(2) J. A. Bertrand and C. E. Kirkwood, *Inorg. Chim. Acta*, **6**, 248 (1972).
(3) E. D. Estes, W. E. Estes, R. P. Scaringe, W. E. Hatfield, and D. J. Hodgson, *Inorg. Chem.*, **14**, 2564 (1975).
(4) R. M. Countryman, W. T. Robinson, and E. Sinn, *Inorg. Chem.*, **13**, 2013 (1974).
(5) R. D. Willett and C. Chow, *Acta Crystallogr., Sect. B*, **30**, 207 (1974).
(6) M. Textor, E. Dubler, and H. R. Oswald, *Inorg. Chem.*, **13**, 1361 (1974).
(7) D. J. Hodgson, P. K. Hale, and W. E. Hatfield, *Inorg. Chem.*, **10**, 1061 (1971).
(8) M. Sundaralingam and J. A. Carrabine, *J. Mol. Biol.*, **60**, 287 (1971); J. P. DeClerq, M. Debbaudt, and M. van Meersche, *Bull. Soc. Chim. Belg.*, **80**, 527 (1971).
(9) R. B. Wilson, W. E. Hatfield, and D. J. Hodgson, *Inorg. Chem.*, **15**, 1712 (1976).
(10) E. Sletten and A. Apeland, *Acta Crystallogr., Sect. B*, **31**, 2019 (1975).
(11) D. H. Svedung, *Acta Chem. Scand.*, **23**, 2865 (1969).
(12) V. F. Duckworth and N. C. Stephenson, *Acta Crystallogr., Sect. B*, **25**, 1795 (1969).
(13) E. D. Estes, W. E. Estes, W. E. Hatfield, and D. J. Hodgson, *Inorg. Chem.* **14**, 106 (1975).
(14) P. Singh, D. Y. Jeter, W. E. Hatfield, and D. J. Hodgson, *Inorg. Chem.*, **11**, 1657 (1972).
(15) E. Luukkonen and A. Pajunen, *Suom. Kemistil. B*, **46**, 292 (1973).
(16) A. R. Hendrickson, R. L. Martin, and D. Taylor, *J. Chem. Soc., Chem. Commun.*, 843 (1975).
(17) R. A. Bream, E. D. Estes, and D. J. Hodgson, *Inorg. Chem.*, **14**, 1672 (1975).
(18) V. C. Copeland, P. Singh, W. E. Hatfield, and D. J. Hodgson, *Inorg. Chem.*, **11**, 1826 (1972).
(19) V. C. Copeland, W. E. Hatfield, and D. J. Hodgson, *Inorg. Chem.*, **12**, 1340 (1973).
(20) J. D. Dunitz, *Acta Crystallogr.*, **10**, 307 (1957).
(21) V. Kupcik and S. Durovic, *Czech. J. Phys.*, **10**, 182 (1960).
(22) B. Morosin, *Acta Crystallogr., Sect. B*, **31**, 632 (1975).
(23) R. D. Willett and K. Chang, *Inorg. Chim. Acta*, **4**, 447 (1970).
(24) M. Laing and E. Horsfield, *Chem. Commun.*, 735 (1968).
(25) M. Laing and G. Carr, *J. Chem. Soc. A*, 1141 (1971).
(26) E. D. Estes and D. J. Hodgson, *J. Chem. Soc., Dalton Trans.*, 1168 (1975).
(27) R. Näsänen, E. Luukkonen, H. Palonen, and M. Sivonen, *Suom. Kemistil. B*, **44**, 93 (1971).
(28) W. R. Busing and H. A. Levy, *Acta Crystallogr.*, **22**, 457 (1967).
(29) D. J. Hodgson and J. A. Ibers, *Inorg. Chem.*, **8**, 326 (1969).
(30) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).
(31) W. R. Busing and H. A. Levy, *J. Chem. Phys.*, **26**, 563 (1957).
(32) For a description of the programs used, see D. L. Lewis and D. J. Hodgson, *Inorg. Chem.*, **13**, 143 (1974).
(33) "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England: (a) Table 2.2A; (b) Table 2.1C.
(34) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
(35) J. A. Ibers and W. C. Hamilton, *Acta Crystallogr.*, **17**, 781 (1964).
(36) W. H. Zachariasen, *Acta Crystallogr.*, **16**, 1139 (1963); *Acta Crystallogr., Sect A*, **24**, 212 (1968); D. J. Hodgson and J. A. Ibers, *Acta Crystallogr., Sect. B*, **25**, 469 (1969).
(37) Supplementary data.
(38) W. E. Estes and W. E. Hatfield, private communication.
(39) D. J. Hodgson, *Prog. Inorg. Chem.*, in press, and references therein.
(40) D. S. Brown, F. W. B. Einstein, and D. G. Tuck, *Inorg. Chem.*, **8**, 14 (1969).
(41) D. J. Hodgson and J. A. Ibers, *Inorg. Chem.*, **8**, 1282 (1969).
(42) T. P. Mitchell, W. H. Bernard, and J. R. Wasson, *Acta Crystallogr., Sect. B*, **26**, 2096 (1970).
(43) L. Pauling, "The Nature of the Chemical Bond", 3d ed, Cornell University Press, Ithaca, N.Y. 1960, p 225.
(44) N. T. Watkins, E. E. Dixon, V. H. Crawford, K. T. McGregor, and W. E. Hatfield, *J. Chem. Soc., Chem. Commun.*, 133 (1973).
(45) H. H. Jaffe, *Chem. Rev.*, **53**, 191 (1953).

