hibit the flattened tetrahedral geometry described above. However, in $UCp_3(NCS)(CH_3CN)$ the Cp-U-Cp angles are close to 120° and the Cp-U-N angles are close to 90°. This clearly represents a geometry different from the flattened tetrahedron characterizing the $MCp_3X$ compounds, including the present one.

While the angles and geometries of the thiocyanato and pyrazolate complexes are distinctly different, there are marked similarities in their bond lengths, which are in turn consistent with the ionic radius calculated for an 11-coordinate uranium(IV) complex. The average U-C distances (2.76 Å) for both compounds and U-N distances (2.40 and 2.36 Å for the pyrazolate vs. 2.40 Å for the thiocyanate) agree well. The reason for the 0.04 Å difference in the U-N distances of the pyrazolate is unclear; the closest intramolecular contact [between N(2) and C(10)] must be expected to make U-N(2) the longer bond, but the opposite is true.

The structure of $Cu(PhN{=}NPh)(CNCMe_3)_2$[22] reveals a roughly analogous, endo-bidentate, $\eta^2$ coordination of an $N_2$ moiety. Structural evidence for a covalent σ-bond formation which affects the π-bond structure of the ligand includes a lengthening of the N-N bond vs. uncoordinated azobenzene (from an average of 1.20 Å to 1.38 Å). However, the N-N bond in the pyrazolate anion should be less susceptible to such an effect because of its incorporation in an aromatic π system. In any case, in $[TiCp_2(pyrazolate)]_2$ the N-N distance [1.312 (6) Å] is quite similar to that observed here [1.318 (10) Å].

In summary, we report the synthesis and first structure analysis of a compound with an endo-bidentate pyrazolate anion. The coordination geometry and the distance in this compound are consistent with a highly ionic description of the bonding.

**Acknowledgment.** We wish to thank Dr. F. J. Hollander for assistance in the structure solution, Dr. S. Simpson for his assistance in obtaining the $^1H$ NMR spectra, and S. Ogden for the mass spectrum. This research was supported by the Division of Nuclear Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, under Contract No. W-7405-Eng-48.

**Registry No.** $UCp_3(C_3H_3N_2)$, 76613-61-1; $UCp_3Cl$, 1284-81-7.

**Supplementary Material Available:** A listing of observed and calculated structure factors and Table V, least-squares plane parameters (17 pages). Ordering information is given on any current masthead page.

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# Studies of Ruthenium(II) Porphyrins Containing Tertiary Diphosphine Ligands, Including the Crystal Structure of (5,10,15,20-Tetraphenylporphinato)bis(bis(diphenylphosphino)methane)ruthenium(II)-Dichloromethane

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*Received September 29, 1980*

The ruthenium(II) porphyrins $Ru(porp)(\widehat{PP})_2$, containing tertiary diphosphine ligands, have been prepared in high yields from $Ru(porp)(CO)(C_2H_5OH)$ [porp = dianion of octaethylporphyrin (OEP) or tetraphenylporphyrin (TPP)] and the $\widehat{PP}$ phosphines $[Ph_2P(CH_2)_nPPh_2$ ($n$ = 1, 2) and $Ph_2P(CH_2)_2N(C_2H_5)(CH_2)_2PPh_2]$. The crystal structure of $Ru(TPP)(Ph_2PCH_2PPh_2)_2$ shows six-coordinate ruthenium situated in the porphyrin plane and coordinated to two axial monodentate phosphine ligands, which each have a free dangling phosphorus atom. The analogous bis(1,2-bis(diphenylphosphino)ethane) complex almost certainly has the same structure and is the first reported case of a compound containing this common diphosphine in a monodentate fashion. The $^{31}P$ NMR spectra of the $Ru(porp)[Ph_2P(CH_2)_nPPh_2]_2$ compounds indicate further structures in solution, including species with a chelated diphosphine. An isolated $Ru(OEP)[Ph_2P(CH_2)_4PPh_2]$ complex is likely a polymer incorporating diphosphine bridges.

## Introduction

During investigations of ruthenium porphyrins containing tertiary phosphines[1-3] we observed highly efficient catalytic decarbonylation of aldehydes by a system involving $Ru(TPP)(PPh_3)_2$[4] (TPP = the dianion of 5,10,15,20-tetraphenylporphyrin). As the mechanism of decarbonylation is usually thought to involve initial oxidative addition of the aldehyde to the catalyst complex,[5] we became interested in studying the potential of ruthenium porphyrins to become greater than six-coordinate. To date, only six-coordinate species of ruthenium(II) porphyrins have been reported, for example, in the X-ray structures of $Ru(TPP)(py)_2$[6] (py = pyridine), $Ru(TPP)(CO)(py)$,[7] and $Ru(TPP)(CO)(C_2H_5OH)$.[8] However, kinetic data have suggested that ruthenium(II) porphyrin complexes containing potentially bidentate ligands (e.g., pyrazoles) may form seven-coordinate species such as I during intramolecular ligand-exchange processes.[9,10]

We set out to prepare a complex with a stereochemistry similar to that of I (L′ = CO, vacant site, or another $\widehat{LL}$

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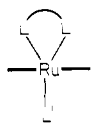

I

$\widehat{L\,L}$ = bidentate ligand
L′ = axial ligand, particularly CO

ligand), and, to this end, we studied the interaction of Ru(TPP)(CO)($C_2H_5OH$) and Ru(OEP)(CO)($C_2H_5OH$) (OEP = dianion of octaethylporphyrin) with the tertiary diphosphine ligands bis(diphenylphosphino)methane (dpm), 1,2-bis(diphenylphosphino)ethane (dpe), 1,4-bis(diphenylphosphino)butane (dpb), and bis((diphenylphosphino)ethyl)ethylamine (pnp). However, complexes in which the ligands were chelated were not isolated; the diphosphines tended to act as monodentate or bridging ligands. A Ru(TPP)$(dpm)_2$ complex is shown to be six-coordinate by single-crystal X-ray diffractometry.

