however, PMDETA has thus far been structurally characterized only in the more usual four-coordinate covalent stereochemistry, exemplified in $[(o\text{-}C_6H_4CH_3(CHSiMe_3))(Li(PMDETA))]$;[9] in the latter, Li-N are only slightly shorter than the present values (Table II), being 2.17 (1), 2.23 (1), and 2.18 (1) Å, with the angles contained by the ligand being 84.1 (4), 84.8 (3), and 114.2 (4)°.

**Acknowledgment.** We gratefully acknowledge receipt of a grant in support of this work from the Australian Research Grants Committee.

**Registry No. 1**, 87729-09-7.

**Supplementary Material Available:** Listings of observed and calculated structure factor amplitudes, thermal parameters, and hydrogen atom parameters (14 pages). Ordering information is given on any current masthead page.

---

(8) M. di Vaira and P. L. Orioli, *Inorg. Chem.*, **8**, 2729 (1969).

(9) M. F. Lappert, C. L. Raston, B. W. Skelton, and A. H. White, to be submitted for publication in *J. Chem. Soc., Dalton Trans.*

---

Contribution from the Department of Chemistry,
University of Southern California, Los Angeles, California 90089-1062

# Preparation and Structural Characterization of $[Ag_2(dpm)_2(NO_3)_2]$ and $[Ag_4(dpm)_4(NO_3)_2]^{2+}[PF_6]^-{}_2$: Conformational Flexibility in the $M_2P_4$ Core Structure of Bis(diphenylphosphino)methane Complexes

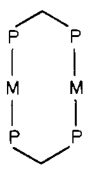
DOUGLAS M. HO and ROBERT BAU*

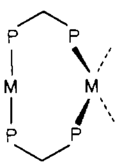
*Received March 16, 1983*

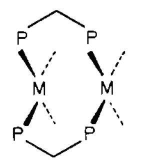
The bis(diphenylphosphino)methane (dpm) silver compounds $[Ag_2(dpm)_2(NO_3)_2]$ and $[Ag_4(dpm)_4(NO_3)_2]^{2+}[PF_6]^-{}_2$ have been synthesized and characterized by IR and $^1H$ NMR spectroscopy and X-ray diffraction. The molecules are found to contain $[Ag_2(dpm)_2]^{2+}$ core structures with the two silver atoms bridged by the dpm ligands to give eight-membered $Ag_2P_4C_2$ rings. The $[Ag_2(dpm)_2]^{2+}$ units exist in a range of conformational forms subject to the nature of additional ligands present (e.g., $NO_3^-$). In $[Ag_2(dpm)_2(NO_3)_2]$ and $[Ag_4(dpm)_4(NO_3)_2]^{2+}[PF_6]^-{}_2$, the $[Ag_2(dpm)_2]^{2+}$ units are significantly folded along the Ag⋯Ag axes in the solid state (P–Ag–P angles from 138 to 152°). $^1H$ NMR data on $[Ag_2(dpm)_2(NO_3)_2]$ in acetonitrile, however, are consistent with a nonfolded structure for the $[Ag_2(dpm)_2]^{2+}$ dication in solution. Crystallographic details are as follows. For $[Ag_2(dpm)_2(NO_3)_2]$: monoclinic space group $C2/c$, $a = 12.687$ (4) Å, $b = 16.997$ (3) Å, $c = 22.627$ (6) Å, $\beta = 100.73$ (3)°, $Z = 4$, $R = 5.0\%$ for 2669 nonzero reflections with $F^2 > 3\sigma(F^2)$. For $[Ag_4(dpm)_4(NO_3)_2]^{2+}[PF_6]^-{}_2$: triclinic space group $P\bar{1}$, $a = 13.703$ (3) Å, $b = 14.516$ (2) Å, $c = 13.402$ (2) Å, $\alpha = 112.21$ (1)°, $\beta = 96.82$ (2)°, $\gamma = 83.56$ (1)°, $Z = 1$, $R = 5.6\%$ for 4555 nonzero reflections.

## Introduction

A key feature in the chemistry of dinuclear bis(diphenylphosphino)methane (dpm) complexes is the relatively stable, intrinsic $M_2(dpm)_2$ framework. In general, this has consisted of trans-bound, bridging dpm ligands to give a planar $M_2P_4$ core structure (I) with the two metal atoms held in close proximity to each other (regardless of whether a metal–metal bond is present or not). This feature is presumably one of the chief reasons for the unusual bonding, reactivity, and catalytic properties of $M_2(dpm)_2$ compounds. The stable $M_2(dpm)_2$ framework, while accepting some conformational changes when interacting with small molecules, places much of the burden for any structural adjustment on the substrate species themselves and on any additional ligands present. This adjustment may be expressed in terms of unique bonding interactions or chemical reactivity. For example, the unusual $\mu_2\text{-}\eta^1,\eta^2$ bridge-binding ($\sigma$, $\pi$) mode for carbon monoxide was first discovered in the homobimetallic dpm complex $[Mn_2(dpm)_2(CO)_5]$,[1] while the rare "unsupported" bridging CO linkage (i.e., without concomitant M–M bonding) can be found in the compounds $[M_2(dpm)_2(\mu\text{-CO})X_2]$ (M = Pd, Pt; X = Cl, Br, I).[2-4] Further, the bridging CO ligands in the latter complexes can be removed and reinserted reversibly, a phenomenon currently unique to $(dpm)_2$ compounds. Catalytic hydrogenation[5-7] and water gas shift activity[7,8] involving $M_2(dpm)_2$ species have also been reported.


I


II


III

Bis(diphenylphosphino)methane compounds containing alternate forms for the $M_2(dpm)_2$ framework on the other hand are rather uncommon but have also been recently isolated and characterized. $[Pt_2(dpm)_2(CH_3)_3]^{+}$[9] and $[Pt_2(dpm)_2(CH_3)_4]$,[10] for instance, have been found to contain cis-bound phosphorus donor atoms to give the new structural types II and III, respectively. In fact, the discovery of still other structural forms (in addition to types I–III) seems highly probable in light of more recent efforts to systematically synthesize *hetero*bimetallic dpm complexes.[11-15] The $M_2P_4$ core structure of

---

(1) Commons, C. J.; Hoskins, B. F. *Aust. J. Chem.* **1975**, *28*, 1663-1672.

(2) Brown, M. P.; Puddephatt, R. J.; Rashidi, M.; Manojlović-Muir, L.; Muir, K. W.; Solomun, T.; Seddon, K. R. *Inorg. Chim. Acta* **1977**, *23*, L33-L34.

(3) Brown, M. P.; Puddephatt, R. J.; Rashidi, M.; Seddon, K. R. *J. Chem. Soc., Dalton Trans.* **1978**, 1540-1544.

(4) Benner, L. S.; Balch, A. L. *J. Am. Chem. Soc.* **1978**, *100*, 6099-6106.

(5) Sanger, A. R. *Can. J. Chem.* **1982**, *60*, 1363-1367.

(6) Kubiak, C. P.; Woodcock, C.; Eisenberg, R. *Inorg. Chem.* **1980**, *19*, 2733-2739.

(7) Kubiak, C. P.; Eisenberg, R. *J. Am. Chem. Soc.* **1980**, *102*, 3637-3639.

(8) Frew, A. A.; Hill, R. H.; Manojlović-Muir, L.; Muir, K. W.; Puddephatt, R. J. *J. Chem. Soc., Chem. Commun.* **1982**, 198-200.

