Table IV. Positional Parameters

atom	*x*	*y*	*z*
Cu	0.8443 (1)	0.0390 (2)	0.5323 (1)
C(1)	0.9250 (4)	−0.0611 (17)	0.5823 (7)
O(1)	0.9760 (3)	−0.1182 (22)	0.6129 (8)
S	0.7037 (1)	−0.0533 (3)	0.6036 (1)
O(2)	0.7699 (2)	0.0471 (9)	0.6198 (3)
O(3)	0.6635 (3)	0.0716 (8)	0.5194 (3)
O(4)	0.7015 (2)	−0.3441 (9)	0.5927 (3)
C(2)	0.6694 (4)	0.0243 (13)	0.7141 (5)
C(3)	0.6021 (4)	−0.0828 (19)	0.7118 (7)
H(1)	0.679 (3)	0.245 (15)	0.723 (5)
H(2)	0.706 (3)	−0.062 (14)	0.764 (5)
H(3)	0.568 (4)	−0.029 (16)	0.675 (6)
H(4)	0.609 (4)	−0.291 (17)	0.701 (5)
H(5)	0.590 (4)	−0.027 (16)	0.775 (6)

for several hours. When there was no evidence of the CO complex remaining, the white solid that had formed was isolated by filtration. After the solid was washed with additional THF and pentane and then dried, 0.6 g of product was obtained.

$Cu_2(COD)(CH_3SO_3)_2$ and $Cu_2(COD)_3(CH_3SO_3)_2$. A solution of 1 g (9.24 mmol) of 1,5-cyclooctadiene in 25 mL of methylene chloride was added dropwise to a suspension of 1.72 g (9.22 mmol) of $Cu(CO)CH_3SO_3$ in 50 mL of methylene chloride, and the mixture was stirred at room temperature overnight. The white solid that resulted was filtered off, washed with methylene chloride, and dried. A 1.0-g yield of product identified as $Cu_2(COD)(CH_3SO_3)_2$ was obtained. The filtrate was evaporated to dryness and the white solid residue washed several times with pentane and dried. The yield of $Cu_2(COD)_3(CH_3SO_3)_2$ was 1.3 g.

X-ray Diffraction Data. A pale green crystal of $Cu(CO)C_2H_5SO_3$ with approximate dimensions of 0.20 × 0.25 × 0.30 mm was selected for the experiment and was mounted in a thin-walled glass capillary. Initially, 25 reflections were automatically located and centered on an Enraf-Nonius CAD4 diffractometer using Mo Kα (λ = 0.71073 Å) radiation. A least-squares fit of the 2θ values of these reflections gave a monoclinic unit cell with dimensions of a = 20.630 (4) Å, b = 5.004 (1) Å, c = 13.410 (3) Å, and β = 97.42 (2)°.[18]

Data were collected in the range $2\theta \leq 50°$ by utilizing the diffractometer in an ω–2θ scan mode with a variable scan rate of 2–13° in 2θ/min. The scan of each intensity was begun 1.0° below the Kα_1 angle and terminated 1.0° above the Kα_2 angle, with a total background counting time equal to half the total scan time and evenly divided on each side of the reflection peak. A total of 1202 unique diffraction maxima were measured, of which 802 were considered to be observed ($I \geq 2\sigma(I)$). Three reflections were monitored at periodic intervals throughout the data collection to ensure that the crystal was not deteriorating and no significant intensity changes were observed.

A calculated density of 1.94 g/cm^3 was obtained for Z = 8 with a unit cell volume of 1372.7 Å^3 and a formula weight of 200.7 for $CuC_3H_5SO_3$. The systematic extinctions ($h0l$, $l = 2n$; hkl, $h + k = 2n$) and the density considerations were consistent with the monoclinic space group $C2/c$ and one $Cu(CO)C_2H_5SO_3$ group per asymmetric unit. Absorption corrections were not applied to the data since inspection of the φ-scan data revealed the effect to be negligible.

The positions of the copper and sulfur atoms in the complex were located by interpretation of a three-dimensional Patterson synthesis. The remaining atoms were located in subsequent difference Fourier maps. Full-matrix least-squares refinement of atomic parameters with anisotropic thermal parameters for all non-hydrogen atoms and fixed isotropic temperature factors for the hydrogen atoms converged to the standard crystallographic residuals of R = 4.5% and R_w = 5.7%. The quantity minimized in the least-squares refinement was $\sum w(|F_o| - |F_c|)^2$ where $w = \sigma(F_o)^{-2}$ and $\sigma(F_o) = \sigma(I)/2|F_o|Lp$, where L and p are the Lorentz and polarization corrections. The largest peak in the final difference Fourier synthesis had an electron density equal to 0.7 e/Å^3. Table IV gives a list of the atomic coordinates.