Contribution from the Department of Chemistry,
The University of Canterbury, Christchurch, New Zealand

Crystal and Molecular Structure of Di-μ-bromo-bis[dibromo(diethyl sulfoxide)nitrosylruthenium(II)]

J. E. FERGUSSON,* C. T. PAGE, and WARD T. ROBINSON

Received February 6, 1976 AIC601028

The crystal and molecular structures of di-μ-bromo-bis[dibromo(diethyl sulfoxide)nitrosylruthenium(II)], $[RuBr_3(NO)(Et_2SO)]_2$, have been determined from three-dimensional x-ray data obtained by counter methods. The compound crystallizes in the centrosymmetric space group $P\bar{1}$ of the triclinic system, with 1 formula unit in a unit cell of dimensions $a = 8.042$ (1) Å, $b = 11.020$ (2) Å, $c = 7.324$ (1) Å, $\alpha = 104.83$ (1)°, $\beta = 102.31$ (1)°, and $\gamma = 88.54$ (1)°. Full-matrix least-squares refinement of the structure has led to a final R value of 0.047 for the 1337 independent reflections having $F_o^2 > 3\sigma(F_o^2)$. The dimeric molecules consist of octahedrally coordinated ruthenium atoms sharing one edge through the two bridging bromine atoms, two coordinated to each ruthenium atom. Above and below this plane are nitrosyl and diethyl sulfoxide groups trans to each other on each ruthenium atom with a crystallographic center of symmetry imposed on the whole molecule. The nitrosyl ligand is linearly coordinated as expected for NO^+ complexes of Ru(II). This sulfoxide complex was formed from the $RuBr_3(NO)(Et_2S)_2$ complex dissolved in chloroform and exposed to sunlight. The oxidation was achieved by dioxygen dissolved in the chloroform assisted by the presence of ethanol. The diethyl sulfoxide ligand is coordinated to the Ru(II) atom through the oxygen atom.

Introduction

During the study of a series of complexes $RuX_3(NO)L_2$ (X = Cl, Br, I; L = Me_2S, PhMeS, Et_2S, PhEtS, Et_2Se, PhEtSe, $(n\text{-}Pr)_2S$, Ph-n-PrS)[1] it was observed that a chloroform solution of $RuBr_3(NO)(Et_2S)_2$ changed color from light yellow to dark red in sunlight. After a period of a few weeks a small quantity of dark red-brown crystals was separated from the solution. The infrared spectrum of these crystals contained a strong absorption at 920 cm^{-1} absent in the parent compound. This suggested the existence of a sulfoxide group bonded to the metal atom through its oxygen atom. The product of this ready conversion seemed best characterized by a crystal structure analysis. This analysis has confirmed the existence of sulfoxide ligands coordinated to ruthenium atoms. The source of the oxygen has also been investigated.

