short time, filtered, washed with absolute ethanol and ether, and dried *in vacuo*. No complexes were isolated from reactions with anhydrous halides of nickel(II) and zinc(II). Complexes of undefined composition precipitated from the reaction of BMO with anhydrous halides of palladium(II) and platinum(II). BPO and PMO did not react with any metal salts. The complexes are insoluble in all common solvents, slightly soluble in dimethylformamide and trace soluble in acetone and acetonitrile. The properties and analytical data for the oxygen-bridged complexes are summarized in Table I.

Reactions of Sulfur-Bridged Ligands.—When a solution of BMS in absolute ethanol was added to a solution of cadmium(II) or mercury(II) salts, a colorless precipitate formed immediately. These compounds were identified as bis(dimethyldithiophosphinate) salts from comparison of their ir spectra with those of authentic complexes prepared from reaction of the metal salt with sodium dimethyldithiophosphinate.[31] When a solution of PMS in absolute ethanol was added to a solution of zinc(II), cadmium(II), or mercury(II) halides, a colorless precipitate formed immediately. Analytical data revealed that these were bis(diphenyldithiophosphinate) salts.[31] BPS did not react with any metal salts.

Conductance Measurements.—These were carried out on 10^{-3}–10^{-4} *M* dimethylformamide or acetonitrile solutions of the complexes with an Industrial Instruments Model RC-1613 conductivity bridge (see Table I). Purification of dimethylformamide and acetonitrile was accomplished by literature procedures.[32,33]

Infrared Spectra.—Spectra were obtained with a Perkin-Elmer Model 337 grating spectrometer and a Perkin-Elmer Model 521 grating spectrometer (1000–500-cm^{-1} region) using Nujol mulls between KBr plates. The Perkin-Elmer 521 spectra were recorded under conditions of 1-cm^{-1} resolution and with gaseous CO_2 as calibrant. Ir spectra of ligands and complexes are presented in Table II.

TABLE II

INFRARED SPECTRA OF DIPHOSPHINOTHIOYL CHELATES AND COMPLEXES (CM^{-1})

Compound	$\nu_{P=S(methyl)}$	$\nu_{P=S(phenyl)}$	ν_{POP}
PMM	579	601	
Cd(PMM)Br_2	543	581	
Hg(PMM)Br_2	542	579	
Pd(PMM)Cl_2	534	575	
Pt(PMM)Cl_2	533	567	
BPM		606	
Hg(BPM)Br_2		571	
Pd(BPM)Cl_2		568	
Pt(BPM)Cl_2		557	
BMO	597		885
Cd(BMO)Br_2	563		900
Hg(BMO)Br_2	562		897
[Cu(BMO)$_2$][CuBr_2]	568		893
BPO		655	924, 908
PMO	607	625	940, 893
BMS	576		
BPS		642	
PMS	595	650	

Proton Nmr Spectra.—Spectra were obtained on a Varian Associates A-60 spectrometer with dimethylformamide as solvent. Chemical shifts were calibrated with tetramethylsilane as an internal standard and the dimethylformamide resonance peak at δ 8.02.[34] Coupling between phosphorus and substituent methyl or methylene protons on ligands and complexes was calibrated by the standard audiooscillation side-band technique. The phosphorus-31 nmr spectra of PMM and PMO in methylene chloride were obtained on a Varian Associates DP-60 spectrom-

---

[29] L. Almasi and L. Paskucz, *Chem. Ber.*, **102**, 1489 (1969).

[30] Prepared in 60% yield by treatment of diphenyldithiophosphinic acid with ammonia.

[31] W. Kuchen, J. Metten, and A. Judat, *Chem. Ber.*, **97**, 2306 (1964).

[32] D. P. Ames and P. G. Sears, *J. Phys. Chem.*, **59**, 16 (1955).

[33] R. L. Dutta, D. W. Meek, and D. H. Busch, *Inorg. Chem.*, **9**, 1215 (1970).

[34] N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, "NMR Spectra Catalogue," Varian Associates, Palo Alto, Calif., 1962.

