CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
VANDERBILT UNIVERSITY, NASHVILLE, TENNESSEE 37203

Metal Complexes of *sym*-Diethyl Tetramethyldiamidopyrophosphate

BY MICHAEL F. PRYSAK[1] AND MELVIN D. JOESTEN

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Metal complexes of *sym*-diethyl tetramethyldiamidopyrophosphate (SYM) which have been isolated include $Mg(SYM)_3(ClO_4)_2$, $Ba(SYM)_2(ClO_4)_2$, $Co(SYM)_3(ClO_4)_2$, $Ni(SYM)_3(ClO_4)_2$, $Cu(SYM)_3(ClO_4)_2$, and $Zn(SYM)_3(ClO_4)_2$. These complexes are much less stable than the corresponding complexes of octamethylpyrophosphoramide (OMPA). Over-all stability constants have been determined in acetone solution for complexes of Co(II) and Ni(II) with both SYM and OMPA. The values for OMPA are consistently larger than those for SYM. This is just the opposite of the order obtained for Dq toward Ni(II) [SYM, 741 cm^{-1}; OMPA, 726 cm^{-1}].

Introduction

The complexing ability of the pyrophosphate anion has been studied extensively in solution.[2] However, relatively few metal complexes of the pyrophosphate linkage have been isolated from solution. We have initiated a systematic study of the coordinating power of the pyrophosphate linkage $R_1R_2P(O)OP(O)R_3R_4$ where R_1–R_4 are various combinations of organic functional groups. We became interested in studying the influence of organic functional groups on the coordinating ability of the pyrophosphate linkage after our discovery of the versatility of octamethylpyrophosphoramide [OMPA, $R_1 = R_2 = R_3 = R_4 = N(CH_3)_2$] as a ligand.[3]

We are particularly interested in isolating metal complexes of organic pyrophosphates with sufficient stability to allow complete structure determination by X-ray analysis. A knowledge of the bonding and orientation of the pyrophosphate linkage with respect to metal ions may lead to a better understanding of the function of metal ions in enzymatic phosphate-transfer reactions of adenosine phosphates.[4]

The present paper is a report of the isolation and characterization of metal complexes of *sym*-diethyl tetramethyldiamidopyrophosphate (SYM, $R_1 = R_3 = OC_2H_5$; $R_2 = R_4 = N(CH_3)_2$). Since OMPA forms complexes with over 30 metal ions and attempts to isolate metal complexes of tetraethyl pyrophosphate ($R_1 = R_2 = R_3 = R_4 = OC_2H_5$) have failed,[5] we decided to study the coordinating ability of SYM.

Experimental Section

A. Ligand Preparation.—*sym*-Diethyl tetramethyldiamidopyrophosphate (SYM) was prepared according to the procedure of Holmstedt.[6] The preparation involved the sequence

$$C_2H_5OP(O)Cl_2 + 2HN(CH_3)_2 \longrightarrow C_2H_5OP(O)N(CH_3)_2Cl + H_2N(CH_3)_2{}^+Cl^-$$

$$C_2H_5OP(O)N(CH_3)_2Cl + H_2O + C_5H_5N \longrightarrow (C_2H_5O)[(CH_3)_2N]P(O)OP(O)[N(CH_3)_2](OC_2H_5) + C_5H_5NH^+Cl^-$$

Ethyl phosphorodichloridate was obtained from Aldrich Chemical Co. Ethyl dimethylphosphoramidochloridate [bp 60–70° (2 mm)] and SYM [bp 126° (0.45 mm)] were purified by fractional distillation. SYM was stored in a desiccator.

B. Complex Preparation.—The complexes were prepared by dehydrating the aquated metal perchlorate in an excess of 2,2′-dimethoxypropane, adding SYM in fourfold molar excess, and stirring for a sufficient time to ensure complete complexation. Excess ether precipitated the complex as an oil which was solidified by a second extraction. All complexes were filtered under nitrogen, washed with anhydrous ether, and dried *in vacuo* at room temperature. The complexes are quite hygroscopic.

