it must be slow in relation to the dissociative process. The second point which needs to be made about the equality of rate constants in these two processes is that the toluene solutions correspond to case B, in which the solvent-caged monomers proceed preferentially to the solvent-separated species, as opposed to recombination. The reason for this behavior in toluene lies in the strongly Lewis acid character of the monomeric species, coupled with the donor character of the aromatic system.[17]

The cyclopentane data correspond to case A, in which the solvent-caged monomers preferentially recombine as opposed to forming solvent-separated species. The rate constant for bridge–terminal exchange is about ten times larger than the effective rate constant for trimethylaluminum–trimethylgallium exchange. This implies that the ratio k_2/k_{-1} is about 10, which is in very reasonable accord with information available from studies of free-radical systems for the relative propensities of recombination *vs.* solvent separation in a relatively inert solvent.

The apparent Arrhenius activation energies obtained in this work fully support the proposed mechanism. It is to be expected that in both toluene and cyclopentane the activation energy for exchange is that associated with formation of the solvent-caged monomers. The identity of the rate-determining process for bridge–terminal exchange with that for trimethylaluminum exchange with trimethylgallium or trimethylindium is thus reflected in the essentially identical values obtained for the activation energies.

The assumption that the rate-determining process for bridge–terminal exchange is dissociation of the dimer into solvent-caged monomers raises the question of how well the activation energy for dissociation, on the order of 15–16 kcal/mole, compares with the heat of dissociation of $Al_2(CH_3)_6$ in the gas phase, about 20 kcal/mole. It is difficult to assess the absolute error in either of these estimates, but the comparison does not seem unreasonable. It is unlikely that the activation energy for dissociation is much greater than the enthalpy of dissociation, and some decrease in the latter may be expected in a condensed phase as opposed to the gas phase. Nevertheless it would be of interest to have further data regarding the thermodynamics of dissociation of trialkylaluminum systems, in both the gas and condensed phases.

The present results are important for a correct understanding of certain other exchange data in the literature. Intermolecular exchange between trimethylaluminum and dimethylcadmium has been observed[18] and was interpreted in terms of a bimolecular rate-determining process. The present results make it extremely unlikely, however, that the exchange is a simple second-order process. Brunner, Wailes, and Kaesz[19] have observed that the adduct $(C_5H_5)_2WH_2Al(CH_3)_3$ undergoes rapid exchange with $Al_2(CH_3)_6$. From the reported temperature dependence it appears that the exchange may involve dissociation of the dimer as the rate-determining step.

The solvent cage effect should be operative in a variety of organometallic exchange systems in which a rate-determining dissociation is operative. The much slower exchange between *t*-butyllithium and lithiomethyltrimethylsilane in cyclopentane as compared with toluene[20] no doubt results from a cage effect.

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The Donor Properties of Pyrophosphate Derivatives. III. A Colorless Copper(II) Complex

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Abstract: Complexes of octamethylpyrophosphoramide (OMPA) with Cu(II), Co(II), Fe(III), Ag(I), and Hg(II) have been prepared and characterized. These include $[Cu(OMPA)_3](ClO_4)_2$, $[Cu(OMPA)_2][CuBr_4]$, $[Ag(OMPA)_2]ClO_4$, $[Hg(OMPA)_3](ClO_4)_2$, $[Co(OMPA)_3][CoBr_4]$, and $[Fe(OMPA)_3](ClO_4)_3$. The most unique compound of these is $[Cu(OMPA)_3](ClO_4)_2$, believed to be the first cationic, six-coordinate complex of Cu(II), which is colorless.

We have previously reported the isolation of complexes of octamethylpyrophosphoramide (OMPA) with a wide variety of metal ions.[2,3] Octamethylpyrophosphoramide is believed to form a six-membered ring with the metal ion[4] in which the phosphoryl oxygens are the donor sites. We have attributed the stability of metal complexes of OMPA

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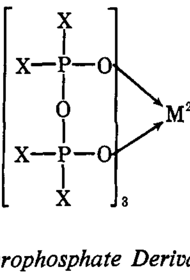
(4) In the form



where X = $N(CH_3)_2$.

