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Synthesis and X-ray Structure Determination of Di- μ -chloro-bis{chloro[bis(diethyl phosphonito)]nitrosylruthenium(II)}, [RuCl₂(NO)[(EtO)₂PO]₂H]₂

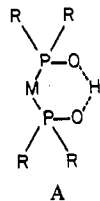
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The complexes [RuCl₂(NO)[R(EtO)PO][R(EtO)POH]₂ (R = OEt or Ph) have been prepared in one step from RuCl₃·3H₂O in ethanol by using Diazald as a nitrosyl source. One isomer was obtained when R was the phenyl group. Single crystals of the other derivative (R = OEt) were obtained directly from the reaction solution. Three-dimensional X-ray data were collected by counter methods. The compound crystallizes in the space group *P* $\bar{1}$ with *Z* = 1 and *a* = 9.370 (2) Å, *b* = 10.248 (5) Å, *c* = 10.933 (6) Å, α = 93.89 (3)°, β = 101.83 (4)°, and γ = 113.82 (6)°. Full-matrix least-squares methods refined the structure to *R* = 0.043 from 4004 nonzero independent reflections. Ruthenium atoms are octahedrally coordinated and are linked together by two chlorine atoms. The nitrosyl ligand is linearly bonded to ruthenium(II). The dinuclear molecule lies on a center of symmetry and shows two unsymmetrical RuPOHOP moieties.

Introduction

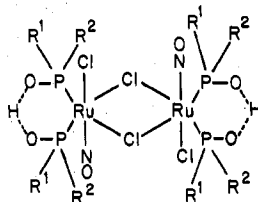
A variety of square-planar derivatives of platinum, palladium, and nickel containing a six-membered ring (A), cor-



responding to the coordinated bis(phenyl phenylphosphinite) or bis(dialkyl phosphonite) groups, have now been isolated. They were produced either by addition of phosphinous acids or of their salts to suitable metal complexes¹⁻⁴ or by solvolysis of phosphinoacetylenes,⁵ tertiary phosphinites, or phosphites^{3,6,7} coordinated in the *cis* position. Spectroscopic⁹ and X-ray studies^{5,7} have brought important information concerning the possibility of a symmetrical heterometallic cycle such as A with short O...O distances (~2.4 Å) which implies a strong hydrogen bonding.

Moreover the interest of these complexes has recently been shown in the synthesis of inorganic oligomers with chains of mixed-metal atoms, by formal replacement of protons in moieties of type A by a metal cation.^{4,8-10}

In this article we present (i) the preparation of a novel type of compound containing the heterometallic cycle A, the binuclear six-coordinated nitrosylruthenium(II) derivatives **1a** and **1b**, in a one-step synthesis starting with RuCl₃·3H₂O and



1a, R¹, R² = OEt
1b, R¹ = OEt, R² = Ph

(ii) the X-ray structure determination of **1a** which shows that two unsymmetrical moieties (A) are bridged by two chlorine atoms.

Experimental Section

Synthesis. Di- μ -chloro-bis{chloro[bis(diethyl phosphonito)]nitrosylruthenium(II)}, [RuCl₂(NO)[(EtO)₂PO]₂H]₂ (**1a**). **Method A.** A mixture of 1.05 g (4 mmol) of RuCl₃·3H₂O, 1.58 g (6 mmol)

of commercial Diazald (*N*-methyl-*N*-nitroso-*p*-toluenesulfonamide), and 8 mL (excess) of triphenyl phosphite was dissolved in 60 mL of absolute ethanol. Reflux was maintained for 24 h under nitrogen atmosphere. The solution turned progressively from brown to green and then orange. After removal of the solvent the residual oil was dissolved in a small volume of diethyl ether and then hexane was added. Bright yellow crystals (1.0 g, 50%) were obtained after washing with cold carbon tetrachloride and hexane; mp 240–242 °C. Anal. Calcd for C₁₆H₄₂Cl₄N₂O₁₄P₄Ru₂: C, 20.13; H, 4.44; Cl, 14.86; N, 2.94; P, 12.98. Found: C, 20.26; H, 4.44; Cl, 15.06; N, 2.95; P, 12.92. IR: ν (NO) 1900 cm⁻¹ (KBr); ν (Ru–Cl) 342, 287, 237 cm⁻¹ (Nujol).

Method B. A mixture of RuCl₃·3H₂O (1.05 g), Diazald (1.58 g), and triethyl phosphite (4 mL) was dissolved in 25 mL of dry, freshly distilled ethanol. After 8 h of refluxing, the orange solution was allowed to stand and afforded yellow crystals which were washed with cold carbon tetrachloride and hexane and dried under vacuum: mp 241–242 °C; yield 1.40 g (77%).