TABLE III

SOME ^{1}H AND ^{31}P CHEMICAL SHIFTS AND COUPLING CONSTANTS[a]

Compound	$\delta(CH_3)$, ppm	$J(^{31}P-C-^1H_3)$, Hz	$\delta(CH_2)$, ppm	$J(^{31}P-C-^1H_2)$, Hz	$\delta(P(C_6H_5))$,[b,c] ppm	$\delta(P(CH_3))$,[b,c] ppm
BMO	1.93	12.9				
Cd(BMO)Br$_2$	1.85	13.6				
[Cu(BMO)$_2$][CuBr$_2$]	1.77	13.5				
PMO	2.10	13.4			−78.6	−94.2
PMS	2.02	12.9				
BMS	2.25	12.2				
PMM	1.87	13.4	3.93[d]	*e*	−32.8	−35.9
Cd(PMM)Br$_2$	2.04	13.6	4.10[d]	*e*		
Hg(PMM)Br$_2$	2.25	13.7	4.54[d]	*e*		
BPM			4.63[f]	13.2		
Hg(BPM)Br$_2$			5.22[f]	13.7		

[a] Spectra run in DMF unless otherwise noted. [b] Solution in CH_2Cl_2. [c] With respect to external 85% H_3PO_4. [d] Two doublets. [e] Coupling is ambiguous. [f] Triplet.

eter operating at 24.3 Mc with 85% H_3PO_4 as an external standard. The nmr spectra of ligands and complexes are presented in Table III.

Visible and Ultraviolet Spectra.—Spectra of the palladium complexes of BPM and PMM in dimethylformamide solution were taken with a Perkin-Elmer Model 356 recording spectrophotometer using a set of matched 1-cm quartz cells.

Analyses.—Carbon, hydrogen, and sulfur microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Discussion

All of the complexes reported in Table I are new. Except for the complexes with copper, all were nonelectrolytes in dimethylformamide of composition M(chelate)X$_2$ ($X^- = Br^-$ or Cl^-). Reactions with two chelates with one metal ion yielded 1:1 complexes. The conductance values indicate that the complexes are slightly dissociated in dimethylformamide but do fall in the expected range for a nonelectrolyte.[33]

The copper complex with BMO has a conductance in acetonitrile indicative of a 1:1 electrolyte.[33] The most reasonable structure is [Cu^{I}(BMO)$_2$][Cu^{I}Br$_2$] which is analogous to five-membered chelate ring complexes with copper(I) isolated by Meek and Nicpon.[2] Presumably, the copper complexes containing BPM and PMM as ligands have the same type of structure. The oxidized products in these reactions have not been identified but may have involved the alcohol solvent as with similar reductions of copper(II) with phosphine sulfides.[35]

Evidence for coordination through the thiophosphoryl donor sites is provided by the decrease in P=S stretching frequency upon coordination as indicated in Table II. The drop in P=S stretching frequency is nearly the same for the chelate diphosphinothioyls BMO and BPM as for analogous monodentate thiophosphoryl groups containing the same type of substituents.[2,36,37]

Complexes with PMM indicate a much smaller drop in the P=S stretching frequency for the thiophosphoryl group with phenyl substituents than in corresponding BPM complexes. The methyl-substituted thiophosphoryl group is expected to be the better donor to the coordinated metal in PMM thus reducing the attraction of the phenyl-substituted thiophosphoryl group in comparison to BPM complexes.

The uv-visible spectra of the palladium complexes of BPM and PMM indicate that the chelating properties of these two were identical. Both complexes have a λ_{max} at 25,000 cm^{-1} and ϵ_{max} of about 950. The λ_{max} value is lower than the value reported for Pd[((CH$_3$)$_2$N)$_3$P=S]$_2$Cl$_2$,[35] in which the thiophosphoryl groups should be better donors as a result of an increased inductive effect.

