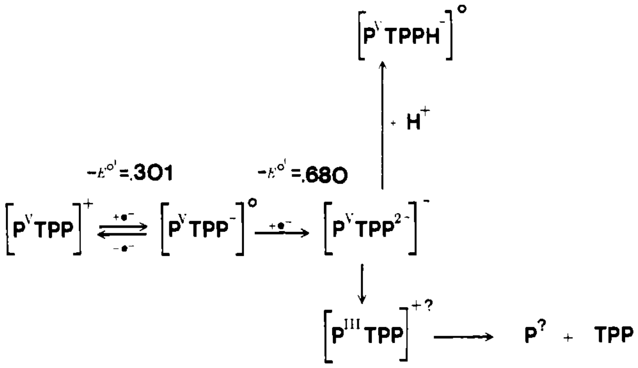
Scheme I



transfers such as that described here can be both irreversible and in one remarkable case reversible and have been reported for three other porphyrin systems.[24-26] All of the other reported examples have involved oxidative reactions, this being the first example to our knowledge of a reductive reaction. The overall electrochemistry is depicted in Scheme I.

Internal electron transfers such as that described here may be important in biological electron transfers involving hemes.[27] It has been suggested that axial ligation can have a strong influence on these internal electron transfers.[26,27] This seems to be the case with these phosphorus systems as well; a report on the electrochemistry of the analogous dihydroxo complex, which is strikingly different, will be forthcoming. We should also add that protonation reactions, as demonstrated here, can also have a substantial effect on the internal electron transfer of reductive processes.

**Acknowledgment.** We wish to thank Prof. W. E. Geiger for the generous loan of his electrochemical equipment without which this work could not have been carried out. We also wish to acknowledge Prof. Geiger and Prof. C. M. Elliott for many helpful discussions concerning various aspects of this work and to thank K. Baptie for assistance with the synthesis and purification of the title compound.

**Registry No.** [(TPP)$P^{V}Cl_2$]Cl, 84896-72-0; [(TPP)$P^{V}(OH)_2$]OH, 85565-87-3; [(TPP)$P^{V}Cl_2$], 84896-73-1; $[(TPP)P^{V}Cl_2]^-$, 84880-35-3.

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# Cadmium Diethyl Phosphate: Structure Determination and Comparison to Cation Phospholipid Complexes

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*Received December 28, 1982*

X-ray diffraction analysis refined to residuals $R_1 = 0.026$ and $R_2 = 0.031$ has shown the structure of $Cd[(EtO)_2PO_2]_2$ to be polymeric with one-dimensional chains of cadmium atoms bridged by oxygen atoms from the phosphates. The compound crystallizes in space group $P\bar{1}$ with $a = 5.316$ (1) Å, $b = 12.867$ (4) Å, $c = 12.963$ (4) Å, $\alpha = 67.93$ (3)°, $\beta = 77.07$ (2)°, $\gamma = 79.13$ (2)°, $Z = 2$, and $V = 795.5$ Å$^3$. In comparison to existing polymeric structures for barium and magnesium analogues, this compound has an unusually short metal–metal distance of 3.50 Å. The concomitant compression of the phosphate–phosphate distances along the chain axis is even more pronounced. Aside from general implications for cadmium coordination chemistry, the variation in these distances is suggested to play a role in selective stimulation of membrane transformations by structurally similar complexes of $Ca^{2+}$ and $Cd^{2+}$ with anionic phospholipids.

## Introduction

Complexes of divalent cations with phosphate esters are important entities in many biological systems. In particular, divalent cations are believed, in several cases, to mediate fusion of natural and artificial membranes with $Ca^{2+}$ often showing enhanced activity over other divalent ions.[1] Correlation of activity with ion size is well documented in at least one model system, a mixed phosphatidylcholine–phosphatidic acid vesicle system.[2] High fusion activities of similar magnitudes were observed for the equivalent-sized ions $Ca^{2+}$ and $Cd^{2+}$. By comparison, lower activities were observed for the larger and smaller ions $Ba^{2+}$ and $Mg^{2+}$. This correlation suggests that structural aspects of the cation–phosphate ester complexes formed may provide a key to understanding ion selectivity in the fusion process.

