

in infrared spectra agree with the existence of two isomers (IVa and IVb, Figure 5). Under these conditions the single methyl nmr signal suggests a dynamical equilibrium between the two isomers; fast rates of interconversion have certainly precluded the observation at -100° of the signals corresponding to each isomer. Assignment of CO frequencies remains however possible. The 1961 (or 1962) cm^{-1} carbonyl frequency is comparable with those observed in *trans*-RhCl(CO)(PR₃)₂³⁵ as in *trans*-RhCl(CO)(α -pic)₂ and is in agreement with structure IVa. In the solid state isomer IVa is only present as shown by CsBr pellets exhibiting a single ν_{CO} at 1950 cm^{-1} and a single $\nu_{\text{Rh-Cl}}$ at 295 cm^{-1} .³⁶ Concerning isomer IVb, as in the case of the RhCl(CO)(C₂H₄)(2,6-lut) compound, we retain the CO and PR₃ groups in mutually *cis* positions. The carbonyl stretching frequency at 1979 (and 1981) cm^{-1} appears, when compared to those of *trans* isomers, surprisingly high. Some such compounds are known: *cis*-RhCl(CO)(PPh₃)₂⁴² (ν_{CO} 1980 cm^{-1} in Nujol), *cis*-(Ph₂PCH₂CH₂PPh₂)Rh(CO)Cl⁴³ (ν_{CO} 2010 cm^{-1} in CH₂Cl₂) (see also ref 44), and *cis*-(1,10-phen)Rh(CO)Cl¹² (ν_{CO} 1989 cm^{-1} in CHCl₃). *Trans* influences⁴⁵ of ligands in isomers IVa and IVb justify the observed order of the CO frequencies, but clearly the high polarizable CO ligand appears to afford a particularly strong response to this influence.

Conclusions

The previously reported synthesis of [RhCl(CO)(PR₃)₂]₂¹

- (42) J. Blum, E. Oppenheimer, and E. D. Bergmann, *J. Amer. Chem. Soc.*, **89**, 2338 (1967).
 (43) W. Hieber and R. Kummer, *Chem. Ber.*, **100**, 148 (1967).
 (44) W. O. Siegl, S. J. Lapporte, and J. P. Collman, *Inorg. Chem.*, **10**, 2158 (1971).
 (45) F. R. Hartley, *Chem. Soc. Rev.*, **2**, 163 (1973).

compounds and the present results permit the same rationalization. Addition of a nucleophilic molecule to [RhCl(CO)(C₂H₄)₂]₂ leads to a dinuclear-pentacoordinated transition state whatever the basicity and hardness of the entering ligand; isolation of the W₂ compounds whose geometry is probably strongly related to the transition state supports this proposition. Isolation of the RhCl(CO)(C₂H₄)(2,6-lut) complex shows that two paths are in competition when [RhCl(CO)L]₂ species are prepared from [RhCl(CO)(C₂H₄)₂]. By loss of ethylene in W₂ the [RhCl(CO)L]₂ compounds (Y₂) are obtained. When comparison was made to the chemistry of amines with platinum(II)-olefin complexes,^{46,47} no addition on the olefin was detected leading to the conclusion that ethylene appears to be the softest of the two electrophilic centers.

Acknowledgments. A. M. thanks the D.G.R.S.T. for a research grant. We are indebted to Professor J. Barrans and Mr. J. Roussel for the use of the HA100 spectrometer.

Registry No. [RhCl(CO)(C₂H₄)(NH(C₂H₅)₂)₂]₂, 52613-54-4; [RhCl(CO)(NH(C₂H₅)₂)₂]₂, 52613-55-5; [RhCl(CO)(NH₂-*n*-C₃H₇)₂]₂, 52613-56-6; [RhCl(CO)(NC₃H₇)₂]₂, 52613-57-7; [RhCl(CO)(3,5-(CH₃)₂NC₅H₃)₂]₂, 52613-58-8; RhCl(CO)(2-(CH₃)NC₅H₄)₂, 52647-44-6; *cis*-RhCl(CO)(C₂H₄)(2,6-(CH₃)₂NC₅H₃)₂, 52613-59-9; *trans*-RhCl(CO)(C₂H₄)(2,6-(CH₃)₂NC₅H₃)₂, 52646-57-8; *cis*-RhCl(CO)(P(CH₃)₃)(2,6-(CH₃)₂NC₅H₃)₂, 52613-60-2; *trans*-RhCl(CO)(P(CH₃)₃)(2,6-(CH₃)₂NC₅H₃)₂, 52646-58-9; *cis*-RhCl(CO)(P(CH₃)₂C₆H₅)(2,6-(CH₃)₂NC₅H₃)₂, 52613-61-3; *trans*-RhCl(CO)(P(CH₃)₂C₆H₅)(2,6-(CH₃)₂NC₅H₃)₂, 52646-59-0; [RhCl(CO)(C₂H₄)₂], 12306-60-4; pyridine, 110-86-1; 2-methylpyridine, 109-06-8; P(CH₃)₃, 594-09-2; [RhCl(CO)P(CH₃)₃]₂, 49634-24-4.

