of the MP_2 fragments about the metal–metal axis. For the complexes $[Pd_2(dpm)_2Br_2]$ and $[Pt_2(dpm)_2Cl_2]$, a twist of about 39° has been reported.[2,29,30] Structural studies involving dinuclear $(dpm)_2$ species of other transition metals (Mn,[1] Re,[31] Mo[32]) have been much less frequent but, in general, also reveal the common trans binding of the two dpm ligands, linear P–M–P fragments, and planar M_2P_4 skeletal units. For the d^{10} complexes IX and X, however, the P–M–P units are distinctly nonlinear.

Prior to our own studies, the best example of an M_2P_4 core approaching the folded structure of the syn conformation X was that of the carbonylated A-frame (distorted type VII) complex $[Rh_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_2(dpm)_2]^+$.[7] The distortion of the A-frame structure resulted in a P–Rh–P angle of 155.2 (1)°, a value surprisingly similar to the P–Au–P angle in $[Au_2(dpm)_2Cl_2]$.[28] This agreement is however strictly coincidental. X-ray structural characterization of the silver complexes $[Ag_2(dpm)_2(NO_3)_2]$ and $[Ag_4(dpm)_4(NO_3)_2]^{2+}[PF_6]^-_2$, reported here, clearly reveals that the P–M–P angles in $(dpm)_2$ compounds are not restricted by steric crowding of the dpm phenyl rings to a minimum value of 155°. The P–Ag–P angles in $[Ag_2(dpm)_2(NO_3)_2]$, in particular, are much more bent [138.3 (1)°] than the corresponding P–M–P values found in $[Au_2(dpm)_2Cl_2]$ and $[Rh_2(\mu\text{-}H)(\mu\text{-}CO)(CO)_2(dpm)_2]^+$. The two silver compounds mentioned above are, to our knowledge, the only examples of $(dpm)_2$ complexes having M_2P_4 core structures in the syn conformation X. Why the sterically larger nitrate groups should bind the metal atoms to give the conformation X in $[Ag_2(dpm)_2(NO_3)_2]$ rather than the anti conformation IX as in $[Au_2(dpm)_2Cl_2]$ is not intuitively obvious, and we can forward no explanation for this preference at this time.

In summary, the doubly bridged bis(diphenylphosphino)methane complexes $[Ag_2(dpm)_2(NO_3)_2]$ and $[Ag_4(dpm)_4(NO_3)_2]^{2+}[PF_6]^-_2$ have been structurally characterized by single-crystal X-ray methods and found to contain folded M_2P_4 core structures in the heretofore unknown syn conformation X. The $M_2(dpm)_2$ framework in these compounds is found to be quite flexible, exhibiting folding angles ranging from 138 to 152° in the solid state. In addition, the nitrate ligands in $[Ag_2(dpm)_2(NO_3)_2]$ are apparently labile, dissociating in solution to form the planar dicationic species $[Ag_2(dpm)_2]^{2+}$. The flexibility of the M_2P_4 core and the coordinative unsaturation of the $[Ag_2(dpm)_2]^{2+}$ dimer are particularly intriguing in that these features should facilitate the uptake and binding of larger substrate species than presently possible with known $M_2(dpm)_2$ (M = Rh, Ir, Pd, Pt) complexes, which are generally restricted to a square-planar coordination geometry. In addition, the tetrameric nature of $[Ag_4(dpm)_4(NO_3)_2]^{2+}[PF_6]^-_2$, suggests yet another mode for the binding of small ligands by $M_2(dpm)_2$ complexes. The ability of the $[Ag_2(dpm)_2]^{2+}$ unit to fold along the Ag⋯Ag axis allows the close approach of two of these dinuclear units to produce an enclosed central cavity. In $[Ag_4(dpm)_4(NO_3)_2]^{2+}[PF_6]^-_2$, this cavity or pocket is occupied by two nitrate anions. However, it should also be possible to introduce other species into this central cavity, as well as carry out reactions on the captured molecules. Stable silver carbonyls, hydrides, and compounds containing Ag–Ag bonds have also not yet been fully established. The $[Ag_2(dpm)_2]^{2+}$ unit should provide a very convenient entry point for the synthesis and study of such molecules.

Supplementary Material Available: Listings of the temperature factors (Tables A and B) for the two structure determinations and listings of the observed and calculated structure factors (Tables C and D) (32 pages). Ordering information is given on any current masthead page.

