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The Donor Properties of Pyrophosphate Derivatives. I. Complexes of Octamethylpyrophosphoramide

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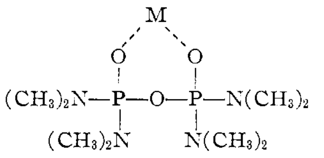
Received October 2, 1963

New complexes of octamethylpyrophosphoramide (OMPA) with $Co(ClO_4)_2$, $Ni(ClO_4)_2$, $Zn(ClO_4)_2$, $CoCl_2$, $FeCl_3$, and $CuCl_2$ have been prepared. The compounds have been characterized as $[Co(OMPA)_3](ClO_4)_2$, $[Ni(OMPA)_3](ClO_4)_2$, $[Zn(OMPA)_3](ClO_4)_2$, $[Co(OMPA)_3][CoCl_4]$, $[Fe(OMPA)_3][FeCl_4]_3$, and $[Cu(OMPA)_2][CuCl_4]$. The ligand field parameters Dq and β are reported for octamethylpyrophosphoramide toward Ni(II).

Introduction

Many new coordination compounds in which the ligand contains the phosphoryl donor site have been synthesized. Coordination compounds with ligands such as substituted phosphine oxides,[1] hexamethylphosphoramide,[2] and bis(diisopropoxyphosphinyl)-methane[3] are examples.

In the present study octamethylpyrophosphoramide $[(CH_3)_2N]_2OPOPO[N(CH_3)_2]_2$, was used. This ligand is similar to the above ligands in that P=O donor sites are available for coordination. However, OMPA is capable of forming a six-membered ring in which the members of the ring include only phosphorus, oxygen, and the metal. This structure is similar to that proposed for complexes of the pyrophosphate anion.



Well-characterized complexes of the pyrophosphate anion are difficult to isolate, and most of the studies have involved physical measurements on solutions of pyrophosphate complexes.[4-9] Octamethylpyrophosphoramide (OMPA) was chosen as a ligand since it has two phosphoryl groups, can coordinate as a neutral ligand, and has donor sites which are more basic than those of the pyrophosphate anion.

Experimental

Reagents.—A 70% solution of octamethylpyrophosphoramide from K and K Laboratories was purified by fractional vacuum distillation. The fraction distilling between 130 and 140° (0.2 mm.) was used for making complexes. *Octamethylpyrophosphoramide is extremely toxic and should be handled with care.* Hydrated metal perchlorates were obtained from the G. Frederick Smith Chemical Co.

Preparation of Complexes. (1) **General.**—All of the complexes except those of $CuCl_2$ and $FeCl_3$ were prepared by the same method. The aquated metal perchlorate or chloride (0.005 mole) was dehydrated with an excess of 2,2′-dimethoxypropane.[10] After stirring the solution for 2 hr. at room temperature, 0.020 mole of octamethylpyrophosphoramide was added and stirring was continued for 10 min. Excess ether was added to precipitate the complex. The mixture was filtered, washed with anhydrous ether, and dried *in vacuo* over Drierite. Elemental analyses for the OMPA complexes are given in Table I.

The complexes are soluble in nitrobenzene, nitromethane, acetone, and chloroform; moderately soluble in methanol; and insoluble in benzene, toluene, and carbon tetrachloride. The metal chloride complexes, especially $[Co(OMPA)_3][CoCl_4]$, are more soluble than the metal perchlorate complexes. The complexes are also soluble in water, but the color changes to that of the hydrated metal perchlorate or chloride immediately. None of the complexes is hygroscopic.

(2) **$[Fe(OMPA)_3][FeCl_4]_3$.**—Anhydrous $FeCl_3$ (0.003 mole) was dissolved in 30 ml. of absolute ethanol. An excess of OMPA (0.012 mole) was added, and the complex began to precipitate immediately. After 30 min., the mixture was filtered and washed with ether.

(3) **$[Cu(OMPA)_2][CuCl_4]$.**—Anhydrous $CuCl_2$ (0.005 mole) was dissolved in 4.5 ml. of absolute ethanol. After OMPA was added, the color of the solution changed from yellowish green to reddish brown. When an excess of ether was added, a red oil was formed. After 24 hr., the red oil solidified. The mixture was filtered and washed with ether.