## Experimental Section

All solvents were spectroscopic grade and were distilled prior to use; all manipulations were carried out under an atmosphere of argon with use of Schlenk techniques. Proton-decoupled $^{31}P$ NMR spectra were recorded on a Varian WP-80 in the Fourier transform mode at 40.5 MHz, with $CDCl_3$, $C_6D_6$, or $CD_3C_6D_6$ as solvent; all shifts (upfield positive) are given relative to external $P(OCH_3)_3$ in $C_6D_6$. UV/visible spectra were recorded with a Cary 17D using freshly distilled toluene or $CH_2Cl_2$. The ruthenium was obtained from Johnson, Matthey Ltd. as $RuCl_3{\cdot}3H_2O$; $Ru_3(CO)_{12}$ was prepared according to a literature procedure.[11] TPP,[12] OEP,[13] and the Ru(porphyrin)(CO)($C_2H_5OH$) precursors[8] were prepared according to literature procedures. The phosphines were Strem products; pnp was a gift from Professor G. Dobson. Microanalyses were performed by Mr. P. Borda of this department and by the Canadian Microanalytical Service Ltd.

**Preparation of Compounds. Ru(TPP)(dpm)$_2$ (1).** Ru(TPP)(CO)($C_2H_5OH$) (0.11 g, 0.14 mmol) and dpm (0.11 g, 0.29 mmol) were dissovled in 50 mL of $CH_2Cl_2$, and the mixture was stirred for 1 h at 20 °C. The reaction was monitored via the UV/visible spectrum. The solvent was removed and the product (ca. 82%) crystallized from $CH_2Cl_2$/hexane. Crystals dried under vacuum analyzed for Ru(TPP)$(dpm)_2$, while crystals used for the X-ray study analyzed for Ru(TPP)$(dpm)_2{\cdot}CH_2Cl_2$. Anal. Calcd for $C_{94}H_{72}N_4P_4Ru$: C, 76.15; H, 4.89; N, 3.78; P, 8.36. Found: C, 75.34; H, 4.85; N, 3.99; P, 8.3. Calcd for $C_{95}H_{74}N_4P_4Cl_2Ru$: C, 72.79; H, 4.25; N, 3.57. Found: C, 73.42; H, 5.16; N, 3.78. On standing, the solvated crystals slowly lose $CH_2Cl_2$.

**Ru(OEP)(dpe)$_2$ (2).** Ru(OEP)(CO)(EtOH) (2.00 g, 2.8 mmol) and dpe (2.39 g, 6.0 mmol) were dissolved in 80 mL of toluene/dichloromethane (1:1 v/v), and the solution was gently refluxed for 4 h, when the solvent was removed. The product was washed with ethanol and then hexane and dried (ca. 90%). Solutions of the product turn cloudy, thought to be due to the formation of a small amount of [Ru(OEP)(dpe)]$_n$, which can be filtered off. Some solvent in complex **2** is indicated by the analyses. Anal. Calcd for $C_{92}H_{92}N_4P_4Ru{\cdot}{}^1/_2CH_2Cl_2$: C, 73.09; H, 6.16; N, 3.68; P, 8.15. Found: C, 73.15; H, 6.17; N, 3.82; P, 8.68.

**[Ru(OEP)(dpb)]$_n$ (3).** The complex was prepared from Ru(OEP)(CO)(EtOH) and dpb in $CH_2Cl_2$ as described for **1**. The product precipitated out of solution on stirring, and the precipitate was washed with ethanol and hexane (ca. 75%). Anal. Calcd for $C_{64}H_{72}N_4P_2Ru$: C, 72.50; H, 6.84; N, 5.28. Found: C, 72.68; H, 7.11; N, 4.87.

**Ru(TPP)(pnp)$_2$ (4).** The complex (ca. 65% yield) was prepared in a manner similar to that described for **1**, from Ru(TPP)(CO)(EtOH) and pnp. Anal. Calcd for $C_{101}H_{94}N_6P_4Ru{\cdot}{}^1/_2CH_2Cl_2$: C, 74.02; H, 5.64; N, 4.98; P, 7.30. Found: C, 74.85; H, 6.21; N, 4.94; P, 6.5.

Table I. Crystal Data and Experimental Conditions for Data Collection

$C_{95}H_{74}ClN_4P_4Ru$
$a = 13.138\ (2)$ Å
$b = 13.188\ (2)$ Å
$c = 12.989\ (3)$ Å
$\alpha = 94.41\ (2)°$
$\beta = 119.27\ (2)°$
$\gamma = 91.52\ (1)°$

fw 1567.56
space group $P\bar{1}$
$Z = 1$
$V = 1951.94$ Å$^3$
$D_{calcd} = 1.333$ g cm$^{-3}$
$\mu = 3.94$ cm$^{-1}$ (Mo K$\bar{\alpha}$)

radiation: Mo K$\bar{\alpha}$; graphite monochromator, $2\theta = 12.20°$
scan: $\omega$–$2\theta$; range $(0.60 + 0.35 \tan\theta)°$ in $\omega$, extended 25% for backgrounds; speed 0.7–10.1° min$^{-1}$ to give $I/\sigma(I) \geqslant 20$
aperture: 4 × 4 mm, 173 mm from crystal
standards: reflections $1\bar{6}0$, $\bar{3}1\bar{2}$, and $\bar{2}0\bar{2}$ monitored every hour of exposure time for intensity fluctuations; three reflections recentered every 100 reflections for orientation control
data collected: $\pm h,\pm k,l$ for $0 < 2\theta \leqslant 40°$
$\sigma(I)$: $[\mathrm{INT} + 4(\mathrm{BG}) + (0.04I)^2]^{1/2}$; INT is the integrated intensity, BG is the sum of the background counts, and $I$ is the intensity
boundary planes: six faces; {100}, {010}, and {001}
transmission factors: 0.9807 maximum and 0.9348 minimum

**Single-Crystal Diffractometry.** A parallelepiped crystal, of approximate dimensions 0.26 × 0.23 × 0.05 mm, possessing six faces, {100}, {010}, and {001} was mounted with $c^*$ approximately along the spindle axis on an Enraf-Nonius CAD4 computer-controlled diffractometer. The automatic peak search and reflection indexing programs in conjunction with a cell reduction program showed the crystal to be triclinic with the space group being either $P1$ or $P\bar{1}$. The latter space group was chosen and shown to be correct by the successful refinement of the structure. Cell constants and an orientation matrix were defined from a least-squares fit to 15 reflections having $12 < 2\theta < 23°$. The crystal data and conditions for data collection are summarized in Table I. During data collection the standard reflections were observed to undergo a nonlinear reduction in intensity which resulted in a 15.1–28.6% decrease over 42 h of exposure time. At this time the crystal quality had degraded to the point that it was decided to cease data collection, having measured 86% of the available reflections with $2\theta < 40°$. Attempts to find other crystals of similar quality were unsuccessful. There were a total of 3307 unique reflections measured, and these were corrected[14] for background, Lorentz, polarization, and absorption[15] effects to give 1974 reflections having $I > 3\sigma(I)$, which were used in the structure solution and refinement; no corrections were made for the effects of decomposition.