- (46) A. de Renzi, G. Paiaro, A. Panunzi, and V. Romano, *Chim. Ind. (Milan)*, **55**, 248 (1973), and references quoted therein.
 (47) D. Hollings, M. Green, and D. V. Claridge, *J. Organometal. Chem.*, **54**, 399 (1973).

Contribution from the Departments of Chemistry, University of Rochester, Rochester, New York 14627, and Brown University, Providence, Rhode Island 02912

Sulfate Coordination. Molecular Structure of Chlorosulfatonitrosylbis(triphenylphosphine)ruthenium(II), RuCl(SO₄)(NO)(PPh₃)₂

JOSEPH REED,^{1a} STUART L. SOLED,^{1b} and RICHARD EISENBERG^{*1a,c}

Received May 23, 1974

AIC40331Z

The crystal and molecular structure of chlorosulfatonitrosylbis(triphenylphosphine)ruthenium(II), RuCl(SO₄)(NO)(PPh₃)₂, has been determined from three-dimensional X-ray data collected by counter methods using the θ - 2θ scan technique. The complex crystallizes in space group *Pbcn* (*D*_{2h}¹⁴) of the orthorhombic system with four molecules in a unit cell of dimensions $a = 19.65$ (1) Å, $b = 10.79$ (1) Å, $c = 15.73$ (1) Å; $V = 3334$ Å³; $\rho_{\text{exptl}} = 1.55$ (2) g/cm³ and $\rho_{\text{calcd}} = 1.55$ g/cm³ for $Z = 4$. The structure was solved by standard Patterson and Fourier methods and has been refined by least squares to an agreement factor R of 0.054 based on 86 variables and 1192 reflections having $F_o^2 > 2\sigma(F_o^2)$. The coordination geometry in the complex is a distorted octahedron with the sulfate ligand coordinating in a bidentate manner. Because the complex is crystallographically required to have a twofold axis of symmetry, the chloride and nitrosyl ligands are disordered as has been observed in several similar structures. The refinement procedure allows for one-half chloride and one-half nitrosyl at each position. With regard to the sulfate coordination, the average Ru-O bond length is 2.079 (7) Å, and the O-Ru-O bond angle is 68.7 (4)°. Moreover, the ruthenium, sulfur, and coordinating oxygen atoms are coplanar. As expected, the sulfate is a slightly distorted tetrahedron. Other important structural parameters are S-O(coordinating) = 1.552 (8) Å, S-O(noncoordinating) = 1.451 (8) Å, Ru-P = 2.454 (3) Å, Ru-N(nitrosyl) = 1.80 (3) Å, and Ru-N-O = 175 (3)°.

Introduction

The catalyzed oxidation of sulfur dioxide to sulfate using transition metal complexes is an interesting and important chemical reaction whose relevance to industrial oxygenation

processes may help in controlling SO₂ in exhaust gases. To date, studies on this oxidation reaction have focused on group VIII metal complexes, particularly those containing dioxygen as a ligand, and general reactions 1 and 2 have been

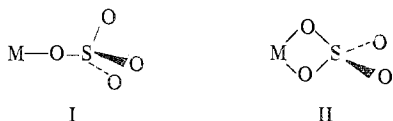
(1) (a) University of Rochester. (b) Brown University.
 (c) Alfred P. Sloan Foundation Fellow, 1972-1974.





investigated.²⁻⁷ It is found that reaction 1 which involves free SO₂ and a metal-dioxygen complex always yields the corresponding sulfate but that the complementary reaction, reaction 2, between free O₂ and a metal-SO₂ complex proceeds in only a limited number of instances.^{4,5}

To date, the principal method used in studying the sulfate complexes and their formation has been infrared spectroscopy. This is based on the fact that the ν_3 and ν_4 normal modes of the sulfate ion are split upon coordination due to a lowering of the symmetry.⁸ When coordinated in a monodentate manner of C_{3v} symmetry, I, the sulfate ion gives rise to two bands apiece for ν_3 and ν_4 . When coordinated as a bidentate ligand of C_{2v} symmetry, II, the sulfate ion shows three bands apiece for ν_3 and ν_4 .



The use of the number of infrared bands to establish the mode of sulfate coordination has been most notably demonstrated by Horn, Weissberger, and Collman,⁴ who also employed doubly labeled ¹⁸O₂ as a means of elucidating the mechanism of reaction 1. These investigators used Ir(O₂)-I(CO)(PPh₃)₂ as the metal-dioxygen complex in that reaction and assigned a bidentate coordination to the product sulfate based on ir data. The analogous ruthenium complex, Ru(SO₄)(CO)₂(PPh₃)₂, was prepared by Laing and Roper following reaction 2 and was independently assigned by them as also having a bidentate sulfate group.³ Finally, the complex Ru(SO₄)Cl(NO)(PPh₃)₂ was prepared by Stiddard and Townsend⁹ and independently by Roper¹⁰ according to reaction 1. The agreement between the sulfate bands in these complexes is excellent.