Di- μ -chloro-bis{chloro[bis(ethyl phenylphosphinito)]nitrosylruthenium(II)}, [RuCl₂(NO)[(PhEtO)PO]₂H]₂ (**1b**). A mixture of RuCl₃·3H₂O (0.52 g), Diazald (0.77 g), and diethyl phenylphosphonite (1 g) was dissolved in 12 mL of dry ethanol. After 8 h of refluxing, the mixture was allowed to cool. The pale yellow crystals were washed with dry ethanol and dried under vacuum. Recrystallization in a dichloromethane–hexane mixture afforded 650 mg (57%) of one isomer, dec pt 250–255 °C. Anal. Calcd for C₃₂H₄₂Cl₄N₂O₁₀P₄Ru₂: C, 35.50; H, 3.91; N, 2.59; P, 11.45. Found: C, 35.48; H, 3.99; N, 2.58; P, 11.18. IR: ν (NO) 1895 cm⁻¹ (KBr); ν (Ru–Cl) 341, 283, 229 cm⁻¹ (Nujol).

Trichloronitrosylbis(triphenyl phosphite)ruthenium(II), RuCl₃-(NO)(P(OPh)₃)₂ (**2**). A solution of RuCl₃·3H₂O (0.26 g), Diazald (0.39 g), and triphenyl phosphite (2 mL) was refluxed in *tert*-butyl alcohol (60 mL) for 1 h during which time the solution changed from brown to dark green. After removal of the solvent and addition of diethyl ether, a green product precipitated which was washed with hexane: mp 161 °C; yield 0.4 g (47%).¹¹ Anal. Calcd for C₃₆H₃₀Cl₃NO₃P₂Ru: C, 50.30; H, 3.52; N, 1.63. Found: C, 48.71; H, 3.35; N, 1.38. IR: ν (NO) 1887 cm⁻¹ (Nujol).

X-ray Analysis. Collection and Reduction of the X-ray Data. The triclinic Laue group was shown by Weissenberg and precession photographs. Second harmonic generation gave no signal and the success of the structure analysis in the space group *P* $\bar{1}$ confirmed the existence of the center of symmetry.

Unit cell parameters refined from 25 accurately centered diffractometer reflections are *a* = 9.370 (2) Å, *b* = 10.248 (5) Å, *c* = 10.933 (6) Å, α = 93.89 (3)°, β = 101.33 (4)°, γ = 113.82 (6)°, and *V* = 928.9 Å³. The calculated density (*d*_{calcd}) = 1.71 g cm⁻³ is in good agreement with the observed density (*d*_{meas}) = 1.69 (3) g cm⁻³ obtained by the flotation method in a mixture of 1,2-dibromoethylene and carbon tetrachloride, for 1 empirical formula/unit cell.

Suitable crystals for X-ray analysis were difficult to find due to twinning. The study of twinned crystals showed that the two crystals were related by a mirror in the plane (110). Attempts to recrystallize the product in various solvents were not successful; nevertheless, a

Table I. Fractional Coordinates and Anisotropic Thermal Parameters ($A \times 10^4$) for Nonhydrogen Atoms^a