(9) Brown, M. P.; Cooper, S. J.; Frew, A. A.; Manojlović-Muir, L.; Muir, K. W.; Puddephatt, R. J.; Seddon, K. R.; Thomson, M. A. *Inorg. Chem.* **1981**, *20*, 1500-1507.

(10) Puddephatt, R. J.; Thomson, M. A.; Manojlović-Muir, L.; Muir, K. W.; Frew, A. A.; Brown, M. P. *J. Chem. Soc., Chem. Commun.* **1981**, 805-806.

(11) Pringle, P. G.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1982**, 81-82.

(12) McEwan, D. M.; Pringle, P. G.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1982**, 859-861.

0020-1669/83/1322-4073$01.50/0 © 1983 American Chemical Society

[(PhC≡C)$_2$Pt(dpm)$_2$AgI], for example, exhibits trans coordination at the platinum atom but a nonlinear, bent coordination at silver [P–Ag–P = 126.4 (10)°].[13] The chemistry of complexes containing these new structural forms, however, remains largely undeveloped in comparison to that of the type I compounds above.

In our own laboratories, and as an extension of our studies on metal hydrides,[16] we have also been involved with introducing silver atoms into the $M_2(dpm)_2$ moiety. In particular, we have been intrigued with the possibility of isolating stable molecular silver hydride complexes based on the $M_2(dpm)_2$ support structure. The dpm ligand has served to stabilize a variety of such hydridic species involving other metal atoms, e.g., $[Pt_2(dpm)_2(H)_3]^+$[17] and $[Rh_2(dpm)_2(CO)_3H]^+$,[7] and we are pursuing the idea that analogous $[Ag_2(dpm)_2H_x]$ molecules might also prove isolable. Along these lines, we have synthesized two new silver dpm complexes as possible starting materials.[18] We report here the preparation of $[Ag_2(dpm)_2(NO_3)_2]$ and $[Ag_4(dpm)_4(NO_3)_2]^{2+}[PF_6]^-_2$ and the first structural details on the homobimetallic $Ag_2(dpm)_2$ moiety. As in the heterobimetallic complex [(PhC≡C)$_2$Pt(dpm)$_2$AgI],[13] dpm coordination to silver in the $Ag_2(dpm)_2$ units of $[Ag_2(dpm)_2(NO_3)_2]$ and $[Ag_4(dpm)_4(NO_3)_2]^{2+}[PF_6]^-_2$ is found to be of a nonlinear form. In addition, the $M_2(dpm)_2$ core structures in these molecules are apparently quite flexible, exhibiting varying degrees of folding along the M···M axis in the solid state. Spectroscopic evidence, however, supports a trans-bound (type I) solution structure for the coordinatively unsaturated $[Ag_2(dpm)_2]^{2+}$ dication.[19]

## Experimental Section

**General Considerations.** Bis(diphenylphosphino)methane was purchased from Pressure Chemical Co. and used without further purification. Infrared spectra were recorded on a Perkin-Elmer 281 spectrophotometer and calibrated against polystyrene. Room-temperature $^1H$ NMR spectra were taken on a Varian XL-100 spectrometer operating at 100.1 MHz in the Fourier-transform mode. Elemental analyses were performed by the Caltech Analytical Facility, Pasadena, CA.

**Preparation of $[Ag_2(dpm)_2(NO_3)_2]$.** $AgNO_3$ (1.70 g, 10 mmol) and dpm (3.84 g, 10 mmol) in methanol (500 mL) were refluxed under nitrogen in the dark for 30 min. The solution was then concentrated under vacuum to approximately 100 mL. The pale yellow microcrystalline product obtained was filtered off in air and recrystallized from methanol as colorless prisms: yield 2.74 g (58%); mp 206–208 °C dec. Anal. Calcd for $C_{50}H_{44}N_2O_6P_4Ag_2$: C, 54.17; H, 4.00; N, 2.53. Found: C, 53.56; H, 4.00; N, 2.62.

**Preparation of $[Ag_4(dpm)_4(NO_3)_2]^{2+}[PF_6]^-_2$.** In an attempt to prepare $[Ag_2(dpm)_2]^{2+}[PF_6]^-_2$, a twofold excess of $K[PF_6]$ (0.037 g, 0.20 mmol) was added with stirring to a solution of $[Ag_2(dpm)_2(NO_3)_2]$ (0.111 g, 0.10 mmol) in 40 mL of absolute methanol. The resulting clear and colorless solution was subsequently allowed to evaporate slowly at room temperature to a final volume of 5–10 mL. Multifaceted, colorless crystals of $[Ag_4(dpm)_4(NO_3)_2]^{2+}[PF_6]^-_2$ were obtained, which were separated by filtration, washed with methanol, and dried in air: yield 0.094 g (79%); mp 216–217 °C dec. Anal. Calcd for $C_{100}H_{88}F_{12}N_2O_6P_{10}Ag_4$: C, 50.40; H, 3.72; N, 1.18. Found: C, 50.19; H, 3.71; N, 1.21.

**Collection and Reduction of X-ray Data for $[Ag_2(dpm)_2(NO_3)_2]$.** A colorless rhombohedral crystal of dimensions 0.32 × 0.32 × 0.37 mm was mounted on a glass fiber and manually centered on a Syntex P2$_1$ automated four-circle diffractometer. Fifteen reflections (9° < 2$\theta$ < 25°) were then machine centered until angular changes for each reflection were less than 0.02° in 2$\theta$, 0.01° in $\omega$, and 0.04° in $\chi$. These results were then used in the calculation of the unit cell parameters (Table I) and the orientation matrix for data collection.

Table I. Crystal Data for $[Ag_2(dpm)_2(NO_3)_2]$

| | |
|---|---|
| crystal type | monoclinic |
| space group | $C2/c$ (No. 15) |
| unit cell parameters | |
| $a$, Å | 12.687 (4) |
| $b$, Å | 16.997 (3) |
| $c$, Å | 22.627 (6) |
| $\beta$, deg | 100.73 (3) |
| $V$, Å$^3$ | 4794 (2) |
| formula units per unit cell, $Z$ | 4 |
| mol wt | 1108.54 |
| $\rho$(calcd), g cm$^{-3}$ | 1.54 |
| $\rho$(obsd), g cm$^{-3}$ | 1.49 ($CCl_4/CHCl_3$) |
| abs coeff ($\mu$), cm$^{-1}$ (for Mo K$\alpha$ X-rays) | 9.80 |