C. Spectral Measurements.—Infrared spectra were obtained as KBr pellets on a Beckman IR-10 spectrophotometer. Visible and near-infrared spectra were obtained with a Beckman DK-2A spectrophotometer. Spectral parameters were calculated according to the method of Drago.[7] Acetone stored over molecular sieves was the solvent used in all visible and near-infrared spectral measurements. Spectral data are contained in Tables I and II.

D. Conductance Measurements.—Conductance measurements were carried out according to the method of Feltham and Hayter.[8] Spectrograde nitromethane (Fisher) was stored over molecular sieves prior to use as the solvent for conductance measurements. A conductance bridge manufactured by Industrial Instruments, Inc., and equipped with a platinum dip-type cell (cell constant 0.110 cm^{-1}) was used. Conductance data are summarized in Table II.

E. Analyses.—Carbon, hydrogen, and nitrogen analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Analytical data for SYM and its complexes can be found in Table III.

F. Stability Constant Measurements.—Stability constant measurements were made for both the SYM and OMPA complexes of Co(II) and Ni(II) in acetone. Mole ratio plots for the hydrated metal perchlorate mixed with SYM and OMPA show breaks at a 3:1 ratio of ligand to metal ion. The interactions between the ligands and the metal ions in solution were examined spectrophotometrically. Molar absorptivities of $Co(SYM)_3(ClO_4)_2$, $Ni(SYM)_3(ClO_4)_2$, $Co(OMPA)_3(ClO_4)_2$, $Ni(OMPA)_3(ClO_4)_2$, $Co(ClO_4)_2\cdot 6H_2O$, and $Ni(ClO_4)_2\cdot 6H_2O$ were determined from Beer's law plots of these species in acetone. Perchlorate salts were used to minimize the possibility of anion competition. The temperature range was 24 ± 1°. A Cary 14 spectrophotometer was used for these measurements.

Calculation of an over-all stability constant was based on[9]

$$M(solv)^{2+} + nA = MA_n{}^{2+}$$

This reaction may be expressed by

$$\beta_n = \frac{[MA_n]}{[M][A]^n}$$

where β_n is the overall formation constant and is equal to the product of the stepwise formation constants, *i.e.*, $(K_1)(K_2)\cdot$

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(1) NDEA Fellow, 1966–1969.

(2) J. R. Van Wazer and C. F. Callis, *Chem. Rev.*, **58**, 1011 (1958).

(3) M. D. Joesten, *Inorg. Chem.*, **6**, 1598 (1967), and papers cited therein.

(4) R. Phillips, *Chem. Rev.*, **66**, 501 (1966).

(5) K. P. Lannert and M. D. Joesten, unpublished results.

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(7) R. S. Drago, "Physical Methods in Inorganic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1965, p 410.

(8) R. D. Feltham and R. G. Hayter, *J. Chem. Soc.*, 4587 (1964).

(9) J. F. Forbes, Ph.D. Thesis, Southern Illinois University, 1968.

TABLE I

VISIBLE AND NEAR-INFRARED DATA FOR SYM COMPLEXES

Compound	λ_{max}, mμ (cm^{-1})	ε
$Co(SYM)_3(ClO_4)_2$	540 (18,518)	17
	711 (14,064)	1
	1460 (6849)	3
$Cu(SYM)_3(ClO_4)_2$[a]	945 (10,582)	17
	1125 (8888)	13
$Ni(SYM)_3(ClO_4)_2$	424 (23,585)	15
	800 (12,500)	6
	1350 (7407)	5

[a] Resolved by the procedure of J. Bjerrum, C. J. Ballhausen, and C. K. Jørgensen, *Acta Chem. Scand.*, **8,** 1275 (1954).