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ru	3309 (0)	3634 (0)	3774 (0)	383 (0)	424 (0)	316 (0)	171 (0)	35 (0)	10 (0)
Cl(1)	3704 (1)	5384 (1)	5648 (1)	404 (3)	614 (4)	485 (6)	213 (4)	49 (4)	-128 (5)
Cl(2)	3201 (1)	1937 (1)	5094 (1)	738 (7)	636 (4)	496 (6)	361 (4)	164 (4)	202 (5)
P(1)	547 (1)	2658 (1)	3381 (1)	397 (3)	562 (4)	451 (6)	167 (4)	66 (4)	84 (5)
P(2)	3042 (1)	1912 (1)	2171 (1)	553 (17)	480 (4)	406 (6)	210 (4)	66 (4)	-40 (5)
N	3316 (4)	4843 (3)	2747 (3)	533 (17)	411 (17)	457 (17)	190 (16)	106 (13)	79 (15)
O(1)	3272 (4)	5605 (4)	2045 (3)	943 (24)	744 (22)	744 (23)	388 (19)	244 (18)	375 (20)
O(2)	-305 (4)	1030 (3)	2913 (3)	487 (17)	575 (17)	767 (23)	505 (16)	111 (13)	-49 (15)
O(3)	2 (3)	3493 (3)	2379 (3)	432 (14)	948 (22)	609 (17)	295 (16)	62 (13)	311 (15)
O(4)	-137 (3)	2975 (3)	4486 (3)	574 (17)	692 (17)	609 (17)	279 (16)	248 (13)	173 (15)
O(5)	1586 (4)	488 (3)	1983 (3)	658 (17)	493 (17)	699 (17)	124 (16)	97 (13)	-143 (15)
O(6)	4572 (3)	1612 (3)	2287 (3)	651 (17)	571 (17)	665 (17)	318 (16)	195 (13)	0 (15)
O(7)	3037 (4)	2644 (3)	954 (2)	940 (24)	697 (17)	321 (11)	384 (16)	97 (13)	-5 (10)
C(1)	-1696 (7)	3177 (9)	1928 (8)	540 (31)	1337 (56)	1325 (62)	404 (39)	66 (35)	489 (49)
C(2)	-1879 (11)	3759 (15)	788 (12)	1051 (63)	2220 (99)	1680 (90)	668 (70)	421 (66)	835 (94)
C(3)	-289 (7)	2207 (8)	5548 (5)	898 (38)	1129 (43)	705 (34)	570 (39)	394 (31)	425 (35)
C(4)	-1187 (9)	2668 (9)	6290 (7)	968 (45)	1419 (61)	789 (39)	508 (47)	187 (40)	306 (44)
C(5)	4833 (8)	551 (7)	2999 (6)	940 (42)	896 (39)	789 (39)	574 (35)	151 (31)	138 (30)
C(6)	4860 (11)	-569 (8)	2184 (8)	1782 (80)	922 (48)	1291 (68)	896 (58)	625 (58)	272 (44)
C(7)	2753 (9)	1809 (8)	-274 (5)	1525 (59)	1147 (48)	395 (23)	691 (50)	137 (35)	-94 (30)
C(8)	2826 (13)	2714 (10)	-1208 (6)	1841 (84)	1467 (69)	451 (28)	889 (66)	301 (40)	143 (35)

^a In the form $\exp[-2\pi^2 \sum_{ij} U_{ij} h_i h_j a_i^* a_j^*]$.

suitable monocrystal of dimensions (0.3 × 0.1 × 0.1 mm) was mounted on an automatic four-circle Nonius diffractometer controlled by a PDP 8 computer.

An $\omega/2\theta$ scan was employed with a scan angle (in degrees) given by $S = 1.00 + 0.35 \tan \theta$ increased by 25% at each end for the background count. The crystal-counter distance was 173 mm; the counter aperture was calculated from $d = 2.50 + 0.4 \tan \theta$ (in mm). By use of the above conditions and graphite-monochromated Mo K α radiation, the intensities and estimated standard deviations of the 4004 unique reflections, collected to $(\sin \theta)/\lambda < 0.7 \text{ \AA}^{-1}$, are given by the formulas

$$I_{\text{net}} = N - 2B$$

$$\sigma_I = (N + 4B)^{1/2}$$

where N = total count and B = (background left + background right).

Three standard reflections were monitored every 100 min of exposure; no significant variation was observed. All the reflections were corrected for Lorentz and polarization effects but not for absorption ($\mu R_{\text{max}} = 0.4$) by the program MAXE.¹²

Solution and Refinement of the Structure. The positions of the heaviest atoms (Ru, Cl, and P) were found with the aid of the program MULTAN^{13a} in the most probable set and confirmed from the Patterson function. From three-dimensional electron density difference maps the positions of the remaining nonhydrogen atoms were obtained. After successive least-squares refinement with anisotropic thermal parameters the positions of all the hydrogen atoms were obtained from an electron density difference map using the reflections below $(\sin \theta)/\lambda = 0.3 \text{ \AA}^{-1}$. Full-matrix least-squares refinement^{13b} with anisotropic thermal parameters for nonhydrogen atoms and constant isotropic thermal parameters for the hydrogen atoms converged to

$$R = \sum \Delta F / \sum |F_o| = 0.043$$

and

$$R_w = (\sum w(\Delta F)^2 / \sum w F_o^2)^{1/2} = 0.044$$

with

$$\Delta F = |F_o - F_c|$$

The isotropic thermal parameters for the hydrogen atoms were taken as the equivalent isotropic thermal parameters of the atoms bearing the protons, except for H(21), the bridging hydrogen atom, whose isotropic thermal parameter was refined.

