Crystal Structure and Magnetic Behavior of Copper(II) Dimethylphosphinate: A Chain Polymer Containing Triangular Trimetallic Bis(μ-dimethylphosphinato)copper(II) Units

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Introduction

Earlier studies on the dialkylphosphinates of copper(II) showed these materials to have interesting magnetic properties, different compounds exhibiting either ferromagnetic or antiferromagnetic exchange interactions. Ligand-mediated exchange was indicated by single-crystal X-ray diffraction studies on several of the compounds which revealed extended chain polymeric structures in which metal ions in compressed tetrahedral environments are doubly bridged by phosphinate ligands.[1] Accordingly, the variable-temperature magnetic behavior of these compounds agreed well with that predicted by theory for extended chains of $S = \frac{1}{2}$ metal ions.[2] Although the dimethylphosphinate of copper(II) was studied in the earlier work,[3] the variable-temperature susceptibilities were found to be at variance from theory for linear chains. We have now obtained the compound in crystalline form suitable for single-crystal X-ray diffraction studies.

Copper(II) dimethylphosphinate belongs to an interesting class of copper compounds, the structures of which contain linear or triangular trimetallic units. Studies on such systems have revealed magnetic properties ranging from ferromagnetic behavior, as in the recently reported μ_3-CO_3^{2-} triangular array complex, (μ_3-CO_3)[$Cu_3(Medpt)_3(ClO_4)_3$](ClO$_4$) (where Medpt is bis(3-aminopropyl)methylamine),[4] to antiferromagnetic behavior in a number of complexes. Examples of the latter are the imidazolate-bridged triangular [$L_3Cu_3(Im)_3$](ClO$_4$)$_3$ (where L is 1,4,7-trimethyl-1,4,7-triazacyclodonane and Im is imidazolate),[5] several reported triangular μ_3-X complexes,[6] and the linear trimetallic [$Cu(pdz)_3(NO_3)_3$]$_2$Cu (where pdz is py-

ridazine).[7] The antiferromagnetic systems are of particular interest because the coupling leads to uncompensated spin in the ground state, a situation that has been termed molecular spin frustration.[5] The structure of copper(II) dimethylphosphinate, reported here, is particularly interesting in that it involves triangular bis(μ-dimethylphosphinato)copper(II) units linked in extended chains. This creates the possibility of additional exchange interactions propagated along the chain.

Experimental Section

Physical Measurements. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) studies were made using a TA 2000 instrument with a DSC 910s cell and TGA 51 unit. Infrared (IR) spectra and electronic spectra were recorded on Bomen Fourier-transform and Cary 5 instruments, respectively. Samples were mulled in Nujol and pressed between KRS-5 plates (Harshaw Chemical Co.) for the IR measurements and quartz glass plates for the electronic spectra. X-ray powder diffractograms were recorded in the range $2\theta = 4-60°$ on a Rigaku rotating anode powder X-ray diffractometer using Cu Kα radiation. Samples were prepared by grinding with *n*-octane to obtain a slurry, applying to a glass slide, and then allowing the n-octane to evaporate. Electron paramagnetic resonance (EPR) spectra on powdered samples at room temperature were recorded on a Varian Associates E3 spectrometer using 100 kHz field modulation. The X-band microwave frequency was monitored on a Hewlett-Packard 5245L electronic counter equipped with a 3−12.4 GHz frequency converter. Carbon and hydrogen microanalyses were performed by P. Borda at UBC, and copper was determined by EDTA titration.

Variable-temperature magnetic susceptibilities were measured over the temperature range 4.2−80 K using a vibrating sample magnetometer and 80−300 K using Gouy equipment and methods described previously.[8] Experimental susceptibility data were corrected for the diamagnetism of all atoms (-11×10^{-6} and -42×10^{-6} cm^3 mol^{-1} for copper(II) and dimethylphosphinate, respectively) and for the temperature-independent paramagnetism of copper(II) (60×10^{-6} cm^3 mol^{-1}).

