valent cation and a neutral water molecule in dilute solutions.[10] Solubility limitations precluded the extension of the study to higher ionic strengths in the case of added nitrate ion. It is clear that sulfate ion in concentrations 8-fold or greater than the initial complex concentration tends to accelerate the aquation reaction. This observation can be explained by assuming that the *cis*-dibromobis(ethylenediamine)cobalt(III) cation forms ion pairs with the sulfate anion which promotes removal of the coordinated bromide ion by an S$_N$1 dissociation type mechanism. Light was routinely excluded in this study since the aquation rates of some cobalt complexes are accelerated by light.[11] However, the control experiment does not indicate that the reaction is affected by light from an incandescent lamp.

Tobe, *et al.*,[4,12] have investigated the steric course of a large number of octahedral aquation reactions of the type $[Co(en)_2AX]^{+n}$ where X represents the ligand being replaced and A is the orienting ligand. In every case it was found that the aquation of the *cis* complexes appears to be stereospecific and only the *cis* isomer of the product is obtained. On the other hand, *trans* complexes are aquated with steric change if the orienting ligand can exhibit an electropositive conjugative effect, *i.e.*, transfer electrons to the metal in the transition state. Since these conditions prevail in most reactions which have been studied, steric change is usually observed in the aquation of *trans* complexes of Co(III). Quinn and Garner[13] have reported similar results for *cis* isomers of Cr(III) complexes, but the relatively small number of *trans* isomers, which have been examined thus far, were found to give predominantly or wholly *trans* product. The configuration of the aquation product in the present study was not determined but no evidence was obtained to indicate that the stereospecific rule for *cis* complexes is violated here. Chan and Tobe[4] also observed a 5- to 6-fold increase in the aquation rate when X is changed from Cl to Br. However, these authors noted that the *trans*-dibromo complex aquates about 4 times faster than the *trans*-dichloro complex at 25°. This latter observation is consistent with the results obtained in the present study. Moreover, these results are in accord with the observation[2] that in comparison with the *trans* isomers, the rates of aquation of the *cis* isomers of Co(III) complexes are often about an order of magnitude greater.

The aquation rate of *cis*-$[Cr(en)_2Br_2]^+$ at 25° is about three times greater than the aquation rate of the Co(III) analog studied here. Crystal field theory predicts a lower activation energy for the Cr(III) d^3 system compared to the Co(III) d^6 system when solvent effects are ignored.[14] However, Arrhenius activation parameters are not available for the Cr(III) complex and one is not justified in drawing further conclusions concerning the relative rates of these two complexes.

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The Donor Properties of Pyrophosphate Derivatives. II. Complexes of Octamethylpyrophosphoramide with Nontransition Metals[1]

By CARL J. POPP[2] and MELVIN D. JOESTEN[3]

New complexes of octamethylpyrophosphoramide (OMPA) with alkali metal salts, alkaline earth salts, Al(ClO$_4$)$_3$, Pb(ClO$_4$)$_2$, Cd(ClO$_4$)$_2$, and SbCl$_5$ have been prepared. The following compounds have been synthesized: LiClO$_4$·2OMPA, LiNO$_3$·OMPA·3H$_2$O, LiCl·OMPA·2H$_2$O, NaClO$_4$·OMPA, Mg(ClO$_4$)$_2$·3OMPA, Mg(NO$_3$)$_2$·2OMPA·2H$_2$O, MgCl$_2$·2OMPA·2H$_2$O, Ca(ClO$_4$)$_2$·3OMPA, Ca(NO$_3$)$_2$·2OMPA, CaCl$_2$·OMPA·4H$_2$O, Ba(ClO$_4$)$_2$·2OMPA, Al(ClO$_4$)$_3$·3OMPA, Cd(ClO$_4$)$_2$·3OMPA, Pb(ClO$_4$)$_2$·3OMPA, and 2SbCl$_5$·OMPA. Elemental analyses, infrared spectra, conductivity measurements, and X-ray powder patterns were used to characterize the complexes.

