Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number AIC40605I.

References and Notes

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(20) In addition to local programs for the CDC 7600 computer, modifications of the following programs were used: Ibers' NUCLS, a group least-squares version of the Busing–Levy ORFLS program; Zalkin's FORDAP Fourier program; ORFFE, a function and error program by Busing, Martin, and Levy; Johnson's ORTEP thermal ellipsoid plot program; MULTAN, a direct-methods program by Main, Woolfson, and Germain.

(21) In all refinements the function minimized was $\sum w(|F_o| - |F_c|)^2$, where F_o and F_c are the observed and calculated structure factors. The weighting factor, *w*, is $4F_o^2/\sigma^2(F_o^2)$. The atomic scattering factors for Co, Cl, O, N, and C were taken from the tabulations of Cromer and Mann.[22] Hydrogen scattering factor values were those calculated by Stewart, Davidson, and Simpson.[23] Corrections for anomalous dispersion effects for Co were made using the $\Delta f'$ and $\Delta f''$ values of Cromer.[24]

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Synthesis and Structural Characterization of Sodium Tetra-μ-sulfato-dirhenate(III) Octahydrate

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A compound of composition $Na_2Re_2(SO_4)_4{\cdot}8H_2O$ is obtained in about 90% yield from the reaction of $[(n\text{-}C_4H_9)_4N]_2Re_2Cl_8$ with Na_2SO_4 and H_2SO_4 in $(CH_3OCH_2CH_2)_2O$. The pale blue substance is air sensitive. It is soluble in water and in the more polar organic liquids. Recrystallization from a 10:1 mixture of methanol and 48% aqueous HBF_4 yielded blue-green crystals suitable for X-ray structure determination. Crystal data are as follows: space group $P2_1/n$; unit cell dimensions $a = 7.739$ (1) Å, $b = 13.212$ (3) Å, $c = 11.077$ (2) Å, $\beta = 100.58$ (1)°, $V = 1113.3$ (4) Å^3, $Z = 2$. Using 1331 reflections for which $I > 3\sigma(I)$ in the range $0° < 2\theta < 50°$ the structure was solved and refined anisotropically to $R_1 = 0.042$ and $R_2 = 0.052$. The structure contains $Re_2(SO_4)_4^{2-}$ ions which lie on crystallographic centers of symmetry and have virtual symmetry C_{4h}. They are essentially similar to the $Mo_2(SO_4)_4^{4-}$ ions previously described. The bridging sulfato ligands are appreciably distorted, with S–O distances of 1.54 (1) Å for coordinated oxygen atoms and 1.43 (1) Å for noncoordinated oxygen atoms and with O–S–O angles ranging from 104 to 117°. There are coaxially coordinated water molecules at an Re–O distance of 2.28 (1) Å, while the average of the eight Re–O(sulfate) distances is 2.01 (1) Å. The Re–Re distance is 2.214 (1) Å, which is very similar to those in other species containing quadruply bonded pairs of Re(III) atoms. The compound is very reactive and may serve as a useful starting material for the preparation of other complexes of Re_2^{6+}.

Introduction

The existence of a quadruple bond was first recognized in a dirhenium(III) compound, namely, a salt of $Re_2Cl_8^{2-}$, about a decade ago.[1-3] Since then a great variety of ligand-exchange reactions in which the quadruply bonded Re_2^{6+} core remains intact have been carried out. In some of these, the Cl^- ligands are partly or wholly replaced by bidentate bridging ligands. These have been, in most cases, carboxylato ions,[4-7] although more recently we have prepared and structurally characterized compounds with $Ph_2PCH_2PPh_2$ and $PhNC(Ph)NPh^-$ as bridging ligands.[8] Still, the number of bridging ligands which are known to occur in Re_2^{6+} complexes is less than for Mo_2^{4+} and Cr_2^{4+} species, where xanthate ions,[9] CO_3^{2-} ions,[10] and sulfate ions[11] have all been found. In an effort to see if similar complexes of Re_2^{6+} can be prepared, we have studied the reaction of $Re_2Cl_8^{2-}$ with sulfate-containing media, and the new compound $Na_2Re_2(SO_4)_4{\cdot}8H_2O$ has been isolated and structurally characterized.