Experimental Section

Preparations. Nitric oxide was bubbled through an ethanol solution of $RuBr_3 \cdot 3H_2O$ for several hours, and then diethyl sulfide was added in slight excess. The solution was heated under reflux for 1 h. Crystals of $RuBr_3(NO)(Et_2S)_2$ formed as ethanol was removed in vacuo. A chloroform solution of $RuBr_3(NO)(Et_2S)_2$ was allowed to evaporate slowly over a period of a few weeks, while exposing the solution to sunlight. The mother liquor was poured off and the crystals obtained in low yield were dried in vacuo. Dark red-brown crystals, of empirical formula $RuBr_3(NO)(Et_2SO)$, formed.

Study of the Reaction. Exposure of chloroform solutions of $RuBr_3(NO)(Et_2S)_2$ to sunlight which first passed through color filters (Ilford) indicated that radiation within the wavelength range 380–480 nm was necessary.

The color change which was observed also corresponded to changes in the ^1H NMR and electronic spectra of the solution. The form of the ^1H NMR spectrum suggested that at least two other products were formed during the course of the reaction. Whether one of these corresponds to the dimeric crystalline compound is not known as the low solubility of the material prevents the running of its ^1H NMR spectrum. One product may correspond to a diethyl sulfone (Et_2SO_2) complex, but work on this is currently in progress. There is no evidence to suggest that free diethyl sulfide is present in the solution.

The compound $RuBr_3(NO)(Et_2S)_2$ was dissolved in chloroform under the following conditions: (a) chloroform free of ethanol (still containing dissolved oxygen); (b) chloroform free of dissolved oxygen (still containing ethanol); (c) chloroform free of ethanol and dissolved oxygen; (d) reagent grade chloroform.

When the solutions were exposed to sunlight, the color change occurred within 2 min in (d), occurred only faintly in (a), and occurred not at all in (b) and (c). However, addition of ethanol to (a) and oxygen to (b) brought about a color change within a few minutes. No color change was observed in (c) until both oxygen and ethanol had been added. This indicates that both dissolved oxygen and ethanol are necessary before the oxidation of the sulfide will occur. The color change was also observed when acetic acid was added instead of ethanol to (a); also, in the case of acetaldehyde addition the change was observed but was slower.

Collection and Reduction of the X-Ray Data. On the basis of precession photography using Cu Kα x radiation it was established that the crystals belong to the triclinic system. The success of this analysis has confirmed that the correct space group is $P\bar{1}$.

Unit cell dimensions of $a = 8.042$ (1) Å, $b = 11.020$ (2) Å, $c = 7.324$ (1) Å, $\alpha = 104.83$ (1)°, $\beta = 102.31$ (1)°, and $\gamma = 88.54$ (1)° [30] were obtained from a least-squares refinement of the setting angles of 12 reflections accurately centered in a 5-mm diameter, circular receiving aperture set 23 cm from the crystal mounted on a Hilger and Watts four-circle, computer-controlled diffractometer [λ(Mo K$\bar{\alpha}$) 0.7107 Å; 23 °C]. All numbers in this paper refer to this unit cell which can be related to the reduced cell of dimensions $a = 8.04$ Å, $b = 11.02$ Å, $c = 11.57$ Å, $\alpha = 142.26°$, $\beta = 96.36°$, and $\gamma = 91.46°$, by the matrix

$$\begin{matrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 1 & 1 \end{matrix}$$

An experimental density of 2.56 (±0.03) g cm^{-3} obtained by the flotation method, using aqueous zinc bromide solution, is in good agreement with the calculated density of 2.59 g cm^{-3} for 2 empirical formula units in the unit cell. Thus the one dimeric molecule found has a crystallographic center of symmetry imposed on it in space group $P\bar{1}$.

The crystal used for data collection was of dimensions 0.13 × 0.33 × 0.09 mm. Its suitability for intensity measurement was examined by means of open-counter ω scans at a takeoff angle of 3°. Under these conditions typical scan widths, at half-height, for intense low-angle reflections were 0.12° and peak profiles were symmetric. Zirconium-filtered Mo Kα radiation and the θ–2θ scan technique were used to collect the intensities of all of the independent reflections in the positive h hemisphere of reciprocal space for which $0 < 2\theta \leq 50°$. The scintillation counter had a circular receiving aperture 5 mm in diameter. A symmetric scan range of 1.20° in 2θ, centered on the calculated peak position [λ(Mo Kα) 0.7107 Å], was composed of 60 steps each of 1-s duration. Stationary-crystal, stationary-counter background counts of 15 s were measured at each end of the scan range. Attenuation was necessary for nine reflections when the count rate exceeded 8000 counts/s during the scan. By the end of the data collection, the intensities of three standard reflections, monitored at intervals of every 50 reflections, were found to have dropped to 83% of their original values. These observations were used to place all of the intensities on the same relative scale.