While the bidentate mode of sulfate coordination in these systems thus seemed probable, it was by no means certain. Horn, *et al.*,⁴ had pointed out that the lowest ν_3 bands in these two sulfate complexes, as well as the ν_1 bands, were significantly lower than the corresponding frequencies in cobalt(III)-bidentate sulfate complexes, and an alternative possible assignment of the observed infrared bands in the complexes IrX(SO₄)(CO)(EPh₃)₂ (X = Cl, Br, I; E = P, As) was even discussed by Levison and Robinson⁶ consistent with the monodentate type of coordination. While this proposal was rejected in favor of the bidentate type of coordination on the basis of molecular weight data, it did underscore the need for a structure determination of a representative member of this class of sulfate complexes.

In this paper we describe the crystal and molecular structure of RuCl(SO₄)(NO)(PPh₃)₂. This complex, which was originally synthesized *via* reaction 1,^{9a} also forms by (a) the

addition of SO₂ to the highly reactive complex RuCl(NO)-(PPh₃)₂^{9a} and (b) the addition of SO₂ to the nitrosyl hydride complex RuH(NO)(PPh₃)₃¹¹ in a halo-hydrocarbon solvent. Our study unequivocally establishes the bidentate nature of the sulfate coordination in RuCl(SO₄)(NO)(PPh₃)₂ and, by extension, in the Ir(III) complexes of the type IrX(SO₄)(CO)(EPh₃)₂.

Experimental Section

General Methods and Materials. Reactions were carried out using a modified Schlenk apparatus. Vacuum and argon sources were provided *via* a double manifold. Solvents were dried and distilled under N₂ (benzene over LiAlH₄ and ethanol over Mg). In most instances, solvents were degassed just prior to use. The ligands employed in the study were triphenylphosphine (Aldrich) and anhydrous 99% SO₂ (Merck). RuCl₃·xH₂O was used as purchased from Matthey Bishop Co.

Preparation of RuCl(SO₄)(NO)(PPh₃)₂. **Method A.** A 0.76-g sample of RuCl₃(NO)(PPh₃)₂¹² was suspended in 50 ml of benzene containing 3 g of a Zn-Cu couple. The mixture was refluxed for 1 hr during which time the dark green color characteristic of RuCl(NO)(PPh₃)₂ developed.⁹ After removal of the Zn-Cu couple and other insolubles by filtration, SO₂ was bubbled through the solution which rapidly became red-orange. A 50-ml amount of *n*-hexane was then added, the solution was cooled in an ice bath, and a fine yellow solid was removed by filtration. From the orange filtrate, crystals of RuCl(SO₄)(NO)(PPh₃)₂ were grown by the evaporation of solvent. The sulfate complex may be recrystallized from a 1:1 solution of methylene chloride and *n*-hexane. As yet, the fine yellow precipitate is unidentified although its infrared spectrum is similar to that of the sulfate complex.

Anal. Calcd for C₃₆H₃₀ClNO₃P₂RuS: C, 55.03; H, 3.82; N, 1.78; P, 7.77. Found: C, 55.99; H, 4.05; N, 2.14; P, 8.11.

Characteristic infrared absorptions for RuCl(SO₄)(NO)(PPh₃)₂ are observed at 1850 (ν_{NO}), 1300, 1170, 885, and 860 cm⁻¹. The last four bands are assigned to sulfate vibrations.

Method B. A 0.60-g sample of RuH(NO)(PPh₃)₃¹¹ was dissolved in 150 ml of degassed methylene chloride. SO₂ was then bubbled through the solution for 30 min, followed by the addition of 60 ml of methanol. The red-orange solution was filtered and crystals of the sulfate complex were grown by the slow evaporation of the solution in air. The infrared spectrum of the product is identical with that found using method A. The yield is 70%.

Collection and Reduction of the X-Ray Data. The orange crystals used for the structure determination were made by the preparation under Method B. Weissenberg and precession photographs showed the complex to crystallize in the orthorhombic system in a cell of dimensions $a = 19.65$ (1) Å, $b = 10.79$ (1) Å, $c = 15.73$ (1) Å, and $V = 3334$ Å³. The unit cell constants were determined at ambient room temperature from a least-squares refinement of the angular settings of 20 strong reflections centered on a Picker four-circle diffractometer using Mo K α radiation (λ 0.7107 Å). The observed density of 1.55 (2) g/cm³ obtained by the flotation method agrees with a calculated value of 1.55 g/cm³ for 4 formula weights of RuCl(SO₄)(NO)(PPh₃)₂ per unit cell. Systematic absences of $0k1$ reflections for k odd, of $h0l$ reflections for l odd, and of hkl reflections for $h + k$ odd uniquely determine the space group to be $Pbcn$ (No. 60, D_{2h}^{14}).¹³ The complex is therefore required to have minimum crystallographic symmetry of either a twofold rotation axis or an inversion center. In view of the composition of the complex, the former was clearly the required symmetry element.