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Preparation and Structure of $[Cu_3(dpm)_3(OH)]^{2+}[BF_4]^-_2$

DOUGLAS M. HO and ROBERT BAU*

The first coordinatively unsaturated triangulo $Cu_3(dpm)_3$ derivative, $[Cu_3(dpm)_3(OH)]^{2+}[BF_4]^-_2$, has been prepared and characterized by a single-crystal X-ray analysis. The $[Cu_3(dpm)_3(OH)]^{2+}$ cation consists of a triangular array of copper atoms, with dpm ligands ($Ph_2PCH_2PPh_2$) bridging each edge of the triangle and a triply bridging OH group bound to one face of the Cu_3 unit. The Cu_3 core is situated in a "picket-fence-like" environment with the remaining face of the metallic core exposed. This exposed face of the Cu_3 triangle contains, formally, three sites of unsaturation positioned in a hydrophobic cavity. Crystallographic details for $[Cu_3(dpm)_3(OH)]^{2+}[BF_4]^-_2$: triclinic space group $P\bar{1}$, a = 14.741 (5) Å, b = 21.236 (6) Å, c = 12.396 (3) Å, α = 90.49 (2)°, β = 113.07 (2)°, γ = 93.25 (2)°; final R factor 6.8% for 6041 nonzero reflections $[F^2 > 3\sigma(F^2)]$.

Introduction

In light of the growing interest in binuclear bis(diphenylphosphino)methane (dpm) complexes,[1] the small number of reported cluster derivatives of this particular diphosphine is somewhat surprising. To our knowledge, 14 cluster compounds containing the dpm molecule as a ligand have been structurally characterized,[2–12] with the majority of these compounds having group 1b (Cu, Ag, Au) metal atom core structures [the exceptions being $Ru_3(dpm)(CO)_{10}$,[2a] $Ru_3(dpm)_2(CO)_8$,[2b] Rh_6-

(1) See the Introduction of the preceding paper in this issue.

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$(dpm)_3(CO)_{10}$,[3b] and $Pt_4(dpm)_3(Ph_2PCH_2P(:O)Ph_2)(CO)_2^{4+}]$. For the group 1b elements, multinuclear dpm compounds with three,[5–7] four,[8–10] five,[11] and thirteen[12] metal atoms have now been crystallographically confirmed.

As in the binuclear $(dpm)_2$ complexes, the dpm ligand is again found to stabilize a number of unusual features. For instance, the first example of a tetrahedral core of gold atoms was recently revealed in the molecular structure of the fascinating pentagold compound $[Au_5(dpm)_3(dpm-H)]^{2+}$-$[NO_3]^-{}_2$;[11] the notation (dpm-H) is used here to indicate the monoanion $[(Ph_2P)_2CH]^-$ that results from deprotonation of one of the bound dpm ligands. The remaining fifth gold atom in that molecule is found bonded to one of the four vertices of the tetrahedron. Similarly, the first example of a 13-atom gold cluster, $[Au_{13}(dpm)_6](NO_3)_4$, was also isolated as a dpm derivative.[12] This complex is the largest gold cluster currently known and consists of a centered icosahedron of metal atoms. The centered icosahedral geometry of the Au_{13} core is in agreement with the theoretically predicted structure forwarded by Mingos in 1976[13] and provides an interesting contrast to the centered cuboctahedral geometry of the $[H_{5-n}Rh_{13}-(CO)_{24}]^{n-}$ $(n = 2, 3, 4)$ clusters.[14–17]

Intrigued by this apparent ability of the dpm ligand to impart unusual properties and stability to multinuclear complexes, we have recently expanded our own studies of cluster carbonyls and hydrides[18] to include selected dpm derivatives. Over the last few years, we have successfully isolated a few unsaturated multinuclear dpm compounds of copper and silver.[19] We report here the preparation of a new trinuclear dpm derivative, $[Cu_3(dpm)_3(OH)]^{2+}[BF_4]^-$, and its molecular structure as determined by a single-crystal X-ray analysis. The molecule is found to contain a coordinatively unsaturated triangular array of copper atoms enclosed by a "picket-fence-like" arrangement of dpm phenyl rings. Alternatively, the molecule may be viewed as containing a triangular metal surface situated in a hydrophobic cavity.

Experimental Section

General Considerations. $Cu(BF_4)_2 \cdot xH_2O$ was obtained from Alfa Inorganics and bis(diphenylphosphino)methane from Pressure Chemical Co. The melting point determination (uncorrected) was

Table I. Crystal Data for $[Cu_3(dpm)_3(OH)]^{2+}[BF_4]^-{}_2$

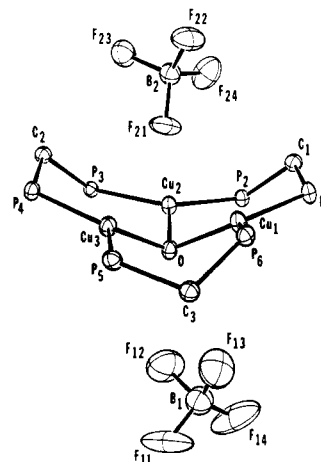|	
crystal type	triclinic
space group	$P\bar{1}$ (No. 2)
unit cell parameters	
a, Å	14.741 (5)
b, Å	21.236 (6)
c, Å	12.396 (3)
α, deg	90.49 (2)
β, deg	113.07 (2)
γ, deg	93.25 (2)
V, Å^3	3562 (2)
formula units per unit cell, Z	2
mol wt	1534.44
ρ(calcd), g cm^{-3}	1.43
ρ(obsd), g cm^{-3}	1.37 (hexane/CHCl$_3$)
abs coeff (μ), cm^{-1} (for Mo Kα X-rays)	11.2