The POP stretching frequencies help to establish a chelate structure for BMO complexes. The POP stretching frequency for BPO has been reported[10] slightly above 900 cm^{-1} and accordingly the band at 885 cm^{-1} was assigned to the POP stretching frequency for BMO. This band shifted upward upon coordination indicating a higher bond order in the POP grouping as a result of increased $p_\pi-d_\pi$ overlap of oxygen onto phosphorus.[38]

The chemical shifts of the methyl or methylene substituents on BPM and PMM are deshielded upon coordination as indicated in Table III whereas the chemical shifts of the methyl groups on BMO are shielded. Bonding *via* the thiophosphoryl group is expected to deshield the substituent methyl or methylene protons. This appears to occur in PMM and BPM complexes whereas the delocalization of the electrons on oxygen *via* $p_\pi-d_\pi$ overlap onto phosphorus may shield the methyl substituents or give rise to a neighboring paramagnetic effect[39] that shields these methyl groups. This same shielding effect has been observed with the "imidodiphosphinates"[10] which are even more highly delocalized.

Not all of the ligands prepared in this study reacted to form six-membered ring chelate complexes. The ligands, BPO, PMO, and BPS did not form complexes of any kind. The presence of phenyl groups and an oxygen bridge must substantially reduce the donor properties of BPO and PMO. Although BPS and BPM are expected to behave similarly, the bridging sulfur in BPS has a much smaller bond angle than the methylene bridge in PBM. This must crowd the two thiophosphoryl groups so close together that chelation is sterically hindered.

On the other hand, both BMS and PMS cleave during the reaction to form stable four-membered ring phosphinodithionate complexes.[31] In reactions with PMS, the inductive effect of the phenyl groups tends to weaken the sulfur bridge on the methyl-substituted side allowing easy formation of the diphenyldithiophos-

---

(35) W. E. Slinkard and D. W. Meek, *Inorg. Chem.*, **8**, 1811 (1969).

(36) M. G. King and G. P. McQuillan, *J. Chem. Soc. A*, 898 (1967).

(37) J. A. W. Dalziel, A. F. le C. Holding, and B. E. Watts, *ibid.*, 358 (1967).

(38) C. J. Popp and M. D. Joesten, *Inorg. Chem.*, **4**, 1418 (1965).

(39) R. S. Drago, "Physical Methods in Inorganic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1965, p 257.

phinate anion whose metal derivative was the only species isolated.

Acknowledgment.—We wish to thank Professor Richard C. Lord, Massachusetts Institute of Technology, for making his PE 521 available to us and to Professor Samuel O. Grim, University of Maryland, for running the ^{31}P nmr spectra.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
WASHINGTON STATE UNIVERSITY, PULLMAN, WASHINGTON 99163

Five-Coordinate, Square-Pyramidal Chelate Complexes of a Novel Tetradentate Amino Acid Like Ligand

BY DONALD F. AVERILL, J. IVAN LEGG,* AND DAVID L. SMITH[1]

Received December 13, 1971

The chemistry of a novel tetradentate aminecarboxylic acid ligand, 1,5-diazacyclooctane-*N,N'*-diacetate (dacoda), is reported. Due to the steric makeup of its chelates, an alkyl proton effectively blocks a coordination site on the metal ion which allows the coordination of only one additional ligand. Consequently a five-coordinate, square-pyramidal complex results. The complexes [M(dacoda)(H_2O)] (M^{2+} = Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}) were prepared, and their spectroscopic and magnetic properties were compared with those of the octahedral, diaquo complexes of ethylenediamine-*N,N'*-diacetate (EDDA), a ligand of comparable crystal field strength. The five-coordinate nature of [M(dacoda)(H_2O)] (M^{2+} = Co^{2+}, Ni^{2+}) both in the solid state and in aqueous solution was established by comparison of X-ray powder patterns and solid and solution spectra. The Zn^{2+} complex is isomorphous. The crystal structure of the Ni(II) complex has been determined in this laboratory. The Co(II)–dacoda complex is stable to oxidation under conditions normally employed to obtain facile oxidation of amino acid–cobalt(II) complexes.