A crystal of dimensions 0.06 × 0.05 × 0.11 mm was mounted along the b^* axis and used for the intensity data collection. The mosaic spread of the crystal was surveyed using the narrow-source, open-counter ω -scan technique.¹⁴ The width at half-height for typical strong reflections was satisfactorily narrow and in the range of 0.07–0.09°. An independent set of intensity data was collected by the θ - 2θ scan technique using Zr-filtered Mo K α radiation at a takeoff angle of 2.5°. The receiving aperture was positioned 21 cm from the crystal. An unsymmetrical scan range in 2θ was used from

(2) C. D. Cook and G. S. Jahaul, *J. Amer. Chem. Soc.*, **89**, 3066 (1967).

(3) K. R. Laing and W. R. Roper, *J. Chem. Soc. A*, 1889 (1969).

(4) R. W. Horn, E. Weissberger, and J. P. Collman, *Inorg. Chem.*, **9**, 2367 (1970).

(5) J. Valentine, D. Valentine, Jr., and J. P. Collman, *Inorg. Chem.*, **10**, 219 (1971).

(6) J. J. Levison and S. D. Robinson, *J. Chem. Soc. A*, 762 (1971).

(7) M. H. B. Stiddard and R. E. Townsend, *J. Chem. Soc. A*, 2719 (1970).

(8) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley, New York, N. Y., 1963, p 161.

(9) (a) M. H. B. Stiddard and R. E. Townsend, *Chem. Commun.*, 1372 (1969); (b) J. Reed, C. G. Pierpont and R. Eisenberg, *Inorg. Syn.*, **16**, in press.

(10) W. R. Roper, private communication as quoted in ref 4.

(11) S. T. Wilson and J. A. Osborn, *J. Amer. Chem. Soc.*, **93**, 3068 (1971).

(12) M. B. Fairy and R. J. Irving, *J. Chem. Soc. A*, 475 (1966); J. Chatt and B. L. Shaw, *ibid.*, 1811 (1966).

(13) "International Tables for X-Ray Crystallography," Vol. I, Kynoch Press, Birmingham, England, 1952, p 149.

(14) T. C. Furnas, "Single Crystal Orienter Manual," General Electric Co., Milwaukee, Wis., 1957, Chapter 10.

Table I. Final Positional, Thermal, and Group Parameters for RuCl(SO₄)(NO)(PPh₃)₂

Atomic Positional and Isotropic Thermal Parameters						
Atom	x	y	z	B, Å ²		
Ru	0.0000	0.1654 (1) ^a	0.2500	b		
Cl ^c	-0.0520 (6)	0.0380 (12)	0.3466 (8)	4.6 (3)		
S	0.0000	0.4185 (4)	0.2500	b		
P	0.1058 (2)	0.1643 (3)	0.3328 (2)	b		
O(1) ^c	-0.0527 (14)	-0.0196 (25)	0.3634 (17)	8.2 (9)		
O(2)	-0.0309 (4)	0.3244 (7)	0.3138 (5)	b		
O(3)	0.0545 (4)	0.4893 (8)	0.2890 (5)	b		
N ^c	-0.0356	0.0514 (27)	0.3211 (17)	3.9 (9)		
Anisotropic Thermal Parameters ^d						
Atom	β ₁₁	β ₂₂	β ₃₃	β ₁₂	β ₁₃	β ₂₃
Ru	0.00169 (4)	0.0034 (1)	0.00359 (7)	0.0000	0.00027 (7)	0.0000
S	0.0019 (1)	0.0050 (4)	0.0046 (3)	0.0000	-0.0005 (3)	0.0000
P	0.0019 (1)	0.0038 (3)	0.0034 (2)	0.0004 (2)	0.0002 (1)	0.0004 (2)
O(2)	0.0023 (3)	0.0047 (8)	0.0040 (4)	0.0003 (4)	0.0008 (3)	-0.0011 (5)
O(3)	0.0021 (3)	0.0072 (9)	0.0057 (5)	-0.0013 (5)	-0.0013 (3)	-0.0006 (6)
Group Parameters ^e						
Group	x _c	y _c	z _c	φ	θ	ρ
R1	0.1033 (3)	0.3678 (5)	0.4816 (3)	1.958 (5)	-2.833 (5)	-2.282 (5)
R2	0.1338 (2)	-0.0939 (5)	0.4318 (3)	2.491 (8)	2.263 (5)	-0.848 (8)
R3	0.2412 (2)	0.2149 (5)	0.2239 (3)	-2.656 (5)	-2.750 (5)	0.608 (5)

^a Numbers in parentheses here and in succeeding tables are estimated standard deviations in the least significant figures. ^b Atoms refined anisotropically. ^c Because of disorder, atoms were refined isotropically with multipliers of 0.5. ^d The form of the anisotropic thermal ellipsoid is $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. ^e $x_c, y_c,$ and z_c are the fractional coordinates of the rigid-group centers. The angles $\phi, \theta,$ and ρ have been previously defined: S. J. La Placa and J. A. Ibers, *Acta Crystallogr.*, **18**, 511 (1965).