Table I. Elemental Analyses and Conductivity Data

Compound	Carbon, % Calcd	Carbon, % Found	Hydrogen, % Calcd	Hydrogen, % Found	Nitrogen, % Calcd	Nitrogen, % Found	Λ_M,[a] cm^2 ohm^{-1} mole^{-1}
$[Cu(OMPA)_3](ClO_4)_2$[b]	25.8	26.0	6.45	6.32	15.0	15.4	168
$[Cu(OMPA)_2][CuBr_4]$[c]	18.8	18.6	4.71	4.70	11.0	10.2	92
$[Ag(OMPA)_2]ClO_4$	24.6	24.4	6.16	5.92	14.4	14.2	94
$[Hg(OMPA)_3](ClO_4)_2$	22.9	22.6	5.73	5.79	13.4	12.9	182
$[Co(OMPA)_3][CoBr_4]$	22.2	21.2	5.55	5.50	13.0	13.5	121
$Fe(OMPA)_3](ClO_4)_3$	23.8	24.0	5.95	6.09	13.9	13.5	280

[a] Conductivity measurements of 10^{-3} *M* nitromethane solutions at 25°. [b] *Anal.* Calcd: Cu, 5.67. Found: Cu, 5.65. [c] *Anal.* Calcd: Cu, 12.5 Found: Cu, 13.0.

to a chelate effect since the ligand field parameters place OMPA at the lower end of both the spectrochemical and nephelauxetic series.[2]

We now wish to report the isolation and characterization of several additional complexes of OMPA with Cu(II), Co(II), Fe(III), Ag(I), and Hg(II). The most interesting complex of these ions is $[Cu(OMPA)_3](ClO_4)_2$ which is colorless.

Experimental Section

Reagents. Fisher reagent grade nitromethane was used for spectral and conductance measurements. Freshly distilled reagent grade acetonitrile was used as the solvent for ultraviolet spectral measurements. Hydrated metal perchlorates were obtained from G. F. Smith Chemical Co. We are grateful to Pennsalt Chemicals for supplying us with 91% OMPA. This solution was distilled under vacuum as reported previously.[2]

Preparation of Complexes. 1. $[Cu(OMPA)_3](ClO_4)_2$. OMPA (5 g, 0.016 mole) was added to 1.5 g of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.004 mole) in acetone. A white solid precipitated from the solution. Further precipitate was obtained by adding anhydrous ether to the solution. The product was recrystallized from acetone, mp 207–209°.

2. $[Cu(OMPA)_2][CuBr_4]$. Anhydrous $CuBr_2$ (1 g, 0.005 mole) and 2.0 g (0.007 mole) of OMPA were dissolved in 20 ml of acetonitrile. After reducing the total volume to 5 ml, anhydrous ether was added. After the volume was further reduced and cooled, black crystals formed on the walls of the flask, mp 111–113°.

3. $[Ag(OMPA)_2]ClO_4$. Hydrated silver perchlorate (2.5 g, 0.011 mole) was dissolved in 25 ml of acetone, and OMPA (10 g, 0.035 mole) was added. The volume was reduced to 10 ml by using a water aspirator. Ether was added and an oil separated from solution. After the ether was drawn off, crystals separated from solution. The product was contaminated with black particles, presumably free silver. The product was dissolved in 5 ml of acetone and a spatula tip of decolorizing charcoal was added. The solution was heated on a steam bath and filtered while hot. After cooling, ether was added to the filtrate. Further cooling of the filtrate caused crystals to form. The colorless crystals were dried in a vacuum oven at 40° for 3 hr, mp 78–80°.

4. $[Hg(OMPA)_3](ClO_4)_2$. Hydrated mercury(II) perchlorate (1.4 g, 0.002 mole) was dissolved in 20 ml of absolute ethanol, and OMPA (4 g, 0.014 mole) was added dropwise. The volume was then reduced to 5 ml. White crystals appeared after several minutes. The product was washed with ether and dried in a vacuum oven at 60° for 4 hr, mp 137° (violent decomposition).

5. $[Co(OMPA)_3][CoBr_4]$. $CoBr_2 \cdot 6H_2O$ (1 g, 0.003 mole) was dissolved in 20 ml of absolute ethanol, and OMPA, (2 g, 0.007 mole) was added. The volume was reduced to 5 ml. Anhydrous ether was added and the blue product precipitated from solution, mp 198–201°.

6. $[Fe(OMPA)_3](ClO_4)_3$. $Fe(ClO_4)_3 \cdot 6H_2O$ (1 g, 0.003 mole) was dissolved in 15 ml of 2,2-dimethoxypropane and stirred for 15 min. Acetone (10 ml) was added along with 3.0 g (0.010 mole) of OMPA. Ether was added to precipitate the product. The yellow product was filtered and then recrystallized from acetone, mp 214° (violet decomposition).