Experimental Section

Preparation. $[(n\text{-}C_4H_9)_4N]_2Re_2Cl_8$ was prepared according to a

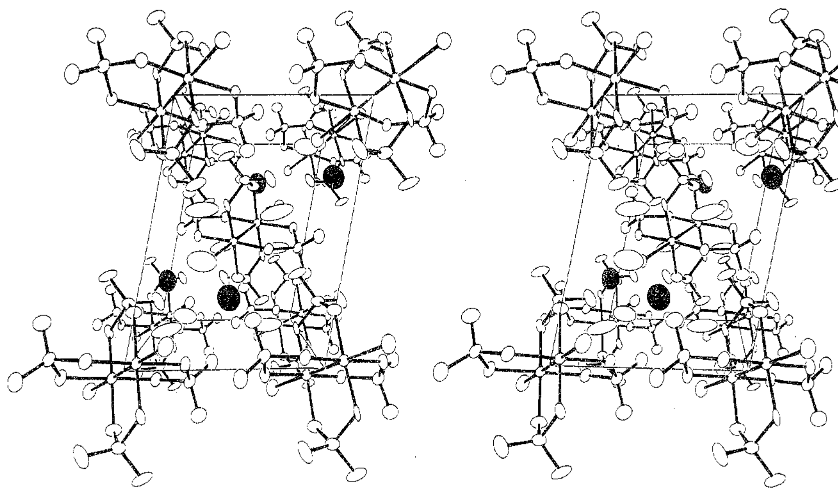

Figure 1. Stereoscopic ORTEP view of the unit cell, in which atoms are represented by their ellipsoids of thermal vibration drawn to enclose 50% of the electron density. The sodium ions are represented by the filled ellipsoids.

published method.[12] All of the following operations were carried out under an atmosphere of nitrogen. $[(n\text{-}C_4H_9)_4N]_2Re_2Cl_8$ (1.0 g) and Na_2SO_4 (0.12 g) were added to a mixture of 60 ml of $(CH_3OCH_2CH_2)_2O$ and 4 ml of concentrated sulfuric acid. The blue slurry which soon formed a blue solution was stirred and heated at 140° until the blue color of the liquid phase disappeared and a blue precipitate had formed. This usually required about 1 hr. The pale blue precipitate was collected on a frit in a Schlenk tube[13] and pumped dry. It was then washed with THF. Yields were typically 90% or more. Recrystallization was carried out by dissolving the pale blue powder in the minimum quantity of a 10:1 mixture of methanol and 40% aqueous HBF_4 and slowly removing the methanol under vacuum. The resultant blue-green crystals are stable in air for only a few minutes. Microscopic examination indicated that the recrystallized material contained many single crystals suitable for an X-ray structural study. One such crystal was transferred to a glass capillary and sealed therein.

Collection of Crystallographic Data. The approximate dimensions of the crystal selected were 0.26 × 0.14 × 0.06 mm, and the developed faces were $11\bar{1}$, $\bar{1}\bar{1}1$, 021, $0\bar{2}\bar{1}$, $1\bar{1}1$, and $\bar{1}1\bar{1}$, with the last two being the largest ones. Data were collected on a Syntex $P\bar{1}$ four-circle automatic diffractometer. ω scans of several reflections gave a peak width at half-height of 0.2°. Computer-guided centering on 15 reflections followed by least-squares refinement gave an orientation matrix which was used to determine unit cell dimensions and to calculate setting angles.

The cell constants, at 24 ± 1°, are $a = 7.739$ (1) Å, $b = 13.212$ (3) Å, $c = 11.077$ (2) Å, $\beta = 100.58$ (1)°, and $V = 1113.3$ (4) Å^3. The formula weight of 946.6 and an assumed value of $Z = 2$ give a calculated density of 2.82 g/cm^3.

Intensities were measured at 24 ± 1° using the θ–2θ scan method. With Mo Kα radiation, 2217 independent reflections were measured in the 2θ range from 0 to 50°. A graphite crystal monochromator was placed in the incident beam. Scan speeds varied from 4 to 24° min^{-1} depending on the intensity of the reflection, and the scan range was from 1° below the Kα_1 peak to 1° above the Kα_2 peak. Absorption corrections were required since the absorption coefficient is 120 and transmission factors varied from 0.218 to 0.523. The crystal was carefully measured on an optical goniometer. Programs for data reduction and absorption corrections as well as those used subsequently in the structure analysis are listed below.[14]