Synthesis and Characterization. Dimethylphosphinic acid was prepared as described previously.[1a] Copper(II) dimethylphosphinate was prepared in relatively large quantities, in powder form, by the following procedure.[3] As a precaution against hydrolysis and the formation of basic salt impurities, all vessels were purged with dry nitrogen and transfers were done in a stream of nitrogen gas. Dimethylphosphinic acid (4.68 g, 49.7 mmol), dissolved in acetone (150 mL, dried by refluxing over K$_2$CO$_3$), was filtered into a flask equipped with a magnetic stirrer. Copper(II) benzoate (5.11 g, 16.7 mmol) was dissolved in dry acetone (120 mL) and filtered into an addition funnel. The copper solution was added, over a period of 3 h, to the stirring acid solution. A flocculent light blue precipitate appeared after the addition of the first 10 mL of the copper solution. After the addition was complete, the solid was separated by filtration, washed repeatedly with a total of 500 mL of dry acetone, and then dried *in vacuo* for several hours at room temperature. Yield: 2.06 g. Anal. Calcd for C$_4$H$_{12}$P$_2$O$_4$Cu: C, 19.25; H, 4.85; Cu, 25.5. Found: C, 19.15; H, 4.85; Cu, 25.6. IR (Nujol mull, PO$_2$ stretching region, values ± 2 cm^{-1}): 1159, 1108, 1055, 1032. UV−vis−NIR (Nujol mull): 790 ± 10 nm, broad. EPR: broad signal at $g = 2.22$. Thermal analysis (DSC and TGA): melting with decomposition at 250 °C. X-ray powder diffraction *d*-spacings (Å) with relative intensities in brackets, four strongest lines: 9.07(100), 4.59(14), 4.36(7), 3.44(11).

Later work showed the powdered form of the compound can be obtained more conveniently than as described above by using acetone containing 10% 2,2-dimethoxypropane as solvent and slowly adding a solution of Cu(NO$_3$)$_2$·3H$_2$O to a solution of dimethylphosphinic acid neutralized with triethylamine.

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Table 1. Crystallographic Data[a]

compd	{Cu₃[(CH₃)₂PO₂]₆}ₓ
formula	$C_{12}H_{36}Cu_3O_{12}P_6$
fw	748.89
cryst system	monoclinic
space group	$C2/c$ (No. 15)
a, Å	10.957(1)
b, Å	18.300(1)
c, Å	14.907(1)
β, deg	108.973(9)
V, Å³	2826.7(5)
Z	4
ρ_{calc}, g/cm³	1.760
T, °C	21
radiation	Mo
μ, cm⁻¹	26.25
R	0.030
R_w	0.029

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2}$.

Table 2. Atom Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients (Å² × 10²) for the {Cu₃[(CH₃)₂PO₂]₆}ₓ[a]

atom	x	y	z	B_{eq}
Cu(1)	5000	3416.19(3)	2500	205.8(9)
Cu(2)	4713.8(3)	5128.3(2)	1111.1(2)	202.9(6)
P(1)	6371.2(7)	3777.8(4)	993.3(5)	218(1)
P(2)	2717.4(7)	3803.0(4)	742.9(5)	223(1)
P(3)	3191.6(7)	5985.0(4)	2236.8(5)	228(1)
O(1)	6358(2)	3576(1)	1972(1)	267(4)
O(2)	5447(2)	4379.1(10)	491(1)	222(4)
O(3)	3732(2)	3248(1)	1272(1)	255(4)
O(4)	3116(2)	4594(1)	895(2)	307(5)
O(5)	3899(2)	5943(1)	1515(1)	238(4)
O(6)	3599(2)	5466(1)	3071(1)	257(4)
C(1)	7971(3)	4059(3)	1102(3)	411(9)
C(2)	6019(4)	2985(2)	255(3)	342(8)
C(3)	1287(3)	3706(2)	1064(3)	346(8)
C(4)	2255(4)	3591(2)	-485(2)	353(8)
C(5)	1503(3)	5842(3)	1656(3)	406(9)
C(6)	3336(5)	6917(2)	2623(3)	350(9)

^{a} $B_{eq} = (8/3)\pi^2\Sigma\Sigma U_{ij}a^*_i a^*_j(\mathbf{a}_i\cdot\mathbf{a}_j)$.