Figure 1. Illustration of the chair and boat conformations of the three fused six-membered rings in the central structure of $[Cu_3(dpm)_3-(OH)]^{2+}[BF_4]^-{}_2$ and the close approach of the F(21) atom to the Cu$_3$ triangle.

carried out on a MEL-TEMP apparatus from Laboratory Devices, Cambridge, MA. The ^{1}H NMR spectrum was recorded on a Varian XL-100 spectrometer. Analyses were performed by the Caltech Analytical Facility, Pasadena, CA.

Preparation of $[Cu_3(dpm)_3(OH)]^{2+}[BF_4]^-{}_2$. A reaction mixture of $Cu(BF_4)_2 \cdot xH_2O$ (0.137 g, 0.50 mmol), Cu powder (0.2 g, excess), and 50 mL of acetonitrile was refluxed for 2 h under nitrogen to give a pale blue solution, which was subsequently separated from unreacted copper metal by filtration. This step presumably yields the reactive species $[Cu(CH_3CN)_4]^+$.[20] The bidentate diphosphine dpm (0.384 g, 1.0 mmol) was then added under a nitrogen flush to the filtrate, and the clear pale blue solution stirred an additional 24 h at room temperature. A second filtration was then performed, followed by removal of the solvent under reduced pressure to give an off-white residue. This solid was redissolved in 100 mL of hot methanol, and the volume of the resulting very pale yellow solution reduced under vacuum. The white microcrystalline product formed was filtered off, washed with methanol, and dried for 6 h in vacuo: yield 0.349 g (65%); mp 199–200 °C. ^{1}H NMR: δ 3.16 (6 H, br m, CH$_2$ protons of dpm); δ 6.84–7.06 (60 H, m, C$_6$H$_5$ protons of dpm). Anal. Calcd for $C_{75}H_{67}B_2F_8OP_6Cu_3$: C, 58.71; H, 4.40. Found: C, 58.73; H, 4.50.

Collection and Reduction of the X-ray Data for $[Cu_3(dpm)_3-(OH)]^{2+}[BF_4]^-{}_2$. A colorless crystal with dimensions of 0.36 × 0.24 × 0.07 mm was selected for the X-ray analysis and mounted at the end of a glass fiber. Accurate unit cell parameters were obtained by careful machine centering of 15 strong reflections ($14° < 2\theta < 25°$) on a Syntex P2$_1$ automated four-circle diffractometer. These are presented together with other relevant crystal data in Table I. One hemisphere of data ($+h,\pm k,\pm l$) was collected by using the θ–2θ scan technique and Mo Kα radition up to a 2θ(max) value of 45°. A variable scan speed was employed with lower and upper limits of 2.5

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Table II. Final Atomic Positions (Fractional Coordinates) for [Cu₃(dpm)₃(OH)]²⁺[BF₄]⁻₂