The weights $w = 1/\sigma_{F^2}$ were calculated as¹⁴

$$\sigma_{F^2} = \frac{1}{4} \frac{\sigma_{I^2} + (0.041I)^2}{I}$$

Table II. Selected Intramolecular Distances (Å)

Ru-Cl(1)	2.494 (1)	N-O(1)	1.138 (5)
Ru-Cl(1')	2.484 (1)	O(2)···O(5)	2.432 (5)
Ru-Cl(2)	2.318 (1)	O(3)-C(1)	1.462 (6)
Ru-P(1)	2.301 (1)	O(4)-C(3)	1.444 (6)
Ru-P(2)	2.302 (1)	O(6)-C(5)	1.450 (7)
Ru-N	1.727 (3)	O(7)-C(7)	1.459 (6)
Ru-Ru'	3.672 (1)	C(1)-C(2)	1.428 (16)
P(1)-O(2)	1.526 (2)	C(3)-C(4)	1.458 (12)
P(1)-O(3)	1.566 (3)	C(5)-C(6)	1.418 (12)
P(1)-O(4)	1.549 (3)	C(7)-C(8)	1.419 (11)
P(2)-O(5)	1.508 (2)	O(2)···H(21)	1.00 (5)
P(2)-O(6)	1.567 (3)	O(5)···H(21)	1.45 (5)
P(2)-O(7)	1.571 (3)		

Table III. Selected Bond Angles (deg)

Cl(1)-Ru-P(1)	93.45 (4)	P(1)-Ru-P(2)	88.51 (4)
Cl(1)-Ru-P(2)	174.74 (4)	P(1)-Ru-Cl(2)	86.84 (4)
Cl(1)-Ru-Cl(2)	88.65 (4)	P(1)-Ru-N	91.25 (10)
Cl(1)-Ru-N	92.95 (8)	P(2)-Ru-Cl(2)	86.59 (4)
Cl(1)-Ru-Cl(1')	84.92 (4)	P(2)-Ru-N	91.88 (10)
Ru-Cl(1)-Ru'	95.08 (4)	Cl(2)-Ru-N	177.58 (10)
Ru-P(1)-O(2)	114.96 (10)	P(1)-O(3)-C(1)	120.85 (31)
Ru-P(1)-O(3)	105.72 (9)	P(1)-O(4)-C(3)	124.58 (25)
Ru-P(1)-O(4)	115.76 (10)	P(2)-O(6)-C(5)	123.18 (81)
Ru-P(2)-O(5)	115.24 (10)	P(2)-O(7)-C(7)	120.51 (28)
Ru-P(2)-O(6)	113.38 (9)	P(1)-O(2)-H(21)	109.5 (16)
Ru-P(2)-O(7)	105.15 (9)	P(2)-O(5)-H(21)	108.8 (16)
Ru-N-O(1)	177.60 (24)		

The estimated standard deviation (esd) of an observation of unit weight was 1.30 and no significant peak remained on a final electron density difference map, and no shifts greater than 0.5 esd were observed on the hydrogen atom parameters in the final refinement.

The final positional and thermal parameters with their esd's are listed in Table I for nonhydrogen atoms; bond distances and angles are given in Tables II and III.

Results and Discussion

Synthesis. In an attempt to prepare the analogous phosphite derivatives of $\text{RuCl}_3(\text{NO})(\text{PPh}_3)_2$ (2)¹¹ the general procedure using *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (DiazaId) as the nitrosyl source led us actually to a dinuclear nitrosyl ruthenium compound. When we treated a mixture of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ with 1.5 equiv of DiazaId and an excess of triphenyl phosphite in refluxing dry ethanol for 24 h, according to reaction 1, we obtained in addition to phenol the bright yellow derivative **1a** in 55% yield instead of the expected $\text{RuCl}_3(\text{NO})[\text{P}(\text{OR})_3]_2$.



With the ¹H NMR indicating the incorporation of ethoxy groups in compound **1a**, a similar reaction was performed by using triethyl phosphite instead of triphenyl phosphite and in that way the derivative **1a** was isolated in 77% yield.

Infrared spectra of **1a** showed a broad absorption at 1900 cm⁻¹ which was consistent with a linear nitrosyl ligand and absorptions which could be attributed to vibrations of RuCl bonds both terminal (342 cm⁻¹) and bridging (287 and 237 cm⁻¹).

A proton-decoupled ³¹P NMR spectrum showed only one singlet at 79.1 ppm downfield from H₃PO₄ in CDCl₃ at 308 K and the ³¹P nuclei still appeared equivalent when the temperature of a sample of CD₂Cl₂ was lowered to 180 K. However, two types of ethoxy groups could be detected at 300 K in the ¹H NMR (CDCl₃): a broad multiplet at δ 4.4 appeared for the methylene protons and two triplets were observed for the methyl protons at δ 1.37 and 1.43 (³J_{H-H} = 7 Hz). As the phosphorus nuclei were equivalent, different environments for the ethoxy groups bonded to a phosphorus atom were anticipated. Of special interest in the ¹H NMR spectrum was the presence of a broad singlet at 13.25 ppm, which disappeared on addition of D₂O and was attributed to a P-OH group, and the relative intensities indicated four ethoxy groups for one P-OH group. The presence of two P-O-H groups was confirmed by a conductometric titration of **1a** against a standard solution of potassium hydroxide in ethanol. The plot of conductance against volume of base added showed two distinct breaks corresponding to the addition of 1 and then 2 equiv of base.