Table II. Final Atomic Positions (Fractional Coordinates) for $[Ag_2(dpm)_2(NO_3)_2]$

| atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| Ag | 0.084 95 (4) | 0.145 93 (3) | 0.308 41 (2) |
| P(1) | 0.219 54 (13) | 0.186 92 (10) | 0.250 78 (8) |
| P(2) | 0.044 89 (13) | 0.206 07 (10) | 0.139 99 (8) |
| O(1) | 0.100 84 (40) | 0.004 39 (30) | 0.314 50 (25) |
| O(2) | 0.220 88 (53) | 0.053 01 (39) | 0.382 96 (26) |
| O(3) | 0.221 49 (54) | −0.069 93 (38) | 0.364 90 (31) |
| N | 0.183 72 (52) | −0.005 03 (38) | 0.354 59 (30) |
| C(1) | 0.161 72 (51) | 0.251 28 (38) | 0.187 58 (29) |
| C(11) | 0.296 17 (52) | 0.114 55 (39) | 0.217 76 (30) |
| C(12) | 0.266 14 (67) | 0.035 71 (47) | 0.218 88 (38) |
| C(13) | 0.322 79 (82) | −0.022 02 (62) | 0.192 57 (49) |
| C(14) | 0.410 35 (75) | 0.000 68 (58) | 0.166 57 (47) |
| C(15) | 0.440 89 (77) | 0.077 19 (56) | 0.166 64 (44) |
| C(16) | 0.381 19 (72) | 0.134 91 (49) | 0.192 00 (38) |
| C(21) | 0.320 89 (50) | 0.247 86 (37) | 0.296 58 (28) |
| C(22) | 0.356 14 (60) | 0.222 53 (45) | 0.355 63 (35) |
| C(23) | 0.434 66 (68) | 0.266 03 (51) | 0.394 22 (39) |
| C(24) | 0.475 18 (73) | 0.332 89 (53) | 0.372 66 (42) |
| C(25) | 0.438 86 (68) | 0.359 96 (46) | 0.314 57 (38) |
| C(26) | 0.362 83 (60) | 0.316 03 (44) | 0.276 70 (34) |
| C(31) | 0.100 74 (53) | 0.141 31 (38) | 0.089 04 (30) |
| C(32) | 0.077 63 (78) | 0.063 37 (59) | 0.090 10 (45) |
| C(33) | 0.119 73 (98) | 0.012 10 (75) | 0.049 73 (58) |
| C(34) | 0.181 15 (77) | 0.041 17 (58) | 0.012 22 (45) |
| C(35) | 0.204 78 (84) | 0.117 18 (64) | 0.011 20 (49) |
| C(36) | 0.163 40 (81) | 0.170 71 (60) | 0.050 57 (46) |
| C(41) | −0.012 26 (52) | 0.285 94 (38) | 0.091 03 (30) |
| C(42) | −0.122 27 (64) | 0.284 50 (48) | 0.069 35 (37) |
| C(43) | −0.166 97 (79) | 0.341 14 (55) | 0.026 97 (45) |
| C(44) | −0.103 22 (71) | 0.396 40 (53) | 0.006 44 (40) |
| C(45) | 0.004 52 (70) | 0.398 41 (51) | 0.029 79 (40) |
| C(46) | 0.048 82 (64) | 0.344 99 (44) | 0.072 01 (36) |

One quadrant of data (±$h$,+$k$,+$l$) was collected at room temperature by using the fixed-detector/moving-crystal ($\omega$-scan) method and Mo K$\alpha$ radiation ($\lambda$ = 0.71069 Å). The minimum and maximum 2$\theta$ limits employed were 3.0 and 45.0°, respectively. Reflections were measured with a scan speed ranging from 2.5 to 29.3°/min. The particular scan speed for each reflection was set approximately proportional to its intensity as estimated by a fast preliminary 2-s scan through the peak prior to actual collection. Three standard reflections—$(0\bar{4}1)$, $(5\bar{3}\bar{6})$, $(\overline{10},0,\bar{4})$—were monitored for every 50 reflections collected and gave no indication of any instrumental instability or sample decomposition. A total of 3183 reflections were measured of which 3093 were unique. Of these, 2669 reflections had $F^2$ values greater than $3\sigma(F^2)$. The intensity data were corrected for Lorentz and polarization effects but not for absorption. Analysis of the intensity values of an axial reflection ($\chi$ = 90°) vs. spindle angle $\phi$ indicated only a 5% variation in intensities. On this basis, an absorption correction was deemed unnecessary.

**Structure Solution and Refinement of $[Ag_2(dpm)_2(NO_3)_2]$.** The structure was solved in the monoclinic space group $C2/c$ (No. 15) by conventional heavy-atom methods. The position of the lone silver atom in the asymmetric unit was determined from a Patterson map while the remaining non-hydrogen atoms were located from subsequent

---

(13) McDonald, W. S.; Pringle, P. G.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1982**, 861–864.

(14) Pringle, P. G.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1982**, 956–957.

(15) McEwan, D. M.; Pringle, P. G.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1982**, 1240–1241.

(16) Teller, R. G.; Bau, R. *Struct. Bonding (Berlin)* **1981**, *44*, 1–82.

(17) Brown, M. P.; Puddephatt, R. J.; Rashidi, M.; Seddon, K. R. *J. Chem. Soc., Dalton Trans.* **1978**, 516–522.

(18) Ho, D. M. Ph.D. Dissertation, University of Southern California, 1981.

(19) van der Ploeg, A. F. M. J.; van Koten, G. *Inorg. Chim. Acta* **1981**, *51*, 225–239.

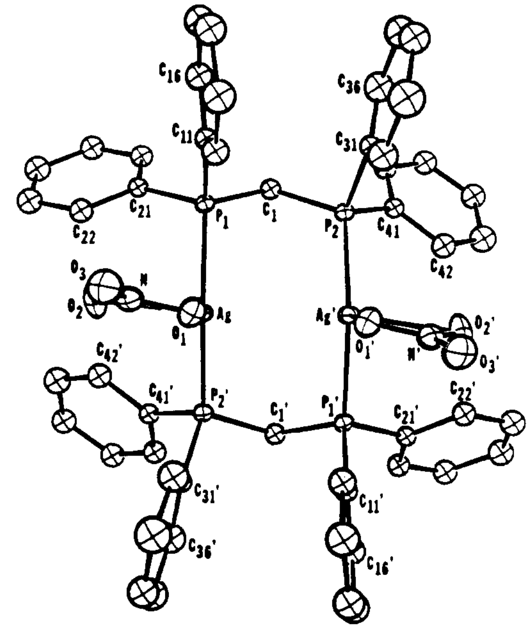


**Figure 1.** Molecular structure and atom labeling for $[Ag_2(dpm)_2(NO_3)_2]$.

Table III. Crystal Data for $[Ag_4(dpm)_4(NO_3)_2]^{2+}[PF_6]^-_2$

| | |
|---|---|
| crystal type | triclinic |
| space group | $P\bar{1}$ (No. 2) |
| unit cell parameters | |
| $a$, Å | 13.703 (3) |
| $b$, Å | 14.516 (2) |
| $c$, Å | 13.402 (2) |
| $\alpha$, deg | 112.21 (1) |
| $\beta$, deg | 96.82 (2) |
| $\gamma$, deg | 83.56 (1) |
| $V$, Å$^3$ | 2443.9 (8) |
| formula units per unit cell, $Z$ | 1 |
| mol wt | 2382.99 |
| $\rho$(calcd), g cm$^{-3}$ | 1.62 |
| $\rho$(obsd), g cm$^{-3}$ | 1.58 |
| abs coeff ($\mu$), cm$^{-1}$ (for Mo K$\alpha$ X-rays) | 10.1 |

difference-Fourier syntheses.[20] This was followed by several cycles of full-matrix least-squares refinement in which all non-carbon atoms were assigned anisotropic temperature factors. Convergence resulted in final agreement factors of $R = 0.050$ and $R_w = 0.071$.[21] In the refinement, the function minimized was $\sum w^2(F_o^2 - F_c^2)^2$, where $w = 1/\sigma(F^2)$. A final difference-Fourier map showed no residual peaks greater than 0.6 e Å$^{-3}$. No attempt was made to locate or calculate the phenyl hydrogen positions. The final positional parameters are given in Table II, and a molecular plot is shown in Figure 1. The final thermal parameters and a listing of observed and calculated structure factors are available as supplementary material.