-0.60 to +0.75° of the Mo K α peak with allowances made for the K α_1 -K α_2 separation. The data set was collected within the angular range $5^\circ < 2\theta < 50^\circ$. Attenuators were inserted automatically if the count rate of the diffracted beam exceeded about 9000 counts/sec during the scan. The attenuators used were of brass foil having thickness sufficient to give an approximate attenuation factor of 3.0.

During data collection the intensities of three reflections in different regions of reciprocal space were monitored after every 100 reflections measured. No decrease in the intensities of these standard reflections was noted.

The data were then processed in the usual way for Lorentz and polarization effects and reduced to a set of structure factor amplitudes F_o . The value of the linear absorption coefficient is only 7.3 cm⁻¹ and no absorption correction was made. The intensities of a total of 3121 reflections were measured, of which 1192 were observed to have $F_o^2 > 2\sigma(F_o^2)$ with the estimated standard deviations σ being calculated according to the equation given in the next section.

Solution and Refinement of the Structure. A three-dimensional Patterson synthesis using 403 independent reflections of a partial data set gave the Ru, P, and S atom positions.¹⁵ One cycle of least-squares refinement of the Ru, P, and S positional and isotropic thermal parameters reduced the discrepancy indices $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ and $R_1 = (\Sigma w(|F_o| - |F_c|)^2 / \Sigma wF_o^2)^{1/2}$ to 33.6 and 45.6%, respectively. From a succession of difference Fourier maps and least-squares refinements, the positions of all nonhydrogen atoms in the structure were determined.

The trial structure was refined with the complete data set by a least-squares procedure in which the function minimized was $\Sigma w \cdot (|F_o| - |F_c|)^2$ and the weights w were taken as $4F_o^2 / \sigma^2(F_o^2)$. The standard deviations $\sigma(F_o^2)$ were estimated from counting statistics according to the formula

$$\sigma(F_o^2) = (1/Lp)[C + 0.825 + 0.25(t_c/t_b)^2(B_1 + B_2 + 1.65) + q^2(C^2 + (B_1 + B_2)^2)]^{1/2}$$

where Lp is the Lorentz-polarization factor, C is the estimated total count obtained in time t_c , B_1 and B_2 are the estimated background counts each obtained in time t_b , and q is the uncertainty parameter¹⁶

(15) The programs used in this study were PICKLST refinement and setting program and local versions of the Busing-Levy ORFLS least-squares program, the Ibers-Doedens group refinement least-squares program, the Zalkin FORDAP Fourier program, the Busing-Martin-Levy ORFFE function and error program, and C. K. Johnson's ORTEP plotting program. All computing was performed on the Brown University IBM 360/67 computer.

(16) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

with a value of 0.03 for this structure. Because the Picker instrument truncates the least significant figure from the scaler without proper round-off, the estimated total count C is the recorded total count $C' + 0.45$, and the estimated background count B_i is the recorded background count $B_i' + 0.45$ where $i = 1$ or 2 . The constants 0.825 and 1.65 appear in the equation for $\sigma(F_o^2)$ as estimates of the errors associated with the 0.45 term which is added to each raw count in calculating F_o^2 as a means of eliminating the systematic error resulting from the truncation. It should be noted that the 0.45 term is not a constant but only a best estimate of the truncated number.

In all calculations, the atomic scattering factors for the nonhydrogen atoms were taken from Cromer and Waber¹⁷ while the hydrogen scattering factor was taken from Stewart, *et al.*¹⁸ The effects of anomalous dispersion were included in the calculated structure factors with the appropriate values of $\Delta f'$ and $\Delta f''$ for the Ru, S, and P atoms taken from the report of Cromer.¹⁹ Throughout all refinements, the phenyl rings were treated as rigid groups of D_{6h} symmetry ($d(C-C) = 1.392$ Å) in the manner described previously.²⁰ The solution of the structure established that the complex did indeed have C_2 crystallographic symmetry which meant a disorder of the chlorine and nitrosyl positions. This was treated by assigning multipliers of 0.5 to the independent nitrosyl and chlorine atom positions and by refining these atoms independently assuming isotropic thermal motion. The Cl, N, and O positions were readily established from difference Fourier maps.