Spectral Measurements. Infrared spectra were obtained as Nujol mulls. Infrared spectra were recorded on a Beckman IR-5 spectrophotometer. Visible and near-infrared spectra of nitromethane solutions of the complexes were measured with a Beckman DK-1 spectrophotometer. The visible and near-infrared spectrum of $[Cu(OMPA)_2][CuBr_4]$ in the solid state was obtained by using a Nujol mull according to a technique reported by Lee, Griswold, and Kleinberg.[5]

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.

Magnetic Susceptibility Measurements. Magnetic susceptibilities were measured with a Gouy magnetic balance. Gouy tubes were calibrated with $Hg[Co(CNS)_4]$. Values for Pascal's constants were used in calculating the corrected magnetic susceptibility.[6] The measured diamagnetic susceptibility for OMPA was -168×10^{-6} cgs units compared to a value of -180×10^{-6} calculated from Pascal's constants.

Analyses. Carbon, hydrogen, and nitrogen analyses were performed by Alfred Bernhardt, Max Planck Institute, Mulheim, Germany. Copper was analyzed by electrodeposition in our laboratory.

Results and Discussion

The most unique property of the complexes listed in Table I is the lack of color of solid $[Cu(OMPA)_3](ClO_4)_2$. We were unable to obtain a Nujol mull spectrum of this complex in the visible and near-infrared region. A nitromethane solution of the complex is pale blue, but the spectrum of such a solution still has no peak in the visible region (Figure 1). However, a characteristic, broad asymmetric band does appear in the near-infrared region. Copper(II) complexes generally have a broad absorption band in the 600–800-mμ region which imparts a blue to green color to the complexes. The peak for $[Cu(OMPA)_3](ClO_4)_2$ at 920 mμ represents the largest shift into the near-infrared region of any known six-coordinate Cu(II) complex. The reflectance spectrum of anhydrous $CuSO_4$ has a peak at 880 mμ.[7] Since the shift to the near-infrared region is an indication of the weakness of the ligand field, Cu(II) interacts with OMPA even less strongly than with sulfate ion. The interesting difference is that $[Cu(OMPA)_3](ClO_4)_2$ is not hygroscopic and can be recrystallized from acetone. This appears to be further support for the stability of the six-membered ring in complexes of OMPA with metal ions.

Bjerrum, Ballhausen, and Jørgensen[7] have found that the asymmetry of absorption bands for six-coordinate Cu(II) complexes can provide a measure of the tetragonality of the complex. They assume that an absorption band will follow a Gaussian error curve if the band is a result of a single energy transition. Bands of

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Table II. Spectral Data

Compound	Infrared, cm^{-1} $\nu_{P=O}$	ν_{P-O-P}	ν_{P-N_1}	ν_{P-N_2}	Visible and near-infrared λ_{max}, mμ (cm^{-1})	ϵ
OMPA	1238	914	988	756		
$[Cu(OMPA)_3](ClO_4)_2$	1191	930	1000	769	290 (33,400)[a]	1390
					920 (10,880)[b]	26
$[Cu(OMPA)_2][CuBr_4]$	1192	928	1001	767	310 (32,300)[a]	7600
				790	360 (27,800)[c]	...
					500 (20,000)	...
					640 (15,600)	...
					925 (10,800)	
$[Ag(OMPA)_2](ClO_4)$	1196	925	998	782		
				761		
$[Hg(OMPA)_3](ClO_4)_2$	1186	931	1000	769		
$[Co(OMPA)_3][CoBr_4]$	1196	913	1002	765	610 (16,400)[b]	585
				791	665 (15,050)	830
					680 (14,700)	895
$[Fe(OMPA)_3](ClO_4)_3$	1179	929	1005	773	222 (45,000)[a]	8500
				790		

[a] In acetonitrile. [b] In nitromethane. [c] Nujol mull.

Cu(II) complexes are resolved in a manner similar to that shown in Figure 1. The ratio of λ_2/λ_1 is used as a measure of the degree of tetragonality[7] (octahedral, $\lambda_2/\lambda_1 = 1$; square pyramid, $\lambda_2/\lambda_1 = 1.6$; square, $\lambda_2/\lambda_1 = 2$).

The two symmetrical curves which appear under the asymmetric band in Figure 1 can be used to determine the degree of tetragonality of $[Cu(OMPA)_3](ClO_4)_2$. The two peak maxima at 920 and 1250 mμ give a value for λ_2/λ_1 of 1.36 which is the same as that reported[7] for $[Cu(H_2O)_6]^{2+}$ and $[Cu(NH_3)_6]^{2+}$.