**Collection and Reduction of the X-ray Data for $[Ag_4(dpm)_4(NO_3)_2]^{2+}[PF_6]^-_2$.** A colorless specimen of dimensions 0.14 × 0.29 × 0.16 mm was chosen for the analysis and mounted on the end of a glass fiber. Accurate unit cell parameters were obtained by carefully centering 15 reflections ($14° < 2\theta < 22°$) on a Syntex $P2_1$ diffractometer and are presented together with other relevant crystal data in Table III. One hemisphere of data ($\pm h,\pm k,+l$) was collected at room temperature by the $\omega$-scan method with Mo K$\alpha$ radiation ($\lambda = 0.71069$ Å). The minimum and maximum $2\theta$ limits were set to 3.5 and 45.0°, respectively. The scan speed was varied from 2.0 to 29.3°/min. Three check reflections—$(\bar{3}10)$, $(2\bar{6}6)$, (408)—were monitored at 50-reflection intervals throughout the data collection and revealed no significant changes in their intensities. Of the 6242 reflections collected, 5945 were unique and a total of 4555 reflections had $F^2$ values greater than $3\sigma(F^2)$. The intensity data were corrected for Lorentz and polarization effects. However, an absorption correction was not applied, since the intensity of an axial reflection varied by only 3% as a function of $\phi$.

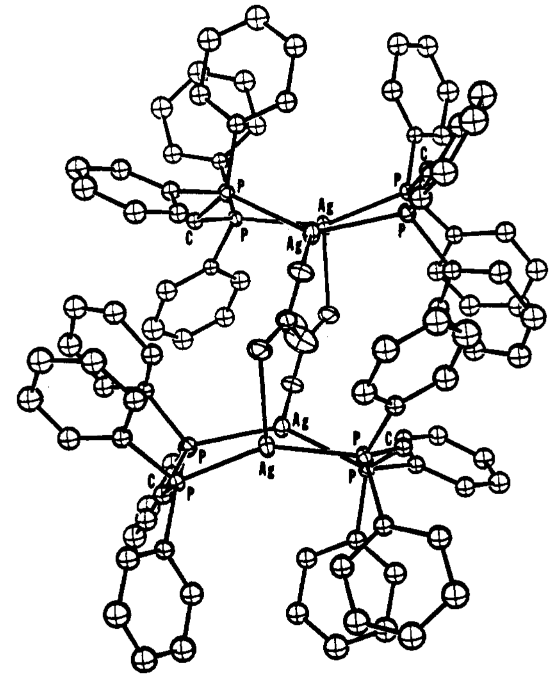


**Figure 2.** View of the $[Ag_4(dpm)_4(NO_3)_2]^{2+}$ dication showing the folded geometry of the $[Ag_2(dpm)_2]^{2+}$ subunits and occupation of the enclosed central cavity by the two nitrate anions.

**Structure Solution and Refinement of $[Ag_4(dpm)_4(NO_3)_2]^{2+}[PF_6]^-_2$.** The structure was solved in the centrosymmetric space group $P\bar{1}$ (triclinic, No. 2) by the heavy-atom method. The coordinates of the two independent silver atoms were determined from a Patterson synthesis, and the positions of the remaining atoms estimated from subsequent difference-Fourier maps.[20] Several cycles of isotropic least-squares refinement were then undertaken to test the correctness of the trial structure. Observed shifts in the positional parameters and a majority of the isotropic temperature factors were, as a whole, quite normal. However, the temperature factors for the six fluorine atoms refined to uncomfortably large values, indicating a possible disorder of the $[PF_6]^-$ anion (a very common phenomenon). Consequently, a difference-Fourier map was generated at this point: six additional peaks were located near the phosphorus atom and were treated as alternate positions for the six fluorine atoms. No additional peak in the difference-Fourier map could be found that might have been attributed to a fragment of the original phosphorus atom. The phosphorus atom of the anion was thus assigned the usual 100% occupancy value while the 12 fluorine positions were initially given 50% occupancy values. Isotropic refinement was subsequently resumed, followed by several cycles of least-squares refinement in which the silver, phosphorus, nitrogen, and oxygen atoms were assigned anisotropic temperature factors.

During the refinement, the occupancies of the disordered fluorine atoms were treated as two interrelated groups of six half-fluorines with the individual occupancy of each fluorine in a given set being required to be the same as that of the remaining five fluorine atoms of that group. The sum of the occupancies of the two groups was further constrained to be equal to 1.0.

The final agreement factors are $R = 0.056$ and $R_w = 0.069$.[21] No attempt was made to locate or calculate the phenyl hydrogen positions. The final difference-Fourier map contained a residual peak of 1.2 e Å$^{-3}$ near the disordered $PF_6^-$ anion, which can be attributed to the fact that the fluorine atoms were not refined anisotropically. The final refined coordinates are listed in Table IV, and various molecular plots are shown in Figures 2–4. The final thermal parameters and the observed and calculated structure factors are available as supplementary material.

## Results

**Synthesis and Properties.** Reaction of $AgNO_3$ with an equimolar quantity of bis(diphenylphosphino)methane in

---

(20) 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.

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

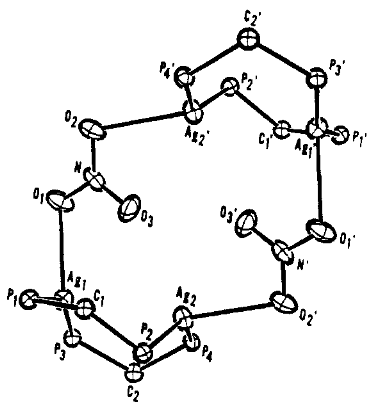


**Figure 3.** Core structure of the $[Ag_4(dpm)_4(NO_3)_2]^{2+}$ dication showing the anti–anti bridge-bonding mode of the nitrate ligands.

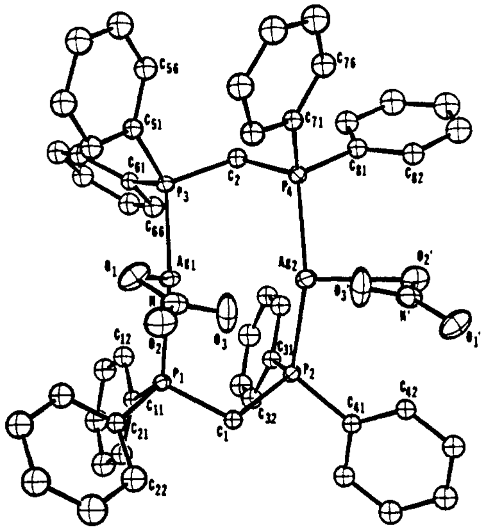


**Figure 4.** Plot that shows approximately half of the tetranuclear $[Ag_4(dpm)_4(NO_3)_2]^{2+}$ cation and features the atom-labeling scheme used in the structure determination. A center of symmetry exists at the midpoint of the O(3)···O(3′) vector. This diagram is included for the purpose of comparing the $[Ag_2(dpm)_2(NO_3)_2]$ portion of the structure of $[Ag_4(dpm)_4(NO_3)_2]^{2+}$ with that of neutral $[Ag_2(dpm)_2(NO_3)_2]$ itself (Figure 1).

methanol (MeOH) affords, in reasonable yield, the new homobimetallic (dpm)₂ complex $[Ag_2(dpm)_2(NO_3)_2]$ (eq 1).

$$2AgNO_3 + 2dpm \xrightarrow{MeOH} [Ag_2(dpm)_2(NO_3)_2] \qquad (1)$$

The product is an air-stable, colorless crystalline material, soluble in polar solvents such as MeOH, acetonitrile, dimethylformamide, and dimethylsulfoxide. It is, however, insoluble in water. The complex has limited solubility in the chlorinated hydrocarbons $CH_2Cl_2$ and $CHCl_3$ and is insoluble in toluene, acetone, ether, and tetrahydrofuran. Solid samples and solutions of the compound show no sensitivity to light.