Data processing included the application of Lorentz and polarization corrections and the calculations of $\sigma(I) = [c + 0.25(t_c/t_b)^2(B_1 + B_2) + (PI)^2]^{1/2}$ where $I = c - (t_c/2t_b)(B_1 + B_2)$ and c is the total integrated peak count obtained in scan time t_c; B_1 and B_2 are the background counts, each obtained in time t_b. P was initially given the value of 0.05 (this was changed to 0.065 to render $\sum w|F_o - F_c|^2$ independent of $|F_o|$ and $(\sin\theta)/\lambda$ at the end of the structure refinement) and is the factor included to avoid overweighting the more intense reflections. The data set consisted of 2165 unique reflections of which 1337 had $F_o^2 > 3\sigma(F_o^2)$. An absorption correction was applied [μ(Mo Kα) = 117.49 cm^{-1}], using Gaussian integration (4^3 grid points) with transmission factors ranging from 0.18 to 0.40.

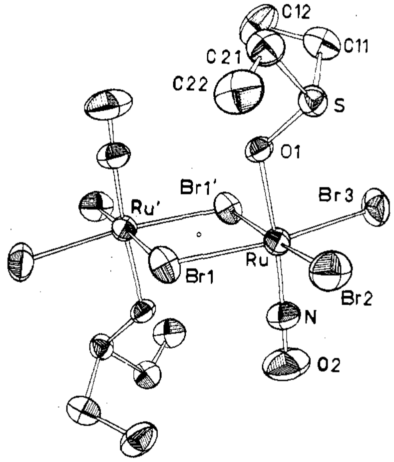


Figure 1.

Solution and Refinement of Structure.[2] A three-dimensional Patterson synthesis was carefully analyzed since the exact composition of the compound was not known. It indicated a triangular arrangement of one ruthenium and two terminal bromine atoms. By carrying out a three-dimensional vector superposition of two Patterson maps the positions of the ruthenium and three bromine atoms as well as the nitrosyl N atom and the sulfur and oxygen atoms of the sulfoxide ligand were determined. Full-matrix least-squares refinement was begun using the ruthenium and bromine atom positions and isotropic thermal parameters using those data for which $F_o^2 > 3\sigma(F_o^2)$. The function $\sum w(|F_o| - |F_c|)^2$ was minimized where the weights w were taken as $4F_o^2/\sigma^2(F_o^2)$; $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes. The agreement factors are defined as

$$R_1 = \Sigma||F_o| - |F_c||/\Sigma F_o$$

$$R_2 = [\Sigma[w(|F_o| - |F_c|)^2]/\Sigma(wF_o^2)]^{1/2}$$

these reduced to 0.243 and 0.325, respectively. Difference Fourier syntheses and full-matrix least-squares refinements were used to determine the positions of all of the nonhydrogen atoms. Atomic scattering factors were those reported by Cromer and Mann[3] for neutral atoms. Anomalous dispersion effects for the Ru, Br, and S atoms were included using the $\Delta f'$ and $\Delta f''$ values reported by Cromer.[4]

Using isotropic temperature factors, refinement of this model converged with R_1 and R_2 at 0.097 and 0.128, respectively. The difference Fourier maps had shown regions of high electron density (up to 5 e/Å^3) around the heavy atoms. Accordingly final least-squares refinements were carried out with all atoms assigned anisotropic thermal vibrational parameters. These refinements, using 1337 reflections for which $F_o^2 > 3\sigma(F_o^2)$, converged to give agreement factors $R_1 = 0.047$ and $R_2 = 0.058$.

The estimated standard deviation of an observation of unit weight was 1.34 electrons and the highest peak in a final difference Fourier synthesis was approximately one-fourth of the height of a typical carbon atom found during this analysis. Structure factor calculations for the 828 reflections having $F_o^2 < 3\sigma(F_o^2)$ showed no large discrepancies between $|F_c|$ and $|F_o|$. There was no evidence for secondary extinction.