The molecular weight (942 ± 20) calculated from the unit cell volume and experimental density (1.69) were consistent with a binuclear ruthenium complex. Elemental analysis and spectroscopic data led us to suggest the formula [RuCl₂(NO)[(EtO)₂PO]₂H₂ for **1a** (calculated mol wt 954.57).

The formation of this novel type of binuclear nitrosyl ruthenium derivative appears to be a general method. When the diethyl phenylphosphonite was used, several isomers were formed as indicated by ¹H NMR but by crystallization only one pale yellow isomer, **1b** (R¹, R² = Ph, OEt), was isolated in an overall yield of 57% for which the nitrosyl absorption band appeared at 1895 cm⁻¹ (KBr). The NMR (CDCl₃) indicated equivalent phosphorus nuclei at δ +110.2 (downfield of H₃PO₄) and only one type of ethoxy group by the appearance of only one triplet at δ 1.20 (³J_{HH} = 7.0 Hz). In this case the POH protons could not be observed as for compound **1a**. Although it was not possible to know which isomer was isolated, its formation indicated that the apical nitrosyl group selectively allows the proximity of either the phenyl or the ethoxy substituent at the phosphorus atom.

The synthesis of derivatives **1** can be understood by the initial formation of the expected mononuclear nitrosyl complexes RuCl₃(NO)[R₂POR¹]₂. When the same reaction was performed in dry *tert*-butyl alcohol instead of ethanol with triphenyl phosphite after 1 h of reflux, RuCl₃(NO)[P(OPh)₃]₂¹¹ could be isolated.

The exchange of phenoxy by ethoxy groups at coordinated phosphorus atom occurs easily and the subsequent solvolysis of ethoxy groups could take place. Examples of solvolysis of phosphinoacetylenes,⁵ tertiary phosphinites, or phosphites^{3,6,7} coordinated in the *cis* position to palladium or platinum have already been reported.

The most significant aspect of the present synthesis is probably the formation of the centrosymmetric dinuclear complex with only two bridging chlorine atoms, since it has been established that Ph₂POMe adds to RuCl₂(C₇H₈)_n to afford in refluxing methanol the tri-*μ*-chloro-bridged dinuclear cation [(Ph₂POMe)₃RuCl₃Ru(Ph₂POMe)₃]Cl,¹⁶ which on

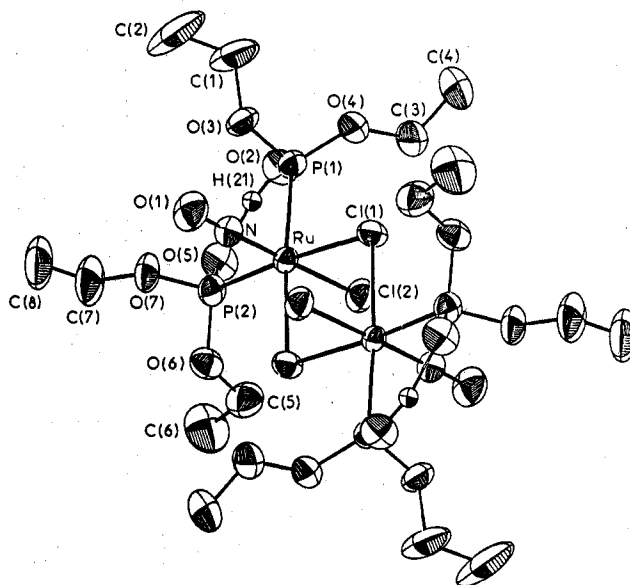


Figure 1. ORTEP³⁰ diagram of compound **1a** with H atoms omitted for clarity.

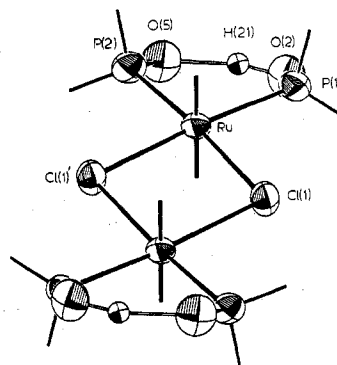


Figure 2. The heavy-atom skeleton and metallocycle of compound **1a**.

pyrolysis gives the unsymmetrical derivative (Ph₂POMe)₂(Ph₂POH)RuCl₃Ru[(Ph₂PO)₃H₂].¹⁷

In the present case the formation of the RuCl₃Ru bridge is probably prevented by the presence of the nitrosyl ligand on ruthenium. The selection of the neighboring group bonded at the phosphorus atoms, the phenyl or the ethoxy group as in **1b**, and the control of the formation of a centrosymmetrical product in the described reaction add to the significant role already known for a nitrosyl ligand.