Refinement of the complete structure was carried out using the 1192 reflections with $F_o^2 > 2\sigma(F_o^2)$. Anisotropic thermal motion was assumed for the Ru, P, and sulfate group atoms while individual isotropic thermal parameters were assigned to the phenyl ring carbon atoms. Inclusion of fixed contributions for the phenyl ring hydrogen atoms in the final cycles of least-squares refinement led to convergence with discrepancy indices R and R_1 of 0.054 and 0.060, respectively, for 86 variables and 1192 observations. The estimated standard deviation of an observation of unit weight was 1.30. A final difference synthesis showed no peaks with density greater than 0.8 e/Å³.

The parameters obtained from this last refinement are taken as the final parameters for the structure and are presented in Table I along with their estimated standard deviations as obtained from the

(17) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).

(18) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(19) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).

(20) S. J. La Placa and J. A. Ibers, *Acta Crystallogr.*, **18**, 511 (1965); R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **4**, 773 (1965).

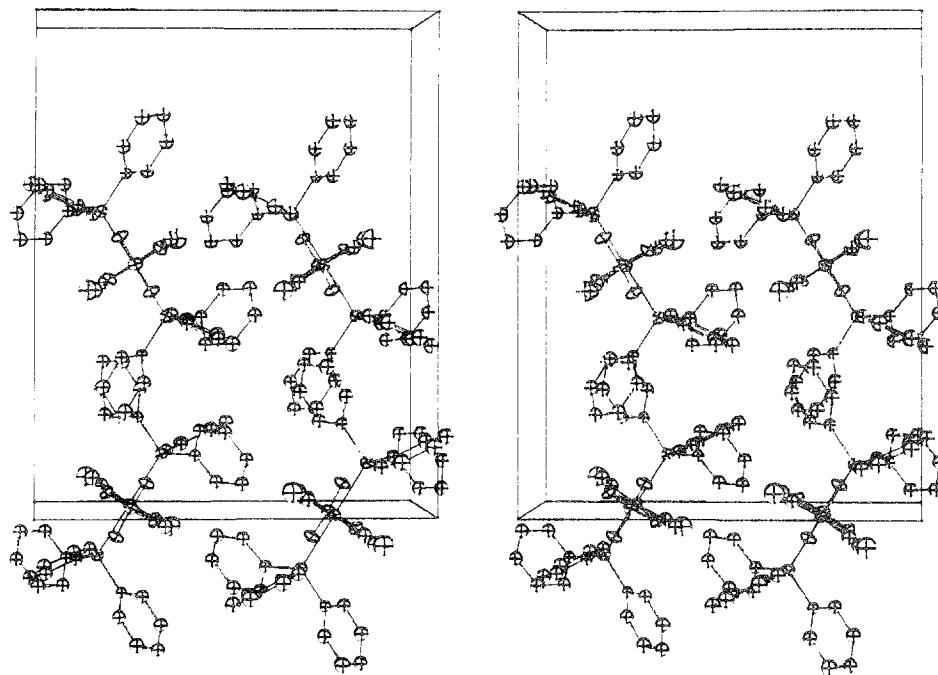


Figure 1. Stereoscopic view of the packing of the $\text{RuCl}(\text{SO}_4)(\text{NO})(\text{PPh}_3)_2$ molecules. The view is down b with a vertical in the field of view.

Table II. Derived Positional and Isotropic Thermal Parameters for Group Carbon Atoms of $\text{RuCl}(\text{SO}_4)(\text{NO})(\text{PPh}_3)_2$

Group atom	x	y	z	$B, \text{\AA}^3$
R1C(1)	0.1056 (5)	0.2786 (6)	0.4177 (4)	2.8 (3)
R1C(2)	0.1585 (3)	0.3634 (7)	0.4264 (5)	3.4 (3)
R1C(3)	0.1561 (4)	0.4526 (7)	0.4903 (6)	3.9 (3)
R1C(4)	0.1008 (5)	0.4569 (6)	0.5455 (4)	3.7 (3)
R1C(5)	0.0479 (4)	0.3721 (7)	0.5368 (5)	3.8 (3)
R1C(6)	0.0504 (4)	0.2829 (7)	0.4729 (5)	3.6 (3)
R2C(1)	0.1213 (7)	0.0169 (6)	0.3894 (5)	2.9 (3)
R2C(2)	0.1513 (6)	0.0183 (6)	0.4696 (5)	3.9 (3)
R2C(3)	0.1638 (4)	-0.0926 (8)	0.5120 (4)	4.5 (3)
R2C(4)	0.1464 (8)	-0.2048 (6)	0.4742 (6)	5.0 (4)
R2C(5)	0.1164 (6)	-0.2061 (6)	0.3941 (6)	4.9 (4)
R2C(6)	0.1039 (4)	-0.0953 (9)	0.3517 (4)	3.9 (3)
R3C(1)	0.1826 (3)	0.1903 (8)	0.2707 (4)	2.5 (3)
R3C(2)	0.1855 (4)	0.2939 (7)	0.2181 (5)	3.4 (3)
R3C(3)	0.2441 (4)	0.3184 (6)	0.1713 (5)	4.0 (3)
R3C(4)	0.2999 (3)	0.2395 (9)	0.1772 (5)	3.6 (3)
R3C(5)	0.2971 (4)	0.1359 (7)	0.2298 (6)	4.7 (3)
R3C(6)	0.2384 (4)	0.1113 (6)	0.2766 (5)	3.9 (3)