Small quantities of blue crystals suitable for single-crystal X-ray diffraction studies were obtained over a period of about 3 weeks from a solution prepared by mixing CuCl₂·2H₂O (85 mg, 0.50 mmol) in dimethylformamide (DMF, 10 mL) with a solution of dimethylphosphinic acid (188 mg, 2.0 mmol, neutralized with 0.14 mL triethylamine) in DMF (10 mL).

X-ray Crystallographic Analysis of {Cu₃[(CH₃)₂PO₂]₆}ₓ. Crystallographic data appear in Table 1. The final unit-cell parameters were obtained by least squares on the setting angles for 25 reflections with $2\theta = 25.3-32.8°$. The intensities of three standard reflections, measured every 200 reflections throughout the data collection, showed only small random fluctuations. The data were processed[9] and corrected for Lorentz and polarization effects and absorption (empirical, based on azimuthal scans, relative transmission factors 0.80−1.00).

The structure analysis was initiated in the centrosymmetric space group $C2/c$ on the basis of the E-statistics, this choice being confirmed by the subsequent successful solution and refinement of the structure. The structure was solved by direct methods. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were refined with isotropic thermal parameters. A secondary extinction correction was applied (Zachariasen type, isotropic); the final value of the extinction coefficient was 7.6(3) × 10⁻⁸. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from ref 10 Final atomic coordinates and

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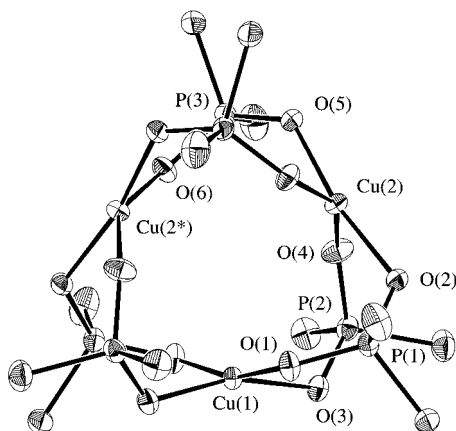
Table 3. Selected Bond Lengths (Å) and Angles (deg) for the Compound {Cu₃[(CH₃)₂PO₂]₆}ₓ[a]

Bond Lengths			
Cu(1)−O(1)	1.918(2)	Cu(1)−O(3)	1.929(2)
Cu(2)−O(2)	1.965(2)	Cu(2)−O(2)^b	2.505(2)
Cu(2)−O(4)	1.938(2)	Cu(2)−O(5)	1.932(2)
Cu(2)−O(6)^c	1.955(2)		

Bond Angles			
O(1)−Cu(1)−O(1)^c	162.5(1)	O(1)−Cu(1)−O(3)	92.89(8)
O(1)−Cu(1)−O(3)^c	89.89(8)	O(3)−Cu(1)−O(3)^c	161.6(1)
O(2)−Cu(2)−O(2)^b	73.46(7)	O(2)−Cu(2)−O(4)	93.17(8)
O(2)−Cu(2)−O(5)	170.39(8)	O(2)−Cu(2)−O(6)^c	93.77(8)
O(2)^b−Cu(2)−O(4)	104.10(8)	O(2)^b−Cu(2)−O(5)	97.07(7)
O(2)^b−Cu(2)−O(6)^c	103.86(7)	O(4)−Cu(2)−O(5)	87.53(8)
O(4)−Cu(2)−O(6)^c	152.03(9)	O(5)−Cu(2)−O(6)^c	90.04(8)