atom	x	y	z	atom	x	y	z
Cu(1)	0.1090 (1)	0.2699 (1)	-0.4387 (1)	C(52)	0.5534 (8)	0.4140 (5)	-0.3670 (9)
Cu(2)	0.3238 (1)	0.3288 (1)	-0.3059 (1)	C(53)	0.6038 (8)	0.4751 (5)	-0.3608 (9)
Cu(3)	0.2782 (1)	0.1828 (1)	-0.4204 (1)	C(54)	0.6535 (8)	0.5052 (5)	-0.2552 (9)
P(1)	0.0524 (2)	0.3654 (1)	-0.4460 (2)	C(55)	0.6558 (8)	0.4778 (5)	-0.1530 (10)
P(2)	0.2570 (2)	0.4158 (1)	-0.2783 (2)	C(56)	0.6057 (8)	0.4172 (5)	-0.1573 (9)
P(3)	0.4807 (2)	0.3142 (1)	-0.2739 (2)	C(61)	0.5482 (7)	0.2761 (4)	-0.1355 (8)
P(4)	0.4329 (2)	0.1874 (1)	-0.4107 (2)	C(62)	0.4905 (8)	0.2538 (5)	-0.0740 (9)
P(5)	0.1694 (2)	0.0993 (1)	-0.4921 (2)	C(63)	0.5417 (10)	0.2204 (6)	0.0332 (12)
P(6)	0.0078 (2)	0.1892 (1)	-0.5436 (2)	C(64)	0.6376 (10)	0.2129 (6)	0.0655 (11)
Oᵃ	0.2418 (4)	0.2463 (2)	-0.3273 (5)	C(65)	0.6947 (9)	0.2345 (6)	0.0098 (11)
F(11)	0.1798 (10)	0.1147 (4)	-0.0655 (8)	C(66)	0.6477 (8)	0.2677 (5)	-0.1002 (9)
F(12)	0.2542 (8)	0.1979 (5)	-0.0994 (9)	C(71)	0.4387 (7)	0.1599 (4)	-0.5464 (8)
F(13)	0.1088 (7)	0.1723 (5)	-0.2139 (8)	C(72)	0.4099 (8)	0.1982 (5)	-0.6420 (9)
F(14)	0.1386 (12)	0.2080 (6)	-0.0342 (12)	C(73)	0.4023 (9)	0.1750 (6)	-0.7550 (10)
F(21)	0.2607 (5)	0.3064 (3)	-0.5372 (5)	C(74)	0.4245 (9)	0.1129 (6)	-0.7642 (11)
F(22)	0.2098 (5)	0.3395 (4)	-0.7184 (5)	C(75)	0.4496 (10)	0.0752 (6)	-0.6742 (12)
F(23)	0.3696 (5)	0.3495 (3)	-0.6065 (6)	C(76)	0.4585 (8)	0.0973 (5)	-0.5587 (9)
F(24)	0.2656 (6)	0.4082 (4)	-0.5698 (8)	C(81)	0.5146 (7)	0.1383 (4)	-0.2994 (8)
B(1)	0.1662 (14)	0.1743 (9)	-0.0992 (16)	C(82)	0.4796 (7)	0.1067 (5)	-0.2248 (9)
B(2)	0.2756 (9)	0.3486 (6)	-0.6078 (11)	C(83)	0.5455 (9)	0.0670 (6)	-0.1378 (10)
C(1)	0.1435 (6)	0.4339 (4)	-0.4061 (8)	C(84)	0.6372 (9)	0.0607 (5)	-0.1329 (10)
C(2)	0.5027 (6)	0.2660 (4)	-0.3844 (7)	C(85)	0.6736 (9)	0.0918 (6)	-0.2057 (11)
C(3)	0.0465 (6)	0.1101 (4)	-0.4875 (7)	C(86)	0.6118 (9)	0.1315 (5)	-0.2915 (10)
C(11)	-0.0287 (7)	0.3802 (4)	-0.5986 (8)	C(91)	0.1414 (7)	0.0611 (4)	-0.6349 (8)
C(12)	-0.1319 (8)	0.3735 (5)	-0.6344 (10)	C(92)	0.0784 (8)	0.0070 (5)	-0.6711 (9)
C(13)	-0.1911 (9)	0.3737 (6)	-0.7587 (10)	C(93)	0.0594 (8)	-0.0212 (5)	-0.7828 (10)
C(14)	-0.1489 (9)	0.3797 (6)	-0.8380 (10)	C(94)	0.0997 (9)	0.0060 (6)	-0.8510 (10)
C(15)	-0.0482 (10)	0.3896 (6)	-0.8032 (11)	C(95)	0.1609 (9)	0.0609 (6)	-0.8215 (10)
C(16)	0.0141 (8)	0.3878 (5)	-0.6802 (10)	C(96)	0.1830 (7)	0.0905 (5)	-0.7082 (8)
C(21)	-0.0231 (7)	0.3763 (5)	-0.3637 (8)	C(101)	0.2176 (7)	0.0370 (4)	-0.3857 (8)
C(22)	-0.0710 (8)	0.4318 (5)	-0.3689 (10)	C(102)	0.2634 (8)	-0.0125 (5)	-0.4138 (9)
C(23)	-0.1310 (10)	0.4369 (6)	-0.3166 (10)	C(103)	0.3121 (9)	-0.0550 (6)	-0.3166 (11)
C(24)	-0.1397 (10)	0.3907 (7)	-0.2355 (12)	C(104)	0.3102 (9)	-0.0440 (6)	-0.2121 (11)
C(25)	-0.0878 (12)	0.3349 (7)	-0.2203 (13)	C(105)	0.2651 (10)	0.0046 (6)	-0.1852 (11)
C(26)	-0.0287 (9)	0.3279 (6)	-0.2888 (10)	C(106)	0.2179 (8)	0.0460 (5)	-0.2768 (9)
C(31)	0.3332 (7)	0.4904 (4)	-0.2527 (8)	C(111)	-0.0180 (6)	0.1828 (4)	-0.6987 (7)
C(32)	0.3851 (8)	0.5149 (5)	-0.1410 (9)	C(112)	0.0360 (8)	0.2243 (5)	-0.7403 (9)
C(33)	0.4494 (8)	0.5709 (6)	-0.1231 (10)	C(113)	0.0242 (9)	0.2170 (6)	-0.8598 (10)
C(34)	0.4588 (9)	0.5987 (6)	-0.2159 (11)	C(114)	-0.0404 (9)	0.1699 (6)	-0.9312 (10)
C(35)	0.4025 (10)	0.5766 (7)	-0.3304 (12)	C(115)	-0.0931 (8)	0.1280 (5)	-0.8879 (10)
C(36)	0.3421 (9)	0.5188 (6)	-0.3484 (10)	C(116)	-0.0814 (7)	0.1349 (5)	-0.7705 (8)
C(41)	0.2182 (7)	0.4118 (4)	-0.1568 (8)	C(121)	-0.1125 (6)	0.1921 (4)	-0.5352 (7)
C(42)	0.2479 (8)	0.3628 (5)	-0.0813 (9)	C(122)	-0.1872 (7)	0.2212 (4)	-0.6227 (8)
C(43)	0.2134 (9)	0.3553 (6)	0.0117 (10)	C(123)	-0.2765 (8)	0.2292 (5)	-0.6063 (10)
C(44)	0.1512 (9)	0.3978 (6)	0.0232 (10)	C(124)	-0.2891 (9)	0.2094 (6)	-0.5093 (11)
C(45)	0.1219 (9)	0.4487 (6)	-0.0503 (10)	C(125)	-0.2128 (10)	0.1795 (6)	-0.4204 (11)
C(46)	0.1570 (8)	0.4554 (5)	-0.1410 (9)	C(126)	-0.1233 (8)	0.1711 (5)	-0.4347 (10)
C(51)	0.5567 (6)	0.3857 (4)	-0.2653 (7)				