Conductance Measurements.—A conductivity bridge manufactured by Industrial Instruments, Inc., was used to measure conductivities of the complexes in nitrobenzene and nitromethane. A cell with a constant of 0.100 was used. All measurements were made at 25°. Conductivity data are summarized in Table II.

Spectral Measurements.—Infrared spectra were obtained as Nujol mulls with a Perkin-Elmer Infracord, Model 137. Electronic solution spectra were measured with a Cary Model 14M recording spectrophotometer. Spectrograde nitromethane was used as the solvent. Solid reflectance spectra were obtained with the reflectance attachment on a Bausch and Lomb Spectronic 505. Magnesium carbonate blocks were used as the standard. Spectral data are summarized in Table III.

Calculation of Dq and β.—The procedure reported by Meek, Drago, and Piper[11] was used to calculate Dq and β. The Dq value of OMPA toward Ni(II) is 726 cm.$^{-1}$ ($10Dq = 7257$ cm.$^{-1}$). The calculated P–F term splitting is 14,070 cm.$^{-1}$. The calculated value for β, which is defined as the percentage lowering of the P–F term splitting in the complex compared to the value of the gaseous ion with no crystalline field, is 11.17%. The calculated frequency of the second band is 12,265 cm.$^{-1}$, which is in good agreement with the experimental value of 12,269 cm.$^{-1}$.

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TABLE I

ANALYTICAL DATA[a] FOR OMPA COMPLEXES

Compound	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found	Color	M.p.,[b] °C.	Yield %
$[Ni(OMPA)_3](ClO_4)_2$	25.82	25.98	6.50	6.36	15.06	14.92	Yellow	...	95
$[Co(OMPA)_3](ClO_4)_2$	25.82	26.06	6.50	6.09	15.06	15.12	Lavender	...	87
$[Zn(OMPA)_3](ClO_4)_2$	25.50	25.70	6.47	6.22	14.98	15.15	White	...	98
$[Co(OMPA)_3][CoCl_4]$	25.82	25.30	6.49	6.45	15.05	14.47	Blue	154	51
$[Fe(OMPA)_3][FeCl_4]_3$	19.12	19.65	4.81	4.91	11.51	11.43	Yellow	234	65
$[Cu(OMPA)_2][CuCl_4]$	22.85	22.55	5.76	5.91	13.33	12.97	Brown	80	20

[a] Carbon, hydrogen, and nitrogen analyses were performed by Weiler and Strauss Microanalytical Laboratory, Oxford, England.
[b] Uncorrected melting points.

TABLE II

ELECTROLYTIC CONDUCTIVITY DATA FOR OMPA COMPLEXES

Compound	Concn. × 10^3, M	Λ_{molar} (25°) in nitrobenzene	Λ_{molar} (25°) in nitromethane
$[Ni(OMPA)_3](ClO_4)_2$	3.08		181
$[Co(OMPA)_3](ClO_4)_2$	2.42		183
$[Zn(OMPA)_3](ClO_4)_2$	2.04		184
$[Co(OMPA)_3][CoCl_4]$	1.12		105
$[Fe(OMPA)_3][FeCl_4]_3$	0.76		261
$[Ni(OMPA)_3(ClO_4)_2$	1.66	61.1	
$[Co(OMPA)_3](ClO_4)_2$	8.97	51.3	
	3.84	55.4	
	1.79	61.3	
	0.71	69.0	
$[Zn(OMPA)_3](ClO_4)_2$	1.32	61.0	
$[Co(OMPA)_3][CoCl_4]$	1.37	12.7	
$[Fe(OMPA)_3][FeCl_4]_3$	5.43	43.1	
	2.94	51.1	
	1.47	55.5	
	0.79	57.4	
	0.22	59.9	
$[Cu(OMPA)_2[CuCl_4]$	2.10	22.1	