**Structure Solution and Refinement.** A three-dimensional Patterson synthesis revealed the positions of the two independent N atoms and one of the P atoms, with the Ru assumed to be at the center of symmetry at (0, 0, 0). The remaining non-H atoms were located after several least-squares refinement cycles and difference Fourier syntheses.

Refinement of atomic parameters was carried out by full-matrix techniques on $F$, minimizing the function $\sum w(|F_o| - |F_c|)^2$ where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes, respectively, and the weighting factor $w$ is given by $w = 4F_o^2/\sigma^2(F_o^2)$. The neutral-atom scattering factors were calculated from the analytical expression for the scattering factor curves.[16] The $f'$ and $f''$ components of anomalous dispersion were those of Cromer and Liberman[17] and were included in the calculations for the Ru and P atoms. The agreement residuals are defined as $R_1 = \sum(||F_o| - |F_c||)/\sum|F_o|$ and $R_2 = (\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2)^{1/2}$.

During the preliminary stages of refinement, all atoms were assigned isotropic thermal parameters and the phenyl rings were refined as rigid groups (C–C = 1.392 Å, $D_{6h}$ symmetry). The agreement factors

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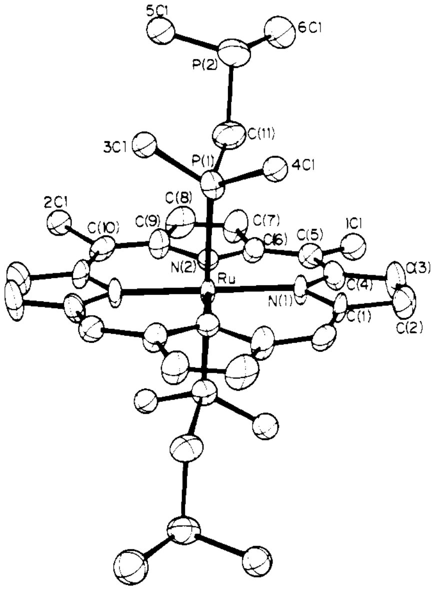

**Figure 1.** Perspective drawing, using 50% probability thermal ellipsoids, of Ru(TPP)(dpm)$_2$. The numbering scheme for the unique atoms is shown. For clarity, H atoms have been omitted and only the $\alpha$-carbons of the phenyl rings are drawn. The phenyl groups are numbered sequentially about each ring.

at this stage of the refinement were $R_1 = 11.4\%$ and $R_2 = 16.1\%$. Removing the rigid-group constraints but retaining the isotropic thermal parameters for these atoms, while assigning anisotropic thermal ellipsoids to the others, reduced the residuals to 10.0% and 14.2%, respectively.

The contributions to the structure factors of the 36 H atoms were included in the calculations using "ideal" positional parameters (C–H = 0.95 Å and regular $C_{sp^2}$ and $C_{sp^3}$ geometry) and isotropic thermal parameters 10% greater than those of the C atom to which they are bonded.

A difference Fourier revealed an area of electron density which was presumed to arise from the presence of a molecule of $CH_2Cl_2$ postulated to be present from an elemental analysis. This electron density sits very close to a center of symmetry at ($^1/_2$, $^1/_2$, 0) and appears to be from a molecule thoroughly disordered among several orientations (the appearance of the disorder may be worsened by the effects of crystal decomposition and the truncated data set). Attempts to accurately describe the disorder were unsuccessful, and it was decided to put three atoms at the positions of the three highest peaks, assigning them as C atoms with isotropic thermal parameters of 6.0 Å$^2$, and refine their occupancies. This approximation resulted in an immediate decrease in the residuals to $R_1 = 6.5\%$ and $R_2 = 8.2\%$.

Prior to the final cycles the positions of the H atoms were recalculated. Two cycles of full-matrix refinement of 289 variables using 1974 data gave agreement factors of 0.061 and 0.075, respectively, for $R_1$ and $R_2$. The error in an observation of unit weight was 2.015 e. The maximum shift of any parameter in the final cycle was 0.74 times its estimated standard deviation and was associated with the $y$ coordinate of atom 6C4. The final populations for the three "solvent" peaks were 0.663, 0.459, and 1.290. An analysis of $R_2$ in terms of $F_o$, $\lambda^{-1}$ sin $\theta$, and combinations of Miller indices showed no unusual trends. Table II contains the final atomic parameters for the nonhydrogen atoms with the H atoms listed in Table III. A list of $F_o$ and $F_c$ for the final model is given in Table IV.[18]

## Results and Discussion

**Structure Description.** The Ru atom is constrained, by virtue of occupying a crystallographic inversion center, to lie in the plane of the four nitrogens of the tetraphenylporphinato (TPP) ligand. Above and below this plane lie two monodentate dpm ligands which complete the approximately octahedral coordination of the metal atom. A drawing of the complex, including the atomic numbering scheme for the unique portion of the molecule, is presented in Figure 1. Figure 2 is a drawing of the porphyrin skeleton showing averaged bond distances and angles. A list of selected interatomic distances and angles is given in Table V.

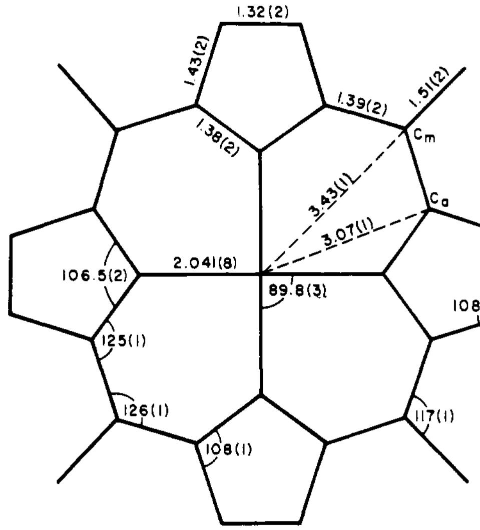

**Figure 2.** Diagram of the porphyrin skeleton including the mean distances and angles. The number in parentheses is the error on the mean when larger than the error on an individual measurement.