Table III. Root-Mean-Square Amplitudes of Vibration (\AA) of Anisotropically Refined Atoms

Atom	Min	Intermed	Max
Ru	0.142 (2)	0.178 (3)	0.215 (2)
S	0.173 (7)	0.187 (9)	0.245 (8)
P	0.144 (7)	0.191 (6)	0.211 (6)
O(2)	0.145 (17)	0.200 (14)	0.248 (11)
O(3)	0.146 (18)	0.228 (14)	0.287 (12)

inverse matrix. The derived positional and isotropic thermal parameters for the group carbon atoms are tabulated in Table II. In Table III the root-mean-square amplitudes of thermal motion for the anisotropically refined atoms are presented. A tabulation of the final values of F_o and $|F_c|$ (in electrons $\times 10$) for the 1192 reflections included in the refinement is available.²¹

Description of the Structure

The crystal structure described by the unit cell constants, the symmetry of the space group, and the parameters of Table I consists of the packing of discrete molecules of the sulfate complex $\text{RuCl}(\text{SO}_4)(\text{NO})(\text{PPh}_3)_2$. A stereoscopic

view of the packing in the crystal is presented in Figure 1. All intermolecular contacts appear normal.

The coordination geometry in the complex is best described as a distorted octahedron with trans phosphine ligands as shown in Figure 2. Principal intramolecular distances and angles are tabulated in Table IV. The most important aspect of the structure is the mode of coordination of the sulfate group which we confirm to be bidentate. The Ru-O distance is 2.079 (7) \AA and the O-Ru-O bond angle 68.7 (4) $^\circ$. These parameters imply that the sulfate ligand is not as strongly chelated as other bidentate ligands because of the strain involved in the four-membered RuOSO ring and the preference of Ru(II) for phosphine and nitrogen-donor ligands.

The sulfate is a distorted tetrahedron with independent O-S-O bond angles of 98.3 (6), 109.3 (4), 111.1 (4), and 116.4 (7) $^\circ$. As one might anticipate, the S-O bond length of the terminal oxygen atom is significantly shorter than the corresponding bond length involving the coordinating oxygen atom (1.451 (8) vs. 1.552 (8) \AA). The angular distortions in the tetrahedron can then be easily rationalized in terms of a Gillespie-Nyholm model²² in which it is assumed that the S-O terminal bonds have greater bond order than those in the chelate ring and hence achieve a maximum angular separation. Additionally, the S-O bonds of the chelate ring show the smallest angular separation as a consequence of both chelation and minimized repulsions between the bonding electrons in the coordinating oxygen-sulfur bonds. For comparison bond distances in ionic sulfates are in the range 1.45-1.51 \AA with a best averaged value of 1.475 (10) \AA .²³

The Ru-P distance of 2.454 (3) \AA is in the upper range of six-coordinate ruthenium(II)-phosphine distances reported for which the trans ligand is also a phosphine. These values include 2.429 (4) and 2.438 (4) \AA in $\text{RuCl}_3(p\text{-N}_2\text{C}_6\text{H}_4\text{Me})(\text{PPh}_3)_2$,²⁴ 2.435 (6) \AA in $\text{RuCl}_3(\text{NO})(\text{PMePh}_2)_2$,²⁵ and 2.363

(22) R. J. Gillespie, *J. Chem. Educ.*, **47**, 18 (1970).

(23) G. D. Andretti, L. Cavalca, and A. Musatti, *Acta Crystallogr., Sect. B*, **24**, 683 (1968), and references cited therein.

(24) J. V. McArdle, A. J. Schultz, B. J. Corden, and R. Eisenberg, *Inorg. Chem.*, **12**, 1676 (1973).

(21) See paragraph at end of paper regarding supplementary material.