Introduction

The first paper of this series[4] reported the formation of coordination compounds of several transition metal ions with the ligand octamethylpyrophosphoramide (OMPA). The structure of OMPA is

$$(CH_3)_2N-\overset{\overset{O}{\|}}{P}-O-\overset{\overset{O}{\|}}{P}-N(CH_3)_2$$
$$\underset{(CH_3)_2N}{|}\underset{N(CH_3)_2}{|}$$
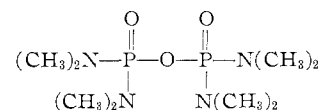
The present work is concerned with OMPA complexes of nontransition elements, especially the alkali and

TABLE I

ANALYTICAL DATA FOR OMPA COMPLEXES

Compound	% carbon Calcd.	Found	% hydrogen Calcd.	Found	% nitrogen Calcd.	Found	% magnesium or calcium Calcd.	Found	M.p.,[a] °C.	% yield
NaClO$_4$·OMPA	23.53	23.50	5.92	6.00	13.71	13.75			121–128	95
LiClO$_4$·2OMPA	28.34	28.14	7.14	6.91	16.53	16.22			141–146	75
Mg(ClO$_4$)$_2$·3OMPA	26.66	26.48	6.71	6.90	15.55	15.45			261–263	97
Ba(ClO$_4$)$_2$·2OMPA	21.16	21.43	5.33	5.44	12.34	12.19			228–241	81
Ca(ClO$_4$)$_2$·3OMPA	26.30	26.64	6.61	6.55	15.31	14.81	3.65	3.31	253–257[b]	96
Al(ClO$_4$)$_3$·3OMPA	24.37	24.43	6.13	6.55	14.21	14.51			249[b,c]	75
Cd(ClO$_4$)$_2$·3OMPA	24.67	24.48	6.21	6.01	14.37	14.21			279[b]	92
Pb(ClO$_4$)$_2$·3OMPA	22.64	22.01	5.74	5.65	13.28	12.99			213–216[b]	80
LiNO$_3$·OMPA·3H$_2$O	23.49	23.90	7.39	7.03	17.11	17.29			105–109	62
Mg(NO$_3$)$_2$·2OMPA·2H$_2$O	25.43	25.33	6.94	7.46	18.59	18.81	3.21	3.44	150–153	72
Ca(NO$_3$)$_2$·2OMPA	26.13	26.03	6.56	6.55	19.05	18.65	5.45	5.38	132–138	55
LiCl·OMPA·2H$_2$O[d]	26.35	27.39	7.74	8.08	15.36	14.51			158–160	65
MgCl$_2$·2OMPA·2H$_2$O[e]	27.38	27.21	7.47	7.73	15.96	16.25	3.46	3.48	135–139	72
CaCl$_2$·OMPA·4H$_2$O[f]	20.47	20.39	6.88	7.16	11.73	11.31	8.54	6.89	58–61	79
2SbCl$_5$·OMPA	10.88	10.71	2.74	3.23	6.34	5.83			161–164[b]	76

[a] Uncorrected melting points.   [b] Decomposed.   [c] Violent decomposition.   [d] Calcd.: Cl, 9.73. Found: Cl, 9.97.   [e] Calcd.: Cl, 10.10. Found: Cl, 10.96.   [f] Calcd.: Cl, 15.12. Found: Cl, 14.50.

alkaline earth elements. Few stable complexes of alkali metals have been isolated. Sidgewick and Brewer prepared complexes of the alkali metals with β-diketone derivatives, o-nitrophenol, and salicylaldehyde.[5,6] The sodium and lithium compounds ranged from hydrated ionic salts such as Na(acac)·2H$_2$O to adducts such as Na(sal)·Hsal (Hsal = salicylaldehyde). A complex of sodium perchlorate with 1,10-phenanthroline has been isolated.[7,8] Recently, a complex of N,N-dimethylacetamide with lithium perchlorate has been prepared which has the composition LiClO$_4$·DMA·2H$_2$O.[9] Brady and Badger[10] have presented evidence for chelation in sodium salts of o-hydroxybenzaldehydes.

None of the previously isolated complexes of alkali metals makes use of a pyrophosphate derivative as the ligand. However, Lambert and Watters[11] have reported formation constants for the association of alkali metal ions with the pyrophosphate anion in aqueous solution. Log K for Li(P$_2$O$_7$)$^{3-}$ is 2.39 and for Na-(P$_2$O$_7$)$^{3-}$ it is 1.0. Formation constants have also been reported for the interaction of the pyrophosphate anion with alkaline earth metal ions.[12] Since OMPA is structurally similar to the pyrophosphate anion, we decided to extend our studies of OMPA by studying reactions of OMPA with nontransition metal ions.

Experimental

Reagents.—We are grateful to Pennsalt Chemicals for supplying us with 91% OMPA. This solution was distilled under vacuum as reported previously.[4] Metal perchlorates were obtained from G. Frederick Smith Chemical Co.