The first bands of the corresponding complexes of Ni(II) and Cu(II) have also been used as a measure of the degree of distortion from an octahedral field.[8] The assumption is that Ni(II) has a perfect octahedral configuration, and if $\lambda_{Ni}/\lambda_{Cu} = 1$, the configuration around Cu(II) would also be octahedral. For OMPA, $\lambda_{Ni}/\lambda_{Cu} = 1.50$ which is the same ratio as that obtained when ethylenediamine is the ligand.[8]

The color of some of the other complexes isolated in this study is also of interest. The intense charge-transfer bands of $[CuCl_4]^{2-}$ and $[CuBr_4]^{2-}$ are the cause of the brown and black colors of $[Cu(OMPA)_2][CuCl_4]$ and $[Cu(OMPA)_2][CuBr_4]$, respectively (Table II). The yellow color of $[Fe(OMPA)_3](ClO_4)_3$ is due to an intense absorption at 222 mμ. Thus far, complexes of OMPA with transition metal halides result in the formation of the tetrahalometalate anion. The spectra of $[Cu(OMPA)_2][CuBr_4]$ and $[Co(OMPA)_3][CoBr_4]$ contain peaks characteristic of the anions (Table II). A previous publication from this laboratory reported additional examples.[2] The ease with which these complexes are isolated is of interest. Although anhydrous metal halides were generally used, the Co(II) complex described in this paper was obtained by using the hydrated salt.

In the preparation of OMPA complexes of Cu(II), Ag(I), and Hg(II) perchlorates it was not necessary to remove the water prior to adding the ligand (see Experimental Section). The complexes were easily isolated and purified. This is rather unusual since complexes such as $[Ag(OMPA)_2](ClO_4)$ and $[Hg(OMPA)_3](ClO_4)_2$ would be expected to be unstable because of their uncommon coordination numbers of 4 and 6, respectively.

The changes in the P=O, P–O–P, and P–N infrared stretching frequencies are similar to those obtained previously.[2,3] The decrease in $\nu_{P=O}$ in the complexes is support for coordination of the metal ion to the phosphoryl oxygens. The increases in both ν_{P-O-P} and ν_{P-N} are support for a chelate structure.[3]

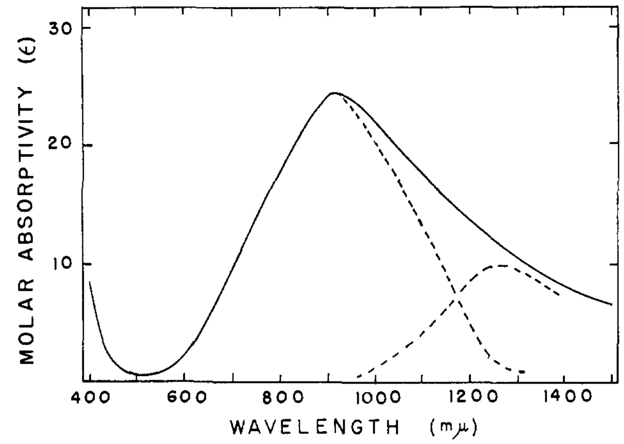

Figure 1. Visible and near-infrared spectrum of $[Cu(OMPA)_3](ClO_4)_2$ in nitromethane. Solid line is experimental curve and dashed lines are resolved curves.

The magnetic susceptibility data are summarized in Table III. The value of 2.12 BM for $[Cu(OMPA)_3](ClO_4)_2$ is higher than the calculated spin-only value of 1.73 BM but is within the range of values (1.7–2.2) reported for other Cu(II) complexes.[6] The experi-

Table III. Magnetic Susceptibility Data

Compound	$\chi_M \times 10^6$	χ_{diamag} (cor) $\times 10^6$	$\chi_M' \times 10^6$	μ_{eff}, BM Exptl (28°)	Calcd[a]
$[Cu(OMPA)_3](ClO_4)_2$	1,240	617	1,857	2.12	1.73
$[Hg(OMPA)_3](ClO_4)_2$	−585	604	19	0.0	...
$[Cu(OMPA)_2][CuBr_4]$	2,913	513	3,426	2.88	2.83
$[Cu(OMPA)_2][CuCl_4]$[b]	2,925	518	3,443	2.89	2.83
$[Co(OMPA)_3][CoBr_4]$	21,767	806	22,573	7.41	6.94
$[Co(OMPA)_3][CoCl_4]$[b]	21,854	725	22,579	7.41	6.94
$[Fe(OMPA)_3](ClO_4)_3$	15,126	649	15,775	6.23	5.92

[a] Calculated from $\mu_{eff} = \sqrt{n(n+2)}$ BM. [b] Data from ref 2.