(. . .)(K_n), [A] is the ligand concentration, [M] is the metal ion concentration, and [MA_n] is the complex concentration. The following expressions may be written

$$C_M = [M] + [MA_n]$$

$$C_A = [A] + n[MA_n]$$

$$A/b = \epsilon_M[M] + \epsilon_{MA_n}[MA_n] + \epsilon_A[A]$$

where A is the absorbance, b is the cell path (5 cm), and ϵ_M, ϵ_{MA_n}, and ϵ_A are the molar absorptivities of the respective species. The ϵ_A[A] term is zero since neither ligand absorbs in the spectral regions of study. These equations are solved to yield the overall stability constant relation

$$\beta_3 = \frac{(A/b) - \epsilon_M C_M}{[\epsilon_{MA_n}C_M - (A/b)]\left[C_A - 3\left(\frac{(A/b) - \epsilon_M C_M}{\epsilon_{MA_3} - \epsilon_M}\right)\right]^3}$$

As mentioned above, n was found to be 3 from mole ratio plots. The mole ratio of ligand to metal ion was kept between 3:1 and 4:1 to minimize further the concentration of 1:1 or 2:1 complexes. The peak maxima of each complex was chosen for calculations. A typical run consisted of preparation of a metal perchlorate solution and a ligand solution of similar molarities. The perchlorate solution (4 ml) was pipetted into each of three 25-ml volumetric flasks. Then 11-, 12-, and 13-ml samples of ligand solution were pipetted into the three flasks and each flask was filled up to volume with solvent. The absorbance of the resulting solutions was then measured on the Cary 14.

Results and Discussion

One cannot help but be struck by the obvious ease with which OMPA complexes are isolated. Frequently, addition of excess ether is not even necessary for their precipitation. However, this is not the case for metal complexes of SYM. We have observed the marked tendency of freshly precipitated SYM complexes to become oils before solidifying. Also, the solid complexes are quite hygroscopic [especially $Cu(SYM)_3(ClO_4)_2$]. If we accept the ease of isolation of a complex as an indication of complex stability, although admittedly an arbitrary one, then we must conclude *a priori* that SYM complexes are less stable than OMPA complexes, and, hence, SYM is of less coordinating ability than its completely dimethylamidated counterpart.

TABLE II

CONDUCTANCE AND INFRARED DATA

Compound	Concn range × 10^4, M	Slope[a]	Λ_0 at 25°, ohm^{-1} cm^2	ν(P=O),[b] cm^{-1}
$Co(SYM)_3(ClO_4)_2$	3.7–23	363	119.4	1253 (1240)
$Ni(SYM)_3(ClO_4)_2$	3.0–28	330	117.6	1253 (1934)
$Mg(SYM)_3(ClO_4)_2$	3.3–28	392	120.9	1236 (1262)
$Cu(SYM)_3(ClO_4)_2$	4.1–25	318	110.1	1260 (1230)
$Zn(SYM)_3(ClO_4)_2$	4.7–20	407	121.4	1253 (1240)
$Ba(SYM)_2(ClO_4)_2$	4.1–23	519	93.2	1256 (1234)
$Co(OMPA)_3(ClO_4)_2$	5.1–25	342	120.1	. . .
$Ba(OMPA)_2(ClO_4)_2$	6.9–27	478	101.7	. . .
SYM	. . .	. . .	. . .	1259

[a] Λ_e *vs.* $\sqrt{C}$. [b] Nujol mulls. Shoulders given in parentheses.

TABLE III

ANALYTICAL DATA FOR SYM AND ITS COMPLEXES

Compound	Color	% C		% H		% N	
		Calcd	Found	Calcd	Found	Calcd	Found
$Co(SYM)_3(ClO_4)_2$	Lavender	25.7	25.5	5.9	6.1	7.5	7.6
$Ni(SYM)_3(ClO_4)_2$	Yellow	25.7	25.7	5.9	5.9	7.5	7.3
$Zn(SYM)_3(ClO_4)_2$	White	25.5	25.4	5.9	6.5	7.4	7.4
$Cu(SYM)_3(ClO_4)_2$	White	25.6	25.9	5.9	6.3	7.5	7.0
$Ba(SYM)_2(ClO_4)_2$	White	21.1	21.3	4.9	5.1	6.1	6.2
$Mg(SYM)_3(ClO_4)_2$	White	26.5	26.5	6.1	6.2	7.7	7.7
SYM	Colorless	33.3	33.1	7.7	7.8	9.7	9.5