Solution and Refinement of the Structure. The systematically absent reflections indicated space group $P2_1/n$. The rhenium atom position was ascertained from a three-dimensional Patterson map. One cycle of refinement of this atom alone gave discrepancy indices of $R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0.23$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.31$. A difference electron density map was then calculated and this revealed the positions of all other nonhydrogen atoms except for three oxygen atoms and the sodium atom. Three cycles of isotropic least-squares refinement reduced R_1 and R_2 to 0.105 and 0.142, respectively. The remaining four atoms were found on a difference electron density map, and one cycle of refinement was run on the now complete set of atoms. The absorption corrections were applied at this point, and only the 1331 reflections for which $I > 3\sigma(I)$ were used subsequently. Three cycles of least-squares refinement with anisotropic temperature parameters were then carried out, with 145 variables, and converged to final R_1 and R_2 values of 0.042 and 0.052, respectively. The parameter p used in the expression for $\sigma(I)$ was assigned a value of 0.06 until the penultimate cycle. An analysis of $\sum w(|F_o| - |F_c|)^2$ *vs.* (F_o) suggested that this was too low a value and 0.07 was used in the last cycle. The error in an observation of unit weight after the last cycle was 1.10. A difference electron density map did not reveal any hydrogen atoms. After application of the absorption corrections, the Re, S, and Na atoms were treated as anomalous scatterers using f' and f'' values taken from the tabulation of Cromer and Liberman.[15] The ordinary scattering factors for all atoms were those of Cromer and Waber.[16] No untoward trends were found in the values of $\sum w(|F_o| - |F_c|)^2$ as a function of Miller indices, classes of Miller indices, $\lambda^{-1} \sin \theta$, or $|F_o|$.

Table I. Interatomic Distances Considered in Assigning Peaks to O and Na Atoms

From	To	Value, Å	From	To	Value, Å
Na	O(12)	2.62	O(10)	O(12)	2.50
Na	O(1)	2.74	O(10)	O(3)	2.77
Na	O(8)	2.92	O(10)	O(4)	2.78
Na	O(3)	2.99	O(10)	O(7)	3.03
Na	O(4)	3.05	O(10)	O(9)	3.12
Na	O(2)	3.11	O(10)	O(11)	3.13
Na	O(7)	3.17			
			O(12)	O(11)	2.50
O(11)	O(12)	2.50	O(12)	O(10)	2.50
O(11)	O(5)	3.04	O(12)	Na	2.62
O(11)	O(7)	3.13	O(12)	O(7)	3.20
O(11)	O(10)	3.13			

A peculiar difficulty in dealing with this structure arose because a sodium cation and a water molecule have the same number of electrons, and in this case, where hydrogen atoms were not located, the two were essentially indistinguishable on X-ray criteria alone. The decision was made by invoking chemical criteria. The peaks finally assigned to O(11) and O(12) have only four other peaks within a radius of 3.2 Å (see Table I), and since we expect Na^+ to have a coordination number higher than 4, we concluded that they must be OH_2 and not Na^+. The peak finally assigned to O(10) was so identified by noting (a) that it, like O(11), is 2.5 Å from O(12), with an O(10)–O(12)–O(11) angle of 112°, and (b) that whether one chose 3.0, 3.1, or even 3.2 Å as the limit to the coordination sphere, the remaining peak, identified as Na^+, has a higher coordination number. In the unit cell drawing, Figure 1, the Na^+ ions are indicated by heavy black dots.

The observed and calculated structure factor amplitudes, expressed as $10|F_o|$ and $10|F_c|$ are available.[17] Atomic positional parameters and anisotropic thermal parameters are listed in Tables II and III.

Properties. This new compound is quite reactive. It is air-sensitive as a crystalline solid, decomposing perceptibly after a few minutes' exposure, and in solution it is immediately decomposed on exposure

Table II. Atomic Positional Parameters

	x	*y*	*z*
Re	0.56708 (8)	0.56034 (4)	0.45677 (5)
S(1)	0.5637 (6)	0.6108 (3)	0.7302 (4)
S(2)	0.8330 (5)	0.3956 (3)	0.5726 (4)
O(1)	0.7075 (16)	0.6857 (9)	0.3707 (11)
O(2)	0.6446 (14)	0.6332 (8)	0.6165 (10)
O(3)	0.4190 (16)	0.6775 (9)	0.7275 (12)
O(4)	0.7013 (18)	0.6152 (10)	0.8364 (11)
O(5)	0.5026 (15)	0.5003 (8)	0.7130 (10)
O(6)	0.7983 (13)	0.4851 (8)	0.4834 (10)
O(7)	0.9118 (17)	0.4297 (10)	0.6906 (11)
O(8)	0.9327 (15)	0.3227 (9)	0.5189 (11)
O(9)	0.6489 (14)	0.3523 (8)	0.5766 (10)
O(10)	0.6336 (33)	0.1533 (11)	0.4232 (15)
O(11)	0.7291 (34)	0.3747 (13)	0.9118 (15)
O(12)	0.2149 (31)	0.5266 (12)	0.8926 (17)
Na	0.5380 (17)	0.8435 (10)	0.2389 (12)