Crystal and Molecular Structure. The dimeric complex [RuCl₂(NO)[(EtO)₂PO](EtO)₂POH₂ (**1a**) exists as discrete molecules lying on a center of symmetry. An illustration of one of these molecules is shown in Figure 1 with its heavy-atom skeleton and metallocycles in Figure 2. The coordination around the ruthenium atoms is approximately octahedral; however, the plane defined by the bridging halogens and the ruthenium atom makes an angle of 6.24° with the plane defined by the ruthenium atom and the coordinating atoms of the ligands trans to the bridging halogens. This angle is similar to that observed in other dimeric ruthenium complexes having two halogen bridges (7.8° for [RuBr₃(NO)(Et₂SO)₂]¹⁸ and 5.2° for [RuBr₂(CO)₃]₂¹⁹). As expected, the ruthenium-bridging chlorine distances, Ru-Cl(1) and Ru-Cl(1)' (2.494 (1) and 2.484 (1) Å, respectively), are longer than that of Ru-Cl(2), the ruthenium-terminal chlorine distance. The nitrosyl ligand which is trans to Cl(2) gives a virtually linear arrangement with the ruthenium atom. The Ru-N-O angle of 177.60° is similar to other values reported for linear nit-

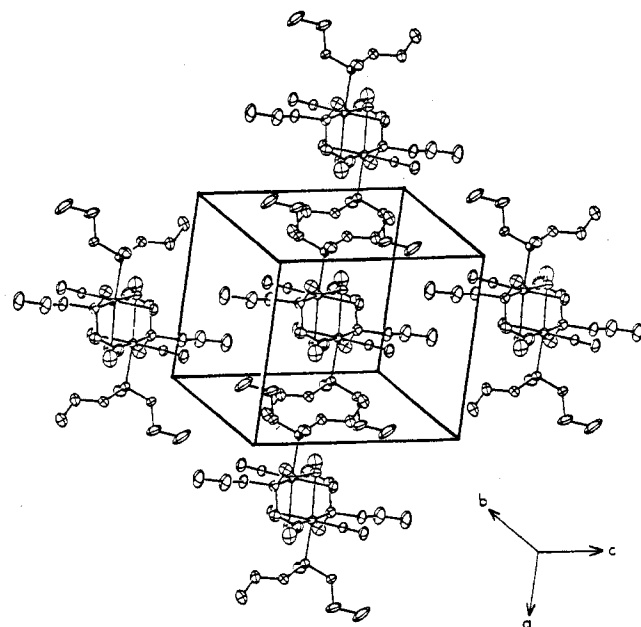


Figure 3. The molecular packing of compound 1a.

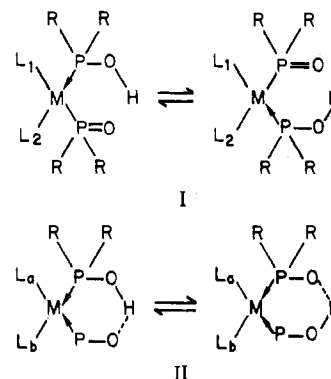
rosyls.^{18,20,21} The distances N–O(1) (1.138 (5) Å) and Ru–N (1.727 (3) Å) are in the same range of values reported in the literature for linear RuNO as in $\text{RuCl}_3(\text{NO})(\text{PPh}_3)_2$ ²⁰ (e.g., 1.142 and 1.737 Å, respectively). A linear nitrosyl ligand is consistent with the coordination of NO^+ . This is confirmed by a short Ru–N bond as expected for a strong π back-donating group and by the nitrosyl absorption at 1900 cm^{-1} .

The most significant aspect concerns the data for the heterometallic cycle. The bond length for P(1)–O(2) (1.526 (2) Å) is significantly shorter than those for the phosphorus–ethoxy group bonds P(1)–O(3) (1.566 (3) Å) and P(1)–O(4) (1.549 (3) Å). Around the second phosphorus atom the P–O bonds for the phosphorus ethoxy groups are equal (P(2)–O(6) = 1.567 (3) Å and P(2)–O(7) = 1.571 (3) Å) and considerably longer than P(2)–O(5) (1.508 (2) Å). Moreover the comparison of P(1)–O(2) and P(2)–O(5) bond lengths shows that in the metallocycle RuPOHOP the P–O bond lengths are significantly different, both being shorter than those found in analogous metallocycles, only reported for square-planar complexes of palladium,^{5a,7} where the average P–O distance is in the region of 1.54 Å. This difference in the phosphorus atoms in the solid state is also reflected in the slight but significant difference in the Ru–Cl(1) and Ru–Cl(1') bond lengths. However, the difference in the phosphorus atoms which was observed in the solid state could not be detected in CD_2Cl_2 solution at 180 K.