Registry No. $Cu(CO)CF_3SO_3$, 81967-72-8; $Cu(CO)C_2H_5SO_3$, 86689-38-5; $Cu(CO)CH_3SO_3$, 86689-26-1; $Cu(CO)CH_3C_6H_4SO_3$, 81967-73-9; $Cu(bpy)(CO)CF_3SO_3$, 86689-27-2; $Cu(tmed)(CO)CH_3SO_3$, 86689-28-3; $Cu(phen)(CO)CF_3SO_3$, 86689-29-4; $Cu(C_2H_4)CH_3SO_3$, 86689-30-7; $Cu(C_7H_{10})CH_3SO_3$, 86689-31-8; $Cu_2(PhC{\equiv}CPh)_3(CH_3SO_3)_2$, 86689-32-9; $Cu_2(COD)_3(CF_3SO_3)_2$, 86689-33-0; $Cu_2(COD)_3(CH_3SO_3)_2$, 86689-34-1; $Cu_2(C_3H_7C{\equiv}CCH_3)(CH_3SO_3)_2$, 86689-35-2; $Cu_2(C_7H_8)(CH_3SO_3)_2$, 86689-36-3; Cu_2O, 1317-39-1.

Supplementary Material Available: Tables of thermal parameters and observed and calculated structure factors (5 pages). Ordering information is given on any current masthead page.

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[18] All calculations were performed with use of the Enraf-Nonius structure determination package, an integrated set of crystallographics computer programs for PDP II series computers.

Contribution from the Department of Chemistry,
Lehigh University, Bethlehem, Pennsylvania 18105

Syntheses and Crystal and Molecular Structures of $M_6(Ph_2PCH_2CH_2CO_2)_{12}$ (M = Ni(II), Co(II))

GREGG E. LEWIS and CHARLES S. KRAIHANZEL*

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The isostructural complexes $M_6(Ph_2PCH_2CH_2CO_2)_{12}$ (M = Ni(II), Co(II)) have been prepared by the interfacial reaction of solutions of $Ph_2PCH_2CH_2CO_2H$ in CH_2Cl_2 and $M(NO_3)_2$ in aqueous $NaHCO_3$. Satisfactory crystals of the Ni(II) and Co(II) complexes were obtained from CH_2Cl_2/C_6H_{14} and acetone, respectively. The complexes crystallize in space group $R\bar{3}$ with Z = 3. For M = Ni(II): $a = b$ = 27.559 (5) Å, c = 21.607 (4) Å, V = 14212 (8) Å^3, ρ(calcd) = 1.205 g cm^{-3} with mol wt 3439.3. For M = Co(II): $a = b$ = 27.597 (4) Å, c = 21.425 (4) Å, V = 14131 (7) Å^3, ρ(calcd) = 1.213 g cm^{-3} with mol wt 3440.6. The common structure is based on a M_6O_6 ring with a nearly octahedral field of five oxygen atoms and one phosphorus atom about each M. Half of the $Ph_2PCH_2CH_2CO_2^-$ is coordinated through the carboxylato oxygens to two M sites (average M–O = 2.04 ± 0.03 Å) in a conventional syn–syn manner, with the phosphorus donor site remaining uncoordinated. The other $Ph_2PCH_2CH_2CO_2^-$ ligands chelate the metal sites through P and O2 with M–O2 = 2.128 (3) and 2.169 (5) Å for Ni(II) and Co(II), respectively. The carboxylato oxygen O2 also bridges to a second metal site with M′–O2 = 2.069 (3) and 2.116 (5) Å for Ni(II) and Co(II), respectively. The second carboxylato oxygen atom (O1) bridges to still a third metal atom (M–O1 = 2.034 (3) and 2.037 (5) Å for Ni(II) and Co(II), respectively) to complete a η^3 bonding scheme. The M–M distances of 3.510 (1) Å for Ni(II) and 3.557 (1) Å for Co(II) preclude any type of direct metal–metal bonding.

Introduction

Individually, tertiary phosphines and carboxylate anions constitute two important and well-studied classes of ligands. Frequently, both types of ligands are incorporated into the same complex,[1-3] and in recent years ligands containing both functions have gained attention.[4-26] The bifunctional ligands

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[1] Marko, L. *Pure Appl. Chem.* **1979**, *51*, 2211.