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mental determination of this moment is somewhat difficult due to the small percentage of Cu(II) present (5.7%). The measurements for the diamagnetic complex, $[Hg(OMPA)_3](ClO_4)_2$, are included for comparison. The magnetic moments of $[Cu(OMPA)_2][CuBr_4]$ and $[Cu(OMPA)_2][CuCl_4]$ are in excellent agreement with the calculated value for two unpaired electrons. The magnetic moment of $[Fe(OMPA)_3](ClO_4)_3$ is slightly higher than the spin-only value for five unpaired electrons. This is further evidence for the weak field property of OMPA that was noted earlier in complexes of Ni(II) and Co(II).[2]

The present work provides evidence that OMPA is not only a versatile ligand, but also a ligand that can fulfill the maximum coordination number of a metal ion even though spectral evidence (colorless Cu(II), low *Dq* parameter toward Ni(II)[2]) indicates weak bonding.

The Synthesis and Chemistry of a Novel Macrocyclic Schiff Base Dihydrogen Perchlorate by Condensation of $Fe(en)_3^{2+}$ with Acetone

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Contribution from the Department of Chemistry, Boston University, Boston, Massachusetts 02215. *Received July 5, 1966*

Abstract: A new quadridentate Schiff base dihydrogen perchlorate has been prepared by means of the reaction of $[Fe(en)_3](ClO_4)_2$ with acetone. The physical and chemical evidence indicates that this compound is a protonated Schiff base having a cyclic structure. The two protons of the protonated macrocycle may be displaced by metal ions in basic solution. The Schiff base dihydrogen perchlorate has proved to be a very useful intermediate in the preparation of macrocyclic complexes of several metals.

In recent years there have been a number of different kinds of condensation reactions reported in which a transition metal ion functions as a template, holding the condensing ligand molecules in a suitable orientation to facilitate the formation of products.[1-8] Curtis and co-workers[3-5] have reported and extensively investigated the formation of macrocyclic Schiff base amine complexes of Cu(II) and Ni(II) by means of the template condensation of acetone with an amine complex of the metal (eq 1). Analogous reactions for

$$[M(en)_n](ClO_4)_2 + 4CH_3COCH_3 \longrightarrow [M(C_{16}H_{32}N_4)](ClO_4)_2 + (n\text{-}2)en + 4H_2O \quad (1)$$

Co(II) and Fe(II) amines have not been reported. The chemistry of the macrocyclic Schiff base complexes of the latter two metals is of particular interest owing to their similarity with such biologically important systems as vitamin B_{12} and hemoglobin.

One of the most interesting features of the chemistry of the macrocyclic Schiff base complexes, $M(C_{16}H_{32}N_4)^{2+}$, of Ni(II) and Cu(II) is their unusual inertness to hydrolysis or substitution even in the presence of strong mineral acids or CN^-.[3-6] This is distinctly in contrast to the usual substitution lability of most Ni(II) and Cu(II) amine complexes[7] and is reminiscent of the behavior of the corresponding metalloporphyrin complexes.[8] It is to be noted, however, the Curtis' macrocyclic Schiff base amine complexes do differ from the metalloporphyrins in that Schiff base amine ligands cannot derive any stability from a conjugated system of double bonds. In fact the macrocyclic Schiff base amine ligands are more closely related to the well-known aliphatic Schiff bases than to the porphyrins. Since aliphatic Schiff bases are generally hydrolyzed rapidly by aqueous acid,[9] we have been surprised that a stable macrocyclic Schiff base dihydrogen perchlorate, $C_{16}H_{32}N_4 \cdot 2HClO_4$, can be obtained in excellent yield from reaction 1 when M = Fe(II). We have been primarily interested in using this Schiff base dihydrogen perchlorate (I) as an intermediate in the preparation of macrocyclic complexes of several metal ions. The preparation, synthetic uses, and some preliminary observations of the chemistry of this Schiff base dihydrogen perchlorate are the subject of this report.

Experimental Section

Infrared spectra were determined from Nujol and hexachlorobutadiene mulls of the dry solids, using both the Perkin-Elmer Models 137 and 237 spectrometers. Visible and ultraviolet absorption spectra were measured with a Cary 14 recording spectrometer. A Varian A-60 high-resolution nmr spectrometer was used to obtain the proton resonance spectra.

Elemental analyses were performed by Spang and/or Schwartzkopf microanalytical companies. Schwartzkopf Microanalytical Company determined molecular weights in pyridine using a vapor pressure osmometer.

Preparations. 5,7,7,12,14,14-Hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene Dihydrogen Perchlorate, $C_{16}H_{32}N_4 \cdot 2HClO_4$. This preparation seemed to be very sensitive to the presence of

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