could well be that the energy difference between the octahedron and the trigonal prism is small in a very large number of cases and that the reason the Bailar twist mechanism is not generally observed is due, not to its unfavorable activation energy, as suggested by some authors,[10,11] but rather to its unusually low frequency factor.

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Metal Complexes of Octamethylmethylenediphosphonic Diamide

BY KENT P. LANNERT AND MELVIN D. JOESTEN

Octamethylpyrophosphoramide (OMPA) has been found to form complexes with a large number of metal ions.[1-5] X-Ray and infrared studies have shown OMPA to be a bidentate ligand with the phosphoryl oxygens as the donor sites.[6] This results in the formation of six-membered chelate rings which are essentially planar in the tris-OMPA complexes of cobalt(II),[7] magnesium(II),[7] and copper(II).[6] Since the bridging oxygen has two lone pairs of electrons available for delocalization into the chelate ring by $d\pi-p\pi$ bonding with the phosphorus atoms, it was decided to see what effect replacing the bridging oxygen by groups with one or no lone pairs of electrons would have on the coordinating ability of the ligand.

The oxygen bridge was first replaced by a methyl-substituted nitrogen which had only one lone pair of electrons available for delocalization into the chelate ring.[8] This ligand is nonamethylimidodiphosphoramide (NIPA). Essentially no difference was noted in its coordinating properties compared to those of OMPA.

The subject of this paper is the preparation of metal complexes from octamethylmethylenediphosphonic diamide (PCP). In PCP the oxygen bridge of OMPA is replaced by a methylene group. The methylene group has no lone pairs of electrons or orbitals of suitable energy to participate in $d\pi-p\pi$ bonding within the chelate ring. The methylene bridge would be expected to be somewhat more rigid than the oxygen or nitrogen

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(5) M. D. Joesten, *Inorg. Chem.*, **6**, 1598 (1967).

(6) M. D. Joesten, M. S. Hussain, P. G. Lenhert, and J. H. Venable, Jr., *J. Am. Chem. Soc.*, **90**, 5623 (1968).

(7) M. D. Joesten and P. G. Lenhert, to be submitted for publication.

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bridges of OMPA and NIPA. Complexes of selected metal ions with PCP have been prepared and will be discussed in this paper. The structure of the ligand is


OMPA, X = O
NIPA, X = NCH₃
PCP, X = CH₂
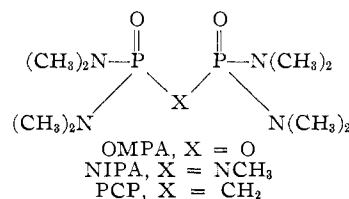
Experimental Section

Preparation of the Ligand.—The preparation of PCP has not been reported. The compound was prepared by first making tetraisopropylmethylene diphosphonate by a Michaelis–Arbuzov reaction from triisopropyl phosphite and methylene bromide.[9]

$$2(RO)_3P + CH_2Br_2 \longrightarrow [(RO)_2P(O)]_2CH_2 + 2RBr$$
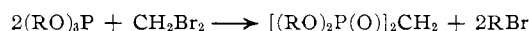
The ester was then converted to the acid by refluxing for several hours with concentrated hydrochloric acid.[9] An equimolar mixture of methylenediphosphonic acid and tetraisopropyl-

$$[(RO)_2P(O)]_2CH_2 + 4HCl \longrightarrow [(HO)_2P(O)]_2CH_2 + 4RCl$$
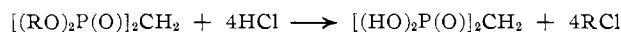
methylene diphosphonate was then treated with PCl₅ to form the acid chloride–methylenediphosphonic dichloride[10]

$$[(RO)_2P(O)]_2CH_2 + [(HO)_2P(O)]_2CH_2 + PCl_5 \longrightarrow$$
$$2[Cl_2P(O)]_2CH_2 + 4HCl + 4RCl + 8POCl_3$$
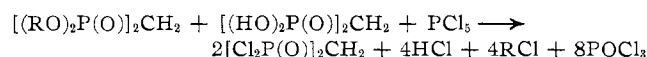
A solution of 75 g (0.3 mol) of methylenediphosphonic dichloride in 1.5 l. of dry benzene was placed in a 2-l. flask fitted with a condenser, a stirrer, and a gas-bubbling tube. The gas-inlet tube should have an opening of approximately 1 cm so that it will not become stopped up with the amine hydrochloride formed during the reaction. The reaction flask was cooled in