The correctness of the above reasoning could conceivably be verified by comparison of ligand field parameters.[3,10–12] From the visible and near-infrared spectrum of $Ni(SYM)_3(ClO_4)_2$, Dq and $\beta°$ values are calculated to be 741 cm^{-1} and 12.6%, respectively. Good evidence for O_h symmetry is obtained by the agreement of the calculated (12,481 cm^{-1}) and experimental (12,500 cm^{-1}) values for the middle band ($^3A_{2g} \rightarrow {}^3T_{1g}(F)$) and the low molar absorptivity values for $Co(SYM)_3(ClO_4)_2$ and $Ni(SYM)_3(ClO_4)_2$. An apparent anomaly appears when the spectral parameters of OMPA are examined. As can be seen from Table IV, both parameters indicate that SYM is a stronger ligand than OMPA. We feel that the differences in Dq and $\beta°$ are outside experimental error. If we now consider bis(diisopropoxyphosphinyl)methane (L_1) and octamethylmethylenediphosphonic diamide (PCP) from the same table, we again encounter the same anomaly.

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(10) J. T. Donoghue and R. S. Drago, *Inorg. Chem.*, **1**, 866 (1962).

(11) M. F. Prysak and M. D. Joesten, unpublished results.

(12) J. A. Walmsley and S. Y. Tyree, *Inorg. Chem.*, **2**, 312 (1963).

TABLE IV

LIGAND FIELD PARAMETERS FOR SELECTED LIGANDS

Ligand	Abbreviation	Metal	*Dq*,[a]	β°,[b] %	Ref
$((CH_3)_2N)(C_2H_5O)P(O)OP(O)(OC_2H_5)(N(CH_3)_2)$	SYM	Ni(II)	741	12.6	This work
$((CH_3)_2N)_2P(O)OP(O)(N(CH_3)_2)_2$	OMPA	Ni(II)	726	11.2	3
$(C_3H_7O)_2P(O)CH_2P(O)(OC_3H_7)_2$	L_1	Ni(II)	722	9.97	13
$((CH_3)_2N)_2P(O)CH_2P(O)(N(CH_3)_2)_2$	PCP	Ni(II)	707	10.4	13
$P(O)(N(CH_3)_2)_3$	HMPA	Co(II)	364	20.0	10
$((CH_3)_2N)_2P(O)(CH(CH_3)_2)$	IPR	Co(II)	415	26.3	11

[a] Values toward Ni(II) are in the octahedral field and those for Co(II) are in the tetrahedral field. [b] $\beta^\circ = 100(1-\beta)$.

TABLE V

STABILITY CONSTANT DATA[a]

Ni(SYM)$_3$(ClO$_4$)$_2$			Ni(OMPA)$_3$(ClO$_4$)$_2$		
[Ni(ClO$_4$)$_2$], *M*	[SYM], *M*	β_3	[Ni(ClO$_4$)$_2$], *M*	[OMPA], *M*	β_3
0.004466	0.01228	1.15×10^7	0.004489	0.01230	9.23×10^8
0.00446	0.01340	1.13×10^7	0.004489	0.01342	5.61×10^8
0.005521	0.01518	4.45×10^6	0.005521	0.01522	2.40×10^8
0.005521	0.01656	3.11×10^6	0.005521	0.01660	2.11×10^8
0.005021	0.01794	2.18×10^6	0.005521	0.01798	1.31×10^8
0.006853	0.01885	2.62×10^6	0.006865	0.01895	1.26×10^8
0.006853	0.02056	2.00×10^6	0.006865	0.02067	8.48×10^7
0.006853	0.02228	2.01×10^6	0.006865	0.02239	6.90×10^7