The final positional and vibrational parameters are presented in Table I along with their estimated standard deviations as obtained from the inverse matrix in the course of the least-squares calculations. Table II contains root-mean-square amplitudes of thermal motion for those atoms refined with anisotropic thermal parameters. A table of the final values of $|F_o|$ and $|F_c|$ for the 1337 reflections included in the refinement is available.[5]

Description and Discussion

The dimeric complex $[RuBr_3(NO)(Et_2SO)]_2$ exists as discrete molecules, one of which is illustrated in Figure 1. Selected interatomic distances and bond angles are listed in Tables III and IV. The shortest nonbonding intermolecular contact not involving hydrogen atoms is 3.1 Å. The coor-

Table I. Final Positional[a] and Thermal[b] Parameters for $[RuBr_3(NO)(Et_2SO)]_2$

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ru	0.1382 (1)	0.1387 (1)	0.0407 (1)	0.0314 (6)	0.0277 (5)	0.0437 (6)	0.0032 (4)	0.0082 (5)	0.0107 (4)
Br(1)	−0.0306 (2)	0.0510 (1)	0.2366 (2)	0.0605 (9)	0.0338 (7)	0.0435 (8)	0.0022 (6)	0.0195 (7)	0.0079 (6)
Br(2)	0.2147 (2)	0.3310 (1)	0.3083 (2)	0.064 (1)	0.0411 (8)	0.0621 (9)	−0.0049 (7)	−0.0038 (8)	0.0031 (7)
Br(3)	0.2711 (2)	0.2242 (1)	−0.1774 (2)	0.0496 (9)	0.0572 (9)	0.090 (2)	0.0049 (7)	0.0342 (8)	0.0324 (8)
S	−0.1012 (4)	0.3465 (2)	−0.0977 (4)	0.037 (2)	0.031 (2)	0.044 (2)	0.001 (2)	0.011 (2)	0.012 (2)
O(1)	−0.0874 (9)	0.2155 (6)	−0.058 (1)	0.025 (5)	0.032 (4)	0.047 (5)	0.002 (4)	0.003 (4)	0.011 (4)
O(2)	0.434 (1)	0.014 (1)	0.188 (2)	0.057 (8)	0.094 (8)	0.104 (9)	0.028 (7)	0.001 (7)	0.034 (7)
N	0.316 (1)	0.0661 (9)	0.127 (2)	0.038 (7)	0.053 (7)	0.058 (7)	0.007 (6)	0.003 (6)	0.020 (6)
C(11)	−0.177 (2)	0.315 (1)	−0.359 (2)	0.061 (9)	0.053 (8)	0.047 (8)	0.009 (7)	0.009 (7)	0.019 (7)
C(12)	−0.320 (2)	0.211 (1)	−0.442 (2)	0.045 (9)	0.10 (2)	0.044 (9)	−0.011 (8)	0.005 (7)	−0.001 (8)
C(21)	−0.292 (2)	0.405 (1)	−0.010 (2)	0.045 (8)	0.043 (7)	0.052 (8)	0.015 (6)	0.021 (7)	0.011 (6)
C(22)	−0.267 (2)	0.422 (1)	0.203 (2)	0.057 (9)	0.09 (2)	0.042 (9)	0.018 (8)	0.024 (8)	0.011 (8)

[a] x, y, and z are in fractional coordinates. [b] The form of the thermal ellipsoid expression is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$; $U_{ij} = (\beta_{ij}/2\pi^2)a_i^*a_j^*$ (Å^2).