The dpm ligands coordinate in a monodentate fashion, which is not the most commonly observed coordination mode for this ligand; bidentate at one metal center or at two metal centers (bridging) is usually found.[19-23] Indeed, the only other example we know of is in the seven-coordinate complex Mo(CO)$_2$Cl$_2$(dpm)$_2$ for which a crystal structure[21] has shown one monodentate dpm ligand and one bidentate. But in terms of the usual coordination geometry of Ru(II) and the steric requirements of relatively bulky ligands such as dpm and TPP, it is not surprising in retrospect to find the phosphine has adopted a conformation in which it lies away from the TPP ligand. The similarity of the conformations of the phosphines in Ru(TPP)(dpm)$_2$ and the monodentate dpm in Mo(CO)$_2$Cl$_2$(dpm)$_2$ (see Table VI) and the lack of any particularly short intermolecular contacts support the idea that simple steric requirements within the complex and not crystal-packing forces probably determine the observed configuration of the complex in the solid state. However, the NMR spectral data in solution may be interpreted in terms of a different arrangement (vide infra).

The Ru–P distance of 2.398 (3) Å is typical for trans P atoms on Ru,[24-27] and the mean P–C distance of 1.83 ± 0.01 Å is also normal. The P(1)–C(11)–P(2) angle, 118.7 (6)°, has opened up considerably from the approximately 93° observed when this ligand chelates to a single metal atom,[21-23] which reflects the degree of strain induced when this ligand forms a four-membered ring with a metal.

The geometry of the TPP ligand (Table V and Figure 2) is closely similar to that observed in two other Ru(TPP) structures[6,7] and in general to other metalloporphyrins with TPP.[6,28,29]

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**Table II.** Atomic Positional and Thermal Parameters[a]

| atom | $x$ | $y$ | $z$ | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Ru | 0 | 0 | 0 | 31 (1) | 17.6 (8) | 30 (1) | 2.6 (7) | 23 (1) | 0.3 (7) |
| P(1) | 1857 (3) | 419 (2) | 1755 (3) | 34 (3) | 26 (2) | 36 (3) | 5 (2) | 21 (2) | 3 (2) |
| P(2) | 3505 (3) | 2298 (2) | 3437 (3) | 41 (3) | 44 (2) | 47 (3) | 1 (2) | 19 (3) | −5 (2) |
| N(1) | 806 (8) | 373 (6) | −939 (8) | 45 (7) | 23 (6) | 38 (7) | −5 (5) | 35 (7) | 1 (5) |
| N(2) | −406 (8) | 1474 (6) | 83 (8) | 33 (7) | 16 (5) | 32 (7) | −3 (4) | 22 (6) | −4 (5) |
| C(1) | 1318 (10) | −296 (8) | −1395 (10) | 35 (9) | 36 (8) | 31 (8) | 6 (6) | 28 (8) | 1 (6) |
| C(2) | 1722 (10) | 270 (9) | −2060 (11) | 48 (10) | 37 (8) | 56 (10) | 5 (7) | 40 (9) | −3 (7) |
| C(3) | 1469 (11) | 1220 (9) | −1975 (12) | 68 (11) | 38 (9) | 72 (11) | −6 (7) | 60 (10) | 6 (7) |
| C(4) | 849 (10) | 1291 (9) | −1329 (11) | 43 (9) | 33 (8) | 50 (9) | −4 (6) | 35 (9) | −3 (7) |
| C(5) | 386 (10) | 2186 (7) | −1083 (10) | 47 (9) | 17 (7) | 33 (8) | −3 (6) | 21 (9) | 4 (6) |
| C(6) | −199 (10) | 2258 (8) | −433 (11) | 45 (9) | 21 (7) | 31 (8) | 1 (6) | 23 (8) | 2 (6) |
| C(7) | −532 (11) | 3182 (8) | −92 (12) | 61 (11) | 25 (7) | 50 (10) | 7 (7) | 40 (9) | −2 (7) |
| C(8) | −960 (11) | 2966 (8) | 615 (12) | 60 (11) | 28 (8) | 56 (10) | 14 (7) | 36 (10) | −7 (7) |
| C(9) | −919 (10) | 1896 (8) | 734 (11) | 49 (10) | 19 (7) | 44 (9) | 2 (6) | 35 (9) | −2 (6) |
| C(10) | −1300 (10) | 1349 (8) | 1355 (10) | 35 (9) | 25 (7) | 27 (8) | 4 (6) | 20 (8) | −5 (6) |
| C(11) | 2150 (10) | 1796 (9) | 2111 (11) | 30 (9) | 46 (8) | 33 (8) | 8 (7) | 8 (8) | 6 (7) |

| atom | $x$ | $y$ | $z$ | $U$, Å$^2$ | atom | $x$ | $y$ | $z$ | $U$, Å$^2$ |
|---|---|---|---|---|---|---|---|---|---|
| 1C1 | 472 (11) | 3116 (8) | −1641 (11) | 38 (3) | 1C2 | 1485 (12) | 3676 (10) | −1225 (12) | 57 (4) |
| 1C3 | 1542 (12) | 4591 (10) | −1754 (13) | 55 (4) | 1C4 | 554 (14) | 4799 (10) | −2680 (14) | 62 (4) |
| 1C5 | −480 (14) | 4289 (12) | −3120 (15) | 80 (5) | 1C6 | −529 (13) | 3388 (10) | −2596 (13) | 57 (4) |
| 2C1 | −1696 (11) | 1960 (8) | 2114 (11) | 35 (3) | 2C2 | −943 (12) | 2142 (10) | 3317 (13) | 55 (4) |
| 2C3 | −1268 (13) | 2733 (10) | 4056 (13) | 67 (4) | 2C4 | −2362 (13) | 3073 (10) | 3541 (14) | 61 (4) |
| 2C5 | −3129 (14) | 2915 (11) | 2407 (16) | 77 (5) | 2C6 | −2773 (13) | 2328 (11) | 1650 (14) | 69 (5) |
| 3C1 | 2216 (10) | −6 (8) | 3197 (11) | 32 (3) | 3C2 | 1399 (12) | 97 (9) | 3568 (13) | 54 (4) |
| 3C3 | 1626 (14) | −194 (10) | 4658 (14) | 64 (4) | 3C4 | 2661 (14) | −558 (11) | 5407 (14) | 68 (4) |
| 3C5 | 3494 (13) | −685 (10) | 5048 (14) | 65 (4) | 3C6 | 3254 (12) | −373 (9) | 3949 (12) | 50 (4) |
| 4C1 | 3096 (10) | 9 (8) | 1586 (10) | 31 (3) | 4C2 | 3268 (11) | −1001 (9) | 1582 (11) | 44 (3) |
| 4C3 | 4210 (12) | −1374 (10) | 1466 (13) | 59 (4) | 4C4 | 4897 (13) | −690 (11) | 1313 (13) | 68 (4) |
| 4C5 | 4748 (13) | 287 (11) | 1279 (14) | 71 (5) | 4C6 | 3795 (12) | 678 (9) | 1406 (12) | 52 (4) |
| 5C1 | 2975 (11) | 2638 (9) | 4472 (11) | 40 (3) | 5C2 | 2145 (12) | 3319 (10) | 4291 (13) | 59 (4) |
| 5C3 | 1792 (13) | 3545 (11) | 5124 (14) | 70 (4) | 5C4 | 2274 (14) | 3104 (11) | 6158 (14) | 69 (4) |
| 5C5 | 3084 (14) | 2412 (11) | 6341 (14) | 78 (5) | 5C6 | 3432 (12) | 2180 (10) | 5516 (13) | 61 (4) |
| 6C1 | 3721 (12) | 3570 (9) | 3072 (12) | 51 (4) | 6C2 | 2883 (13) | 4082 (11) | 2240 (14) | 70 (4) |
| 6C3 | 3075 (16) | 5091 (13) | 2028 (16) | 90 (5) | 6C4 | 4217 (18) | 5499 (13) | 2718 (17) | 94 (6) |
| 6C5 | 5059 (16) | 5031 (13) | 3508 (16) | 89 (5) | 6C6 | 4847 (14) | 4038 (12) | 3717 (15) | 79 (5) |