Co(SYM)$_3$(ClO$_4$)$_2$			Co(OMPA)$_3$(ClO$_4$)$_2$		
[Co(ClO$_4$)$_2$], *M*	[SYM], *M*	β_3	[Co(ClO$_4$)$_2$], *M*	[OMPA], *M*	β_3
0.003988	0.01092	6.00×10^8	0.003976	0.01088	4.06×10^9
0.003988	0.01192	2.29×10^8	0.003976	0.01187	7.55×10^9
0.003988	0.01291	1.19×10^8	0.003976	0.01286	4.24×10^9
0.004804	0.01322	1.46×10^8	0.004789	0.01314	2.16×10^9
0.004804	0.01442	1.85×10^8	0.004789	0.01433	2.04×10^9
0.004804	0.01562	2.71×10^8	0.004789	0.01553	1.17×10^9
0.005942	0.01636	9.02×10^7	0.005935	0.01636	1.47×10^9
0.005942	0.01783	7.66×10^7	0.005935	0.01784	5.87×10^8
0.005942	0.01934	8.12×10^7	0.005935	0.01933	6.23×10^8

[a] Measurements made in acetone at 24°.

It should be noted here that the *Dq* value previously reported for L_1[12] is incorrect. A discussion of the spectrum of $Ni(L_1)_3(ClO_4)_2$ will be published in another paper.[13] The recalculated value for L_1 is given in Table V. Inferring from experimental descriptions, PCP complexes appear to be much more easily isolated than those of L_1. Just the opposite would be predicted from the spectral parameters. This anomaly also exists for other organophosphorus ligands. Again from Table IV, *Dq* and β° values indicate that P-isopropyl-N,N,N′,N′-tetramethylphosphonic diamide (IPR) is a better coordinator than hexamethylphosphonic triamide (HMPA). In the course of our laboratory work with these two compounds, we found that complexes of HMPA are easier to isolate and less hygroscopic than the corresponding complexes of IPR. Therefore, we feel the differences in coordinating abilities of these organophosphorus ligands are erroneously mirrored in their relative *Dq* and β° values.

The results of stability constant measurements in acetone support these conclusions. A comparison of over-all stability constants at a given concentration of metal ion shows that β_3 values for OMPA complexes are always larger than the corresponding β_3 values for SYM complexes (Table V). Since the stability constants appear to be concentration dependent, only relative comparisons can be made. Ion pairing is expected to be extensive in acetone. However, the effect of ion pairing on the over-all stability constant is assumed to be the same for SYM and OMPA complexes. The decreasing order of over-all stability constants is $Co(OMPA)_3^{2+} > Co(SYM)_3^{2+} \sim Ni(OMPA)_3^{2+} > Ni(SYM)_3^{2+}$.

Let us examine the anomaly more closely from the standpoint of chemical bonding. The magnitude of *Dq* is affected by (1) electrostatic forces, (2) σ lone pairs on the ligand, (3) metal→ligand $d\pi$–$p\pi$ bonding, and (4) ligand→metal $p\pi$–$d\pi$ bonding.[14] An increase in the first three causes a larger *Dq* while an increase in (4) results in a smaller *Dq*. The difference in *Dq* values for OMPA and SYM can be explained by considering the influence of the organic groups on (1)–(4). The ethoxy group is a much weaker electron donor than a dimethylamino group. Therefore, the P=O bond in SYM complexes will contain more $d\pi$–$p\pi$ bonding than in OMPA complexes. This conclusion is borne out by the infrared spectra which are discussed below. This will cause less repulsions between metal t_{2g} electrons and lone-pair electrons on the oxygen in the SYM complexes. As a result (3) will be greater and (4) smaller for SYM than for OMPA complexes. Thus *Dq* will be greater for SYM. The larger values of β° can also be explained by the importance of (3) since the delocaliza-

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[13] K. P. Lannert and M. D. Joesten, *Inorg. Chem.*, in press.