^{a} Superscripts refer to the following symmetry operations: ^{b} $1 - x$, $1 - y$, $-z$; ^{c} $1 - x$, y, $^1/_2 - z$.
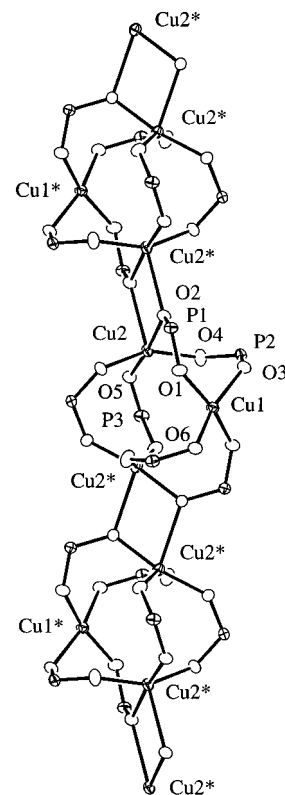
Figure 1. Structure showing a section of the chain and atom numbering scheme, with 33% probability thermal ellipsoids shown.

equivalent isotropic thermal parameters for the non-hydrogen atoms and selected bond lengths and bond angles appear in Tables 2 and 3, respectively. A complete tables of crystallographic data, hydrogen atom parameters, anisotropic thermal parameters, bond lengths and angles, torsion angles, intermolecular contacts, and least-squares planes are included as Supporting Information.

Results and Discussion

Synthesis and Structure of {Cu₃[(CH₃)₂PO₂]₆}ₓ. Somewhat different synthetic methods were employed to obtain powder and single-crystal samples of the compound, and since magnetic studies were done on powder samples, it was important to establish that the powder and single-crystal forms are the same. This was confimed by IR, elemental analysis, thermal analysis, and X-ray powder diffraction.

All X-ray determined structures of binary diorganophosphinates of copper(II) reported to date have revealed linear chains with metal ions doubly bridged by phosphinate groups. In this respect, the structure of copper(II) dimethylphosphinate is

Figure 2. View of the trimetallic unit with 33% probability thermal ellipsoids shown.
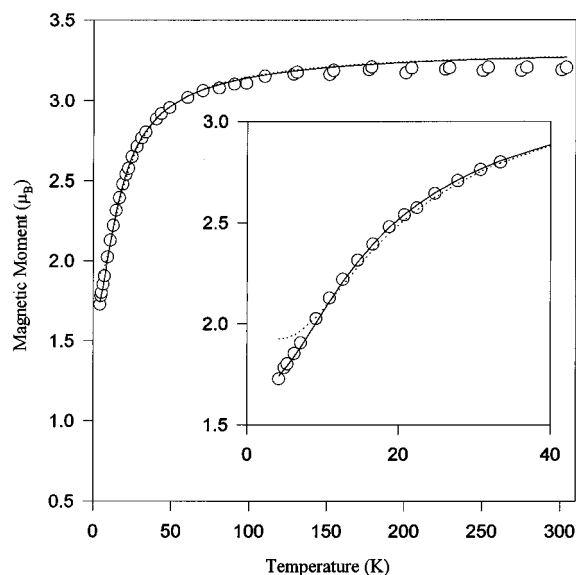

Figure 3. Plot of magnetic moment (per mole of trimetallic unit) versus temperature. The solid lines are calculated from theory by employing a single intratrimer exchange constant plus a molecular field correction as described in the text. The dotted lines are calculated from a modified form of eq 1 as described in the text.