$$[Cl_2P(O)]_2CH_2 + 8(CH_3)_2NH \longrightarrow$$
$$\{[(CH_3)_2N]_2P(O)\}_2CH_2 + 4(CH_3)_2NH_2Cl$$
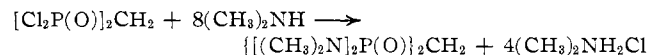
an ice bath and dimethylamine was bubbled in for about 8–10 hr. At the end of this time, the hydrochloride salt was removed by filtering and the benzene was removed on a rotoevaporator connected to a water aspirator. The oily residue was then shaken with ether to give a milky white dispersion and brown solid. The ether was removed on a rotoevaporator and the oily liquid was vacuum distilled. The main fraction was collected at 147° at 0.25 mm ($n_{25}D$ 1.4888). After standing for 1 hr, the liquid solidified. The solid was very hygroscopic and melted over the range 47–60°.

The nmr of a chloroform solution of PCP has a methyl hydrogen doublet at 2.66 ppm. This agrees with the value of 2.58 ppm reported for [(CH₃)₂N]₃PO.[11] A triplet is expected for the methylene protons in the 2.40-ppm region.[12] This region is partially obscured by the methyl protons but it appears that the middle peak of the triplet occurs at 2.38 ppm.

The mass spectrum of PCP shows a parent peak at 284 mass units which agrees well with the calculated value of 284.3.

The triisopropyl phosphite and the dibromomethane were obtained from Aldrich Chemical Co. and used without further purification.

Preparation of Complexes.—The complexes of PCP were prepared by allowing an acetone solution of the hydrated metal perchlorate and excess PCP to evaporate slowly in a desiccator until crystals formed. The crystals were removed from the solution, washed once with ether, and dried *in vacuo*. Analytical data for the complexes are presented in Table I.

Conductance Measurements.—A conductance bridge (Industrial Instruments, Inc.) was used to measure the conductivities

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(12) T. H. Siddall and C. A. Prohaska, *Inorg. Chem.*, **4**, 783 (1965).

TABLE I

ANALYTICAL DATA FOR PCP COMPLEXES

Compound	% carbon Calcd	Found	% hydrogen Calcd	Found	% nitrogen Calcd	Found	Color
Mg(PCP)₃(ClO₄)₂	30.1	30.2	7.31	7.42	15.6	15.4	White
Co(PCP)₃(ClO₄)₂	29.2	29.4	7.08	6.96	15.1	14.5	Pink
Ni(PCP)₃(ClO₄)₂	29.2	29.1	7.08	7.31	15.1	14.9	Yellow
Zn(PCP)₃(ClO₄)₂	29.0	29.1	7.04	6.97	15.1	14.8	White
Cu(PCP)₃(ClO₄)₂	29.1	29.3	7.05	7.21	15.1	15.0	White
Cu(PCP)₂(ClO₄)₂	26.0	26.0	6.31	6.27	13.5	13.3	Blue

of nitromethane solutions of the complexes. A platinum dip-type cell with a cell constant of 0.11 and a bridge frequency of 50–60 cps was used. The conductance data are summarized in Table II.

TABLE II

INFRARED SPECTRAL AND CONDUCTANCE DATA
FOR PCP COMPLEXES

Compound	ν(P=O), cm⁻¹	ν(P—C—P), cm⁻¹	ν(P—N), cm⁻¹	Λ_{molar} (25°), cm² ohm⁻¹ mol⁻¹	Concn × 10³, M
PCP	1197	788	963		
Mg(PCP)₃(ClO₄)₂	1189	788	977	170	1.00
Co(PCP)₃(ClO₄)₂	1187 1163	794	978	170	1.01
Ni(PCP)₃(ClO₄)₂	1170 1185	796	983	170	1.01
Zn(PCP)₃(ClO₄)₂	1173	800	987	170	1.00
Cu(PCP)₃(ClO₄)₂	1185 1150	793	980		
Cu(PCP)₂(ClO₄)₂	1180	807	1005 986	166	1.02

Spectral Measurements.—Infrared spectra were obtained for Nujol mulls of the complexes with a Beckman IR-10 spectrophotometer. The spectrum of the ligand was obtained as a neat sample. The infrared data are summarized in Table II. The visible and near-infrared spectra were obtained for acetone and nitromethane solutions with a Beckman DK-2A spectrophotometer.