Preparation of Complexes.—All of the OMPA complexes with metal perchlorates with the exception of that of Mg(II) were prepared by the same method. The hydrated metal perchlorates

were dehydrated with excess 2,2-dimethoxypropane by stirring for a minimum of 1 hr.[13] An excess of OMPA was added and stirring was continued for 10–20 min. Excess anhydrous ether was added, and precipitates formed immediately for Al(III), Ca(II), Ba(II), Cd(II), and Pb(II). The mixtures were filtered, washed with ether, and dried *in vacuo*. The sodium and lithium perchlorate complexes with OMPA came down as oils which could be worked up by successively evaporating the solvent and treating with ether. They were recrystallized from methanol with great difficulty. All of the metal perchlorate complexes with OMPA are stable in air.

The magnesium(II) perchlorate complex with OMPA was prepared by dissolving anhydrous magnesium perchlorate in methanol and stirring with an excess of OMPA. The complex precipitated from solution upon standing. The OMPA complexes of calcium chloride and lithium chloride were prepared by dissolving the anhydrous chlorides in a minimum amount of methanol, adding an excess of OMPA, and stirring for 1 hr. Anhydrous ether was added and the resulting oils were worked up. Several days were required for crystallization to occur. The method used for hydrated metal perchlorates was also used for hydrated magnesium chloride. The resulting oil was worked up to give a white solid. As is indicated in Table I, completely anhydrous complexes of OMPA with the metal chloride salts could not be isolated.

Hydrated lithium, magnesium, and calcium nitrates were dissolved in a minimum amount of methanol and stirred with an excess of OMPA for 10–20 min. Ether was added and the resulting oils were worked up with ether to form white crystals.

Elemental analyses for all complexes prepared in this study are given in Table I.

Conductance Measurements.—A conductance bridge manufactured by Industrial Instruments, Inc., was used to measure molar conductivities of the complexes in nitromethane. A cell with a constant of 0.100 was used. Conductivity data are summarized in Table II.

Infrared Spectra.—Infrared spectra of Nujol mulls were obtained with a Beckman IR5-A spectrophotometer. The infrared spectral data are summarized in Table II.

X-Ray Measurements.—Recorded spectra of the X-ray powder patterns were obtained by using an HF recorder attachment with a General Electric XRD-5 X-ray diffraction unit. A Cu Kα source with a Ni filter was used. Samples were run as fine powders.

Analyses.—Carbon, hydrogen, and nitrogen analyses were performed by Weiler and Strauss Microanalytical Laboratory, Oxford, England, and the chloride, magnesium, and calcium

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TABLE II
INFRARED SPECTRAL AND CONDUCTANCE DATA FOR OMPA COMPLEXES

| Compound | Infrared[a] | | | | | | Conductance[b] | |
	$\nu P{=}O$, cm.$^{-1}$	$\Delta\nu P{=}O$, cm.$^{-1}$	$\nu P{-}O{-}P$, cm.$^{-1}$	$\Delta\nu P{-}O{-}P$, cm.$^{-1}$	$\nu P{-}N$, cm.$^{-1}$	$\Delta\nu P{-}N$, cm.$^{-1}$	Concn., $M \times 10^3$	Λ_{molar}, cm.^{2} ohm^{-1} mole^{-1}
OMPA	1238	. . .	914	. . .	988	. . .		
Al(ClO₄)₃·3OMPA	1180	−58	937	+23	1018	+30	1.42	273
Pb(ClO₄)₂·3OMPA	1178	−60	932	+18	1003	+15	0.951	206
Cd(ClO₄)₂·3OMPA	1209	−29	938	+24	1006	+18	1.33	209
Mg(ClO₄)₂·3OMPA	1218	−20	920	+6	1002	+14	0.740	201
Ca(ClO₄)₂·3OMPA	1219	−19	930	+16	1003	+15	1.36	206
Ba(ClO₄)₂·2OMPA	1223	−15	926	+12	1004	+16	2.11	154
NaClO₄·OMPA	1225	−13	928	+14	1001	+13	2.87	80.9
LiClO₄·2OMPA	1218	−20	902	−12	991	+3	1.49	85.9
Ca(NO₃)₂·2OMPA	1231	−7	928	+14	1003	+15	1.28	74.4
Mg(NO₃)₂·2OMPA·2H₂O	1213	−25	930	+16	1005	+17	1.63	80.9
LiNO₃·OMPA·3H₂O	1210	−28	924	+10	1000	+12	2.42	27.4
MgCl₂·2OMPA·2H₂O	1210	−28	923	+9	1004	+16	3.03	80.5
CaCl₂·OMPA·4H₂O	1215	−23	933	+19	1000	+12	1.19	50.6
LiCl·OMPA·2H₂O	1230	−8	912	−2	1003	+15	3.22	21.0
2SbCl₅·OMPA	1173	−65	948	+36	1012	+24	0.235	28.3

[a] − indicates shift toward lower frequencies; + indicates shift toward higher frequencies. [b] Measurements made at 25° with nitromethane as solvent.

analyses were done in our laboratory. Chloride was determined by the Volhard method and calcium and magnesium by titration with EDTA.