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Table I. Crystallographic Data and Data Collection Procedures

formula	$Ni_6P_{12}O_{24}C_{180}H_{168}$	$Co_6P_{12}O_{24}C_{180}H_{168}$
mol wt	3439.3	3440.6
space group	$R\bar{3}$	$R\bar{3}$
a, Å	27.559 (5)	27.597 (4)
b, Å	27.559 (5)	27.597 (4)
c, Å	21.607 (4)	21.425 (4)
V, Å^3	14212 (8)	14131 (7)
Z	3	3
d(calcd), g/cm^3	1.205	1.213
μ(Mo Kα), cm^{-1}	7.438	6.730
cryst size, mm	0.3 × 0.3 × 0.3	0.5 × 0.5 × 0.5
diffractometer	Enraf-Nonius CAD4	Enraf-Nonius CAD4
radiation; graphite monochromated	Mo Kα ($\lambda_\alpha = 0.71073$ Å)	Mo Kα ($\lambda_\alpha = 0.71073$ Å)
collecn range	$+h, +k, \pm l$; $0 \leq 2\theta \leq 45°$	$+h, +k, \pm l$; $0 \leq 2\theta \leq 45°$
aperture width	$0.65 + 0.35 \tan\theta$	$0.8 + 0.35 \tan\theta$
max counting time, s	30	30
X-ray exposure time, h	33.2	32.8
cryst decomp, %	0	0
no. of unique data	4168	4204
no. of data with $I \geq 3\sigma(I)$	2597	1950
p	0.05	0.05
no. of variables	334	304
R_1	0.057	0.074
R_2	0.075	0.089
esd	2.082	2.217
largest shift[a]	0.00	0.01
largest peak,[b] e/Å^3	0.62	0.60

[a] Largest Δ_i/σ_i ratio in final refinement cycle. [b] Largest peak in a final difference Fourier.

are of particular interest because they may (i) coordinate to a metal in unidentate fashion (P or O), (ii) form chelate complexes (P,O), or (iii) bridge metal sites (P,O or O,O). Among the most intensely studied phosphine-substituted carboxylic acids, and their respective carboxylate anions, are $Ph_{3-n}P(CH_2CO_2H)_n$[4-18], $P(CH_2CH_2COOH)_3$,[19] $(HO_2CCH_2)_2PCH_2CH_2P(CH_2CO_2H)_2$,[20-23] and $(HO_2CCH_2)(Ph)PCH_2CH_2P(Ph)(CH_2CO_2H)$.[24-26] Spectral and other analytical procedures have been interpreted to show that phosphinoacetic acids bind in either a unidentate manner (P or O) or in chelating fashion depending upon the binding characteristics of the metal (soft vs. hard) and the pH of the solution. However, unequivocal structural evidence for the modes of binding of phosphinoacetic acids is limited. Exclusive P coordination of diphenylphosphinoacetic acid is found in dibromobis(diphenylphosphinoacetic acid)palladium(II).[18] In bis(diphenylphosphinoacetato)palladium(II) the anionic ligands both chelate the metal.[17] Both modes of binding are observed in bromo(diphenylphosphinoacetato)(diphenylphosphinoacetic acid)platinum(II).[16] Exclusive coordination of the carboxylato donor group has been suggested to occur in solution but has not been observed to date.

As a part of our studies on organofunctionalized phosphines, a general synthetic procedure has been developed for ω-(diphenylphosphino)alkanoic acids, $Ph_2P(CH_2)_nCOOH$ (n = 2–8, 11).[27] Although these substances form several different types of complexes,[28] this paper focuses upon the syntheses and unusual molecular structures of the two new complexes $M_6(Ph_2P(CH_2)_2CO_2)_{12}$, where M = Ni(II) and Co(II).

Experimental Section

Synthesis and Crystallization of $M_6(Ph_2PCH_2CH_2CO_2)_{12}$ (M = Ni(II), Co(II)). A solution of $Ph_2PCH_2CH_2CO_2H$ (0.02 mol) in CH_2Cl_2 (50 mL) was shaken vigorously with an aqueous solution (50 mL) containing $NaHCO_3$ (0.03 mol) and $M(NO_3)_2 \cdot 6H_2O$ (0.01 mol) (M = Ni(II), Co(II)) until the metal ion had been extracted into the organic layer as evidenced by the loss of color from the aqueous layer. The deeply colored CH_2Cl_2 layer was separated, dried with anhydrous $MgSO_4$, filtered, and evaporated to dryness to leave the crude product in nearly quantitative yield.

Well-formed green crystals of $Ni_6(Ph_2PCH_2CH_2CO_2)_{12}$ were obtained by the slow cooling of a methylene chloride/hexane solution. Large violet crystals of the cobalt analogue formed slowly upon recrystallization from acetone under nitrogen. The Co(II) complex does not appear to be oxygen sensitive.