X-ray crystal structures of the simple phosphate ester–cation complexes formed by $Mg^{2+}$ and $Ba^{2+}$ with diethyl phosphate have been published.[3,4] A structure of the $Ca^{2+}$ or $Cd^{2+}$ salt should provide a series in which structural correlations with activity could be sought. We present here the structure of the $Cd^{2+}$ salt. $Cd^{2+}$ has been used as a substitute ion for $Ca^{2+}$ in a number of biochemical NMR studies.[5,6] It provides a useful spectroscopic probe in that the $^{113}Cd$ and $^{111}Cd$ isotopes are spin 1/2 with reasonably high NMR receptivity. Thus, in addition to completing a structural series useful in analyzing a possible structural basis for variation in membrane fusion activity, the cadmium–diethyl phosphate structure will provide the basis of solid $^{113}Cd$ NMR studies, which can extend structural characterization to less ordered membrane phases.

## Experimental Section

$Cd[(EtO)_2PO_2]_2$ was crystallized from a solution of potassium-diethyl phosphate and $Cd(NO_3)_2$. $KNO_3$, which precipitates first,

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**Table I.** Experimental Data for X-ray Diffraction Study of $Cd_n[(EtO)_2PO_2]_{2n}$

(A) Crystal Parameters at 24 (2) °C

$a = 5.316$ (1) Å
$b = 12.867$ (4) Å
$c = 12.963$ (4) Å
$\alpha = 67.93$ (3)°
$\beta = 77.07$ (2)°
$\gamma = 79.13$ (2)°
$V = 795.5$ Å$^3$
$Z = 2$
mol wt = 418.59
$d$(calcd) = 1.747 g/cm$^3$
space group: $P\bar{1}$ (No. 2)

(B) Measurement of Intensity Data

radiation: Mo K$\alpha$; $\lambda = 0.710\,73$ Å
monochromator: graphite
detector aperture: horizontal, $A + B \tan\theta$ ($A = 3.0$ mm, $B = 1.0$ mm); vertical, 4.0 mm
reflcns measd: $+h, \pm k, \pm l$
max $2\theta$: 50°
scan type: moving crystal–stationary counter
$\omega$ scan rate: max = 10, min = 1.82°/min
$\omega$ scan width: 1.2°
bkgd: one-fourth additional scan at each end of scan
std reflcns: 3 measd after each 90 min, showing only random fluctuations of ±2%
reflcns measd: 2776
data used ($F^2 \geqslant 3\sigma(F^2)$): 2331

(C) Treatment of Data

abs coeff ($\mu$): 15.924 cm$^{-1}$
$p$ factor: 0.01
final residuals ($R_1, R_2$): 0.026, 0.031
esd of unit wt: 2.3

**Table II.** Positional Parameters and Their Estimated Standard Deviations for $Cd_n[(EtO)_2PO_2]_{2n}$

| atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| Cd | 0.19528 (5) | 0.05469 (2) | 0.05469 (2) |
| P(1) | 0.6681 (2) | 0.22553 (8) | −0.03748 (8) |
| P(2) | −0.3562 (2) | −0.03748 (8) | 0.22555 (8) |
| O(11) | 0.8613 (4) | 0.1262 (2) | −0.0463 (2) |
| O(12) | 0.3859 (4) | 0.2115 (2) | −0.0024 (2) |
| O(13) | 0.6946 (5) | 0.3275 (2) | −0.1535 (2) |
| O(14) | 0.7709 (5) | 0.2636 (2) | 0.0475 (2) |
| O(21) | −0.4409 (4) | −0.0464 (2) | 0.1263 (2) |
| O(22) | −0.0958 (4) | −0.0021 (2) | 0.2111 (2) |
| O(23) | −0.3682 (5) | −0.1537 (2) | 0.3274 (2) |
| O(24) | −0.5815 (5) | 0.0473 (2) | 0.2638 (2) |
| C(11) | 0.952 (1) | 0.3568 (4) | −0.2122 (5) |
| C(12) | 0.933 (1) | 0.4659 (6) | −0.3016 (6) |
| C(13) | 0.641 (1) | 0.3536 (5) | 0.0790 (5) |
| C(14) | 0.778 (1) | 0.3863 (5) | 0.1442 (6) |
| C(21) | −0.596 (1) | −0.2123 (4) | 0.3567 (4) |
| C(22) | −0.597 (1) | −0.3016 (6) | 0.4661 (6) |
| C(23) | −0.573 (1) | 0.0795 (6) | 0.3536 (5) |
| C(24) | −0.809 (1) | 0.1429 (6) | 0.3868 (5) |