Table II. Root-Mean-Square Amplitudes of Vibration (Å)

Atom	Min	Intermed	Max
Ru	0.162 (1)	0.178 (2)	0.210 (1)
Br(1)	0.183 (2)	0.197 (2)	0.250 (2)
Br(2)	0.191 (2)	0.239 (2)	0.295 (2)
Br(3)	0.181 (2)	0.228 (2)	0.310 (2)
S	0.173 (4)	0.190 (5)	0.212 (4)
O(1)	0.15 (1)	0.18 (1)	0.22 (1)
O(2)	0.19 (2)	0.33 (1)	0.34 (1)
N	0.18 (2)	0.23 (1)	0.25 (1)
C(11)	0.20 (2)	0.23 (2)	0.26 (2)
C(21)	0.17 (2)	0.23 (2)	0.24 (2)
C(12)	0.19 (2)	0.22 (2)	0.33 (2)
C(22)	0.17 (2)	0.24 (2)	0.31 (2)

Table III. Intramolecular Distances (Å) for $[RuBr_3(NO)(Et_2SO)]_2$

Ru-N	1.71 (1)	S-C(21)	1.83 (1)
Ru-O(1)	2.050 (7)	N-O(2)	1.16 (1)
Ru-Br(3)	2.476 (2)	C(11)-C(12)	1.55 (2)
Ru-Br(2)	2.477 (2)	C(21)-C(22)	1.49 (2)
Ru-Br(1)	2.535 (2)	Ru-Ru′	3.673 (2)
S-O(1)	1.541 (7)	Br(1)-Br(1)′	3.496 (2)
S-C(11)	1.82 (1)		

Table IV. Intramolecular Angles (deg) for $[RuBr_3(NO)(Et_2SO)]_2$

N-Ru-O(1)	175.3 (4)	Br(1)-Ru-Br(1)′	87.18 (5)
N-Ru-Br(3)	94.9 (4)	Ru-Br(1)-Ru′	92.82 (5)
N-Ru-Br(2)	91.8 (3)	O(1)-S-C(11)	104.3 (5)
N-Ru-Br(1)	93.4 (3)	O(1)-S-C(21)	101.9 (5)
O(1)-Ru-Br(3)	89.4 (2)	C(11)-S-C(21)	101.8 (6)
O(1)-Ru-Br(2)	90.0 (2)	S-O(1)-Ru	123.9 (4)
O(1)-Ru-Br(1)	84.7 (2)	O(2)-N-Ru	177.8 (11)
Br(3)-Ru-Br(2)	92.32 (6)	C(12)-C(11)-S	113.6 (9)
Br(3)-Ru-Br(1)	89.30 (6)	C(22)-C(21)-S	111.6 (9)
Br(2)-Ru-Br(1)	174.46 (6)		

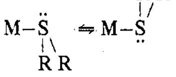
dination about the ruthenium atoms is approximately octahedral, but the plane containing the terminal bromine atoms Br(2) and Br(3) and Ru makes an angle of 7.8° with the plane Ru, Br(1), Ru′, and Br(1)′. The terminal bromine atoms are displaced toward the diethyl sulfoxide group. The Ru_2Br_2 ring geometry is nearly square with diagonals of 3.496 (2) and 3.673 (2) Å.

The bond lengths and angles for the diethyl sulfoxide ligand agree well with those of other sulfoxide structures reported.[6-17] The orientation of the sulfoxide ligand is similar to that reported[11] and appears (Figure 1) to be that expected from a consideration of intramolecular forces. Also C–C and C–S bond lengths and angles agree with those reported for a diethyl sulfide structure.[18] In this structure the oxygen atom of the sulfoxide ligand acts as the donor atom to Ru(II). It may be that steric effects of neighboring groups inhibit the sulfoxide ligand bonding through the sulfur atom. That oxygen is the donor atom is consistent with the infrared spectrum, where the shift is to a lower position for the ν(S–O) absorption (920 cm^{-1}) than that observed for the free sulfoxide (1030 cm^{-1}).[19] When oxygen is the donor atom, a slight weakening of the S–O bond is expected and hence there is a shift of the ν(S–O) absorption to lower energy. This effect has been confirmed by crystal structures of sulfoxide complexes. For sulfoxide ligands coordinated through oxygen the following average S–O bond lengths (in Å) have been reported: $CuCl_2(DMSO)_2$, 1.531 (4);[6] $[FeCl_2(DMSO)_4]FeCl_4$, 1.541 (6);[7] $Me_2SnCl_2(DMSO)_2$, 1.56 (4);[8] $Lu(NO_3)_3(DMSO)_3$, 1.54 (4);[9] $[RuBr_3(NO)(Et_2SO)]_2$, 1.541 (7);[10] $RuCl_2(DMSO)_4$, 1.557 (4).[11] On the other hand, for the sulfur-coordinated sulfoxides the reported average S–O bond lengths (Å) are as follows: $RuCl_2(DMSO)_4$, 1.485 (5);[11] $PdCl_2(DMSO)_2$, 1.476 (5);[12] $[Ru(NH_3)_5(DMSO)](PF_6)_2$, 1.527 (8);[13] $Pd(NO_3)_2(DMSO)_2$, 1.463 (7);[14] $Ir(C_{15}H_{13}O)Cl_2(DMSO)_2$, 1.45 (2);[15] $Na[Rh(DMSO)_2Cl_4]$, 1.47;[16] $(NH_2Me_2)[RuCl_3(DMSO)_3]$, 1.48 (1) Å.[17] The crystal structure analysis of dimethyl sulfoxide[20] (DMSO), at 5 °C, gave an S–O bond length of 1.513 (5) Å which is intermediate between the sulfur-coordinated and oxygen-coordinated S–O bond lengths. Hence, for sulfoxide complexes the ν(S–O) absorption can be used as an indicator of the mode of coordination of the sulfoxide to the metal atom, especially when the S–O bond length differs from that of the free sulfoxide.