Collection and Reduction of X-ray Data. The crystallographic studies were conducted in the same manner for both compounds. Suitable crystals were mounted on glass fibers with epoxy cement and placed on an Enraf-Nonius CAD4 diffractometer. Least-squares refinement of 25 intense reflections in the range 20° < 2θ < 30° gave

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Table II. Positional Parameters and Their Estimated Standard Deviations for $Ni_6(Ph_2PCH_2CH_2CO_2)_{12}$ and $Co_6(Ph_2PCH_2CH_2CO_2)_{12}$[a]

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
			$Ni_6(Ph_2PCH_2CH_2CO_2)_{12}$				
Ni	0.09839 (3)	−0.02796 (3)	0.03499 (4)	C21	0.1419 (3)	−0.1183 (2)	0.1179 (3)
P1	0.10841 (6)	−0.07592 (7)	0.1261 (1)	C22	0.1911 (3)	−0.0953 (3)	0.0827 (4)
P2	0.11852 (8)	−0.25660 (8)	−0.0669 (1)	C23	0.2209 (3)	−0.1240 (3)	0.0763 (5)
O1	−0.0657 (1)	−0.0913 (2)	0.0941 (2)	C24	0.2008 (3)	−0.1754 (3)	0.1053 (5)
O2	0.0100 (1)	−0.0801 (1)	0.0437 (2)	C25	0.1514 (4)	−0.1991 (3)	0.1393 (5)
O3	0.1082 (2)	−0.0820 (2)	−0.0189 (2)	C26	0.1199 (3)	−0.1714 (3)	0.1451 (4)
O4	0.0242 (1)	−0.1600 (2)	−0.0295 (2)	C31	0.0846 (3)	−0.2739 (3)	−0.1417 (4)
C1	−0.0190 (2)	−0.0879 (2)	0.0923 (3)	C32	0.1142 (3)	−0.2802 (3)	−0.1909 (4)
C2	0.0025 (2)	−0.0946 (3)	0.1544 (3)	C33	0.0913 (4)	−0.2965 (3)	−0.2494 (5)
C3	0.0361 (2)	−0.1271 (3)	0.1470 (4)	C34	0.0382 (4)	−0.3036 (4)	−0.2609 (5)
C4	0.0766 (2)	−0.1331 (2)	−0.0325 (3)	C35	0.0089 (4)	−0.2957 (4)	−0.2135 (6)
C5	0.1060 (2)	−0.1640 (2)	−0.0569 (4)	C36	0.0318 (3)	−0.2826 (4)	−0.1533 (5)
C6	0.0834 (3)	−0.2225 (2)	−0.0281 (4)	C41	0.0842 (4)	−0.3246 (3)	−0.0274 (5)
C11	0.1385 (3)	−0.0392 (3)	0.1988 (4)	C42	0.1082 (6)	−0.3270 (4)	0.0277 (7)
C12	0.1733 (3)	0.0182 (3)	0.1968 (4)	C43	0.0890 (9)	−0.3736 (6)	0.0661 (10)
C13	0.1981 (4)	0.0480 (4)	0.2512 (5)	C44	0.0400 (6)	−0.4209 (5)	0.0422 (7)
C14	0.1876 (4)	0.0210 (4)	0.3064 (5)	C45	0.0128 (7)	−0.4226 (4)	−0.0136 (7)
C15	0.1526 (4)	−0.0380 (5)	0.3091 (5)	C46	0.0362 (5)	−0.3713 (4)	−0.0497 (6)
C16	0.1271 (4)	−0.0693 (4)	0.2547 (4)				
			$Co_6(Ph_2PCH_2CH_2CO_2)_{12}$				
Co	0.09981 (5)	−0.02749 (5)	0.03617 (8)	C21	0.1420 (4)	−0.1192 (4)	0.1212 (5)
P1	0.1082 (1)	−0.0772 (1)	0.1301 (2)	C22	0.1921 (4)	−0.0951 (5)	0.0860 (6)
P2	0.1182 (1)	−0.2577 (1)	−0.0661 (2)	C23	0.2203 (5)	−0.1238 (6)	0.0797 (8)
O1	−0.0654 (2)	−0.0913 (3)	0.0949 (3)	C24	0.2005 (5)	−0.1759 (6)	0.1067 (8)
O2	0.0099 (2)	−0.0805 (2)	0.0457 (3)	C25	0.1524 (6)	−0.2007 (5)	0.1420 (8)
O3	0.1083 (3)	−0.0822 (3)	−0.0188 (4)	C26	0.1190 (5)	−0.1736 (5)	0.1487 (7)
O4	0.0258 (3)	−0.1597 (2)	−0.0302 (4)	C31	0.0858 (4)	−0.2732 (4)	−0.1408 (7)
C1	−0.0192 (4)	−0.0891 (4)	0.0940 (5)	C32	0.1145 (5)	−0.2799 (4)	−0.1899 (7)
C2	0.0034 (4)	−0.0961 (5)	0.1572 (5)	C33	0.0902 (6)	−0.2950 (5)	−0.2508 (7)
C3	0.0358 (4)	−0.1283 (4)	0.1504 (6)	C34	0.0374 (6)	−0.3027 (6)	−0.2653 (9)
C4	0.0784 (4)	−0.1322 (4)	−0.0332 (5)	C35	0.0095 (7)	−0.2938 (7)	−0.2172 (10)
C5	0.1077 (4)	−0.1637 (4)	−0.0570 (6)	C36	0.0323 (6)	−0.2821 (7)	−0.1532 (8)
C6	0.0833 (4)	−0.2225 (4)	−0.0257 (6)	C41	0.0815 (6)	−0.3281 (6)	−0.0289 (8)
C11	0.1371 (4)	−0.0413 (5)	0.2029 (6)	C42	0.1091 (9)	−0.3249 (9)	0.0276 (11)
C12	0.1739 (5)	0.0165 (5)	0.2014 (8)	C43	0.0793 (11)	−0.3829 (11)	0.0690 (14)
C13	0.1967 (7)	0.0448 (6)	0.2592 (9)	C44	0.0359 (8)	−0.4228 (8)	0.0387 (10)
C14	0.1837 (7)	0.0178 (6)	0.3129 (9)	C45	0.0093 (9)	−0.4246 (9)	−0.0135 (11)
C15	0.1503 (7)	−0.0381 (8)	0.3153 (8)	C46	0.0348 (8)	−0.3689 (8)	−0.0568 (10)
C16	0.1235 (6)	−0.0725 (7)	0.2595 (7)				