TABLE III

SPECTRAL DATA FOR OMPA COMPLEXES

Compound	ν_{P-O}, cm.$^{-1}$	λ_{max}, mμ (cm.$^{-1}$)	ϵ	Solid reflectance λ_{max}, mμ
OMPA, smear	1234			
$[Ni(OMPA)_3](ClO_4)_2$	1195	424 (23,584)	20	424
		815 (12,269)	7	
		1378 (7257)	5	
$[Co(OMPA)_3](ClO_4)_2$	1200	546 (18,315)	20	545
$[Zn(OMPA)_3](ClO_4)_2$	1203			
$[Co(OMPA)_3][CoCl_4]$	1195	492 (20,330)[a]	~20	444
		520 (19,250)[a]	~50	527
		534 (18,700)[a]	~60	
		593 (16,863)	499	>590[b]
		678 (14,749)	701	
$[Fe(OMPA)_3][FeCl_4]_3$	1183	<400[c]	>10,000	<435[b]
$[Cu(OMPA)_2][CuCl_4]$	1184	~380[c]	>1,200	<400[b]

[a] Shoulder. [b] Off chart. [c] Near solvent cut-off.

This is support for the assignment of an octahedral configuration to the Ni(II) complex in solution.

Magnetic Susceptibility Measurements.—Magnetic susceptibilities were measured with a Gouy magnetic balance. The Gouy tubes were calibrated with $Hg[Co(NCS)_4]$. The moments were measured at 28°. The values for Pascal's constants were taken from Figgis and Lewis.[12] The magnetic data are summarized in Table IV.

Attempted Molecular Weight Measurements.—An attempt was made to measure molecular weights of $[Co(OMPA)_3](ClO_4)_2$ and $[Fe(OMPA)_3][FeCl_4]_3$ in nitrobenzene with a Beckman molecular-weight apparatus. Using $M = 1000K_f g/G\Delta T_f$ where $K_f = 8.1$ for nitrobenzene, g = grams of solute, G = grams of solvent, and ΔT_f temperature change, the values in Table V were obtained. The concentration dependence of these values and the molar conductivity values is evidence for dissociation of the complexes in nitrobenzene.

Discussion

Octamethylpyrophosphoramide can coordinate to metal ions as a monodentate ligand or as a bidentate ligand. If OMPA coordinates as a monodentate ligand, bridging between metal ions could take place.[13] If bridging occurs alone or in combination with chelation, a polymeric structure would result. A monomeric structure would form if OMPA coordinates as a bidentate ligand.

Although accurate molecular weights could not be obtained, the concentration dependence of the molecular weight values and the molar conductance values is evidence for dissociation of the complexes in nitrobenzene. The dissociation process could involve ligand dissociation from the metal ion as well as ionization of the salt.

Recent conductance studies[3] on a variety of complexes in nitrobenzene indicate that 1:1 electrolytes have molar conductance values from 25 to 35 and 2:1 electrolytes from 44 to 60. Data for 3:1 electrolytes are not extensive, but two reported conductance values[3] for Fe(III) complexes are 69.7 and 82.5. The

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(12) B. N. Figgis and J. Lewis, "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, New York, N. Y., 1960, p. 403.

(13) We are grateful to the referees for this suggestion.

TABLE IV

MAGNETIC DATA FOR SOME OMPA COMPLEXES

Compound	$\chi_M \times 10^6$	Diamag. cor. $\times 10^6$	$\chi_M' \times 10^6$	μ_{eff}, B.M. (28°)
$[Ni(OMPA)_3](ClO_4)_2$	3,685	695	4,380	3.26
$[Co(OMPA)_3](ClO_4)_2$	10,620	695	11,315	5.24
$[Co(OMPA)_3][CoCl_4]$	21,854	725	22,579	7.41
$[Fe(OMPA)_3][FeCl_4]_3$	66,892	911	67,803	12.83
$[Cu(OMPA)_3][CuCl_4]$	2,925	518	3,443	2.89

TABLE V

$[Fe(OMPA)_3][FeCl_4]_3$	$[Co(OMPA)_3](ClO_4)_2$
M = 560 for 0.1108 g./25 ml.	M = 636 for 0.2285 g./25 ml.
M = 352 for 0.0552 g./25 ml.	M = 540 for 0.1406 g./25 ml.
M = 230 for 0.0298 g./25 ml.	M = 525 for 0.055 g./25 ml.

conductance values for OMPA complexes in nitrobenzene (Table II) are support for the presence of 1:1 electrolytes for $[Co(OMPA)_3][CoCl_4]$ and $[Cu(OMPA)_2[CuCl_4]$; 2:1 electrolytes for $[Ni(OMPA)_3](ClO_4)_2$, $[Co(OMPA)_3](ClO_4)_2$, and $[Zn(OMPA)_3](ClO_4)_2$; and a 3:1 electrolyte for $[Fe(OMPA)_3][FeCl_4]_3$. The molar conductance values in nitromethane are in good agreement with the expected values for the electrolytes listed above.