The nitrosyl ligand is nearly linear, the Ru–N–O bond angle being 178 (1)°, and the bond lengths correspond to those reported for other linear nitrosyl ligands in reviews on metal nitrosyl complexes.[21,22] The nitrosyl stretching frequency of 1874 cm^{-1} is also consistent with the NO^+ ligand and linear M–N–O grouping found. The Ru–N bond distance of 1.71 (1) Å agrees well with those of other ruthenium–nitrosyl complexes such as 1.74 (2) Å in $[RuCl(NO)_2PPh_3]_2{}^+$,[23] 1.744 (6) Å in $RuCl_3(NO)(PMePh_2)_2$,[24] and 1.738 (2) Å in $[Ru(NO)Cl_5]^{2-}$.[25] When the Ru–N–O group is bent, the Ru–N length is found to be significantly longer, such as 1.85 (2) Å for $[RuCl(NO)_2(PPh_3)_2]^+$.[23]

The short Ru–N distance observed together with the linear Ru–N–O arrangement confirms that strong π back-bonding exists when the nitrosyl ligand is coordinated as NO^+.

The initial complex $RuBr_3NO(Et_2S)_2$ has a trans arrangement of sulfide ligands as shown by its ^{1}H NMR spectrum and supported by crystal structure determinations of related phosphine complexes.[24,26] Hence, considerable steric rearrangement of the ligands is necessary in forming the dimeric structure. Studies of the ^{1}H NMR spectra of the sulfide complexes RuX_3NOL_2 indicate that the sulfide ligands undergo a reasonably facile interconversion


$$M-\ddot{S}(R)(R) \rightleftharpoons M-\underset{..}{S}(R)(R)$$

either by inversion at the S atom or rotation about the M–S bond or by complete bond breaking and re-forming.[1] The interchange is rapid at room temperature (i.e., only one methylene quartet is observed). At low temperatures the ^1H NMR spectrum shows two methylene quartets indicating two sulfide arrangements in the complex. The frequency of the process in $RuBr_3(NO)(Et_2S)_2$ has been found to be 32/s at the temperature of multiplet collapse. The interconversion does not necessarily mean the M–S bond is broken, but it is possible[27] and suggests that considerable ligand rearrangement is quite feasible.

The oxygen responsible for the formation of the sulfoxide appears to be dissolved dioxygen in the chloroform, and the ethanol is probably a source of protons since the replacement of ethanol with other protic sources also gives the same red solution. It is known that sulfides oxidize to sulfoxides under more forcing conditions than those encountered in the present work and in acid-catalyzed conditions and also in the presence of H-bonding reagents.[28]

This appears to be the first report of the mild oxidation of a sulfide, and the metal ion may have an influence similar to that found in the oxidation of phosphines in metal complexes.[29] Attempts to isolate a dioxygen complex have so far been unsuccessful, but a detailed investigation of this possibility is currently under study as well as an investigation of the general occurrence of the reaction in other systems.

Acknowledgment. We wish to thank the New Zealand Universities Grants Committee for equipment grants and for a UGC scholarship to C.T.P.