Calculation of Dq and β^0.—The Dq and β^0 parameters were calculated for the Ni(II) complex by the method given by Drago.[13] The Dq value for PCP is 707 cm⁻¹ ($10Dq = 7070$ cm⁻¹). The value calculated for the P–F term splitting is 14,000 cm⁻¹ and $\beta^0 = 11.0\%$. The frequency of the middle peak in the spectrum was calculated to be 12,000 cm⁻¹ and the experimental value is 12,300 cm⁻¹.

Results and Discussion

The complexes of octamethylmethylenediphosphonic diamide are very similar in appearance and properties to the corresponding complexes of octamethylpyrophosphoramide[1–5] and nonamethylimidodiphosphoramide.[8]

The conductance data and the analytical data of Table I are in support of a coordination number of 6 for all of the complexes except the bis copper(II) complex. These coordination numbers indicate that PCP is acting as a bidentate ligand as expected.

The visible spectrum of Co(PCP)₃(ClO₄)₂ in acetone solution consists of one low-intensity asymmetric peak with a maximum at 541 mμ (19)[14] and a shoulder on the high-frequency side. This spectrum is characteristic of octahedral Co(II) and has been observed for Co(II) complexes of other bidentate organophosphorus lig-

ands.[1,8,15] The visible and near-infrared spectra of Ni(PCP)₃(ClO₄)₂ in acetone solution are typical of octahedral Ni(II) with three weak peaks at 427 mμ (12), 810 mμ (4), and 1415 mμ (4). The $^3A_{2g} \rightarrow {}^3T_{2g}$ transition is assigned to the 1415-mμ (7070-cm⁻¹) peak. Thus, the Dq value for PCP is 707 cm⁻¹.

Similar spectra were obtained for the nickel(II) complexes of OMPA,[1] NIPA,[8] and L₁.[15] The Dq values for OMPA and NIPA were reported as 726 and 727 cm⁻¹. Walmsey and Tyree reported a 10Dq value of 8470 cm⁻¹ for L₁.[15] However, a spectrum of Ni(L₁)₃(ClO₄)₂ run in this laboratory showed that the shoulder at 1185 mμ had been chosen to represent the $^3A_{2g} \rightarrow {}^3T_{2g}$ transition rather than the peak maximum at 1385 mμ. By choosing the latter peak a 10Dq value of 7220 cm⁻¹ or a Dq of 722 cm⁻¹ was obtained. This is in agreement with the other Dq values obtained. A calculation[13] of the frequency expected for the middle peak using the maximum at 1385 mμ resulted in a calculated value of 12,220 cm⁻¹ compared to an observed value of 12,400 cm⁻¹. This is in good agreement and supports the assignment of the 1385-mμ band to the $^3A_{2g} \rightarrow {}^3T_{2g}$ transition. Using the shoulder at 1185 mμ, the calculated frequency of the middle band is 13,850 cm⁻¹. This is not in good agreement with the observed value. The calculated and observed values for the middle band of the Ni(PCP)₃(ClO₄)₂ are 12,000 and 12,300 cm⁻¹, respectively.

A comparison of the Dq values of OMPA, NIPA, and PCP seems to indicate that the substitution of a bridge group with lone-pair electrons (oxygen with two lone pairs, nitrogen with one lone pair) has little effect on the Dq, viz., 727 cm⁻¹ vs. 726 cm⁻¹ for OMPA and NIPA. However, when the methylene group with no lone-pair electrons is placed in the bridge position, the Dq drops by about 20 cm⁻¹. Also a replacement of the dimethylamino groups on the phosphorus by alkoxy groups tends to increase Dq. This is seen by comparing the Dq values of 707 cm⁻¹ for the PCP complex and 722 cm⁻¹ for the L₁ complex. Some other results from this laboratory indicate this trend holds true for the oxygen-bridged complexes as well.[16] It is realized that these differences in Dq values are small and their significance is still in question.