Metathesis of $[Ag_2(dpm)_2(NO_3)_2]$ with excess $K[PF_6]$ in MeOH at room temperature failed to give the straight hexafluorophosphate derivative $[Ag_2(dpm)_2]^{2+}[PF_6]^-{}_2$. Instead, the product isolated is found to be the tetranuclear complex $[Ag_4(dpm)_4(NO_3)_2]^{2+}[PF_6]^-{}_2$ (eq 2). This latter complex is

$$2[Ag_2(dpm)_2(NO_3)_2] \xrightarrow[K[PF_6]\ (excess)]{MeOH} [Ag_4(dpm)_4(NO_3)_2]^{2+}[PF_6]^-{}_2 \qquad (2)$$

obtained as a colorless crystalline material and is light and air stable as a solid and in solution. Its solubility properties are similar to those of $[Ag_2(dpm)_2(NO_3)_2]$, being most soluble in MeOH and MeCN but insoluble in halogenated hydrocarbons.

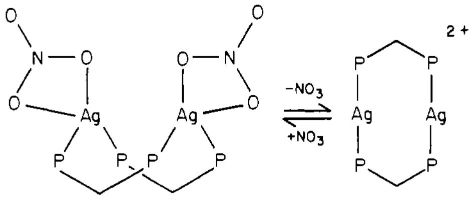
**Table IV.** Final Atomic Positions (Fractional Coordinates) for $[Ag_4(dpm)_4(NO_3)_2]^{2+}[PF_6]^-{}_2$

| atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| Ag(1) | 0.1199 (1) | −0.0339 (1) | −0.2578 (1) |
| Ag(2) | 0.1718 (1) | 0.0446 (1) | −0.0098 (1) |
| P(1) | 0.1670 (2) | −0.2061 (2) | −0.2843 (2) |
| P(2) | 0.2708 (2) | −0.1155 (2) | −0.0578 (2) |
| P(3) | 0.1450 (2) | 0.1197 (2) | −0.2745 (2) |
| P(4) | 0.1660 (2) | 0.2092 (2) | −0.0231 (2) |
| P(5) | 0.6643 (2) | 0.5654 (2) | 0.2435 (3) |
| O(1) | −0.0596 (5) | −0.0509 (6) | −0.2711 (6) |
| O(2) | −0.1580 (5) | −0.1026 (6) | −0.1924 (6) |
| O(3) | −0.0162 (6) | −0.0552 (7) | −0.1149 (6) |
| N | −0.0779 (6) | −0.0691 (6) | −0.1912 (7) |
| F(1) | 0.6093 (12) | 0.5342 (12) | 0.1234 (14) |
| F(2) | 0.7165 (14) | 0.5881 (14) | 0.3573 (16) |
| F(3) | 0.7599 (14) | 0.5813 (15) | 0.1935 (17) |
| F(4) | 0.7101 (11) | 0.4556 (10) | 0.2070 (11) |
| F(5) | 0.5693 (16) | 0.5365 (17) | 0.2712 (17) |
| F(6) | 0.6363 (13) | 0.6787 (12) | 0.2602 (13) |
| F(7) | 0.6380 (18) | 0.4540 (16) | 0.2256 (18) |
| F(8) | 0.7244 (28) | 0.6556 (28) | 0.2844 (31) |
| F(9) | 0.5522 (16) | 0.5967 (17) | 0.2541 (18) |
| F(10) | 0.6678 (16) | 0.5822 (16) | 0.3726 (18) |
| F(11) | 0.7754 (26) | 0.5241 (28) | 0.2541 (30) |
| F(12) | 0.6658 (21) | 0.5511 (20) | 0.1236 (22) |
| C(1) | 0.2094 (6) | −0.2231 (6) | −0.1576 (7) |
| C(2) | 0.2059 (7) | 0.2078 (7) | −0.1499 (7) |
| C(11) | 0.2667 (6) | −0.2589 (7) | −0.3727 (7) |
| C(12) | 0.3123 (8) | −0.1958 (8) | −0.4071 (8) |
| C(13) | 0.3904 (8) | −0.2359 (9) | −0.4733 (10) |
| C(14) | 0.4237 (9) | −0.3328 (9) | −0.5013 (10) |
| C(15) | 0.3789 (9) | −0.3987 (9) | −0.4686 (10) |
| C(16) | 0.2970 (8) | −0.3592 (8) | −0.4033 (9) |
| C(21) | 0.0690 (6) | −0.2848 (6) | −0.3414 (7) |
| C(22) | 0.0522 (8) | −0.3612 (8) | −0.3006 (9) |
| C(23) | −0.0309 (10) | −0.4212 (10) | −0.3495 (11) |
| C(24) | −0.0886 (9) | −0.4070 (9) | −0.4338 (10) |
| C(25) | −0.0731 (8) | −0.3368 (8) | −0.4729 (9) |
| C(26) | 0.0066 (8) | −0.2758 (8) | −0.4252 (9) |
| C(31) | 0.3795 (7) | −0.1070 (7) | −0.1196 (7) |
| C(32) | 0.4391 (8) | −0.1890 (8) | −0.1737 (9) |
| C(33) | 0.5257 (9) | −0.1770 (9) | −0.2163 (10) |
| C(34) | 0.5457 (9) | −0.0819 (9) | −0.2037 (10) |
| C(35) | 0.4870 (8) | 0.0008 (8) | −0.1512 (9) |
| C(36) | 0.4017 (7) | −0.0090 (7) | −0.1058 (8) |
| C(41) | 0.3207 (6) | −0.1620 (6) | 0.0489 (7) |
| C(42) | 0.3016 (7) | −0.1052 (7) | 0.1547 (8) |
| C(43) | 0.3388 (8) | −0.1369 (8) | 0.2387 (8) |
| C(44) | 0.3970 (8) | −0.2264 (8) | 0.2156 (9) |
| C(45) | 0.4121 (8) | −0.2867 (8) | 0.1079 (9) |
| C(46) | 0.3752 (7) | −0.2550 (7) | 0.0241 (8) |
| C(51) | 0.0327 (7) | 0.1846 (7) | −0.3064 (7) |
| C(52) | −0.0458 (8) | 0.1255 (8) | −0.3602 (8) |
| C(53) | −0.1352 (8) | 0.1725 (8) | −0.3831 (9) |
| C(54) | −0.1484 (9) | 0.2752 (9) | −0.3520 (10) |
| C(55) | −0.0707 (9) | 0.3313 (9) | −0.3014 (10) |
| C(56) | 0.0220 (8) | 0.2881 (8) | −0.2798 (9) |
| C(61) | 0.2287 (6) | 0.1097 (6) | −0.3736 (7) |
| C(62) | 0.1952 (8) | 0.1240 (8) | −0.4699 (8) |
| C(63) | 0.2633 (9) | 0.1197 (9) | −0.5415 (10) |
| C(64) | 0.3626 (8) | 0.0978 (8) | −0.5211 (10) |
| C(65) | 0.3965 (8) | 0.0781 (9) | −0.4278 (10) |
| C(66) | 0.3279 (8) | 0.0843 (8) | −0.3539 (9) |
| C(71) | 0.0464 (6) | 0.2806 (7) | −0.0083 (7) |
| C(72) | −0.0345 (7) | 0.2302 (7) | −0.0645 (8) |
| C(73) | −0.1270 (8) | 0.2840 (8) | −0.0648 (9) |
| C(74) | −0.1385 (9) | 0.3822 (9) | −0.0048 (10) |
| C(75) | −0.0555 (9) | 0.4334 (9) | 0.0530 (10) |
| C(76) | 0.0388 (8) | 0.3825 (8) | 0.0505 (9) |
| C(81) | 0.2488 (7) | 0.2945 (7) | 0.0782 (8) |
| C(82) | 0.2380 (7) | 0.3125 (8) | 0.1858 (8) |
| C(83) | 0.2929 (9) | 0.3842 (9) | 0.2680 (10) |
| C(84) | 0.3618 (10) | 0.4311 (10) | 0.2406 (12) |
| C(85) | 0.3772 (10) | 0.4117 (10) | 0.1320 (11) |
| C(86) | 0.3176 (8) | 0.3425 (8) | 0.0481 (9) |