**Table III.** Selected Interatomic Distances (Å) for $Cd_n[(EtO)_2PO_2]_{2n}$[a]

| | | | |
|---|---|---|---|
| Cd- - - -Cd′ | 3.496 (0) | Cd- -O(14)′ | 3.153 (2) |
| Cd- - - -Cd″ | 3.495 (0) | Cd- -O(24) | 3.158 (2) |
| Cd- - - -P(1) | 3.368 (1) | P1–O(11) | 1.504 (2) |
| Cd- - - -P(1)′ | 3.364 (1) | P1–O(12) | 1.492 (2) |
| Cd- - - -P(2) | 3.367 (1) | P1–O(13) | 1.580 (2) |
| Cd–O(22) | 2.225 (2) | P1–O(14) | 1.589 (2) |
| Cd–O(21)′ | 2.446 (2) | P2–O(21) | 1.504 (1) |
| Cd–O(11) | 2.448 (2) | P2–O(22) | 1.489 (2) |
| Cd–O(11)′ | 2.287 (2) | P2–O(23) | 1.581 (2) |
| Cd–O(21) | 2.289 (2) | P2–O(24) | 1.587 (2) |
| Cd–O(12) | 2.227 (2) | | |
| Cd–O$_{av}$ | 2.320 | | |

[a] A prime indicates an atom related by a center of symmetry. A double prime indicates a cadmium in an adjacent unit cell.

**Table IV.** Selected Bond Angles (deg) for $Cd_n[(EtO)_2PO_2]_{2n}$[a]

| | | | |
|---|---|---|---|
| | Cadmium Coordination | | |
| O(11)–Cd–O(11)′ | 84.88 (6) | O(11)–Cd–O(14) | 49.80 (6) |
| O(11)–Cd–O(12) | 98.16 (6) | O(11)–Cd–O(24) | 145.40 (6) |
| O(11)–Cd–O(21) | 164.65 (6) | O(11)′–Cd–O(12) | 153.79 (7) |
| O(11)–Cd–O(21)′ | 82.74 (6) | O(21)′–Cd–O(22) | 153.73 (7) |
| O(11)–Cd–O(22) | 88.82 (6) | | |
| | 8-Membered Rings Cd′–Cd | | |
| O(21)′–Cd–O(22) | 153.73 (5) | O(22)–P(2)–O(21) | 119.3 (1) |
| Cd–O(22)–P(2) | 129.1 (1) | P(2)–O(21)–Cd′ | 131.49 (9) |
| | 8-Membered Rings Cd–Cd″ | | |
| O(11)′–Cd–O(12) | 153.79 (7) | O(12)–P(1)–O(11) | 119.5 (1) |
| Cd–O(12)–P(1) | 128.8 (1) | P(1)–O(11)–Cd″ | 131.39 (9) |
| | 4-Membered Rings Cd′–Cd | | |
| O(11)–Cd–O(11)′ | 84.88 (6) | Cd–O(11)–Cd′ | 95.12 (6) |
| | 4-Membered Rings Cd–Cd″ | | |
| O(21)′–Cd–O(21) | 84.95 (6) | Cd′–O(21)–Cd″ | 95.05 (6) |
| | Phosphates | | |
| O(11)–P(1)–O(12) | 119.5 (1) | O(21)–P(2)–O(22) | 119.3 (1) |
| O(13)–P(1)–O(14) | 105.5 (1) | O(23)–P(2)–O(24) | 105.6 (1) |

[a] A prime indicates an atom related by a center of symmetry. A double prime indicates a cadmium in an adjacent unit cell.