[a] Estimated standard deviations in the least significant digits are shown in parentheses. C11 through C46 are phenyl carbon atoms.

an orientation matrix for calculation of setting angles and cell parameters. An *R*-centered hexagonal cell, later shown by the Patterson map and successful refinement to belong to the space group $R\bar{3}$, was used. The cell parameters are presented in Table I.

Solution and Refinement of the Structures. $\mathbf{Ni_6[(C_6H_5)_2PCH_2CH_2CO_2]_{12}}$. This compound crystallizes in the space group $R\bar{3}$, with each molecule sitting about a $\bar{3}$ axis and the Ni atoms occupying general positions. One nickel atom and two of the ligands constitute the asymmetric unit. The structure was solved by Patterson and Fourier methods and refined[29] by the full-matrix least-squares procedure. The position of the Ni atom was obtained through a three-dimensional Patterson synthesis. Three cycles of isotropic least-squares refinement gave values of $R_1 = 0.47$ and $R_2 = 0.55$ where the R_i are defined as

$$R_1 = \sum(||F_o| - |F_c||)/\sum|F_o|$$

$$R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w(|F_o|)^2]^{1/2}$$

Further least-squares cycles and difference Fourier maps located all 36 remaining non-hydrogen atoms. Isotropic refinement of the atom positions gave discrepancy indices of $R_1 = 0.110$ and $R_2 = 0.149$. Anisotropic refinement including all atoms (except hydrogen) led to convergence at $R_1 = 0.057$ and $R_2 = 0.075$. No attempt was made to include hydrogen atoms in this study.

$\mathbf{Co_6[(C_6H_5)_2PCH_2CH_2]_{12}}$. This Co(II) compound is isomorphous with the Ni(II) compound and was found to be isostructural as shown by successful refinement using the positional parameters from the Ni(II) structure. Relevant crystal and experimental data are listed in Table I.

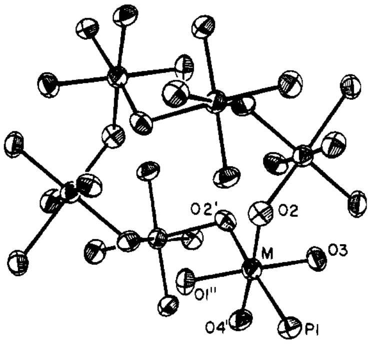

Figure 1. ORTEP drawing of the $M_6O_{24}P_6$ core.

The final atomic positional parameters for the nickel and cobalt compounds are listed in Table II. The thermal parameters and values of F_o vs. F_c are available as supplementary material.