Registry No. $[RuBr_3(NO)(Et_2SO)]_2$, 59492-73-8.

Supplementary Material Available: Listing of observed and calculated structure factor amplitudes (5 pages). Ordering information is given on any current masthead page.

References and Notes

(1) C. T. Page and J. E. Fergusson, *Aust. J. Chem.*, in press.
(2) Calculations were carried out at the University of Canterbury using a Burroughs B6718 computer. The data processing program HILGOUT is based on programs DRED (J. F. Blount) and PICKOUT (R. J. Doedens). Numerical absorption corrections were applied using program DABS which is a modification of DATAPH (P. Coppens). Structure factor calculations and least-square refinements were carried out using program CUCLS and Fourier summations using program FOURIER. These are highly modified versions of the well-known programs ORFLS (W. A. Busing, K. O. Martin, and H. A. Levy) and FORDAP (A. Zalkin), respectively. Other programs include local modifications of Busing and Levy's ORFFE function and error program and C. K. Johnson's ORTEP thermal ellipsoid plotting program.
(3) D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968).
(4) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).
(5) Supplementary material.
(6) R. D. Willett and K. Chang, *Inorg. Chim. Acta*, **4**, 447 (1970).
(7) M. J. Bennett, F. A. Cotton, and D. L. Weaver, *Acta Crystallogr.*, **23**, 581 (1967).
(8) N. W. Isaacs and C. H. L. Kennard, *J. Chem. Soc. A*, 1257 (1970).
(9) L. A. Aslanov, L. I. Soleva, and M. A. Porai-Koshits, *Zh. Strukt. Khim.*, **14**, 1064 (1973), and references therein.
(10) This work.
(11) A. Mercer and J. Trotter, *J. Chem. Soc., Dalton Trans.*, 2480 (1975).
(12) M. J. Bennett, F. A. Cotton, D. L. Weaver, R. J. Williams, and W. H. Watson, *Acta Crystallogr.*, **23**, 788 (1967).
(13) F. C. March and G. Ferguson, *Can. J. Chem.*, **49**, 3590 (1971).
(14) D. A. Langs, C. R. Hare, and R. G. Little, *Chem. Commun.*, 1080 (1967).
(15) M. McPartlin and R. Mason, *J. Chem. Soc. A*, 2206 (1970).
(16) V. I. Sokol, N. D. Rubtsova, and A. Yu. Gribenyuk, *Zh. Strukt. Khim.*, **15**, 318 (1974).
(17) R. S. McMillan, A. Mercer, B. R. James, and J. Trotter, *J. Chem. Soc., Dalton Trans.*, 1006 (1975).
(18) C. I. Branden, *Ark. Kemi.*, **22**, 83 (1964).
(19) W. Kitching and C. J. Moore, *Inorg. Nucl. Chem. Lett.*, **4**, 691 (1968).
(20) R. Thomas, C. B. Shoemaker, and K. Eriks, *Acta Crystallogr.*, **21**, 12 (1966).
(21) J. H. Enemark and R. D. Feltham, *Coord. Chem. Rev.*, **13**, 339 (1974).
(22) R. Eisenberg and C. D. Meyer, *Acc. Chem. Res.*, **8**, 26 (1975).
(23) C. G. Pierpont and R. Eisenberg, *Inorg. Chem.*, **11**, 1088 (1972).
(24) A. J. Schultz, R. L. Henry, J. Reed, and R. Eisenberg, *Inorg. Chem.*, **13**, 732 (1974).
(25) J. T. Veal and D. J. Hodgson, *Inorg. Chem.*, **11**, 1420 (1972).
(26) B. L. Haymote and J. A. Ibers, *Inorg. Chem.*, **14**, 3060 (1975).
(27) R. J. Cross, I. G. Dalgleish, G. J. Smith, and R. Wardle, *J. Chem. Soc., Dalton Trans.*, 992 (1972).
(28) N. Kharasch, "Organic Sulfur Compounds", Vol. 1, D. Barnard, L. Bateman, and J. I. Cunneen, Ed., Pergamon Press, New York, N.Y., 1961, Chapter 21.
(29) L. Vaska, *Science*, **140**, 809 (1963).
(30) Numbers in parentheses here and in succeeding tables are estimated standard deviations in the least significant figure.