Discussion

All of the complexes reported in Table I are new. Spectral and conductance data are given in Table II. Literature values for molar conductance in nitromethane and N,N-dimethylacetamide are in the range of 15–20 or less for nonelectrolytes, 80–90 for 1:1 electrolytes, 130–180 for 2:1 electrolytes, and 200–250 for 3:1 electrolytes.[9,14,15] The complexes of OMPA with monovalent or trivalent metal perchlorates have molar conductance values within the expected ranges. However, the molar conductance values for OMPA complexes with bivalent metal perchlorates are slightly higher than expected.

The low conductivity values for the complexes of OMPA with nitrate and chloride metal salts are an indication of greater association in solution. The conductance of Ca(NO₃)₂·2OMPA is considerably less than that of Ca(ClO₄)₂·3OMPA. A major part of this difference might be attributed to the following equilibrium in nitromethane.

$$[\text{Ca(OMPA)}_2(\text{NO}_3)_2] \rightleftharpoons [\text{Ca(OMPA)}_2]^{2+} + 2\text{NO}_3^{-}$$
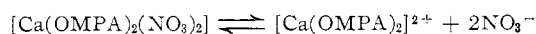
The nitrate and chloride anions are stronger ligands than the perchlorate anion. In preparing complexes in which nitrate and chloride are present, fewer OMPA ligands can be added to the coordination sphere of the metal ion. The conductance data for all of the OMPA complexes of metal nitrates and chlorides are in agreement with the existence of coordinated nitrate and chloride in nitromethane.

The molar conductance values for LiClO₄·2OMPA and LiCl·OMPA·2H₂O are also of interest. If we assume that the coordination number of Li(I) is four, both

should be electrolytes if the perchlorate and chloride ions are not coordinating with the metal ion. The conductance values indicate that LiClO₄·2OMPA is an electrolyte and LiCl·OMPA·2H₂O is a nonelectrolyte. It is possible that OMPA is acting as a chelating ligand in the former and as a bridging ligand in the latter. The bridged structure would give a more highly associated structure, which would account for the low conductance of LiCl·OMPA·2H₂O. However, the infrared evidence is indicative of a nonchelate structure for both complexes.

Evidence for coordination through the phosphoryl donor site and for the chelate structure can be found by examining the infrared spectra. The infrared spectra of pyrophosphates have been studied by several workers. Bergman, et al.,[16] have attributed the characteristic frequency at 900–950 cm.$^{-1}$ to the P–O–P antisymmetrical stretch. Bellamy and Beecher[17] have assigned the frequency at 1210–1250 cm.$^{-1}$ to the P=O stretch. Since coordination is believed to take place through the P=O groups, these frequencies should be affected. The P–N stretch has been assigned[18] to the range 989–1006 cm.$^{-1}$ and will also be examined. These frequencies in OMPA and the corresponding peaks and shifts in the complexes are summarized in Table II.

The shift of the P=O stretch in all cases is in the direction of lower frequency and longer wave length. This is indicative of bond weakening and decrease in double bond character of P=O with electron density being drawn away by interaction with the metal ion.[19] The relative strength of the interaction is indicated by the magnitude of the shift.[20,21] This in itself is evidence for the use of phosphoryl donor sites, but to

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establish the chelate structure the P—O—P stretch must be examined. The frequency shift of the P—O—P stretch in all cases except two is in the direction of higher frequency, which indicates a stronger bond or higher bond order. This may be explained by considering the structures

$$X = N(CH_3)_2$$
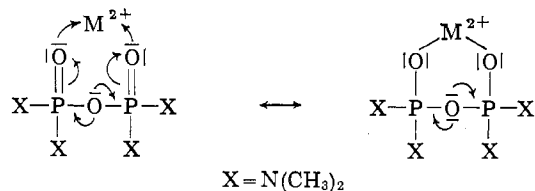
After forming the proposed chelate structure, the polarization effects of the metal ion will tend to decrease the double bond character of P=O and at the same time draw the electron pairs from the P—O—P oxygen into p_π-d_π overlap with phosphorus. The overall effect is to decrease the P=O stretching frequency and increase the P—O—P stretching frequency. The decrease in P=O stretching frequency is observed in all complexes prepared in this study, and all but two show an increase in the P—O—P stretching frequency.