Results and Discussion

The molecular structures of green $Ni_6(Ph_2PCH_2CH_2CO_2)_{12}$ and violet $Co_6(Ph_2PCH_2CH_2CO_2)_{12}$ are remarkably alike. The final atomic coordinates for the two complexes are listed in Table II. Pertinent bond distances and bond angles are given in Table III.

The foundation for the molecular structure is the M_6O_6 ring shown in Figure 1. Each metal ion is surrounded by a nearly

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[29] The crystallographic programs of the Enraf-Nonius Structure Determination Package were employed in the structural solutions and their refinement. A PDP 11/45 computer at B. A. Frenz and Associates, College Station, TX, was used for the calculations.

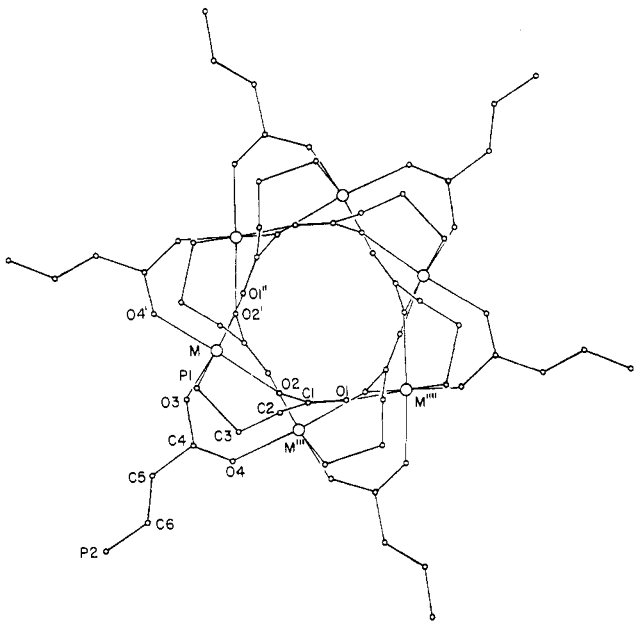

Figure 2. Schematic representation of the $M_6(Ph_2PCH_2CH_2CO_2)_{12}$ molecule, showing the atom-labeling scheme. All phenyl carbons have been omitted for clarity.

octahedral field of five oxygens from carboxylato groups and a single phosphorus atom. The octahedral ligand fields and long M–M distances preclude direct M–M bonding in the complexes.

The twelve 3-(diphenylphosphino)propionato ligands are divided into two groups of six according to their mode of bonding. As can be seen in Figure 2, the more simply described type of ligand has a free phosphorus atom (P2) at the end of the alkane chain (C5,C6). The carboxylato group is bound in a commonly seen fashion as the oxygens (O3 and O4) bridge two metal atoms (M and M''') in a slightly unsymmetrical syn–syn configuration. These ligands are positioned alternately above and below the plane of Figure 2 as a result of the sixfold improper rotation axis perpendicular to the plane. There is nothing unusual regarding the bond distances and bond angles in these ligands.

The mode of binding of the second group of ligands is more complex. An examination of Figure 2 shows these ligands to chelate the metal atoms through phosphorus (P1) and oxygen (O2) with M–O2 distances of 2.128 (3) and 2.169 (5) Å for the Ni(II) and Co(II) complexes, respectively. This same oxygen bridges to a second metal (M''') with slightly shorter respective distances of 2.069 (3) and 2.116 (5) Å. Further binding of the second carboxylato oxygen atom (O1) is seen to a third metal site (M''''). These latter bonds of 2.034 (3) and 2.037 (5) Å for Ni(II) and Co(II), respectively, are almost as short as the M–O3 and M–O4 of the nonchelated ligands and complete a η^3 bonding mode. A close examination of the stereoscopic diagram in Figure 1 shows the M''''–O1 and M'''–O2 bonding to be of a syn–syn type. The positioning of the M''''–O1 and M–O2 bonds is syn–anti. The observed M''''–O1 distances are consistent with the binding to a single metal site while the longer M'''–O2 and M–O2 bonds are consistent with the bridging nature of the M'''–O2–M portion of the molecule. The ability of a carboxylato ligand to bind simultaneously to three different sites has been observed previously in $Mn(CH_3CO_2)_2 \cdot 4H_2O$[30] and $Na_4(VO)_2(CF_3CO_2)_8(THF)_6(H_2O)_2$.[31]

Table III. Bond Distances (Å) and Bond Angles (deg) in $M_6(Ph_2PCH_2CH_2CO_2)_{12}$ As Labeled in Figure 2[a,b]