ᵃ A final difference-Fourier synthesis revealed a residual peak at (0.220, 0.228, -0.298), which is tentatively assigned as the hydroxy hydrogen atom (see text).

and 15.0°/min, respectively. Three standard reflections [(050), (144), (0,10,4)] were collected at 50-reflection intervals throughout data collection to monitor the quality of the crystal and gave no indication of sample decomposition. The data were corrected for Lorentz and polarization effects, but an absorption correction was not applied (the observed variation in ψ-scan intensities was only 8%). Data reduction resulted in 8932 measured reflections of which 8553 were unique. Of these, a total of 6041 reflections had F^2 values greater than $3\sigma(F^2)$, and they were used in the solution and refinement of the structure.

Structure Solution and Refinement of [Cu₃(dpm)₃(OH)]²⁺[BF₄]⁻₂. The structure was successfully solved and refined in the triclinic space group $P\bar{1}$ (No. 2). The initial phasing model was determined by using direct methods (MULTAN[21]), which readily revealed the positions of the three independent Cu atoms. The remaining non-hydrogen atoms were located in subsequent difference-Fourier maps.[22] The resulting model was then refined, first isotropically and then anisotropically (with the Cu, P, F, and O atoms assigned anisotropic temperature factors). The final agreement factors are $R = 0.068$ and $R_w = 0.077$.[23]

No attempt was made to locate or calculate the phenyl hydrogen positions. The largest peak on the final difference-Fourier map had a height of 0.7 e Å⁻³ and was clearly a residual of one of the Cu atoms. A second peak of intensity 0.37 e Å⁻³ was located near the oxygen atom at approximately the position calculated for the hydroxy hydrogen atom, but was not included in the analysis. The final atomic coordinates are listed in Table II. Final temperature factors and observed and calculated structure factors are available as supplementary material.

Description of the Molecular Structure

The structure of [Cu₃(dpm)₃(OH)]²⁺[BF₄]⁻₂ consists of discrete trinuclear dications [Cu₃(dpm)₃(OH)]²⁺ and associated [BF₄]⁻ anions. Plots showing the molecular geometry, and associated ion pairing, are presented in Figures 1–3. A selected listing of relevant distances and angles is given in Table III.

The complex dication [Cu₃(dpm)₃(OH)]²⁺ consists of a triangular array of copper atoms with each edge of the cluster bridged by a dpm ligand and with one of the two faces of the Cu₃ triangle capped by a μ₃-hydroxy ligand (Figure 1). (One

(21) Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A* **1971**, *A27*, 368–376.

(22) The major computations in this work were performed by using CRYM, an amalgamated set of crystallographic programs developed by R. E. Marsh and co-workers at the California Institute of Technology.