Further evidence for coordination through the phosphoryl oxygen is found by looking at the P—N stretching frequency, which shifts to higher frequencies in all cases. The decrease in the P=O bond order that occurs when the metal ion coordinates to the phosphoryl oxygen can cause the lone pair on nitrogen to delocalize into the available d_π orbitals on the phosphorus. This would increase the P—N bond order.

The presence of coordinated water in $Mg(NO_3)_2 \cdot 2OMPA \cdot 2H_2O$, $MgCl_2 \cdot 2OMPA \cdot 2H_2O$, $LiCl \cdot OMPA \cdot 2H_2O$, $LiNO_3 \cdot OMPA \cdot 3H_2O$, and $CaCl_2 \cdot OMPA \cdot 4H_2O$ was established by an absorption peak in the infrared spectrum of each of these compounds in the 3300–3400 cm.$^{-1}$ region.[22] This peak is absent in all of the other complexes.

The positions and relative intensities of d_{hkl} for the

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3:1 complexes are given in Table III. The d_{hkl} values for $Ni(ClO_4)_2 \cdot 3OMPA$ are included for comparison. The X-ray data indicate that the 3:1 complexes are isomorphous. Earlier work with spectra of $Ni(ClO_4)_2 \cdot 3OMPA$ dissolved in nitromethane supported the assignment of an octahedral configuration to this complex in solution.[4] The similarity of the X-ray data for the 3:1 complexes in this study supports the assignment of an octahedral configuration to the metal ions in these complexes.

TABLE III

X-RAY POWDER PATTERN DATA[a]

$Mg(ClO_4)_2 \cdot 3OMPA$		$Ca(ClO_4)_2 \cdot 3OMPA$		$Pb(ClO_4)_2 \cdot 3OMPA$	
d_{hkl}	I/I_{100}	d_{hkl}	I/I_{100}	d_{hkl}	I/I_{100}
11.78	57	11.62	32	11.78	100
9.82	29	9.30	24	9.82	57
7.37	64	7.19	75	7.62	51
6.23	81	6.23	100	5.98	78
5.75	88	5.94	71	5.64	86
4.87	64	4.92	61	4.67	38
4.23	100	4.23	83	4.29	43
3.93	52	3.93	66	3.81	48
3.85	52	3.60	17	3.55	20
3.53	18	3.58	17	3.31	21
3.13	33	3.16	27	2.89	17
2.95	15	2.88	17		
2.79	15				

$Al(ClO_4)_3 \cdot 3OMPA$		$Cd(ClO_4)_2 \cdot 3OMPA$		$Ni(ClO_4)_2 \cdot 3OMPA$	
d_{hkl}	I/I_{100}	d_{hkl}	I/I_{100}	d_{hkl}	I/I_{100}
10.27	78	11.62	65	10.77	77
9.50	62	9.30	32	9.02	25
6.32	100	8.93	33	7.13	99
5.43	79	7.19	100	6.02	63
4.44	57	6.41	70	5.37	100
4.19	47	4.92	47	4.77	46
3.98	60	4.23	64	4.09	77
3.49	19	3.90	82	3.81	60
2.98	10	3.62	14	3.08	31
2.79	11	3.15	29	2.88	19

[a] d_{hkl} is reported in Å.; I_{100} is the most intense line.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF
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The Synthesis of Tetraphosphorus Triselenide: Preliminary Infrared, Nuclear Magnetic Resonance, and Raman Studies

BY KURT IRGOLIC, RALPH A. ZINGARO, AND MOHAN KUDCHADKER

A highly simplified method for the preparation of the soluble modification of P_4Se_3 is described. Very simple apparatus is used and the material is obtained in good yield and a high degree of purity. Some preliminary studies of the infrared, Raman, ^{31}P n.m.r., visible, and ultraviolet spectra of this molecule are reported.

Tetraphosphorus triselenide has been prepared in two ways. Meyer[1] fused a stoichiometric mixture of

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red or yellow phosphorus with selenium and isolated P_4Se_3 as a red solid by distillation at 360–400°. He reported it to be only slightly soluble in carbon disul-