The infrared spectra (in KBr) of both of these complexes exhibit the expected bands due to the dpm ligand. For $[Ag_2(dpm)_2(NO_3)_2]$, these occur at 1482 m, 1435 s, 1184 w, 1161 w, 1095 m, 1027 w, 999 w, 781 m, 737 s, 715 m, and 689 s cm$^{-1}$. For $[Ag_4(dpm)_4(NO_3)_2]^{2+}[PF_6]^-_2$, the corresponding bands are found at 1481 m, 1436 s, 1386 s, 1188 w, 1163 w, 1097 m, 1026 w, 999 m, 779 m, 770 m, 738 s, 718 m, and 689 s cm$^{-1}$. The expected band at about 1385 cm$^{-1}$ was not resolved in the spectrum of $[Ag_2(dpm)_2(NO_3)_2]$ due to the presence of the very intense nitrate band in the same region.

The $^1H$ NMR spectra of $[Ag_2(dpm)_2(NO_3)_2]$ and $[Ag_4(dpm)_4(NO_3)_2]^{2+}[PF_6]^-_2$ in $CD_3CN$ at ambient temperature exhibit phenyl resonances at $\delta$ 7.29 and 7.52 and $\delta$ 7.29 and 7.51, respectively. For $[Ag_2(dpm)_2(NO_3)_2]$, the methylene resonance appears as a quintet ($J_{PH}$ = 5 Hz) with a chemical shift of $\delta$ 3.58, while for $[Ag_4(dpm)_4(NO_3)_2]^{2+}[PF_6]^-_2$ the corresponding resonance occurs as a broad unresolved multiplet at $\delta$ 3.57.

The quintet structure can be rationalized as arising from coupling of the methylene hydrogens with four equivalent phosphorus nuclei.[22] It is thus likely that $[Ag_2(dpm)_2(NO_3)_2]$ undergoes dissociation in solution to give the nonfolded dicationic species $[Ag_2(dpm)_2]^{2+}$ with the dpm ligands now bound trans to one another (eq 3). Virtual coupling of $^{31}P$ nuclei, a phenomenon widely observed in *trans*-diphosphine complexes,[23] then results in each methylene hydrogen in $[Ag_2(dpm)_2]^{2+}$ being coupled to four equivalent phosphorus nuclei. Flipping of the methylene groups from one side of the $Ag_2P_4$ plane to the other is apparently sufficiently rapid on the NMR time scale, such that only a single quintet pattern is observed. For comparison, the methylene resonance of $[Pd_2(dpm)_2Cl_2]$ also occurs as a quintet with a P–H coupling of 4 Hz.[22] The absence of a similar quintet in the $[Ag_4(dpm)_4(NO_3)_2]^{2+}[PF_6]^-_2$ spectrum suggests that for this compound dissociation into $[Ag_2(dpm)_2]^{2+}$ does not readily occur and that the presence of the two nitrate bridges (Figure 3) may have imparted considerable structural integrity to the tetranuclear complex.



(3)

Variable-temperature NMR spectra for $[Ag_2(dpm)_2(NO_3)_2]$ in $CD_3CN$ were recorded from +30 to −10 °C and are also consistent with the formation of the $[Ag_2(dpm)_2]^{2+}$ dication. The experiments were stopped at −10 °C due to the limited solubility of the complex at that temperature. The quintet pattern of the methylene resonance is observed over the entire temperature range, and no indication of a slowing of a dynamic process involving bound nitrate ligands is discernible. Additional studies on the stability and solution chemistry of these compounds are in progress.

**The Molecular Structure of $[Ag_2(dpm)_2(NO_3)_2]$.** The molecular geometry of $[Ag_2(dpm)_2(NO_3)_2]$, which has crystallographic $C_2$ symmetry, is depicted in Figure 1. Selected bond distances and angles are given in Table V. The solid-state structure consists of a neutral dimeric molecular unit with the two silver atoms bridged by a pair of dpm ligands. In addition, each silver atom is terminally bound by a single nitrate anion in an asymmetric bidentate fashion.

Table V

(A) Bond Distances (Å) for $[Ag_2(dpm)_2(NO_3)_2]$

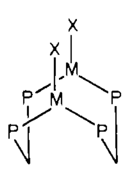
| | | | |
|---|---|---|---|
| | Silver-Ligand | | |
| Ag-P(1) | 2.436 (2) | Ag-O(1) | 2.416 (5) |
| Ag-P(2′) | 2.417 (2) | Ag-O(2) | 2.689 (6) |
| | Nitrogen-Oxygen | | |
| N-O(1) | 1.265 (9) | N-O(3) | 1.208 (9) |
| N-O(2) | 1.223 (9) | | |
| | Phosphorus-Carbon | | |
| P(1)-C(1) | 1.841 (7) | P(2)-C(1) | 1.832 (7) |
| P(1)-C(11) | 1.813 (7) | P(2)-C(31) | 1.830 (7) |
| P(1)-C(21) | 1.819 (7) | P(2)-C(41) | 1.816 (7) |

(B) Bond Angles (deg) for $[Ag_2(dpm)_2(NO_3)_2]$

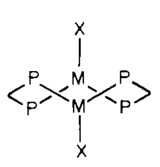
| | | | |
|---|---|---|---|
| | At Silver | | |
| P(1)-Ag-P(2′) | 138.3 (1) | P(2′)-Ag-O(1) | 116.8 (1) |
| P(1)-Ag-O(1) | 104.8 (1) | P(2′)-Ag-O(2) | 111.1 (1) |
| P(1)-Ag-O(2) | 94.1 (1) | O(1)-Ag-O(2) | 48.9 (2) |
| | At Methylene Carbon | | |
| P(1)-C(1)-P(2) | 111.7 (4) | | |
| | At Nitrogen | | |
| O(1)-N-O(2) | 117.6 (6) | O(2)-N-O(3) | 122.3 (7) |
| O(1)-N-O(3) | 120.1 (7) | | |
| | At Oxygen | | |
| N-O(1)-Ag | 102.5 (4) | N-O(2)-Ag | 90.3 (4) |
| | At Phosphorus | | |
| Ag-P(1)-C(1) | 111.6 (2) | Ag′-P(2)-C(1) | 116.3 (2) |
| Ag-P(1)-C(11) | 120.7 (2) | Ag′-P(2)-C(31) | 115.4 (2) |
| Ag-P(1)-C(21) | 110.5 (2) | Ag′-P(2)-C(41) | 112.4 (2) |
| C(1)-P(1)-C(11) | 104.5 (3) | C(1)-P(2)-C(31) | 104.9 (3) |
| C(1)-P(1)-C(21) | 104.0 (3) | C(1)-P(2)-C(41) | 103.5 (3) |
| C(11)-P(1)-C(21) | 104.2 (3) | C(31)-P(2)-C(41) | 102.8 (3) |