(23) $R = \sum|F_o - |F_c||/\sum|F_o|$; $R_w = [\sum w|F_o - |F_c||^2/\sum wF_o^2]^{1/2}$.
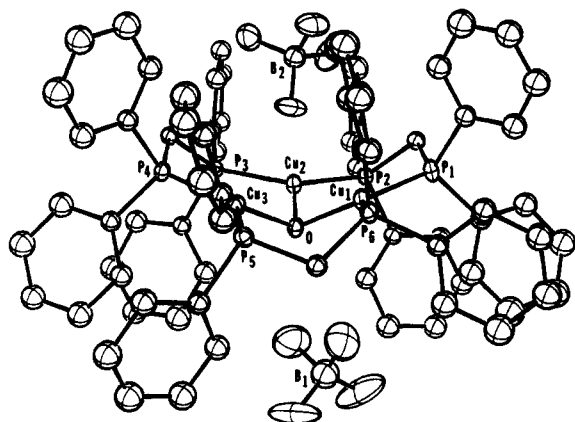
Figure 2. View of $[Cu_3(dpm)_3(OH)]^{2+}[BF_4]^-_2$ showing the "crown" or "picket-fence-like" arrangement of dpm phenyl rings about the Cu_3 core.
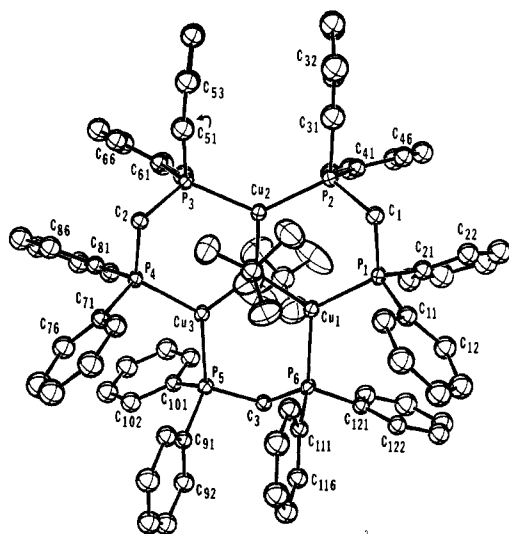
Figure 3. View of the $[Cu_3(dpm)_3(OH)]^{2+}[BF_4]^-_2$ complex approximately normal to the Cu_3 core.

of the $[BF_4]^-$ anions is found situated over the opposite face of the triangle, with one of its fluorine atoms apparently very weakly associated with the three copper atoms (average $Cu\cdots F$ = 2.888 Å)). Two of the edges of the triangle are significantly shorter than the third, with copper-copper distances of 3.120 (2), 3.127 (2), and 3.322 (2) Å for $Cu(1)\cdots Cu(2)$, $Cu(1)\cdots Cu(3)$, and $Cu(2)\cdots Cu(3)$, respectively. A similar set of distances [3.175 (4), 3.175 (4), and 3.281 (3) Å] was previously reported for the related compound $[Cu_3(dpm)_3Cl_2]^+$-$[Cl]^-$.[6a] All of these distances are significantly longer than the range of copper–copper bond lengths [2.494 (5) to 2.674 (5) Å] found in $H_6Cu_6(PPh_3)_6\cdot DMF$,[24] suggesting that the copper atoms in the present compound are not involved in metal–metal-bonding interactions.

Thus, each copper atom is three-coordinate, with phosphorus atoms from each of two bridging dpm ligands occupying two of the coordination sites and the hydroxy oxygen atom occupying the third. The Cu–P distances vary from 2.226 (3) to 2.244 (3) Å, while the mean value for the analogous Cu–P bond distances in $[Cu_3(dpm)_3Cl_2]^+[Cl]^-$ is 2.257 (4) Å. The hydroxy oxygen atom is bound to Cu(1), Cu(2), and Cu(3) at distances of 1.997 (6), 2.026 (6), and 1.996 (6) Å, respectively, and is displaced out of the plane of copper atoms by 0.792 Å. The Cu–O–Cu angles are 101.7 (2), 103.1 (2),

Table III. Selected Distances and Angles in
$[Cu_3(dpm)_3(OH)]^{2+}[BF_4]^-_2$

(A) Bond Distances (Å)

Copper–Ligand

Cu(1)–P(6)	2.238 (3)	Cu(3)–P(5)	2.244 (3)
Cu(1)–P(1)	2.226 (3)	Cu(1)–O	1.997 (6)
Cu(2)–P(2)	2.226 (3)	Cu(2)–O	2.026 (6)
Cu(2)–P(3)	2.228 (3)	Cu(3)–O	1.996 (6)
Cu(3)–P(4)	2.232 (3)		

Boron–Fluorine

B(1)–F(11)	1.34 (2)	B(2)–F(21)	1.33 (1)
B(1)–F(12)	1.36 (2)	B(2)–F(22)	1.34 (1)
B(1)–F(13)	1.34 (2)	B(2)–F(23)	1.38 (2)
B(1)–F(14)	1.27 (2)	B(2)–F(24)	1.38 (2)

Phosphorus–Carbon

P(1)–C(1)	1.847 (10)	P(4)–C(2)	1.866 (9)
P(1)–C(11)	1.841 (10)	P(4)–C(71)	1.812 (9)
P(1)–C(21)	1.801 (11)	P(4)–C(81)	1.819 (9)
P(2)–C(1)	1.861 (9)	P(5)–C(3)	1.862 (10)
P(2)–C(31)	1.838 (10)	P(5)–C(91)	1.824 (9)
P(2)–C(41)	1.810 (10)	P(5)–C(101)	1.843 (9)
P(3)–C(2)	1.841 (9)	P(6)–C(3)	1.857 (9)
P(3)–C(51)	1.811 (9)	P(6)–C(111)	1.810 (9)
P(3)–C(61)	1.835 (9)	P(6)–C(121)	1.822 (10)