Introduction

A useful classification of five-coordinate complexes is in terms of the ligand field strength of the ligands involved.[2] With one exception[3] these complexes are unstable in strong polar solvents and as a consequence many of them have to be prepared under anhydrous conditions.

We have synthesized a tetradentate amino acid like ligand, 1,5-diazacyclooctane-*N,N'*-diacetate (dacoda), which forms five-coordinate, square-pyramidal complexes in aqueous solution and the solid state.[4] This geometry has been established for the Ni(II) complex by an X-ray crystal structure determination.[5] The design of dacoda, Figure 1, was predicated on the stereochemical nature of chelates formed with the parent amine 1,5-diazacyclooctane (daco).[6] The key to the design of ligands which would lead to five-coordinate, square-pyramidal complexes was to take advantage of the unique mode of coordination of daco. When daco is coordinated, a proton on the 3 carbon (or 7 carbon) is forced over the metal ion in order to avoid steric crowding with a proton on the 7 carbon (or 3 carbon), Figure 1. This blocks this position to further coordination. The two six-membered chelate rings of the bicyclic ring system define a chair and boat conformation. Musker and Hussain took advantage of this predicted behavior to prepare square-planar $M(daco)_2^{2+}$ complexes where a proton from each daco blocks an apical position on the octahedron.

By alkylating one or both of the ring nitrogens of daco with a group containing a coordinating ligand, a complex with only one daco unit is anticipated since only one ligand is expected to coordinate. Thus only one position is blocked and a five-coordinate complex is expected to form. Furthermore, the *N*-R substituents must coordinate in the plane of the nitrogens, and consequently the complexes will be square pyramidal.

We have synthesized a series of N-substituted ligands of daco and its closely related homolog 1,4-diazacycloheptane (dach, homopiperazine) most of which are expected to form five-coordinate complexes. The ligands are relatively simple, lacking bulky, dangling groups such as phenyl or ethyl and uncomplicated by the presence of π-acceptor ligating atoms. Hydrolysis under neutral or near-neutral conditions is not anticipated, and thus the geometry should be maintained under aqueous conditions. Our interest in these ligands is related to both the unique stereochemistry involved and the expected behavior of certain of these complexes as models for metalloproteases. This report is concerned with the Co(II), Ni(II), Cu(II), and Zn(II) complexes of 1,5-diazacyclooctane-*N,N'*-diacetate, dacoda. The properties of these complexes were compared with the complexes of ethylenediamine-*N,N'*-diacetate (EDDA), a ligand of similar crystal field strength which was expected to lead to the formation of normal six-coordinate complexes.

Experimental Section

Preparation of Ligands.—Ethylenediamine-*N,N'*-diacetic acid (H_2EDDA) was obtained from K & K Laboratories and was used as received. A previously reported procedure[7] was used to prepare 1,5-diazacyclooctane (daco) and the product was purified as the dihydrobromide salt.[8]

---

* Address correspondence to this author at the Biophysics Research Laboratory, Peter Bent Brigham Hospital, Harvard Medical School, Boston, Mass. 02115.

[1] National Science Foundation Undergraduate Research Participant.

[2] L. Sacconi, *J. Chem. Soc. A*, 248 (1970).

[3] M. Ciampolini and P. Paoletti, *Inorg. Chem.*, **6**, 1261 (1967), and references therein.

[4] For a preliminary report see J. I. Legg, D. O. Nielson, D. L. Smith, and M. L. Larson, *J. Amer. Chem. Soc.*, **90**, 5030 (1968).

[5] D. O. Nielson, M. L. Larson, R. D. Willett, and J. I. Legg, *ibid.*, **93**, 5079 (1971).

[6] W. K. Musker and M. S. Hussain, *Inorg. Chem.*, **5**, 1416 (1966).

[7] E. L. Buhle, A. M. Moore, and F. G. Wiseloge, *J. Amer. Chem. Soc.*, **65**, 29 (1943).

[8] J. H. Billman and L. C. Dorman, *J. Org. Chem.*, **27**, 2419 (1962).