The Ag–P distances in $[Ag_2(dpm)_2(NO_3)_2]$ of 2.417 (2) and 2.436 (2) Å are in good agreement with the range 2.42 (1)–2.47 (1) Å found in $[Ag_3(dpm)_3Br_2]^+[Br]^-$.[24,25] The observed Ag–O distances of 2.416 (5) and 2.689 (6) Å are comparable to the values of 2.438 (7) and 2.628 (7) Å found for the asymmetrically bound nitrate in $Ph_3PAgNO_3$.[26] The Ag···Ag separation of 3.085 (1) Å is significantly shorter than the distances of 3.362 (3), 3.356 (3), and 3.192 (3) Å found in the trinuclear dpm complex $[Ag_3(dpm)_3Br_2]^+[Br]^-$[24,25] but is similar to the nonbonding distances of 2.964 (3) and 3.081 (2) Å in the tetranuclear iminophosphorane complex $[CH_3N(PPh_2AgBr)_2]_2$.[25,27]

The P–Ag–P units are nonlinear and eclipsed, resulting in a folding of the $Ag_2P_4$ core along the Ag···Ag axis (IV). The P(1)–Ag–P(2′) angle of 138.3 (1)° is significantly smaller than the corresponding P(1)–Au–P(2) angle of 155.9 (1)° found in the related dinuclear $(dpm)_2$ complex $[Au_2(dpm)_2Cl_2]$.[28] It should be noted, however, that the P–Au–P units in $[Au_2(dpm)_2Cl_2]$ do not have the eclipsed conformation (IV) as in $[Ag_2(dpm)_2(NO_3)_2]$ but rather the alternative staggered



IV



V

---

[22] Balch, A. L.; Benner, L. S.; Olmstead, M. M. *Inorg. Chem.* **1979**, *18*, 2996–3003.

[23] Jenkins, J. M.; Shaw, B. L. *J. Chem. Soc. A* **1966**, 770–775.

[24] Aly, A. A. M.; Neugebauer, D.; Orama, O.; Schubert, U.; Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 125–126.

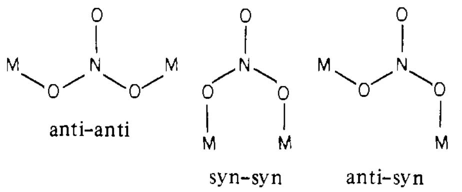
[25] Schubert, U.; Neugebauer, D.; Aly, A. A. M. *Z. Anorg. Allg. Chem.* **1980**, *464*, 217–232.

[26] Stein, R. A.; Knobler, C. *Inorg. Chem.* **1977**, *16*, 242–245.

[27] Schmidbaur, H.; Aly, A. A. M.; Schubert, U. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 846–847.

[28] Schmidbaur, H.; Wohlleben, A.; Schubert, U.; Frank, A.; Huttner, G. *Chem. Ber.* **1977**, *110*, 2751–2757.

Chart I. Known Bridge-Bonding Modes for the Nitrate Anion



conformation (V). The opening of the P–M–P angle in $[Au_2(dpm)_2Cl_2]$ may be the result of an inability of the dpm ligand to comfortably span gauche positions in the staggered conformation.

The nitrate anions are situated syn to each other (IV) in a plane through the silver atoms and are approximately perpendicular to a second plane defined by the four phosphorus atoms. The Ag′···Ag–O(1), Ag′···Ag–O(2), and Ag′···Ag···N angles are 95.0 (1), 143.3 (1), and 119.0 (1)°, respectively, the latter value clearly indicating the nonlinearity of the Ag···Ag···$NO_3$ arrangement.

**The Molecular Structure of $[Ag_4(dpm)_4(NO_3)_2]^{2+}[PF_6]^-_2$.** The solid-state structure of $[Ag_4(dpm)_4(NO_3)_2]^{2+}[PF_6]^-_2$ consists of discrete tetranuclear cations and hexafluorophosphate anions. The complex cation is shown in Figures 2 and 3. Selected bond distances and angles are presented in Table VI.

The tetranuclear complex consists of two $[Ag_2(dpm)_2]^{2+}$ subunits bound together by two bridging nitrate anions (Figure 3). The basic $[Ag_2(dpm)_2]^{2+}$ subunit is similar to that previously described in the dinuclear complex $[Ag_2(dpm)_2(NO_3)_2]$. Each nitrato ligand is involved in the idealized $C_{2v}$ anti–anti bridge-bonding mode (Chart I) with the two silvers bound to different nitrate oxygen atoms. Hence, each silver atom is tricoordinate with a coordination sphere of two phosphorus atoms and a nitrate oxygen.

The Ag–P distances in $[Ag_4(dpm)_4(NO_3)_2]^{2+}[PF_6]^-_2$ vary from 2.390 (3) to 2.456 (3) Å, with a mean of 2.428 (2) Å, in good agreement with the average value of 2.426 (10) Å found in $[Ag_2(dpm)_2(NO_3)_2]$. The Ag(1)–O(1) and Ag(2)–O(2′) distances are 2.478 (7) and 2.541 (8) Å, respectively. The nitrate O(3) and O(3′) atoms are positioned in the central cavity of the tetranuclear complex (Figure 3) and are involved in significantly longer contact distances to the silver atoms. The Ag(1)···O(3), Ag(2)···O(3), and Ag(2)···O(3′) distances are 2.944 (9), 3.026 (9), and 2.819 (9) Å, respectively, and reflect predominantly electrostatic rather than covalent interactions. The Ag(1)···Ag(2) nonbonding distance of 3.099 (1) Å is in excellent agreement with the corresponding distance of 3.085 (1) Å found for the $[Ag_2(dpm)_2]^{2+}$ subunit in $[Ag_2(dpm)_2(NO_3)_2]$.

The two unique P–Ag–P units in $[Ag_4(dpm)_4(NO_3)_2]^{2+}[PF_6]^-_2$ are nonlinear (Figure 2) with values of 152.0 (1) and 141.5 (1)° for P(1)–Ag(1)–P(3) and P(2)–Ag(2)–P(4), respectively. For comparison, the P–Ag–P angles in $[Ag_2(dpm)_2(NO_3)_2]$ are both 138.3 (1)°. Hence, the $Ag_2P_4$ core structures in $[Ag_4(dpm)_4(NO_3)_2]^{2+}[PF_6]^-_2$ are markedly folded, though not as much as that found in $[Ag_2(dpm)_2(NO_3)_2]$.