The Dq value for OMPA (726) is similar to the Dq value for the chloride ion (720)[14] and much lower than the Dq values for other bidentate ligands.

The following portion of the spectrochemical series indicates the position of OMPA with respect to other ligands: $H_2NCH_2CH_2NH_2$, 1150[14]; $(C_4H_9)_2P(O)CH_2P(O)(C_4H_9)_2$, 864[3]; H_2O, 850[14]; $(CH_3)_2N[(CH_3)_2N]OPOPO[N(CH_3)_2]N(CH_3)_2$, 726.

The β value for OMPA (11.2%) is similar to that given for water (11.0%)[14] and much less than the value for chloride ion (28.0%).[14] The Dq value for OMPA is over 100 less than the Dq value for water, and the β value indicates about the same amount of covalent contribution to the bonding as in the case of water. This places octamethylpyrophosphoramide at the lower end of both the spectrochemical series and the nephelauxetic series of ligands.

The decrease in the P=O stretching frequency (Table III) is evidence for coordination of the phosphoryl oxygens to the metal ion. The solid reflectance spectra for OMPA complexes of Ni(II) and Co(II) perchlorate have the same peak maxima as the solution spectra. The similarity between the solid reflectance spectra and the solution spectra indicates that no change in species occurs when the solid complexes are dissolved in nitromethane. The solid reflectance spectra for OMPA complexes of the metal chloride salts are difficult to interpret because of the presence of the strongly absorbing tetrachlorometalate anions.

The low molar absorptivity values for $[Co(OMPA)_3](ClO_4)_2$ and $[Ni(OMPA)_3](ClO_4)_2$ support the presence of an octahedral configuration around Co(II) and Ni(II). The peak maxima and molar absorptivities for the OMPA complexes of $CoCl_2$, $FeCl_3$, and $CuCl_2$ are evidence for the presence of tetrahedral $[CoCl_4]^{-2}$, $[FeCl_4]^-$, and $[CuCl_4]^{-2}$.

The magnetic moments for $[Co(OMPA)_3](ClO_4)_2$ and $[Ni(OMPA)_3](ClO_4)_2$ fall in the range expected for spin-free octahedral complexes.[12] The magnetic moments for the metal chloride complexes are difficult to interpret because of the presence of both octahedral and tetrahedral coordination. The number of unpaired electrons calculated from the spin-only formula and the experimental moment are six for $[Co(OMPA)_3[CoCl_4]$ and two for $[Cu(OMPA)_2][CuCl_4]$.

Although OMPA appears to be a weak ligand, it completely replaces the chloride ion from the coordination sphere of the metal cation. As a result, a tetrachlorometalate anion is formed. The Dq parameter indicates that the chloride ion has about the same coordinating power as OMPA. Therefore, the formation of bridged complexes of $FeCl_3$, $CuCl_2$, and $CoCl_2$ in which all of the chloride ions are replaced by a *bridging* OMPA is highly unlikely. The observation that all chloride ions are replaced by OMPA can be explained by considering the stability gained through chelation. Octamethylpyrophosphoramide can form six-membered rings with the metal ion. The added stability because of chelation enables OMPA to act as a bidentate ligand in forming monomeric coordination compounds.

Acknowledgment.—The authors wish to acknowledge the support of the Cooperative Research Fund of Southern Illinois University and to thank Dr. R. S. Drago for the use of his Gouy balance and Bausch and Lomb Spectronic 505.

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(14) C. E. Schaffer and C. K. Jørgensen, *J. Inorg. Nucl. Chem.*, **8**, 143 (1958).