[a] Estimated standard deviations in this and other tables are given in parentheses and correspond to the least significant digits. The positional parameters are ×$10^4$ and the thermal parameters are ×$10^3$. $U_{ij} = B_{ij}/(2\pi^2 a^*_i a^*_j)$ Å$^2$. The thermal ellipsoid is given by $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$.

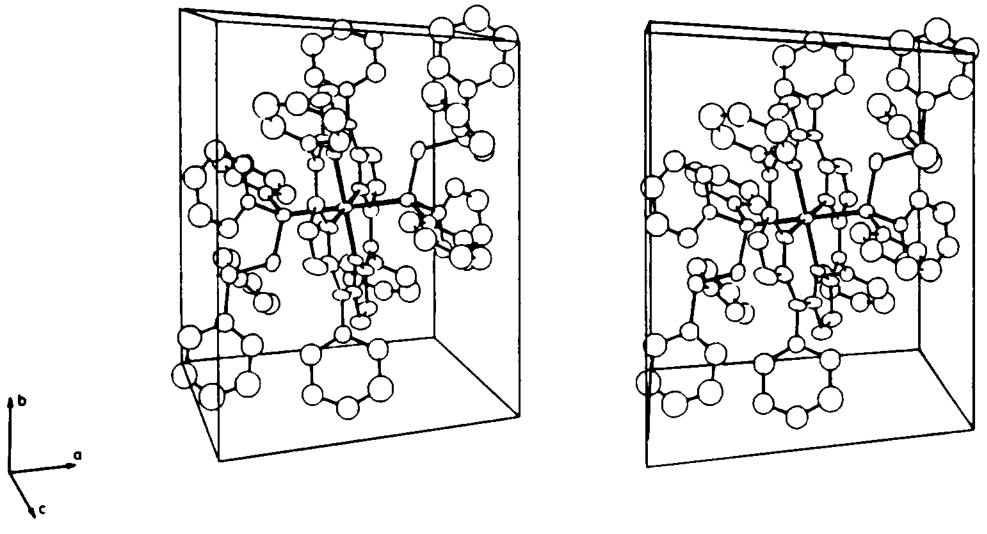
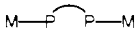


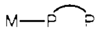
Figure 3. Stereoview of a unit cell contents.

A stereoview of a unit cell is presented in Figure 3. There are no short (<3.0 Å) intermolecular contacts indicating only the usual van der Waals forces between molecules.

**Solution Species.** As well as binding in the usual chelating manner (e.g., I), bidentate phosphines may also act as bridging[19,30–33] (II) or monodentate ligands[19,21,30,32] (III), as found here in the crystal structure of Ru(TPP)(dpm)$_2$.



II



III

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**Table III.** Positional (×10$^4$) and Isotropic Thermal (×10$^3$) Parameters

| atom | *x* | *y* | *z* | *U*, Å$^2$ |
|---|---|---|---|---|
| SOLV1[a] | 4469 | 3525 | −387 | 76 |
| SOLV2 | 4900 | 5055 | −717 | 76 |
| SOLV3 | 4872 | 4046 | −415 | 76 |
| HC(2) | 2100 | −5 | −2470 | 52 |
| HC(3) | 1660 | 1754 | −2311 | 60 |
| HC(7) | −458 | 3839 | −325 | 52 |
| HC(8) | −1280 | 3428 | 945 | 59 |
| H1C(11) | 2148 | 2029 | 1410 | 54 |
| H2C(11) | 1491 | 2034 | 2129 | 54 |
| H1C2 | 2179 | 3469 | −590 | 75 |
| H1C3 | 2249 | 5036 | −1485 | 64 |
| H1C4 | 560 | 5372 | −3057 | 74 |
| H1C5 | −1190 | 4476 | −3804 | 83 |
| H1C6 | −1267 | 2957 | −2939 | 66 |
| H2C2 | −195 | 1898 | 3671 | 68 |
| H2C3 | −793 | 2868 | 4868 | 79 |
| H2C4 | −2617 | 3435 | 4031 | 71 |
| H2C5 | −3931 | 3168 | 2069 | 87 |
| H2C6 | −3327 | 2245 | 806 | 92 |
| H3C2 | 655 | 392 | 3082 | 67 |
| H3C3 | 1064 | −143 | 4936 | 78 |
| H3C4 | 2821 | −757 | 6180 | 82 |
| H3C5 | 4194 | −961 | 5530 | 70 |
| H3C6 | 3863 | −438 | 3758 | 60 |
| H4C2 | 2736 | −1453 | 1662 | 55 |
| H4C3 | 4336 | −2085 | 1513 | 75 |
| H4C4 | 5519 | −930 | 1224 | 88 |
| H4C5 | 5241 | 739 | 1189 | 86 |
| H4C6 | 3589 | 1372 | 1300 | 64 |
| H5C2 | 1724 | 3586 | 3509 | 65 |
| H5C3 | 1238 | 4036 | 4972 | 83 |
| H5C4 | 2033 | 3224 | 6734 | 84 |
| H5C5 | 3440 | 2097 | 7080 | 89 |
| H5C6 | 4033 | 1711 | 5668 | 70 |
| H6C2 | 2125 | 3770 | 1813 | 89 |
| H6C3 | 2526 | 5459 | 1429 | 108 |
| H6C4 | 4470 | 6188 | 2659 | 107 |
| H6C5 | 5803 | 5335 | 3929 | 102 |
| H6C6 | 5421 | 3700 | 4311 | 85 |

[a] The three atoms assigned to the disordered $CH_2Cl_2$ are labeled SOLV1, SOLV2, and SOLV3.