(B) Bond Angles (deg)

At Copper

O–Cu(1)–P(6)	115.0 (2)	O–Cu(3)–P(5)	115.4 (2)
O–Cu(1)–P(1)	124.6 (2)	P(1)–Cu(1)–P(6)	119.9 (1)
O–Cu(2)–P(2)	116.9 (2)	P(2)–Cu(2)–P(3)	129.2 (1)
O–Cu(2)–P(3)	112.4 (2)	P(4)–Cu(3)–P(5)	124.4 (1)
O–Cu(3)–P(4)	118.6 (2)		

At Oxygen

Cu(1)–O–Cu(2)	101.7 (2)	Cu(2)–O–Cu(3)	111.3 (3)
Cu(1)–O–Cu(3)	103.1 (2)		

At Methylene Carbons

P(1)–C(1)–P(2)	110.2 (5)	P(5)–C(3)–P(6)	108.1 (5)
P(3)–C(2)–P(4)	111.5 (5)		

At Phosphorus

Cu(1)–P(1)–C(1)	117.6 (3)	Cu(3)–P(4)–C(2)	118.5 (3)
Cu(1)–P(1)–C(11)	109.0 (3)	Cu(3)–P(4)–C(71)	112.0 (3)
Cu(1)–P(1)–C(21)	115.4 (3)	Cu(3)–P(4)–C(81)	114.0 (3)
C(1)–P(1)–C(11)	102.9 (4)	C(2)–P(4)–C(71)	102.2 (4)
C(1)–P(1)–C(21)	105.9 (5)	C(2)–P(4)–C(81)	104.2 (4)
C(11)–P(1)–C(21)	104.6 (5)	C(71)–P(4)–C(81)	104.4 (4)
Cu(2)–P(2)–C(1)	113.5 (3)	Cu(3)–P(5)–C(3)	114.0 (3)
Cu(2)–P(2)–C(31)	117.0 (3)	Cu(3)–P(5)–C(91)	123.6 (3)
Cu(2)–P(2)–C(41)	113.6 (3)	Cu(3)–P(5)–C(101)	105.0 (3)
C(1)–P(2)–C(31)	102.2 (4)	C(3)–P(5)–C(91)	104.7 (4)
C(1)–P(2)–C(41)	104.3 (4)	C(3)–P(5)–C(101)	102.4 (4)
C(31)–P(2)–C(41)	104.9 (4)	C(91)–P(5)–C(101)	104.8 (4)
Cu(2)–P(3)–C(2)	116.9 (3)	Cu(1)–P(6)–C(3)	114.5 (3)
Cu(2)–P(3)–C(51)	115.1 (3)	Cu(1)–P(6)–C(111)	118.1 (3)
Cu(2)–P(3)–C(61)	113.9 (3)	Cu(1)–P(6)–C(121)	110.0 (3)
C(2)–P(3)–C(51)	102.0 (4)	C(3)–P(6)–C(111)	104.7 (4)
C(2)–P(3)–C(61)	103.7 (4)	C(3)–P(6)–C(121)	102.9 (4)
C(51)–P(3)–C(61)	103.6 (4)	C(111)–P(6)–C(121)	105.2 (4)

and 111.3 (3)° with a mean of 105 (6)°. These values may be compared to the Cu–O distance of 1.99 (1) Å and Cu–O–Cu angle of 108.2 (4)° reported for the triply bridging hydroxy group in the trinuclear copper(II) complex $Cu_3L_3(OH)(SO_4)$, where L is the pyridine-2-carbaldehyde oximato ligand.[25,26] The hydroxy oxygen atom in the latter complex is displaced out of the Cu_3 plane by 0.697 (15) Å. Similar values were also obtained for the complex $[Cu_3L'_3(OH)(ClO_4)]^+[ClO_4]^-$, where L'H is 3-(phenylimino)butanone 2-oxime[27] (the mean Cu–O and Cu–O–Cu values were 1.964 Å and 108.8°, re-

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spectively, while the hydroxy oxygen atom was found 0.695 Å out of the Cu_3 plane).