	Ni(II)	Co(II)
	Distances	
M–M'''	3.510 (1)	3.557 (1)
–P1	2.463 (2)	2.511 (3)
–O1''	2.034 (3)	2.037 (5)
–O2'	2.069 (3)	2.116 (5)
–O2	2.128 (3)	2.169 (5)
–O3	2.013 (3)	2.018 (5)
–O4'	2.069 (3)	2.072 (5)
P1–C3	1.831 (5)	1.832 (8)
–C11	1.827 (6)	1.81 (1)
–C21	1.824 (5)	1.82 (3)
P2–C6	1.852 (5)	1.887 (8)
–C31	1.807 (7)	1.78 (2)
–C41	1.835 (8)	1.86 (2)
O1–C1	1.243 (6)	1.247 (9)
O2–C1	1.271 (6)	1.259 (9)
O3–C4	1.264 (6)	1.242 (9)
O4–C4	1.251 (6)	1.259 (9)
C1–C2	1.515 (7)	1.54 (1)
C2–C3	1.585 (7)	1.55 (1)
C4–C5	1.536 (7)	1.54 (1)
C5–C6	1.539 (7)	1.56 (1)
	Angles	
M–M'''–M''''	102.81 (2)	102.43 (4)
P1–M–O1''	88.0 (1)	88.6 (2)
–O2'	177.8 (1)	176.7 (2)
–O2	87.95 (9)	86.8 (1)
–O3	88.4 (1)	89.0 (2)
–O4'	91.3 (1)	93.0 (2)
O1''–M–O2'	94.2 (1)	94.2 (2)
–O2	86.7 (1)	85.6 (2)
–O3	176.1 (1)	177.6 (2)
–O4'	91.3 (1)	91.6 (2)
O2–M–O2'	92.1 (2)	91.7 (2)
–O3	94.8 (1)	94.1 (2)
–O4'	177.9 (1)	177.2 (2)
O2'–M–O3	89.3 (1)	88.3 (2)
–O4'	88.7 (1)	88.7 (2)
O3–M–O4'	87.2 (1)	88.7 (2)
M–P1–C3	103.8 (2)	104.3 (3)
–C11	122.1 (2)	121.9 (3)
–C21	119.7 (2)	118.6 (7)
C3–P1–C11	103.5 (3)	103.3 (4)
–C21	103.6 (3)	104.0 (6)
C11–P1–C21	101.7 (3)	102.4 (6)
C6–P2–C31	102.0 (3)	102.2 (8)
–C41	100.1 (3)	101.0 (8)
C31–P2–C41	102.2 (4)	100.9 (8)
M''''–O1–C1	139.3 (4)	140.8 (6)
M–O2–M'''	113.5 (2)	112.2 (2)
–C1	126.8 (3)	127.7 (5)
–O2'–C1'	119.5 (3)	119.8 (5)
–O3–C4	133.2 (3)	135.6 (6)
M'''–O4–C4	125.7 (3)	126.1 (5)
O1–C1–O2	125.3 (5)	124.2 (8)
–C2	114.6 (5)	116.8 (8)
O2–C1–C2	120.1 (5)	119.0 (8)
C1–C2–C3	110.7 (4)	112.1 (7)
P1–C3–C2	108.0 (4)	107.4 (6)
O3–C4–O4	126.7 (5)	125.7 (8)
–C5	115.8 (5)	117.7 (8)
O4–C4–C5	117.4 (5)	116.7 (8)
C4–C5–C6	113.2 (4)	111.6 (7)
P2–C6–C5	107.9 (4)	105.9 (6)

[a] Estimated standard deviations in the least significant digits are shown in parentheses. [b] Bond distances and bond angles for phenyl rings are listed in the supplementary material. Carbon atoms C11, C21, C31, C41 shown in this table correspond to the phenyl carbons to which phosphorus is attached.

In addition to the unusual η^3 bonding of the carboxylato groups discussed above, the two complexes of interest are also unusual because of the two different modes of attachment of the $Ph_2PCH_2CH_2CO_2^-$ ligands. Presumably, with the divalent

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metal ions, the preference for maintaining a ligand field with as many hard-base donor ligands as possible appears to be thermodynamically more favorable than formation of smaller molecular weight units with more M–P bonding. The fact that these complexes are unique in their high molecularity without leading to insoluble polymers should be noted inasmuch as simple molecular carboxylato complexes containing more than four metal atoms appear to be unknown.[32]

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Registry No. $Ni_6(Ph_2PCH_2CH_2CO_2)_{12}$, 86711-95-7; $Co_6(Ph_2PCH_2CH_2CO_2)_{12}$, 86711-96-8.