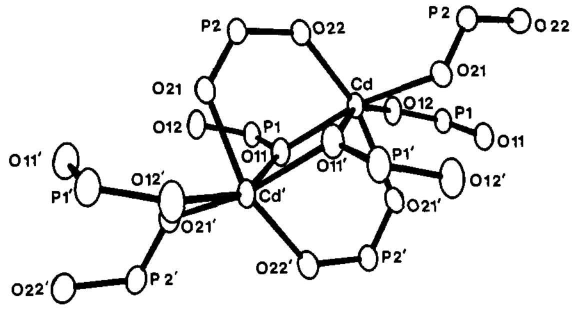

**Figure 1.** ORTEP drawing of the repeating units of cadmium diethyl phosphate showing 50% probability ellipsoids. Ethoxy groups are not shown. Primes indicate atoms related by the center of inversion.

was removed by filtration. Slow evaporation of the remaining ethanol solution resulted in growth of long colorless needles of the desired product. Potassium diethyl phosphate used in the preparation was formed from triethyl phosphate by hydrolysis in 10% ethanolic KOH following the procedure of Kyogoku and Iitaka.[4]

All diffraction measurements were performed on an Enraf-Nonius CAD-4 fully automated four-circle diffractometer using graphite-monochromatized Mo K$\alpha$ radiation. Unit cells were determined from 25 randomly selected reflections by using the CAD-4 automatic search, center, index, and least-squares routines. The space group was assumed to be centric, and the structure was successfully refined in $P\bar{1}$.

All calculations were performed on a DEC PDP 11/23 computer using the Enraf-Nonius SDP program library. The structure was solved by the heavy-atom method. Anomalous dispersion corrections[7a] were added to the neutral-atom scattering factors[7b] used for all non-hydrogen atoms. Full-matrix least-squares refinements minimized the function $\sum w(|F_o| - |F_c|)^2$ where the weighting factor $w = 1/\sigma(F)^2$, $\sigma(F) = \sigma(F_o)^2/2F_o$, and $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (pF_o^2)^2]^{1/2}/Lp$. Crystallographic data and data collection parameters for the structure are listed in Table I.

A crystal of approximate dimensions 0.17 mm × 0.20 mm × 0.50 mm was selected and mounted in a thin-walled glass capillary. The long axis of the crystal was oriented along the $\phi$ axis of the diffractometer with the normal to the 211 plane aligned 3.19° to the $\phi$ axis. From a total of 2776 reflections, 2331 ($F^2 \geq 3.0\ \sigma(F^2)$) were used in the structure solution and refinement. Standard reflections monitored periodically showed only a random (±2%) fluctuation during data collection. Hydrogen atom positions were calculated and included, but not refined. Full-matrix least-squares refinement using anisotropic thermal parameters for the non-hydrogen atoms converged to the final residuals $R_1 = 0.026$ and $R_2 = 0.031$. The largest peak in the final difference Fourier synthesis was 0.61 e/Å$^3$ and was in the vicinity of the metal atoms. The largest value of the shift/error parameter

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(7) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1975; Vol. IV: (a) Table 2.3.1, pp 149–50; (b) Table 2.2B, pp 99–101.

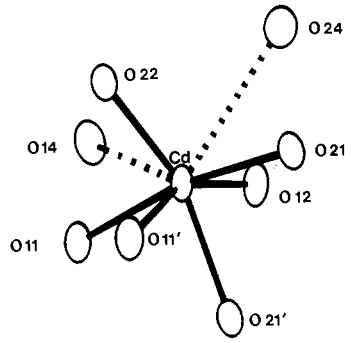

**Figure 2.** Coordination geometry about the cadmium ion.

on the final cycle of refinement was 0.12. The error in an observation of unit weight was 2.27. Final atomic coordinates are listed in Table II. Bond distances and angles with errors from the inverse matrix obtained on the final cycle of least-squares refinement are listed in Tables III and IV.