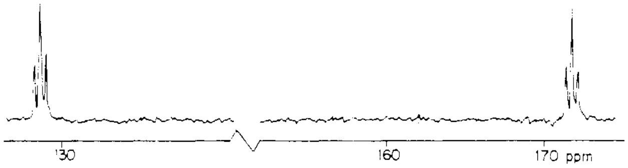


**Figure 4.** $^{31}$P NMR spectrum of $Ru(TPP)(dpm)_2$ in $CDCl_3$, at ambient temperature. Dotted line represents the shift for free dpm.

While dpm and dpb[19–21,30] have been shown to coordinate in any of these three ways, the dpe diphosphine has been found invariably to form the favored five-membered ring system and exhibit only chelating properties.[32] $^{31}$P NMR spectroscopy has been used widely to distinguish the possible modes of binding, and such data on the ruthenium porphyrin phosphine systems will now be considered.

**Table V.** Selected Bond Distances and Angles[a]

Distances (Å)

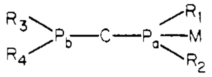
| | | | |
|---|---|---|---|
| Ru-N(1) | 2.045 (8) | C(7)-C(8) | 1.33 (2) |
| Ru-N(2) | 2.038 (8) | C(8)-C(9) | 1.37 (1) |
| Ru-P(1) | 2.398 (3) | C(9)-C(10) | 1.37 (1) |
| N(1)-C(1) | 1.38 (1) | C(1)-C(10)′ | 1.39 (1) |
| N(1)-C(4) | 1.36 (1) | C(5)-1Cl | 1.50 (2) |
| N(2)-C(6) | 1.36 (1) | C(10)-2Cl | 1.52 (1) |
| N(2)-C(9) | 1.41 (1) | C(11)-P(1) | 1.82 (1) |
| C(1)-C(2) | 1.45 (2) | C(11)-P(2) | 1.83 (1) |
| C(2)-C(3) | 1.32 (1) | P(1)-3C(1) | 1.83 (1) |
| C(3)-C(4) | 1.43 (2) | P(1)-4C(1) | 1.84 (1) |
| C(4)-C(5) | 1.43 (2) | P(2)-5C(1) | 1.82 (1) |
| C(5)-C(6) | 1.39 (1) | P(2)-6C(1) | 1.83 (1) |
| C(6)-C(7) | 1.42 (1) | | |

Angles (Deg)

| | | | |
|---|---|---|---|
| N(1)-Ru-N(2) | 89.8 (7) | C(4)-C(5)-1Cl | 117 (1) |
| C(1)-N(1)-C(4) | 106.9 (8) | C(9)-C(10)-C(1)′ | 126.8 (9) |
| C(6)-N(2)-C(9) | 106.1 (8) | C(9)-C(10)-2Cl | 116.4 (9) |
| N(1)-C(1)-C(2) | 108.0 (9) | Ru-P(1)-C(11) | 110.8 (4) |
| N(1)-C(4)-C(3) | 109 (1) | Ru-P(1)-7Cl | 123.2 (4) |
| N(2)-C(6)-C(7) | 110 (1) | Ru-P(1)-4Cl | 113.2 (4) |
| N(2)-C(9)-C(8) | 107 (1) | 3C(1)-P(1)-C(11) | 101.9 (5) |
| C(1)-C(2)-C(3) | 107 (1) | 4C(1)-P(1)-C(11) | 103.9 (5) |
| C(2)-C(3)-C(4) | 109 (1) | 3C(1)-P(1)-4Cl | 101.7 (5) |
| C(6)-C(7)-C(8) | 107 (1) | P(1)-C(11)-P(2) | 118.7 (6) |
| C(7)-C(8)-C(9) | 109 (1) | C(11)-P(2)-5Cl | 101.3 (6) |
| N(1)-C(4)-C(5) | 125 (1) | C(11)-P(2)-6Cl | 101.9 (6) |
| N(1)-C(1)-C(10)′ | 125 (1) | 5Cl-P(2)-6Cl | 99.6 (6) |
| N(2)-C(6)-C(5) | 124.8 (9) | | |
| N(2)-C(9)-C(10) | 124.6 (9) | N(1)-Ru-P(1) | 86.9 (3) |
| C(4)-C(5)-C(6) | 126 (1) | N(2)-Ru-P(1) | 89.8 (2) |

[a] Primed atoms are related to unprimed ones by an inversion center.

**Table VI.** Comparison of Monodentate dpm in the Structures $Ru(TPP)(dpm)_2$ and $Mo(CO)_2Cl_2(dpm)_2$



R = phenyl

| torsion angles[a] | value, deg M = Ru | value, deg M = Mo[21] |
|---|---|---|
| $R_1$-$P_a$-C-$P_b$ | 45.9 | 58.5 |
| $R_2$-$P_a$-C-$P_b$ | −59.4 | −53.4 |
| $R_3$-$P_b$-C-$P_a$ | 155.7 | 162.3 |
| $R_4$-$P_b$-C-$P_a$ | −101.8 | −88.6 |
| $P_b$-C-$P_a$-M | 178.6 | −171.3 |

[a] A positive angle implies a clockwise rotation of atom 1 to eclipse atom 4 when the view is along the atom 2 to atom 3 vector.

**Table VII.** Spectra of the Ruthenium Complexes in Dichloromethane: $\lambda_{max}$, nm (log $\epsilon$)

$Ru(OEP)(dpe)_2$ (**2**): 532.1 (3.79), 506.8 (3.79), 421.5 (5.03), 411 (4.35), 399 (4.08), 353.5 (4.3), 339 (42)
$Ru(TPP)(dpm)_2$ (**1**): 549 (3.83), 519.5 (4.10), 435.1 (5.49), 413.0 (4.54), 358 (4.5)
$Ru(TPP)(pnp)_2$ (**4**): 549.2 (3.71), 519.0 (4.01), 434.3 (5.36), 414.5 (4.55), 359 (4.5)
$[Ru(TPP)(dpb)]_n$:[a] 550, 520.1, 435.0, 355
$[Ru(OEP)(dpb)]_n$: 533.0, 506.5, 421.8, 400, 355, 340
$Ru(TPP)(PPh_3)_2$:[b] 550 (3.38), 515.7 (3.74), 435 (5.02), 413.3 (4.41)

[a] Spectrum taken on warmed solution of a Ru(TPP)(CO)-($C_2H_5OH$)/dpb mixture before precipitation occurred (see text). [b] Reference 3.