unique. Figure 1 shows a section of a chain with the trimetallic units linked via phosphinate O(2) atoms to Cu(2) atoms on neighboring units. Figure 2 gives details of the structure of the trimetallic unit which has exact C_2 symmetry with Cu(1) located on the 2-fold axis. The unique Cu(1) is in a distorted square planar environment of oxygens from four different bridging phosphinate groups. These groups, in pairs, link the unique copper to the other two copper ions, Cu(2). The two phosphinate groups in a pair are different. One, containing P(2), is only involved in the single intratrimer bridging interaction, while the other, containing P(1), is also involved, via O(2), in intertrimer bridging to a Cu(2) atom of a neighboring trimer. The form of coordination shown by the latter phosphinate in which it bridges three metals is rare although it has been reported previously.[11] The two Cu(2) atoms in a given trimetallic unit are bridged by two identical phosphinate groups (containing P(3)). Because of their involvement in the intertrimetallic interactions each Cu(2) atom is bonded to five oxygens in a distorted square pyramidal environment. The extent of the distortion is clear from an examination of bond lengths and angles (Table 3). Of particular note are the Cu(2)−O bond

lengths. The four distances forming the base of the pyramid are on average 1.948(8) Å, comparable to the average of the Cu(1)−O distances (1.924(4) Å) and the average Cu−O distances in Cu[(C$_2$H$_5$)$_2$PO]$_2$[1a] and Cu[(n-C$_6$H$_{13}$)$_2$PO]$_2$[1b] (1.918-(1) and 1.907(3) Å, respectively), while the axial Cu(II)−O distance is, at 2.505(2) Å, considerably longer.

The electronic absorption spectrum consists of a very broad featureless band centered around 790 nm. This absorption no doubt arises from overlap of several transitions arising from copper ions in two different highly distorted environments. Similarly distinct EPR signals for the different copper(II) centers are not seen. A single asymmetric line is seen with a crossover at $g = 2.22$. Moreover the observation of at least four distinct infrared active bands in the infrared spectrum is consistent with the partial overlap of the PO$_2$-stretching vibrations of the three distinct phosphinate groups in this compound.

Magnetic Properties. Magnetic moment data (per mole of trimetallic unit) are plotted versus temperature in Figure 3. Assuming isotropic Heisenberg exchange and the equivalence of g values for an isosceles triangle (ABA) arrangement of three $S = {}^1/_2$ metal centers, the expression for the magnetic susceptibility is[12,13]

$$\chi_M = \frac{Ng^2\mu_B{}^2}{4kT}\frac{\exp(-2J/kT) + \exp(-2J'/kT) + 10\exp(J/kT)}{\exp(-2J/kT) + \exp(-2J'/kT) + 2\exp(J/kT)}$$

$$(1)$$

where J is the exchange integral between the unique copper(II) (compressed tetrahedral ligand chromophore in the compound studied here) and the other two copper(II) ions and J' is the exchange integral between the two equivalent copper(II) ions (square pyramidal chromophore in this case). In examining fits of experimental susceptibilities to eq 1, we fixed g at the value 2.22, obtained from the EPR spectrum, and allowed J and J' to vary. While reasonable fits between experiment and theory could be obtained, the individual J and J' parameters had unacceptably high error limits, in effect making the two parameters indistinguishable. Accordingly we modified eq 1 putting $J' = J$. The best fit to this modified eq was obtained with $J = -7.4 \pm 0.3$ cm^{-1} and $F = 0.059$.[14] There is good agreement between experiment and theory above about 30 K using this model; however, significant deviation occurs in the low-temperature region. This is demonstrated most clearly by the magnetic moment plot, shown by the dotted line in the inset in Figure 3. The experimental moments at low temperature are significantly less than calculated by theory, suggesting the presence of an additional source of antiferromagnetic coupling. This most likely arises from coupling between copper ions in adjacent trimetallic units via the O(2) oxygen. This oxygen occupies a short-bonded (1.965(2) Å) basal position of one copper and a long-bonded (2.505(2) Å) axial position of the other metal. Such a molecular arrangement is unlikely to result in strong magnetic coupling, and we accordingly examined the possibility of allowing for this exchange by employing a