## Results

The important structural features of a dimeric unit of $Cd_n[(EtO)_2PO_2]_{2n}$ are shown in Figure 1. For clarity, ethoxy groups are not shown. There are two molecules in the unit cell related by a center of inversion. The ions are joined along the *a* axis in an infinite one-dimensional chain. Nonesterified phosphate oxygens either serve directly or serve within a phosphate group as bridging atoms between Cd ions. This is a highly interlocking structure with adjacent Cd ions separated by only 3.50 Å (see Figure 3). The coordination about the Cd is a highly distorted octahedron. The six nonesterified oxygens are at an average distance of 2.32 Å. There are, however, two additional esterified oxygens at 3.16 Å situated at the most open faces of the distorted octahedron, as shown in Figure 2 (and not shown in Figure 1).

## Discussion

The possibility of a direct comparison of the Cd structure to the structures of the Mg and Ba complexes seems remote when viewed at either the unit cell or local coordination level. None of the complexes crystallize in the same space group, and cell constants are drastically different. The Cd complex is effectively 6-coordinate with a distorted octahedral geometry, whereas the Mg and Ba complexes are 4- and 8-coordinate, respectively. When the complexes are viewed at the level of a polymeric chain continuing through several unit cells, however, similarities emerge. Figure 3 allows a comparison of the structures of the three complexes, oriented so that each has a horizontal chain of cations. Ethyl groups and noncoordinated oxygens have been deleted for clarity. All three structures show that the polymer chains of metal ions are strongly linked by phosphate bridges in one direction but with chains held in parallel arrays only by van der Waals interaction between ethyl groups in the other two directions. For the Cd structure, each Cd is linked to preceding and succeeding metals by one four-membered ring involving two bridging oxygens and by one eight-membered ring involving two bridging phosphate groups. This leads to a highly interlocked structure.

The Mg and Ba structures can both be derived from this model of the Cd complex. In the case of the barium structure, the same four- and eight-membered rings are present; however, each barium ion is made 8-coordinate by additional bonds to two esterified phosphate oxygen donors. In the Cd structure, the analogous esterified oxygens can be identified as O(24) and O(14) located at distances of 3.16 and 3.15 Å from the metal. Shortening of these distances coupled with lengthening of distances to nonesterified oxygens will produce the coordination environment found in the Ba structure.

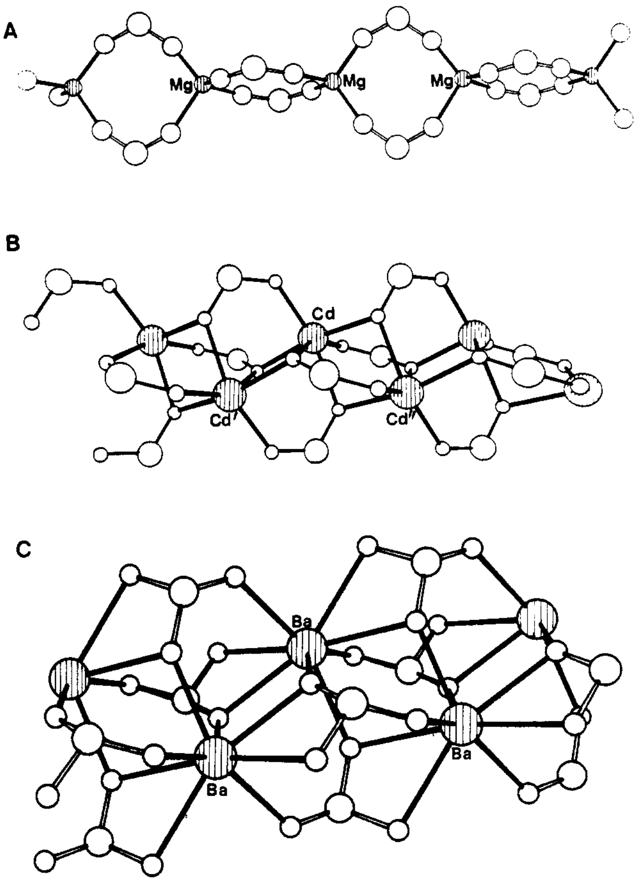

**Figure 3.** Structures of (a) Mg, (b) Cd, and (c) Ba salts of diethyl phosphate. In each case, ethyl groups and noncoordinated oxygens have been omitted. Metal ions are shaded.