The low solubility of the $[Ru(OEP)(dpb)]_n$ complex (**3**) prevented the recording of the $^{31}$P NMR spectra. The complex is thought to be polymeric $[-Ru(OEP)\widehat{PP}-]_n$ formed via species such as III; the UV/visible spectrum of the solution taken during preparation of **3** (and of a mixture of Ru(TPP)(CO)($C_2H_5OH$)/dpb which slowly formed a precipitate similar to **3**) shows the features observed for $Ru(OEP)(dpe)_2$ and $Ru(TPP)(dpm)_2$ (Table VII), while the microanalyses support the bridged polymeric structure.

The solid-state structure of $Ru(TPP)(dpm)_2$ reveals monodentate diphosphine ligands. The $^{31}$P NMR spectrum consists of two triplets (Figure 4) with the dangling phosphorus shifted

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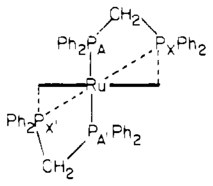
**Table VIII.** $^{31}$P NMR Spectral Data[a]

| complex | $\delta_C$[b] | $\delta_D$[c] | $J_{PP}$, Hz | $\delta_L$[d] |
|---|---|---|---|---|
| Ru(TPP)(dpm)$_2$ (1) | 127.6 (t) | 172.6 (t) | 30.2 | 162.3 |
| Ru(OEP)(dpm)$_2$[e] | 128.8 (t) | 171.0 (t) | 24.6 | 162.3 |
| Ru(OEP)(dpe)$_2$ (2)[f] | 120.3 (d) | 149.2 (d) | 13.0[b] | 148.6 |
| | 120.6 (d) | 149.5 (d) | 14.7[c] | |

[a] At ambient temperature in $C_6D_6$ or $CDCl_3$ unless noted otherwise; d = doublet, t = triplet. [b] Coordinated phosphorus. [c] Dangling phosphorus. [d] Free ligand singlets. [e] Solution of Ru(OEP)(CO)($C_2H_5OH$) with a 2 mol excess of dpm, initially warmed to 50 °C. [f] With a 2 mol excess of dpe in toluene-$d_8$.

upfield by ca. 10 ppm compared to the free ligand (Table VIII); addition of excess dpm to the system simply results in an extra sharp singlet at 162.3 ppm. The NMR pattern is thought to arise from an AA'XX' system ($J_{AX} = J_{A'X'} = 30.2$ Hz) with virtual coupling between $P_A$–$P_{X'}$ and $P_{A'}$–$P_X$.[34,35] The spin system requires $J_{AA'} > 200$ Hz in order to simulate the line widths of the triplets. As expected the shift of the coordinated $P_A$ appears at lower field strength than that of free ligand. The shift of $P_X$ to higher field could result from shielding by the TPP due to ring current effects.[10,36] Such shielding, similar to that observed for the ortho protons of pyridine coordinated to ruthenium(II),[10] requires the phosphorus to be within the field of the delocalized electron system of TPP, which is certainly not true in the solid-state structure where the phosphorus is some 5 Å above the ruthenium porphyrin plane.

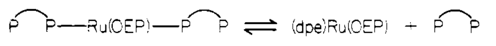
We envisage a solution structure such as IV with weak Ru···$P_X$ and porphyrin···$P_X$ interactions. Strong interaction with the ruthenium implies a chelating dpm ligand, but steric interactions would certainly prevent formation of the four-membered ring system. Solutions of Ru(OEP)(CO)($C_2H_5OH$) and dpm yield a very similar two-triplet $^{31}$P NMR spectrum (Table VIII).



IV

A further possibility is that $\pi$ interactions exist between the porphyrin core and a phenyl group of the uncoordinated phosphine moiety, since $\pi$-complex formation between metalloporphyrins and, for example, substituted benzenes is well-known.[37] High-resolution $^1$H NMR studies are needed to investigate this possibility.

The NMR data for the (dpm)$_2$ complexes and the suggested interpretation provide an interesting contrast with those for the dpe analogue, 2. The $^{31}$P data for Ru(OEP)(dpe)$_2$ with a 1–3 mol excess of dpe show the free ligand singlet and two sets of overlapping doublets that are recognized from the chemical shifts and coupling constants (Figure 5, Table VIII). The excess ligand is needed to maintain the Ru(OEP)(dpe)$_2$ species in solution in an equilibrium such as (1). UV/visible



(1)

2 V

spectral changes with varying phosphine concentration indicate this dissociation reaction (2 and an uncharacterized dissociation product V show Soret maxima at 421 and 405 nm, respectively), which is also found for triphenylphosphine in the Ru(TPP)(PPh$_3$)$_2$ system.[3] The $^{31}$P spectrum is thus assigned to 2 containing inequivalent coordinated ($\delta$ ~120) and inequivalent dangling phosphines ($\delta$ ~149).

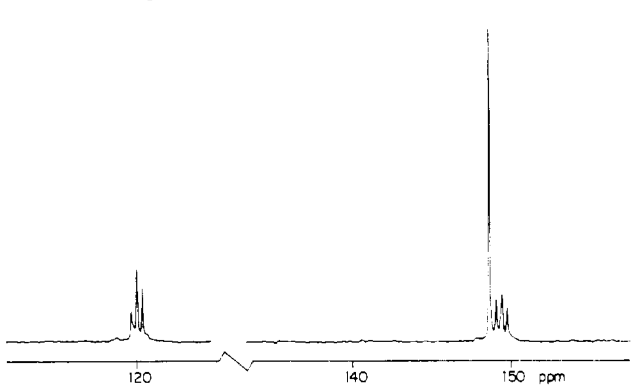
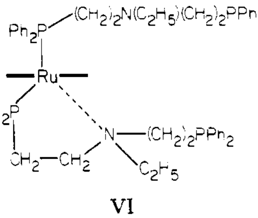


**Figure 5.** $^{31}$P NMR spectrum of Ru(OEP)(dpe)$_2$ in toluene-$d_8$ containing a 2 mol excess of dpe, at ambient temperature.