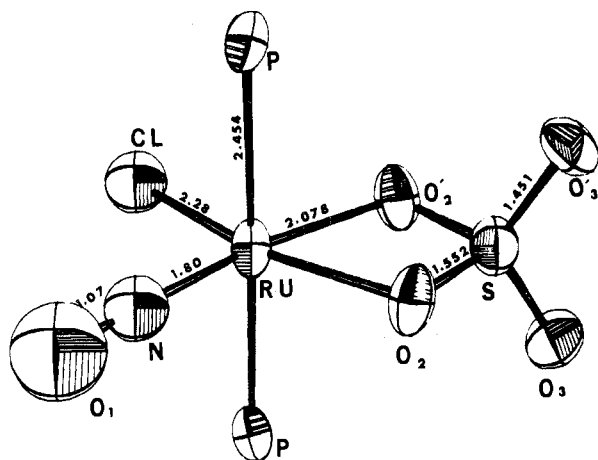


Figure 2. Perspective drawing of the inner coordination geometry of RuCl(SO₄)(NO)(PPh₃)₂ in which the phosphorus substituents have been omitted for clarity. The twofold axis of symmetry passes through Ru and S.

Table IV. Important Intramolecular Distances (Å) and Angles (deg) for RuCl(SO₄)(NO)(PPh₃)₂

Distances			
Ru-P	2.454 (3)	S-O(3)	1.451 (8)
Ru···S	2.731 (5)	N-O(1)	1.07 (4)
Ru-N	1.80 (3)	O(2)···O(2)'	2.35 (1)
Ru-Cl	2.289 (15)	O(2)···O(3)	2.48 (1)
Ru-O(2)	2.079 (7)	O(3)···O(3)'	2.47 (2)
S-O(2)	1.552 (8)		
Angles			
N-Ru-O(2)	98.7 (9)	O(2)-Ru-P	90.7 (2)
N-Ru-Cl	100.0 (8)	O(2)'-Ru-P	89.7 (2)
Cl-Ru-O(2)	92.6 (4)	O(3)-S-O(3)'	116.4 (7)
O(2)-Ru-O(2)'	68.7 (4)	O(3)-S-O(2)	111.0 (4)
Ru-N-O(1)	175 (3)	O(3)-S-O(2)'	109.3 (4)
Cl-Ru-P	88.3 (3)	O(2)'-S-O(2)	98.3 (6)
N-Ru-P	89.8 (3)		
Dihedral Angle between Planes, deg			
(O(2)-S-O(2)')-(O(3)-S-O(3)')		88.6 (5)	

(5) and 2.351 (5) Å in RuH(CH₃COO)(PPh₃)₃.²⁶ The P-Ru-P bond angle of 179.4 (3)° does not differ from the ideal trans value of 180° in the present structure.

As expected, the nitrosyl coordinates in an essentially linear manner with a Ru-N distance of 1.80 (3) Å and a Ru-N-O bond angle of 175 (3)°. Errors in these values are understandably large because of the disorder between the nitrosyl and chlorine atom positions. The Ru-Cl distance of 2.29 (2) Å is significantly shorter than the 2.35–2.39 Å range

(25) A. J. Schultz, R. L. Henry, J. Reed, and R. Eisenberg, *Inorg. Chem.*, 13, 732 (1974).

(26) A. C. Skapski and F. A. Stephens, *J. Chem. Soc., Dalton Trans.*, 390 (1974).

found for corresponding distances in the Ru(II) octahedral structures cited above,^{24–26} and the explanation for this shortening lies in the reduction of interligand repulsions in the equatorial plane of the complex (assuming the phosphine ligands to be axial) owing to the small bite of the bidentate sulfate group.

Discussion

The chelated sulfate complex whose structure is reported here is the first of the group VIII complexes of this type to be studied by X-ray diffraction. The results have confirmed the bidentate mode of sulfate coordination proposed by other investigators based on infrared results. It is noteworthy that RuCl(SO₄)(NO)(PPh₃)₂ is one of the few sulfate systems accessible by either reaction 1 or 2. In each case the parent Ru(O)-NO⁺ complex RuCl(NO)(PPh₃)₂ serves to activate sufficiently the first addendum to make it susceptible to subsequent chemical attack.

We have described in the Experimental Section two methods for the preparation of the title complex. The latter of these leads to higher purity product in better yield and starts with the nitrosyl hydride complex RuH(NO)(PPh₃)₃ in the reaction sequence. We surmise that the hydride ligand is exchanged with a chlorine of the CH₂Cl₂ solvent in the course of the reaction. Precedents for exchange reactions between metal hydrides and halogenated solvents exist.

An interesting parallel to this last reaction has been reported by Levison and Robinson,²⁷ who examined the reaction of MH(CO)(PPh₃)₃ (M = Rh, Ir) with SO₂. Some anomalies in the spectral characterization of these adducts were noted, especially with the Rh system. The lack of any evidence for a hydride bonded to rhodium in CHCl₃ solutions of this system may in fact indicate the formation of a chlorosulfate complex as we have found in the present study.

Acknowledgments. We wish to thank the National Science Foundation (Grants GP-35667X and GP-40088X) for support of this research.

Registry No. RuCl(SO₄)(NO)(PPh₃)₂, 52760-71-1.

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 the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals 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 INORG-74-3001.

(27) J. J. Levison and S. D. Robinson, *J. Chem. Soc., Dalton Trans.*, 2013 (1972).