The coordination geometry about Mg involves only four oxygens placed in a tetrahedral array. The analogous oxygen atoms can be identified as O(11)′, O(12), O(22), and O(21)′ in the Cd system. These oxygen atoms form the eight-membered bridging rings of the Cd and Ba structures. One of the two bonds from each of the bridging oxygens forming the four-membered rings in the Cd and Ba structure is removed so the O–$Mg^{2+}$ distance is lengthened to 5.6 Å.

The ethyl groups not shown in Figure 3 radiate from the central string of phosphate-linked ions in such a way as to form a hydrophobic exterior. This is the case in all three structures, but there are minor differences in ethyl conformation and packing of the parallel arrays of ion channels.

Perhaps the most interesting difference in the structure lies in the metal–metal spacing and the closely related phosphate–phosphate spacing along the chain axis. The metal–metal spacing in the Cd complex is in fact shortest at 3.5 Å, compared to 4.2 and 4.7 Å in the Ba and Mg cases, respectively. Differences in separation of phosphates in a direction parallel to the chain axis are even more pronounced, 5.3 Å in the Cd complex compared to 6.0 and 9.3 Å in the Ba and Mg cases.

Packing of phosphate ester head groups relative to lipid acyl chains in phospholipid systems has often been considered a key factor in determining preferred phospholipid phases. Most phosphoglycerides on dispersion in water spontaneously form the lamellar phases common to biological membranes. Other phases such as a hexagonal phase can exist and have been suggested as important entities for transport, interaction with membrane protein, and membrane–membrane fusion.[8]

The conditions under which head groups occupy a small interfacial area in comparison to the cross-sectional area of lipid acyl chains have been suggested to promote the formation

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(8) Cullis, P. R.; De Kruijff, B. *Biochim. Biophys. Acta* **1979**, *559*, 399–420.

of hexagonal phases.[8] Low-angle X-ray scattering studies of cardiolipin–divalent cation complexes with $Ca^{2+}$, $Mg^{2+}$, and $Ba^{2+}$ have been carried out, but unfortunately $Cd^{2+}$ studies have not. Nevertheless, $Ca^{2+}$ in comparison to $Mg^{2+}$ and $Ba^{2+}$ is found to promote a particularly small area per head group. On the basis of measured spacing between cylinders and estimated partial specific volume of the lipid, an area of 29 $Å^2$ is found. The $Mg^{2+}$ and $Ba^{2+}$ complexes have areas of 38 and 39 $Å^2$, respectively.[9] Preferential formation of hexagonal phases with $Ca^{2+}$ have been explained on this basis.

The parallel rows of bridged cations found in the crystals discussed here are very reminiscent of the arrays of long aqueous channels separated by hydrophobic acyl chains that characterize lipid hexagonal phases. It is instructive, therefore, to view our structures on the basis of a surface area per phosphate at the boundaries of the ion channels. We will define a cylindrical surface passing through all phosphorus atoms. Mg, Cd, and Ba structures have cylinder diameters of 4.6, 5.4, and 5.7 Å and surface areas of 34, 22, and 27 $Å^2$ per phosphate, respectively. The minimum area for Cd and the similarity in magnitude to values observed for the lipid phases in which $Ca^{2+}$ rather than $Cd^{2+}$ was studied suggest that coordination geometries found in simple phosphate complexes may extend to even complex lipid systems. Moreover, these geometries may be at the heart of $Ca^{2+}$ and $Cd^{2+}$ selectivity in membrane transformations. Anticipated work applying $^{113}Cd$ solid NMR techniques to crystalline Cd complexes and lipid dispersions should allow testing of this possibility.

**Acknowledgment.** This work was supported by a grant from the National Institutes of Health, GM 19035, and benefited from an equipment grant from the National Science Foundation.

**Registry No.** $Cd[(EtO)_2PO_2]_2$, 17071-46-4.

**Supplementary Material Available:** A table including *h*, *k*, *l*, $F_o$, and $F_c$ for all reflections collected along with a list of anisotropic thermal parameters (11 pages). Ordering information is given on any current masthead page.