[14] T. M. Dunn in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, New York, N. Y., 1960, p 267.

tion of metal d electrons would result. The same basic argument also applies to the L_1 *vs.* PCP case. Note also the OMPA values as compared to these for PCP. This indicates the bridging group does play some role in the coordination picture. We feel, though, that this bridge effect is of a different nature than the substituent effect discussed above. It probably has more to do with the possibility of electron delocalization; that is, the better the bridge is in facilitating delocalization, the larger the Dq value will be. Thus an oxo-bridged chelate will necessarily contain a more mobile ring-electron cloud than a methylene-bridged chelate. This is reflected in the respective Dq values of OMPA and PCP. The substituent and bridge effects are often in opposition to one another as in OMPA. These opposing effects are a possible explanation for results of X-ray structure studies. The chelate rings of OMPA complexes are planar[15] which would suggest that $d\pi$–$p\pi$ delocalization in the chelate ring is important. However, the phosphoryl oxygen distance of 1.47 Å is too short and the bridging P–O distance of 1.61 Å is too long to be consistent with appreciable electron delocalization in the ring.

The decrease in the P=O stretching frequency is evidence for coordination of the phosphoryl oxygens to the metal ion. Shifts other than that of the P=O stretch upon coordination of SYM are not significant enough to be mentioned. The shift of the P=O stretch in all cases is in the direction of lower frequency and longer wavelength. For SYM complexes this shift is from 20 to 30 cm^{-1}. The relative strength of the interaction is indicated by the magnitude of the shift. For the corresponding OMPA complexes the shift is of the order of 30–60 cm^{-1}.

As with OMPA, the tris-copper(II) complex isolated with SYM is colorless with no spectral peak in the visible region. However, a characteristic, broad asymmetric band does appear in the near-infrared region. For $Cu(OMPA)_3(ClO_4)_2$ this band occurs at 920 mμ and at the time was reported to represent the largest shift into the near-infrared region of any known six-coordinate copper(II) complex.[16] For $Cu(SYM)_3(ClO_4)_2$ the shift is even greater (945 mμ). In acetone $[Cu(SYM)_3](ClO_4)_2$ apparently exhibits only one broad, asymmetric band. However, an examination of the absorption spectrum obtained after addition of excess ligand shows that several bands are present. According to Bjerrum, Ballhausen, and Jørgensen,[17] absorption curves follow a simple Gaussian error curve and, consequently, are symmetrical around their maximum value if the band is arising from a single transition. We used this principle on the $Cu(SYM)_3(ClO_4)_2$ near-infrared spectrum and determined that its absorption curve can be resolved into a minimum of two symmetric absorption curves with maxima at 945 mμ (λ_1) and 1350 mμ (λ_2). The wavelength ratio has been used to indicate the configuration of the complex ions in solution (octahedral, $\lambda_2/\lambda_1 = 1$; square pyramid, $\lambda_2/\lambda_1 = 1.16$; square, $\lambda_2/\lambda_1 = 2$). The λ_2/λ_1 ratio for $Cu(SYM)_3(ClO_4)_2$ is 1.19 compared to 1.26 for $Cu(OMPA)_3(ClO_4)_2$.

The method of Feltham and Hayter was chosen for conductance measurements. The method emphasizes the greater reliability and significance of equivalent conductivity as a function of the square root of the equivalent concentration. Our results are summarized in Table II. The important parameter is the slope of the slope–intercept form of the Onsager equation $\Lambda_e = \Lambda_0 - B\sqrt{C}$. Feltham and Hayter[8] report slopes of 392–510 for 2:1 electrolytes and 151–216 for 1:1 electrolytes in nitromethane. Our slopes have a range of 318–519 which is sufficient evidence that our SYM complexes dissociate as 2:1 electrolytes in nitromethane. Two OMPA complexes were included in the study for comparison.

In summary, the experimental results indicate that the pyrophosphate linkage of SYM forms chelate rings with metal ions. Complexes of SYM are much less stable than the corresponding complexes of OMPA. This decrease in stability is probably due to the greater electron-withdrawing ability of ethoxy groups as compared to that of dimethylamino groups.

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[17] J. Bjerrum, C. J. Ballhausen, and C. K. Jørgensen, *Acta Chem. Scand.*, **8**, 1275 (1954).