to air. When it is placed in refluxing 6 *N* HCl and $(n\text{-}C_4H_9)_4NCl$ is added, $[(n\text{-}C_4H_9)_4N]_2Re_2Cl_8$ can be obtained. It also reacts rapidly with a hot CH_3COOH–$(CH_3CO)_2O$ mixture, forming an orange solid which turns blue upon addition of water. The identity of this product has not been determined, but the color is reminiscent of the compound $Re_2(C_3H_7CO_2)_4(H_2O)_2SO_4$ reported by Taha and Wilkinson[18] and also by Cotton, Oldham, and Robinson.[4]

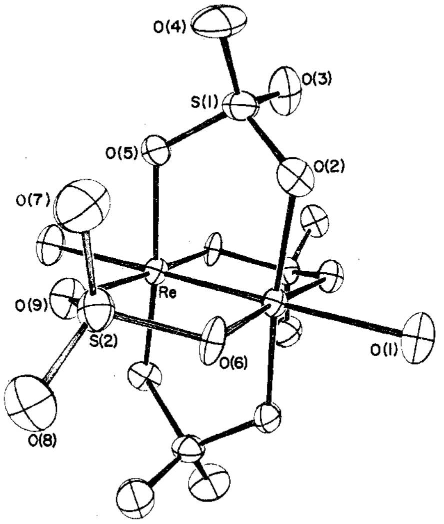

Figure 2. ORTEP drawing of the $Re_2(SO_4)_4(H_2O)_2{}^{2-}$ anion, in which each atom is represented by its ellipsoid of thermal vibration at the 50% level. The atom-numbering scheme is shown. Unlabeled atoms are related to labeled ones by a center of symmetry at the midpoint of the Re–Re bond.

Table III. Anisotropic Temperature Factors[a] (×10⁴)

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Re	57 (1)	21.8 (3)	33.2 (5)	−2.3 (6)	5.3 (5)	3.8 (4)
S(1)	107 (8)	35 (2)	38 (3)	3 (4)	7 (4)	−6 (2)
S(2)	74 (7)	28 (2)	47 (4)	5 (3)	−3 (4)	5 (2)
O(1)	102 (23)	38 (7)	79 (12)	−7 (11)	11 (13)	22 (9)
O(2)	46 (20)	34 (7)	67 (11)	−19 (9)	38 (12)	−8 (7)
O(3)	131 (26)	40 (7)	106 (15)	6 (12)	78 (16)	11 (9)
O(4)	177 (30)	67 (9)	42 (11)	−6 (14)	−38 (15)	−11 (9)
O(5)	134 (24)	24 (6)	41 (10)	−16 (10)	14 (13)	−1 (7)
O(6)	56 (18)	26 (6)	57 (10)	−3 (9)	12 (11)	23 (7)
O(7)	146 (27)	53 (9)	60 (11)	−9 (13)	9 (14)	5 (8)
O(8)	94 (22)	35 (7)	85 (14)	0 (11)	17 (14)	−1 (8)
O(9)	66 (20)	31 (7)	56 (11)	−12 (9)	7 (12)	5 (7)
O(10)	627 (73)	54 (11)	91 (17)	−1 (22)	−95 (27)	−6 (11)
O(11)	682 (85)	76 (13)	76 (17)	51 (26)	−10 (31)	9 (12)
O(12)	492 (64)	65 (12)	122 (21)	−21 (22)	64 (29)	18 (13)
Na	340 (34)	122 (11)	224 (19)	40 (15)	77 (21)	35 (12)

[a] These are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Table IV. Bond Distances and Angles in $Na_2Re_2(SO_4)_4 \cdot 8H_2O$