The $^{31}$P NMR data for 2 in the absence of excess dpe from room temperature to −30 °C are complex, and the system is presently under further investigation. At room temperature, for example, broad signals occur around 110 and 128 ppm, as well as signals in the region expected for free and dangling dpe. Of interest, however, a doublet of doublets pattern is observed at the lower temperatures, $\delta$ 107.0 and 107.9 ($J_{PP}$ = 50.0 Hz), and these are considered likely due to a species with chelated dpe with inequivalent phosphorus atoms (e.g., V in eq 1); the substantially larger downfield shifts seen here, compared to those of monodentate phosphines such as $n$-Bu$_3$P and Ph$_3$P,[3,38] are common in five-membered ring systems.[39,40] The spectrum of the system with excess dpe at −30 °C also shows weak signals at 106–107 ppm.

The $^{31}$P NMR spectrum of Ru(TPP)(pnp)$_2$ at room temperature shows dangling phosphorus as a slightly broadened singlet at 160.9 ppm and coordinated phosphorus as a series of unresolved peaks at about 30 ppm to lower field. This complex pattern is indicative of inequivalent coordinated phosphorus atoms, suggesting perhaps interaction involving the nitrogen atom as in VI (cf. IV).



VI

The UV/visible solution spectra of the TPP complexes 1 and 4 are very similar, but in the corresponding bis(monodentate phosphine) systems the $\alpha$, $\beta$, and Soret bands have about half the intensity [see Table VII; 1, 4, and Ru(TPP)(PPh$_3$)$_2$]. Whether such intensity differences relate to different coordination modes (e.g., a bidentate type as in IV or VI in which the ruthenium is likely to be out of the porphyrin plane) remains to be established.

**Acknowledgment.** We thank the Natural Sciences and Engineering Research Council of Canada and the U.S. National Institutes of Health (Grant AM 17989) for financial support, the University of British Columbia Computing Centre

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for assistance, and Johnson, Matthey Ltd. for the loan of ruthenium. The work is a contribution from the Bioinorganic Chemistry Group.

**Registry No.** 1·$CH_2Cl_2$, 76584-43-5; 2, 76584-44-6; 3, 76584-50-4; 4, 76584-45-7; $[Ru(TPP)(dpb)]_n$, 76584-48-0; $Ru(OEP)(dpm)_2$, 76584-46-8; Ru(TPP)(CO)(EtOH), 41654-56-2; Ru(OEP)(CO)(EtOH), 55059-73-9.

**Supplementary Material Available:** Table IV, a listing of structure factor amplitudes (15 pages). Ordering information is given on any current masthead page.

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Contribution from the Departments of Chemistry,
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# $[Mo_2S_{10}]^{2-}$, a Complex with Terminal Sulfido, Bridging Sulfido, Persulfido, and Tetrasulfido Groups

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*Received October 1, 1980*

The complex $[Mo_2S_{10}]^{2-}$ has been isolated as one product of the reaction between $[NH_4]_2[Mo_2S_{12}]$ and PhSNa (1:16) in $MeOH/Me_2SO$ (10:1). $[AsPh_4]_2[Mo_2S_{10}]\cdot 0.5MeCN$ crystallizes in the triclinic space group $P\bar{1}$ ($Z = 2$), with $a = 10.489$ (2) Å, $b = 11.756$ (2) Å, $c = 21.856$ (4) Å, $\alpha = 77.11$ (2)°, $\beta = 85.46$ (2)°, and $\gamma = 77.92$ (2)°. The structure has been determined from 6774 X-ray counter intensities by Patterson and Fourier techniques and refined by full-matrix least-squares methods to $R = 0.054$ (0.064 weighted). The anion has a terminal sulfido group bonded to each of the molybdenum atoms ($\overline{\mathrm{Mo{-}S}} = 2.110$ (2) Å) which are bridged by two $\mu$-sulfido groups (Mo–S = 2.289 (2)–2.351 (2) Å); one of the molybdenum atoms is also coordinated to a persulfido group ($\overline{\mathrm{Mo{-}S}} = 2.395$ (3), S–S = 2.071 (3) Å) whereas the other is bonded to a tetrasulfido group ($\overline{\mathrm{Mo{-}S}} = 2.406$ (3) Å). The two central atoms of the tetrasulfido group are disordered and this disorder has been refined in terms of an 80–20% distribution of two components; in each case the length of the S–S bond involving the noncoordinated sulfur atoms (1.970 (6) Å for the major component) is significantly shorter than those involving a coordinated sulfur atom (2.018 (5) and 2.116 (5) Å for the major component).

## Introduction

There is much current interest in the study of complexes containing molybdenum and sulfur, not least because of the probable coordination of molybdenum by a group of sulfur atoms in each of the molybdenum-containing enzymes.[2] This generally held view has received considerable support from the interpretations presented for the EXAFS details, associated with the molybdenum *K* edge, for nitrogenase,[3] sulfite oxidase,[4] and xanthine oxidase.[5,6] In nitrogenase, the molybdenum appears to be incorporated into an assembly of iron and sulfur atoms,[3] whereas in sulfite oxidase[4] and xanthine oxidase[5,6] the molybdenum is apparently coordinated by three or four sulfur atoms, which are presumably derived from methioninyl and/or cysteinyl residues of a polypeptide. Furthermore, a comparison of the EXAFS data obtained for active and desulfo xanthine oxidase,[6] indicates that the sulfur atom lost upon the cyanolysis which converts the former to the latter,[7] is immediately adjacent to the molybdenum; the interpretation of these data provides some support for the view[8] that this atom is present as a terminal sulfido group.

Recent developments in molybdenum–sulfur chemistry serve to demonstrate the structural diversity possible for combinations of these elements.[11-29] One interesting aspect developed[12-16] and discussed[17,18] by Müller et al. is the formation of molybdenum–persulfide complexes; $[Mo_2S_{12}]^{2-}$ provides a good example of this ligand's ability to function as a terminal and a bridging group.[12] Herein, we report that $[NH_4]_2[Mo_2S_{12}]$ reacts with PhSNa to give, as one of the products, $[Mo_2S_{10}]^{2-}$; this anion contains two terminal sulfido groups, two $\mu$-sulfido groups, one persulfido group, and one tetrasulfido

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0020-1669/81/1320-1562$01.25/0