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(14) In the least-squares fitting procedure employed the following is the function minimized:

$$F = \left[\frac{1}{n}\sum_{i=1}^{n}\left(\frac{\chi^i{}_{calc} - \chi^i{}_{obs}}{\chi^i{}_{obs}}\right)^2\right]^{1/2}$$

Here n is the number of data points and $\chi^i{}_{obs}$ and $\chi^i{}_{calc}$ are the experimental and calculated molar susceptibilities. The F value gives a measure of the quality of fit between experiment and theory.

molecular field correction to the susceptibilities.[15] The expression for this is

$$\chi_M' = \frac{\chi_M}{1 - (zJ_{mf}/Ng^2\mu_B^2)\chi_M} \qquad (2)$$

where χ_M' is the corrected molar susceptibility, z is the number of nearest interacting units, J_{mf} is the molecular field exchange coupling constant, and χ_M is the susceptibility calculated with eq 1, modified by putting $J' = J$. Using the two variable parameters only, J and zJ_{mf}, we obtained a good fit to the data over the whole temperature range studied with the values $J = -5.9 \pm 0.1$ cm^{-1} and $zJ_{mf} = -0.27 \pm 0.02$ cm^{-1} ($F = 0.021$). These calculated data are shown as solid lines in Figure 3. This analysis of the magnetic data seems reasonable particularly since the molecular field correction is less than 10% of the magnitude of J.[15]

Within the trimetallic units there are three potential pathways for exchange, all involving double phosphinate bridges. The phosphinates containing P(1) and P(2) link the two five-coordinate copper ions to the four-coordinate copper, and the two phosphinates containing P(3) link the five-coordinate metal ions to each other. Analysis of our data permits the determination of a single intratrimetallic exchange constant linking all three metals. Presumably the exchange couplings by the three pathways are not significally different from each other and J for each is close in magnitude to the value obtained from our fit. The intratrimetallic phosphinate bridges observed in the title compound are not significantly different in terms of bond angles or lengths from those reported previously for antiferromagnetically coupled linear chain copper(II) dialkylphosphinates. The exchange coupling constants in these polymers range from $J = -1.3$ cm^{-1} in the ethyl derivative[1b] to $J = -29$ cm^{-1} in the dodecyl derivative.[16] Hence the value $J = -5.9$ cm^{-1}

obtained for the title compound can be considered typical for copper(II) ions exchanging antiferromagnetically via double phosphinate bridges. It was previously noted that the magnitude of exchange does not correlate with bonding parameters associated with the bridging phosphinates but that the chromophore geometry may play a significant role in determining the nature and strength of exchange.[1b,e] The present work shows, however, no significant change in the magnitude of exchange on going from the polymers where all metals are four-coordinate to the title compound where two out of three metal centers are five-coordinate.

Two potential pathways for intertrimetallic exchange involve (i) the Cu(2) ions in different units linked by O(2) and (ii) the Cu(1) from one unit linked via the P(1)-containing phosphinate bridge to a Cu(2) in a neighboring unit. The first, being the shorter pathway, would be expected to dominate; however, exchange via either should be weak since both involve the long (2.505(2) Å) Cu−O link. Adding to the expectation that exchange via this link will be weak is the fact it is orthogonal to the presumed magnetic orbital, d$_{x^2-y^2}$, in the basal plane. Comparisons with related systems are not possible since the form of phosphinate coordination seen here in which one oxygen (O(2)) is bonded to two metal ions has not been previously reported for a magnetically and structurally characterized copper(II) compound.

Supporting Information Available: Tables of structure determination details, crystallographic data, expanded non-H atom coordinates, bond lengths, and bond angles, anisotropic thermal parameters for non-H atoms, calculated positional parameters of H atoms, bond lengths and angles involving hydrogen, torsion angles, nonbonded contacts, and least-squares planes for the compound (15 pages). Ordering information is given on any current masthead page.

IC961365G

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