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Contribution from the Istituto di Chimica Generale and Istituto di Chimica Analitica ed Elettrochimica, University of Pisa, 56100 Pisa, Italy, and Istituto di Chimica Generale, University of Parma, 43100 Parma, Italy

# Studies on Carbonyl Derivatives of Early Transition Elements. A Convenient Method for the Preparation of the $[Nb(CO)_6]^-$ Anion at Atmospheric Pressure and Room Temperature. Crystal and Molecular Structure of $[M(CO)_6]^-$ (M = Nb, Ta) as Their Bis(triphenylphosphine)nitrogen(1+) Derivatives

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*Received August 30, 1982*

A new method is reported for the preparation of $[Nb(CO)_6]^-$ and $[Ta(CO)_6]^-$ by reductive carbonylation of $M_2Cl_{10}$ (M = Nb, Ta) with the magnesium–zinc–pyridine–CO system. In the case of niobium, the reductive carbonylation occurs at atmospheric pressure and room temperature with yields as high as 48%. The tetrahydrofuran-stabilized sodium derivatives $[Na(THF)][M(CO)_6]$ and the bis(triphenylphosphine)nitrogen(1+) derivatives, $PPN[M(CO)_6]$ (M = Nb, Ta), are reported. The crystal and molecular structures of both niobium and tantalum $PPN[M(CO)_6]$ complexes are described. Both compounds are isostructural with the corresponding vanadium derivative: rhombohedral, space group $R\bar{3}$, one molecule per cell; M = Nb, $a = 9.832$ (4) Å, $\alpha = 91.98$ (5)°, $V = 948.7$ (7) $Å^3$, $\rho_{calcd} = 1.399$ g $cm^{-3}$, $R = 0.0391$; M = Ta, $a = 9.814$ (4) Å, $\alpha = 92.02$ (8)°, $V = 943.4$ (7) $Å^3$, $\rho_{calcd} = 1.562$ g $cm^{-3}$, $R = 0.0294$ (Mo K$\alpha$, $\lambda = 0.71069$ Å). The geometry of the two hexacarbonylmetalates is that of an almost perfect octahedron. Chemical and spectroscopic comparisons of the three $[M(CO)_6]^-$ (M = V, Nb, Ta) anions are made.

The chemistry of binary carbonyl derivatives of group 5 metals, especially of niobium and tantalum, is still largely unknown. Vanadium in this group is known to give a neutral compound, namely $V(CO)_6$,[2] while for niobium and tantalum, the hexacarbonylmetalates only, $[M(CO)_6]^-$ (M = Nb, Ta), were reported.[3] The synthesis of $V(CO)_6$ requires the preliminary preparation of $[V(CO)_6]^-$, which can be carried out by reductive carbonylation at elevated temperature and pressure with magnesium–zinc–diiodine in pyridine[4] or with sodium metal in diglyme as solvent.[3] Similarly, all the known methods to produce $[Nb(CO)_6]^-$ require the reduction of $Nb_2Cl_{10}$ by sodium[3] or by the Na–K alloy[5] in diglyme as solvent at superatmospheric pressure of CO. While the carbonylation yield of vanadium is around 80%, the reported yields[5] of $[K(CH_3O(CH_2)_2O(CH_2)_2OCH_3)_3][M(CO)_6]$ (M = Nb, Ta) are 14%.

This paper reports new and simple procedures for preparing the $[M(CO)_6]^-$ (M = Nb, Ta) anions, the former at atmospheric pressure in good yields, and the crystal and molecular structures of both hexacarbonylmetalates as their bis(triphenylphosphine)nitrogen(1+), hereinafter abbreviated as PPN, derivatives, $PPN[M(CO)_6]$. Preliminary results of the structure of $PPN[Nb(CO)_6]$ have been reported in an earlier publication.[6] Whenever possible, comparisons among the hexacarbonylmetalate(−I) anions of group 5 elements are made.

## Experimental Section

Unless otherwise stated, all of the operations were carried out, with the exclusion of air, under carbon monoxide or argon. Commercially

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