The $[Ag_2(dpm)_2]^{2+}$ subunits in $[Ag_4(dpm)_4(NO_3)_2]^{2+}[PF_6]^-_2$ and $[Ag_2(dpm)_2(NO_3)_2]$ exhibit further differences that warrant a brief mention here. In the latter dinuclear complex, the two planes defined by [P(1), P(2′), O(1)] and [P(1′), P(2), O(1′)] (Figure 1) are essentially parallel to one another, and the methylene carbon atoms, C(1) and C(1′), are in a cis conformation directed away from the bound nitrate anions (IV). In contrast, the planes defined by [P(1), P(3), O(1)] and [P(2), P(4), O(2′)] in $[Ag_4(dpm)_4(NO_3)_2]^{2+}[PF_6]^-_2$ are significantly skewed with respect to each other (Figure 4), and the methylene carbon atoms, C(1) and C(2), are found in a trans configuration with C(1) inclined toward the nitrato ligands (Figures 2 and 3). In addition, Figures 1 and 4 clearly reveal substantial differences in the packing arrangement of the dpm phenyl rings in $[Ag_2(dpm)_2(NO_3)_2]$ and $[Ag_4(dpm)_4(NO_3)_2]^{2+}[PF_6]^-_2$, respectively. Thus, the basic $[Ag_2(dpm)_2]^{2+}$ structure appears to be quite flexible, with the specific solid-state conformation dependent on the size and mode of binding of the other ligands (e.g., $NO_3^-$).

Table VI

(A) Bond Distances (Å) for $[Ag_4(dpm)_4(NO_3)_2]^{2+}[PF_6]^-_2$

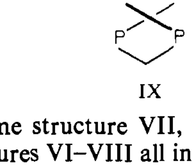
| | | | |
|---|---|---|---|
| Silver-Ligand | | | |
| Ag(1)-P(1) | 2.411 (3) | Ag(2)-P(4) | 2.455 (3) |
| Ag(1)-P(3) | 2.390 (3) | Ag(1)-O(1) | 2.478 (7) |
| Ag(2)-P(2) | 2.456 (3) | Ag(2)-O(2′) | 2.541 (8) |
| Nitrogen-Oxygen | | | |
| N-O(1) | 1.26 (1) | N-O(3) | 1.22 (1) |
| N-O(2) | 1.25 (1) | | |
| Phosphorus-Carbon | | | |
| P(1)-C(1) | 1.826 (10) | P(3)-C(2) | 1.848 (10) |
| P(1)-C(11) | 1.822 (10) | P(3)-C(51) | 1.807 (10) |
| P(1)-C(21) | 1.814 (9) | P(3)-C(61) | 1.811 (9) |
| P(2)-C(1) | 1.839 (9) | P(4)-C(2) | 1.839 (10) |
| P(2)-C(31) | 1.826 (10) | P(4)-C(71) | 1.827 (10) |
| P(2)-C(41) | 1.835 (10) | P(4)-C(81) | 1.829 (11) |

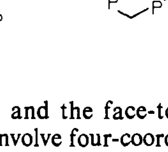
(B) Bond Angles (deg) for $[Ag_4(dpm)_4(NO_3)_2]^{2+}[PF_6]^-_2$

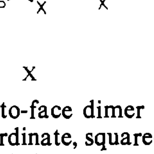
| | | | |
|---|---|---|---|
| At Silver | | | |
| P(1)-Ag(1)-P(3) | 152.0 (1) | P(3)-Ag(1)-O(1) | 108.8 (2) |
| P(2)-Ag(2)-P(4) | 141.5 (1) | P(2)-Ag(2)-O(2′) | 105.3 (2) |
| P(1)-Ag(1)-O(1) | 95.1 (2) | P(4)-Ag(2)-O(2′) | 98.2 (2) |
| At Nitrogen | | | |
| O(1)-N-O(2) | 119.4 (9) | O(2)-N-O(3) | 121.4 (9) |
| O(1)-N-O(3) | 119.2 (9) | | |
| At Oxygen | | | |
| N-O(1)-Ag(1) | 108.0 (6) | N-O(2)-Ag(2′) | 99.4 (6) |
| At Methylene Carbons | | | |
| P(1)-C(1)-P(2) | 113.0 (5) | P(3)-C(2)-P(4) | 115.0 (5) |

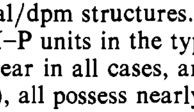
## Discussion

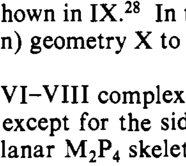
On the basis of studies prior to this investigation, three main structural types have been found for dinuclear $M_2(dpm)_2$ (M = Rh, Ir, Pd, Pt) complexes: the side-by-side form VI, the A-frame structure VII, and the face-to-face dimer VIII.[16] Structures VI–VIII all involve four-coordinate, square-planar metal centers. For three-coordinate (trigonal-planar) $d^{10}$ complexes, the gold(I) compound $[Au_2(dpm)_2Cl_2]$ features the staggered (or anti) arrangement shown in IX.[28] In this work, we have added the eclipsed (or syn) geometry X to the list of known metal/dpm structures.


VI


VII


VIII


IX


X

The P–M–P units in the type VI–VIII complexes are essentially linear in all cases, and except for the side-by-side dimers (VI), all possess nearly planar $M_2P_4$ skeletons. For type VI complexes, contraction of the M–M distance due to metal–metal bond formation, plus steric constraints imposed by the dpm ligands, presumably results in the observed twisting 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.

**Acknowledgment.** We thank the National Science Foundation (Grants CHE-79-26479 and CHE-81-01122) for support of this research.

**Registry No.** $[Ag_2(dpm)_2(NO_3)_2]$, 87801-38-5; $[Ag_4(dpm)_4(NO_3)_2]^{2+}[PF_6]^-{}_2$, 87801-40-9.

**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.

---

(29) Colton, R.; McCormick, M. J.; Pannan, C. D. *Aust. J. Chem.* **1978**, *31*, 1425–1438.

(30) Holloway, R. G.; Penfold, B. R.; Colton, R.; McCormick, M. J. *J. Chem. Soc., Chem. Commun.* **1976**, 485–486.

(31) Cotton, F. A.; Shive, L. W.; Stults, B. R. *Inorg. Chem.* **1976**, *15*, 2239–2244.

(32) Abbott, E. H.; Bose, K. S.; Cotton, F. A.; Hall, W. T.; Sekutowski, J. C. *Inorg. Chem.* **1978**, *17*, 3240–3245.

---

Contribution from the Department of Chemistry,
University of Southern California, Los Angeles, California 90089-1062

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

DOUGLAS M. HO and ROBERT BAU*

*Received March 16, 1983*

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, $\alpha$ = 90.49 (2)°, $\beta$ = 113.07 (2)°, $\gamma$ = 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.

(2) (a) Cotton, F. A.; Hanson, B. E. *Inorg. Chem.* **1977**, *16*, 3369–3371. (b) Lavigne, G.; Lugan, N.; Bonnet, J. J. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1982**, *B38*, 1911–1916.

(3) (a) Carré, F. H.; Cotton, F. A.; Frenz, B. A. *Inorg. Chem.* **1976**, *15*, 380–387. (b) Ceriotti, A.; Ciani, G.; Garlaschelli, L.; Sartorelli, U.; Sironi, A. *J. Organomet. Chem.* **1982**, *229*, C9–C12.

(4) Frew, A. A.; Hill, R. H.; Manojlović-Muir, L.; Muir, K. W.; Puddephatt, R. J. *J. Chem. Soc., Chem. Commun.* **1982**, 198–200.

0020-1669/83/1322-4079$01.50/0 © 1983 American Chemical Society