The two independent $[BF_4]^-$ anions are situated in the hydrophobic cavities above and below the Cu_3 triangle (figures 1 and 2), with a mean B–F distance of 1.34 (1) Å and F–B–F angle of 109 (1)°. One of the $[BF_4]^-$ fluorine atoms, F(21), is positioned over the face of the Cu_3 triangle opposite the hydroxy oxygen atom, with Cu(1)···F(21), Cu(2)···F(21), and Cu(3)···F(21) distances of 3.008 (8), 2.674 (6), and 2.983 (7) Å, respectively. These distances are all significantly longer than reported Cu–F distances involving "semicoordinated" (2.56 Å)[28,29] or "weakly coordinated" (2.31 Å)[30] $[BF_4]^-$ anions. We thus conclude that the $[BF_4]^-$ interactions observed are predominately electrostatic in nature and that the structure of $[Cu_3(dpm)_3(OH)]^{2+}[BF_4]^-_2$ is best described as consisting of associated molecular ions in the solid state.

Discussion

Prior to this study, the only other trinuclear copper(I) dpm complexes structurally characterized were the two related compounds $[Cu_3(dpm)_3Cl_2]^+[Cl]^{-6a}$ and $Cu_3(dpm)_2I_3$.[6b] As in the title compound of this work, the dpm molecules in these other two complexes were also found in bridging positions along the edges of Cu_3 triangles. $[Cu_3(dpm)_3Cl_2]^+[Cl]^-$ and $Cu_3(dpm)_2I_3$ are further similar in that triply bridging halide ligands are found situated over each face of the Cu_3 triangles to give a central trigonal-bipyramidal Cu_3X_2 core in each of these molecules. In contrast, only one of the two faces of the

metallic triangle in $[Cu_3(dpm)_3(OH)]^{2+}[BF_4]^-_2$ is found to be capped, in this case by a μ_3-hydroxy ligand (presumably resulting from the deprotonation of a water of hydration in the $Cu(BF_4)_2 \cdot xH_2O$ starting material). Thus, while the two former compounds contain four-coordinate, closed-shell 18-electron metal centers, the $[Cu_3(dpm)_3(OH)]^{2+}$ dication differs in having three-coordinate, coordinatively unsaturated 16-electron copper atoms. The face of the Cu_3 triangle opposite the hydroxy group in $[Cu_3(dpm)_3(OH)]^{2+}$ may hence be viewed as a sort of a metal surface with three sites of unsaturation (one per copper atom) available for the absorption of small molecules, e.g., carbon monoxide.

In addition to the coordinative unsaturation of the title compound, the placement of the dpm phenyl groups about the metal atoms in $[Cu_3(dpm)_3(OH)]^{2+}$ is worthy of some discussion. As shown in Figures 2 and 3, the three copper atoms are encircled by a cylindrical array of phenyl rings and hence may be said to reside in a "picket-fence-like" environment. In effect, what we have here resembles a small triangular metal surface situated in a hydrophobic cavity. How this cavity or pocket may alter the binding and reactivity of substrate species on the Cu_3 surface is not known at this time. One can speculate about the possible catalytic potential of metal complexes of this type, in addition to their use as suitable precursor molecules from which group 1b cluster carbonyls and hydrides might be obtained.

Supplementary Material Available: Listings of temperature factors (Table A) for this structure determination and observed and calculated structure factors (Table B) (29 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structures of Bis(cyclodecane-1,3-dionato)copper(II) and Bis(cyclotridecane-1,3-dionato)copper(II)

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The crystal and molecular structures of bis(cyclodecane-1,3-dionato)copper(II), $Cu(CDD)_2$, and bis(cyclotridecane-1,3-dionato)copper(II), $Cu(CTDD)_2$, were determined by single-crystal X-ray diffraction analysis. The unit cell of $Cu(CDD)_2$ is monoclinic (space group $P2_1/n$) with dimensions a = 4.9657 (7) Å, b = 14.977 (2) Å, c = 12.670 (2) Å, β = 95.84 (1)°, and Z = 2. The unit cell of $Cu(CTDD)_2$ is also monoclinic (space group $P2_1/c$) with dimensions a = 4.900 (3) Å, b = 28.206 (7) Å, c = 9.060 (3) Å, β = 102.21 (3)°, and Z = 2. In both compounds the copper atom has square-planar coordination with the four oxygen atoms. However, there is a greater degree of distortion in the chelate ring of $Cu(CDD)_2$ as compared to that of $Cu(CTDD)_2$.

Introduction

In a survey of the chelation behavior of a series of macrocyclic 1,3-diketones of the type
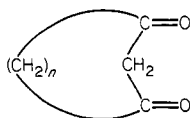
where n = 4, 6, 7, 8, and 10, it was observed that the selectivity of the chelation increased with decreasing ring size.[1] The

thirteen-carbon β-diketone formed chelates readily with many metal ions as expected whereas the ten-carbon diketone formed chelates only with Fe(III) and Cu(II). The seven- and nine-carbon diketones were not observed to form chelates with Be(II), Mg(II), Al(III), Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Pd(II), and Cd(II). This selectivity is in contrast to the nonselective chelation behavior of β-diketones in general. It was also observed that the degree of enolization in this series decreased with decreasing ring size down to n = 4–6 where there was a very limited tendency to enolize.[1–4]

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