The nonbonding O(2)–O(5) distance (2.432 (5) Å) is of the same order as that found in $\text{Me}_2\text{PS}_2\text{Pd}(\text{Ph}_2\text{PO})\text{H}$ (2.41 (2) Å)⁷ and in $[\text{Pd}(\text{SCN})(\text{Ph}_2\text{PO})_2\text{H}]$ ^{5a} (2.421 (7) Å); however, the position of the bridging proton in both these compounds is thought to be symmetrically placed with respect to the two oxygen atoms whereas for $\{\text{RuCl}_2(\text{NO})[(\text{EtO})_2\text{PO}][(\text{EtO})_2\text{POH}]\}_2$ both the P–O bond lengths and the O–H bond lengths (O(2)–H(21) = 1.00 (5) Å and O(5)–H(21) = 1.45 (5) Å) imply a significant asymmetry in the RuPOHOP moiety.

The asymmetry in the metallocycle cannot be explained by packing arguments alone. Figure 3 shows the molecular packing; it can be seen that all the intramolecular interactions appear to be repulsive in nature as the A...H...B angles are all too small²² and that any effects due to packing will be weak.

As was suggested by Serpline and Roundhill,⁸ complexes containing the ligand $(\text{R}_2\text{PO})_2\text{H}$ can be formally represented



as I or II, where R is an alkyl, aryl, alkoxy, or phenoxy group and L_a , L_b , L_1 , and L_2 represent the other ligands coordinated to the metal.

One possible explanation for the symmetry or dissymmetry of these ring systems is in the type of metal–phosphorus bonding and hence the phosphorus–oxygen bonding. If the bonding is represented as in II, the two oxygen atoms are equivalent, both being sp^3 hybridized and separated by approximately 2.45 Å, and the hydrogen will be symmetrically bonded to both oxygen atoms. On the other hand, when the bonding is represented as in I with the oxygen atoms still separated by approximately 2.45 Å the nonequivalence of the oxygen atoms, one being sp^2 hybridized and the other sp^3 hybridized, will induce dissymmetry in the O...H...O bonding.

Thus, for compounds such as $\text{Me}_2\text{PS}_2\text{Pd}[(\text{Ph}_2\text{PO})_2\text{H}]$ or $\{\text{Pd}(\text{SCN})[(\text{Ph}_2\text{PO})_2\text{H}]\}_2$ in which the observed P–O bond lengths are equal and are in the range of P–O single bond lengths (1.53–1.60 Å^{23–29}) observed in transition metal–phosphite complexes, it would appear normal that the O...H...O system is symmetric. Moreover in $\{\text{RuCl}_2(\text{NO})[(\text{EtO})_2\text{PO}]\}_2$, although the Ru–P bond distances are equivalent, the observed P–O bond lengths are not equal, and one is very much shorter than a P–O single bond distance. Therefore it would appear that the bonding is much nearer that represented in I; hence it is normal that the O...H...O system is dissymmetric.

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Registry No. 1a, 69047-60-5; 1b, 71328-87-5; 2, 28577-87-9; RuCl_3 , 10049-08-8; Diazald, 80-11-5.

Supplementary Material Available: A listing of observed and calculated structure factors and tables of fractional coordinates and isotropic thermal parameters for the hydrogen atoms and of the shortest intramolecular interactions and of hydrogen bond lengths (15 pages). Ordering information is given on any current masthead page.

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Synthesis and Crystal and Molecular Structure of $[(C_7H_7)_3P]_4Cu_4W_2O_2S_6$, a Dimer of Bis((tri-*p*-tolylphosphine)copper)oxotrithiotungsten

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Reaction of tri-*p*-tolylphosphine, cuprous chloride, and $(Ph_3PCH_3)_2WO_2S_2$ produced $[(C_7H_7)_3P]_4Cu_4W_2S_8$ and $[(C_7H_7)_3P]_4Cu_4W_2O_2S_6$. The oxotrithiotungsten derivative crystallizes in monoclinic space group $P2_1/n$ with $a = 13.164$ (5) Å, $b = 25.613$ (16) Å, $c = 13.823$ (6) Å, $\beta = 97.25$ (4)°, and $Z = 2$. The X-ray structure ($R = 0.067$) revealed a 12-atom $Cu_4W_2S_6$ cage which may be viewed as consisting of two approximately tetrahedral WOS_3 units bridged on adjacent edges by $[(C_7H_7)_3PCu]$ groups.