Distances, Å

Re–Re	2.214 (1)	S(1)–O(3)	1.42 (1)
Re–O(1)	2.28 (1)	S(1)–O(4)	1.44 (1)
Re–O(2)	2.01 (1)	S(1)–O(5)	1.54 (1)
Re–O(5)	2.02 (1)	S(2)–O(6)	1.53 (1)
Re–O(6)	2.02 (1)	S(2)–O(7)	1.41 (1)
Re–O(9)	2.01 (1)	S(2)–O(8)	1.43 (1)
S(1)–O(2)	1.54 (1)	S(2)–O(9)	1.54 (1)

Angles, deg

Re–Re–O(1)	179.0 (3)	O(2)–Re–O(5)	174.0 (4)
Re–Re–O(2)	93.0 (3)	O(6)–Re–O(9)	173.8 (4)
Re–Re–O(5)	92.9 (3)	O(2)–S(1)–O(3)	107.5 (7)
Re–Re–O(6)	93.2 (3)	O(2)–S(1)–O(4)	108.1 (8)
Re–Re–O(9)	93.0 (3)	O(2)–S(1)–O(5)	104.1 (6)
Re–O(2)–S(1)	122.0 (6)	O(3)–S(1)–O(4)	117.1 (8)
Re–O(5)–S(1)	121.0 (6)	O(3)–S(1)–O(5)	111.3 (7)
Re–O(6)–S(2)	121.3 (6)	O(4)–S(1)–O(5)	107.8 (7)
Re–O(9)–S(2)	121.5 (6)	O(6)–S(2)–O(7)	110.2 (7)
O(1)–Re–O(2)	86.1 (4)	O(6)–S(2)–O(8)	107.2 (7)
O(1)–Re–O(5)	88.0 (4)	O(6)–S(2)–O(9)	104.5 (6)
O(1)–Re–O(6)	86.6 (4)	O(7)–S(2)–O(8)	115.2 (7)
O(1)–Re–O(9)	87.1 (4)	O(7)–S(2)–O(9)	109.6 (7)
O(2)–Re–O(6)	89.6 (4)	O(8)–S(2)–O(9)	109.5 (6)
O(5)–Re–O(9)	89.2 (4)		

Angles between Planes

Plane	Plane	Angle, deg
S(1)–O(2)–O(5)	Re–O(2)–O(5)	22.9
S(2)–O(6)–O(9)	Re–O(6)–O(9)	22.4

The infrared spectrum (in a mineral oil mull) is very complex: 1280 (m), 1160 (br, s), 1110, 1100 (w), 1060 (w), 885 (m), 860 (w), 838 (w), 808 (s), 695 (m) cm⁻¹. Such complexity is not inconsistent with the structure (see later) in which there are two long S–O distances (1.54 Å) and two short ones (1.43 Å), a variety of O–S–O angles from 104 to 117°, hydrogen bonding from water molecules to some sulfate oxygen atoms, and, finally, coordination of some sulfate oxygen atoms to the sodium ions. It may be that the bands from 1060 to 1280 cm⁻¹ are due to the short S–O oscillators and those from 808 to 885 cm⁻¹ to the long S–O oscillators, with the band at 695 cm⁻¹ being of uncertain origin.

Results and Discussion

The structure is built up of Na^+ ions, $[Re_2(SO_4)_4(H_2O)_2]^{2-}$ ions, and additional water molecules, some of which are coordinated to the sodium ion and others hydrogen bonded so as to connect sulfate oxygen atoms of different $[Re_2(SO_4)_4(H_2O)_2]^{2-}$ groups. These features are displayed in Figure 1 which presents a stereoview of the unit cell and its contents. The $Re_2(SO_4)_4(H_2O)_2{}^{2-}$ anion is shown in Figure 2. Table IV lists pertinent interatomic distances and angles.

The general structure of the $Re_2(SO_4)_4(H_2O)_2{}^{2-}$ ion is not surprising in view of the previously described[11] structures of the $Mo_2(SO_4)_4{}^{4-}$ and $Mo_2(SO_4)_4(H_2O)_2{}^{3-}$ ions. In all cases the symmetry is essentially that of point group C_{4h}. The deviation from D_{4h} is due to the nonplanarity of the Re–Re–O–S–O rings, with the sulfur atoms deviating from the plane defined by the two metal and two oxygen atoms. As in the case of the molybdenum species, these displacements of the sulfur atoms are all in the same rotational sense with respect to the metal–metal axis, and the fourfold axis of rotation is thus preserved. The C_{4h} symmetry is, however, only approximate and the rigorous, *i.e.*, crystallographically imposed, symmetry is only that due to the presence of an inversion center midway between the rhenium atoms.