The calculated β^0 values for the OMPA, NIPA, L₁, and PCP complexes of nickel(II) are 11.2, 9.7, 9.8, and 11.0%, respectively. The β^0 and Dq values for these organophosphorus chelates are at the lower end of both the nephelauxetic series (based on β^0) and the spectrochemical series (based on Dq). This indicates that the bonding between the ligands and the nickel(II) ion is essentially electrostatic.

One of the interesting properties of the bidentate organophosphorus ligands OMPA,[3] NIPA,[8] and PCP is their ability to form colorless tris copper(II) complexes as well as blue bis complexes. The visible and near-infrared spectrum of Cu(PCP)₂(ClO₄)₂ contains a single asymmetric peak at 810 mμ (38) characteristic of

(13) R. S. Drago, "Physical Methods in Inorganic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1965, pp 410, 411.

(14) Molar absorptivity values are given in parentheses throughout this paper.

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

(16) M. F. Prysak and M. D. Joesten, *ibid.*, **8**, 1455 (1969).

tetragonal Cu(II).[17] This peak is shifted to longer wavelengths as more ligand is added to the solution. When the amount of ligand added is enough to make the ratio of ligand to metal 3:1, the spectrum is the same as that of $Cu(PCP)_3(ClO_4)_2$. The spectrum of colorless $Cu(PCP)_3(ClO_4)_2$ in nitromethane solution with a slight excess of PCP shows a peak at 930 mμ (30). This is about the same as is obtained for $Cu(OMPA)_3(ClO_4)_2$ and $Cu(NIPA)_3(ClO_4)_2$.

The infrared data are summarized in Table II. The strong peak in the 1190-cm^{-1} region has been assigned to the P=O stretch since the P=O stretch in $[(CH_3)_2N]_2P(O)CH_3$ was reported as 1205 cm^{-1}.[18] Thomas and Chittenden assigned the frequency range 873–1053 cm^{-1} to be that containing the P—N stretch.[19] The PCH$_2$P vibration was assigned to the 780–830-cm^{-1} region.[20]

Coordination is believed to be through the phosphoryl oxygen atom with each PCP molecule forming a six-membered chelate ring. This chelate structure has been shown to be correct for OMPA complexes of Co(II), Mg(II), and Cu(II).[6,7] Thus, one would expect and finds much the same changes in the P=O and P—N stretching frequencies in PCP complexes as were found in OMPA and NIPA complexes.

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(18) R. B. Harvey and J. E. Mayhood, *Can. J. Chem.*, **33**, 1552 (1955).

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Pyridine Complexes of Zinc, Cadmium, and Mercury(II) Nitrates[1]

BY THOMAS J. OUELLETTE AND HELMUT M. HAENDLER[2]

Several studies have been made of the pyridine complexes of zinc, cadmium, and mercury(II) halides, but little work has been reported on the pyridine complexes of the corresponding anhydrous nitrates. Frank and Rogers[3] have reported the far-infrared spectrum of dinitratotris(pyridine)zinc(II), and Bullock and Tuck[4] have recorded the infrared spectrum of dinitratobis-(pyridine)mercury(II). Pyridine often forms a series of complexes with the same metal salt, as demonstrated

with copper(II), cobalt(II), and nickel(II) nitrates,[5,6] and similar behavior might be expected of zinc, cadmium, and mercury(II) nitrates.

Experimental Section

Starting Materials.—Reagent grade methanol was dried by distillation from magnesium activated with iodine. Reagent grade pyridine was dried by distillation from potassium hydroxide and stored over barium oxide. Practical grade 2,2-dimethoxypropane was used without further purification. All other chemicals were of reagent grade and were used without further purification.