Supplementary Material Available: A stereoscopic view of the $M_6(Ph_2PCH_2CH_2CO_2)_{12}$ molecules and tables of structure factors, thermal vibration parameters, and bond distances and angles in the phenyl rings (28 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry,
The University of North Carolina, Chapel Hill, North Carolina 27514

Synthesis of 4-Methylthiazole Complexes of Copper(II) Chloride. Structure of a Mixed-Valent Dimer, $Cu^{II}Cu^{I}(4\text{-Metz})_4Cl_3$

WAYNE E. MARSH, WILLIAM E. HATFIELD, and DEREK J. HODGSON*

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The reaction of 4-methylthiazole (4-Metz), C_3H_5NS, with copper(II) chloride has been investigated. A total of six new complexes has been identified, five of which are discussed in detail. These include the copper(II)–copper(II) dimers $[Cu(4\text{-Metz})_2Cl_2]_2$, $[Cu(4\text{-Metz})_2Cl_2]_2{\cdot}2CH_3OH$, and $[Cu(4\text{-Metz})(DMF)Cl_2]_2$, the copper(II) monomer $[Cu(4\text{-Metz})_3Cl_2]$, and the mixed-valent copper(II)–copper(I) dimer $[Cu^{II}Cu^{I}(4\text{-Metz})_4Cl_3]$. The crystal structure of the mixed-valent dimer is discussed in detail. The complex, $Cu_2(C_3H_5NS)_4Cl_3$, crystallizes in the monoclinic space group $P2_1/n$ with four binuclear species in a cell of dimensions $a = 10.957$ (2) Å, $b = 15.457$ (3) Å, $c = 15.104$ (2) Å, and $\beta = 108.61$ (1)°. The structure has been refined to a final value of the weighted R factor of 0.035 on the basis of 2543 independent data with $I \geq 3\sigma(I)$. The geometry at the Cu(II) center is distorted tetragonal pyramidal, while that at the Cu(I) center is pseudotetrahedral. The two copper centers are bridged by two chloride ligands, the Cu(I)–Cu(II) separation being 3.244 (1) Å.

Introduction

The investigation of the reaction chemistry of 4-methylthiazole with copper(II) chloride has produced several products that not only show some uncommon coordination properties at copper but also indicate some reduction–oxidation chemistry that has not been observed in similar systems of the type CuA_2X_2 (where A is a monodentate ligand and X is a halide). Initial interest in this study was centered on the preparation, and subsequent structural and magnetic characterization, of the dimeric complex $[Cu(4\text{-Metz})_2Cl_2]_2$, which would be analogous to the dimeric copper(II) bromide complex of 4-methylthiazole.[1] However, by use of a synthetic procedure similar to that used for preparing the bromide complex, at least six products were formed and, as a result, several new avenues of study were initiated. Of particular interest was the discovery of a mixed-valence dimer, $Cu^{II}Cu^{I}(4\text{-Metz})_4Cl_3$, which represents a reduction of the parent Cu(II)/Cu(II) dimer with a corresponding loss of chloride ion. This observation is reminiscent of the behavior of a variety of biological macromolecules containing binuclear active sites[2–9] and their synthetic models.[10–17]

Experimental Section

Synthesis of $[Cu(4\text{-Metz})_2Cl_2]_2$ (1). Compound **1** can be prepared in several ways, and depending on certain modifications of the general procedure, other products can be obtained as well (vide infra). For specifically isolating **1**, the following procedure was developed. Copper(II) chloride dihydrate was dehydrated under a vacuum and in the presence of the drying agent P_4O_{10}, and the resultant anhydrous copper(II) chloride was kept in a desiccator until used. The methanol used in the synthesis was distilled over $Mg(OMe)_2$ for 1 h and deaerated with dry N_2 before use. The ligand 4-methylthiazole was obtained from Aldrich Chemical Co. and used without further purification. The complex was prepared by dissolving 1.344 g (0.01 mol) of anhydrous $CuCl_2$ in 20 mL of methanol under a N_2 atmosphere and by adding to this solution under N_2 2.975 g (0.03 mol) of the ligand in methanol. The mixture was stirred constantly for about 10 min and then filtered. The blue-green precipitate that had formed was collected, rinsed with ether, and sealed in small vials to prevent decomposition. The solution was sealed under N_2 and placed in the freezer unit of a refrigerator or allowed to evaporate at room temperature under a steady flow of N_2 for crystallization purposes. The first crystals formed and the initial precipitate were **1** and usually came out of solution immediately; extended periods of crystallization yielded other products (vide infra). Anal. Calcd for $Cu(C_8H_{10}N_2S_2)Cl_2$: C, 28.88; H, 3.03; N, 8.42. Found: C, 28.74; H, 3.03; N, 8.24.

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