The dimensions of the bridging sulfate ions in $Re_2(SO_4)_4(H_2O)_2{}^{2-}$ are also similar to those found in the molybdenum compounds. In each case the S–O bonds that form part of the bridge system are longer than those which do not. In the present case the relevant average S–O distances and the average difference are 1.54 (1), 1.43 (1), and 0.11 (2) Å. In the case of $Mo_2(SO_4)_4{}^{4-}$ the corresponding quantities are 1.51 (1), 1.45 (1), and 0.06 (2) Å, while for $Mo_2(SO_4)_4{}^{3-}$ we found 1.52 (1), 1.44 (1), and 0.08 (2) Å. It appears that the greater the formal charge on the pair of metal atoms, *i.e.*, 6+ for $Re_2(SO_4)_4(H_2O)_2{}^{2-}$, 5+ for $Mo_2(SO_4)_4{}^{3-}$, and 4+ for $Mo_2(SO_4)_4{}^{4-}$, the greater the distortion of the sulfate ions in the sense of having longer S–O bonds inside and shorter ones outside. This is certainly a reasonable observation since the more highly charged metal atoms should form the stronger M–O bonds.

The Re–Re distance here, 2.214 (1) Å, is quite similar to those in other species[19] having quadruple bonds (*i.e.*, Re$\equiv$Re), which have been found to vary from 2.198 (1) to 2.251 (2) Å, with most of them being about 2.23 ± 0.01 Å.

A significant difference between this rhenium species and the two molybdenum ones is in the stronger binding of the coaxial water molecules. Here, the difference between the mean Re–O(S) distance and the Re–O(coax.) distance is only 0.26 Å, whereas in the molybdenum compounds the corresponding differences are 0.45 and 0.48 Å. The ability of the rhenium atoms to bind coaxial ligands more strongly may be at least partly due to the higher formal charge on the metal atoms.

The reactivity of the $Re_2(SO_4)_4{}^{2-}$ ion is greater than that of the $Re_2Cl_8{}^{2-}$ ion. It is therefore more difficult to isolate and handle but it may have the advantage of being a superior starting material in the preparation of other species.

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Registry No. $Na_2Re_2(SO_4)_4\cdot 8H_2O$, 53567-40-1; $[(n\text{-}C_4H_3)_4N]_2Re_2Cl_8$, 14023-10-0.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all the supplementary material for papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th Street, N.W., Washington, D.C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number AIC40616B.

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Platinum Metal Complexes of Amine- and Ether-Substituted Phosphines

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o-Diphenylphosphinoanisole (PO), *o*-diphenylphosphinobenzyl methyl ether (PCO), and *o*-diphenylphosphino-*N*,*N*-dimethylbenzylamine (PCN) have been synthesized. New platinum metal complexes of these ligands and *o*-diphenylphosphino-*N*,*N*-dimethylaniline (PN) have been prepared. Chelate complexes $[Pt(PN)_2](ClO_4)_2$, $PtCl_2(PCN)$, $PdCl_2(PCN)$, $CoCl_2(PCN)$, $RhCl(CO)PCN$, $RuCl_2(PO)_2$, $RuBr_2(PO)_2$, $RuCl_2(PCO)_2$, and $RuCl_2(PN)_2$ have been isolated. ^1H nmr evidence is presented for chelation. The complex $RuCl_2(PO)_2$ will readily undergo carbonylation to give $RuCl_2(CO)(PO)_2$ and $RuCl_2(CO)_2(PO)_2$. The complexes $PtCl_2(PO)_2$, $PtCl_2(PCO)_2$, $PdCl_2(PO)_2$, and $PdCl_2(PCO)_2$ have been prepared, coordination being solely through the phosphines. The position and multiplicity of the metal–chlorine stretching frequencies are used as a guide to stereochemistry. The temperature-dependent ^1H nmr spectrum of $RhCl(CO)PCN$ shows that the two nonequivalent *N*-methyl groups are undergoing fast exchange at room temperature.

Introduction

Recently we have been interested in the synthesis and chemistry of low-valent platinum metal complexes of unsymmetrical chelate ligands.[1,2] The ligands chosen are potentially bidentate, and there is a wide disparity in the coordinating ability of each ligating atom for platinum metals. We have previously shown that a dimethylamino arm of a chelate coordinated to rhodium(I) can readily be displaced by CO, and recent synthetic and kinetic studies by other workers have shown that a similar reaction occurs with other low-valent