Dinitratotris(pyridine)zinc(II).—Granular zinc (7.5 g) was added slowly to a solution of 34 g of silver nitrate in 100 ml of methanol. The mixture was stirred for 32 hr, at which time the solution gave no Ag$^+$ test. The reaction mixture was filtered and 25 ml of pyridine was added to the filtrate. The mixture was evaporated to a final volume of 40 ml. Colorless, transparent crystals formed on refrigeration and were collected on a sintered-glass filter and washed with methanol and finally with ethyl ether. The product was recrystallized from a chloroform–pyridine mixture and dried *in vacuo* over silica gel. *Anal.* Calcd for Zn(py)$_3$(NO$_3$)$_2$: Zn, 15.32; N, 16.42; C, 42.22; H, 3.54. Found: Zn, 15.54; N, 16.41; C, 42.12; H, 3.43.

The compound was also prepared by dehydrating zinc(II) nitrate hexahydrate in 2,2-dimethoxypropane and adding pyridine to the solution at room temperature. It could also be crystallized from methanol–pyridine.

Dinitratobis(pyridine)zinc(II).—A ground and weighed sample of dinitratotris(pyridine)zinc(II) was heated at 115° under a stream of dry nitrogen until no further weight loss was observed (9.5 hr). The final product was a pale pink solid. *Anal.* Calcd for Zn(py)$_2$(NO$_3$)$_2$: Zn, 18.81; N, 16.11; C, 34.53; H, 2.88. Found: Zn, 18.98; N, 16.26; C, 34.13; H, 2.86. Calcd weight loss: 18.54%. Found: 18.83%.

Dinitratotris(pyridine)zinc(II)–Tris(pyridine).—A weighed sample of dinitratotris(pyridine)zinc(II) was placed in a desiccator over pyridine for 15 days at room temperature. The starting material added 3 mol of pyridine. The reaction was completely reversible at 60 Torr. *Anal.* Calcd for Zn(py)$_3$(NO$_3$)$_2$·3py: Zn, 9.85. Found: Zn, 10.29. Microanalytical C, H, and N analyses were not possible because of rapid loss of pyridine from the sample. Calcd weight gain: 55.62%. Found: 54.96%.

Dinitratotris(pyridine)cadmium(II).—An indirect method of oxidizing cadmium in methanol was selected because the oxidation with silver nitrate was very slow, and no Ag$^+$-free solution could be obtained. Bismuth (15 g) was added to a solution of 34 g of silver nitrate in 100 ml of methanol. The mixture was stirred for 30 hr at room temperature. The mixture was filtered to remove suspended solids, the filtrate giving a negative Ag$^+$ test. Cadmium filings (12 g) were added to the bismuth(III) solution, and the mixture was stirred for 30 hr and filtered to remove suspended solids. The resulting cadmium nitrate solution gave a negative test for Bi^{3+}. Pyridine (24 ml) was added to the cadmium(II) solution and the mixture was evaporated to a final volume of 40 ml. Colorless, transparent crystals were obtained on refrigeration. These were washed with ether, recrystallized from chloroform–pyridine, and dried *in vacuo*. *Anal.* Calcd for Cd(py)$_3$(NO$_3$)$_2$: Cd, 23.72; N, 14.78; C, 38.03; H, 3.19. Found: Cd, 24.18; N, 14.84; C, 37.73; H, 3.10.

The compound was also prepared by dehydrating cadmium(II) nitrate tetrahydrate in 2,2-dimethoxypropane and adding pyridine to the solution at room temperature.

Tetranitratotris(pyridine)dicadmium(II).—A ground and weighed sample of dinitratotris(pyridine)cadmium(II) was heated at 115° under a slow stream of dry nitrogen until no further weight loss was observed (24 hr). The weight loss corresponded to the loss of 1.5 mol of pyridine per mole of starting material.

(1) Taken in part from the Ph.D. thesis of Thomas J. Ouellette. Supported by the U. S. Atomic Energy Commission.

(2) To whom communications should be addressed.

(3) C. W. Frank and L. B. Rogers, *Inorg. Chem.*, **5**, 615 (1966).

(4) J. I. Bullock and D. G. Tuck, *J. Chem. Soc.*, 1877 (1965).

(5) R. V. Biagetti, W. G. Bottjer, and H. M. Haendler, *Inorg. Chem.*, **5**, 379 (1966).

(6) R. V. Biagetti and H. M. Haendler, *ibid.*, **5**, 383 (1966).