Introduction

Evidence that reduction-oxidation reactions catalyzed by metalloenzymes occur at sites in which the metal is coordinated to one or more sulfur atoms^{1,2} has stimulated interest in the coordination chemistry of molybdenum and its congeners. It appears that substitution of tungsten for molybdenum in an apoenzyme, when it can be accomplished, as for example in nitrate reductase³ and sulfite oxidase,⁴ produces a protein which is virtually inactive as a catalyst. This may be due to the lower stability of lower oxidation states of tungsten relative to those of molybdenum. Tungsten is also an antagonist to dietary molybdenum.⁵ The utility of model tungsten compounds in helping to understand the chemistry of molybdoenzymes has been pointed out,^{6,7} and group 6B copper ternary sulfides are of current interest in regard to complex interactions between copper, molybdenum, and sulfur in mammalian metabolism. This paper describes the synthesis and structure of a novel ternary metal-sulfur cluster in which the (tri-*p*-tolylphosphine)copper moiety bridges tetrahedral WOS_3 units. A similar complex in which a substituted phosphine-silver moiety bridges tetrahedral WS_4 units has also been prepared and studied by single-crystal X-ray analysis.⁸

Experimental Section

A mixture of 0.95 g of tri-*p*-tolylphosphine (3.1 mmol), 0.2 g (2 mmol) of cuprous chloride, and 100 mL of dichloromethane was stirred until the cuprous chloride dissolved. Then 1.67 g (2 mmol) of $(Ph_3PCH_3)_2WO_2S_2$ was added and stirring continued for 18 h. After refluxing for 1 h, the reaction mixture was filtered, evaporated to a small volume, and applied to a 13 in. \times 1 in. silica gel column. Dichloromethane eluted a broad yellow band. The eluate was evaporated and applied to two 8 in. \times 8 in. silica gel preparative thin

layer chromatography plates which were then developed with benzene to yield two components. The fast yellow band was eluted with dichloromethane to afford 0.55 g (26%) of $[(C_7H_7)_3P]_4Cu_4W_2S_8$. The slower, orange band was eluted with dichloromethane and the product recrystallized by slow evaporation of a dichloromethane-isopropyl alcohol solution to give 0.05 g (2.2%) of $[(C_7H_7)_3P]_4Cu_4W_2O_2S_6$ (1) as orange needles, mp 238–239 °C.

Magnetic susceptibility at 300 K was 0.39×10^{-6} cm³ g⁻¹. Anal. Calcd for $C_{84}H_{84}Cu_4O_2P_4S_6W_2$: C, 48.49; H, 4.10; Cu, 12.32; P, 6.00; S, 9.32; W, 17.85; mol wt 1031. Found: C, 49.14; H, 4.37; Cu, 12.56; P, 5.89; S, 8.21; W, 18.56; mol wt (osmometric in $CHCl_3$) 945. IR (Nujol): strong bands at 940, 930, 446, 428 cm⁻¹. Raman spectrum (4185-Å excitation; 1,2- $C_2H_4Cl_2$ solution): $\Delta\nu$ 456, 467 cm⁻¹. λ_{max} (1,2- $C_2H_4Cl_2$): 400 (sh), 385 (sh) nm. ¹H NMR ($CDCl_3$): -7.6 (m, 4 H), -2.95 ppm (s, 3 H). ¹H³¹P NMR (CH_2Cl_2): broad singlet at -9.4 ppm.⁹

In a similar experiment in which 1.84 g of tri-*p*-tolylphosphine was used, the yields of $[(C_7H_7)_3P]_4Cu_4W_2S_8$ and $[(C_7H_7)_3P]_4Cu_4W_2O_2S_6$ were 0.75 and 0.095 g, respectively; about half of the starting phosphine was recovered.

Experimental details and results of the X-ray crystallographic study are summarized in Tables I–III. A table of observed and calculated structure factors is available as supplementary material.

Results and Discussion

Preparative Chemistry. The reaction of a tertiary phosphine such as diphenylmethylphosphine, copper(I) chloride, and $WO_2S_2^{2-}$ produces the bimetallic net compound $(Ph_2PCH_3)_4Cu_2WS_4$.¹⁰ We found that a like reaction employing tri-*p*-tolylphosphine as both a ligand and reducing agent afforded, in addition to $[(C_7H_7)_3P]_4Cu_4W_2S_8$, a low yield of $[(C_7H_7)_3P]_4Cu_4W_2O_2S_6$, 1, which was isolated by preparative thin-layer chromatography. This material was of interest from the standpoint of the relationship of the M_2MOS_3 core to metalloenzymes and because of the fact that it presented the interesting structural problem of the location of the oxygen atoms in the dimeric structure (vide infra).

Vapor pressure osmometry revealed that the trithiotungstate was a dimer, and the ¹H³¹P NMR spectrum consisted of only

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