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Structure of Chloronitrosyl(η^2-sulfur dioxide)bis(triphenylphosphine)ruthenium–Dichloromethane, $RuCl(NO)(\eta^2\text{-}SO_2)(P(C_6H_5)_3)_2{\cdot}CH_2Cl_2$

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Chloronitrosyl(η^2-sulfur dioxide)bis(triphenylphosphine)ruthenium, $RuCl(NO)(\eta^2\text{-}SO_2)(PPh_3)_2$, on the basis of an X-ray structure determination of its CH_2Cl_2 solvate, is shown to possess η^2 coordination of the SO_2 group to the Ru atom. About the Ru atom are trans axial PPh_3 groups and a basal plane consisting of the Cl ligand, the NO ligand (with Ru–N–O linear), and the S,O bonded SO_2 group. As opposed to the η^2 coordination of CO_2 and CS_2 to transition metals, wherein the metal–ligand systems are planar, atom O(2), which is not bonded to the Ru atom, is 1.24 Å out of the plane of atoms Ru, S, and O(1). Through the use of $S^{18}O_2$ it was established that a weak band at 895 cm^{-1} in the spectrum of the compound containing $S^{16}O_2$ arises from the presence of SO_2. The geometrical features of the present structure are compared with those in $Rh(NO)(\eta^2\text{-}SO_2)(PPh_3)_2$, the only other example where η^2 coordination of SO_2 has been established. The compound $RuCl(NO)(SO_2)(PPh_3)_2{\cdot}CH_2Cl_2$ crystallizes in space group C_i^1-$P\bar{1}$ of the triclinic system with two formula units in a cell of dimensions $a = 13.629$ (2) Å, $b = 15.255$ (3) Å, $c = 10.106$ (2) Å, $\alpha = 92.70$ (1)°, $\beta = 104.41$ (2)°, $\gamma = 65.48$ (1)°, $V = 1848$ Å^3, $\rho_{calcd} = 1.498$ g/cm^3, and $\rho_{obsd} = 1.51$ (1) g/cm^3. The structure has been refined to a conventional R index on F_o of 0.063 on the basis of 182 variables and 5379 observations.

The discovery of the bent mode of coordination of the SO_2 molecule to transition metals[1] was followed shortly by firm characterization of the bent mode of coordination of the NO ligand to transition metals.[2,3] In the ensuing years a considerable body of chemical and structural knowledge has evolved on NO coordination[4] and somewhat less on SO_2 coordination.[5] We[6] recognized that NO and SO_2 are both amphoteric ligands that are capable of acting as Lewis acids (M–L bond mainly σ in character, long M–L bond, bent geometry) or as Lewis bases (multiple and short M–L bond, linear or planar geometry) and that such amphoteric ligands are a convenient probe of the electronic characteristics of the metal system. A question that we asked was how do the acid–base properties of the NO and SO_2 ligands differ from one another. An obvious way to answer this question experimentally is to synthesize and characterize complexes containing both NO and SO_2 ligands. One that has been at hand for a number of years now[7] is $RuCl(NO)(SO_2)(PPh_3)_2$ (where Ph = phenyl), prepared by the addition of SO_2 to $RuCl(NO)(PPh_3)_2$. One could envisage the Ru atom in this complex possessing a square-pyramidal coordination geometry, either with a basal, linear Ru–N–O linkage and an axial, pyramidal Ru–SO_2 geometry or with a basal, planar Ru–SO_2 geometry and an axial, bent R–N–O linkage, depending upon the relative basicities of SO_2 and NO. As is sometimes the case in transition-metal chemistry, the stumbling block in this experiment was our inability to obtain suitable crystals of the complex. After successive tries over a period of years this has now been accomplished, and the results of the structural study are presented here. As often occurs, the geometry we find for the complex is neither of the possibilities we anticipated.

Experimental Section

Compound Preparation and Characterization. Manipulations of all solutions and solids were done under dry N_2 flow. Reactions were carried out under a static N_2 atmosphere. Crystals of $RuCl(NO)(PPh_3)_2$ required an inert-atmosphere drybox for successful manipulation. All solvents were distilled under N_2 from the appropriate drying agents. Infrared spectra were measured in Nujol mulls and C_6H_6 solutions using Perkin-Elmer 727-B and I-R 283 spectrophotometers. Elemental analyses were performed by H. Beck of the Northwestern University Analytical Laboratory.

Chloronitrosylbis(triphenylphosphine)ruthenium. This complex was prepared by the literature method.[7] In a typical run 0.16 g (0.21 mmol) of $RuCl_3(NO)(PPh_3)_2$[8] was dissolved in 40 mL of benzene, and an excess of Zn dust was added. After 2 h under reflux, the dark green solution was filtered and stored at room temperature under N_2 gas. It was used in this way for further syntheses. For estimation of concentrations we assumed that the reduction step was quantitative. Dark green crystals of $RuCl(NO)(PPh_3)_2$ can be grown from such solutions by vapor diffusion, using pentane as the nonsolvent. These crystals show an infrared band at 1735 cm^{-1} (vs), which may be assigned to $\nu_{N=O}$. At the expense of this band, a new nitrosyl band grows at 1768 cm^{-1} if the cell plates are exposed to dioxygen. In addition, a band at 878 cm^{-1}, assignable to the presence of the RuO_2 group, appears. These band positions are for the species $RuCl(NO)(O_2)(PPh_3)_2$.[9] Owing to the instability of crystals of $RuCl(NO)(PPh_3)_2$, no elemental analyses were obtained. However, it was possible to obtain unit cell data: triclinic, space group $P1$ or $P\bar{1}$, $a = 9.16$ Å, $b = 11.03$ Å, $c = 10.73$ Å, $\alpha = 110.0°$, $\beta = 86.5°$, $\gamma = 122.9°$, $V = 838$ Å^3. Since $P\bar{1}$ is the much more common space group and since the assumption of one formula unit per cell yields the reasonable calculated density of 1.37 g/cm^3, it is likely that in the solid state a center of symmetry is imposed on the molecule. Hence, it is probable that the phosphine groups are trans, the coordination about Ru is planar, and the NO and Cl ligands are disordered.

Chloronitrosyl(η^2-sulfur dioxide)bis(triphenylphosphine)ruthenium. This compound was prepared by the original literature method.[7] A freshly prepared solution of 0.21 mmol of $RuCl(NO)(PPh_3)_2$ in 40 mL of benzene was treated with 1 atm of SO_2 gas for 5 min to yield a bright red solution ($\nu_{N=O}$ 1758 cm^{-1} (s), ν_{SO_2} 1150 cm^{-1} (m)). Removal of solvent and excess SO_2 gas under vacuum yielded a powder of the desired material.

Chloronitrosyl(η^2-sulfur dioxide)bis(triphenylphosphine)ruthenium Diethyl Ether Solvate. This compound was obtained by recrystallization of the above powder from diethyl ether–dichloromethane. The compound crystallizes with four formula units in space group C_{2h}^5-$P2_1/n$ of the monoclinic system in a cell of dimensions $a = 16.499$ (3) Å, $b = 23.216$ (4) Å, $c = 10.138$ (2) Å, and $\beta = 96.46$ (1)°. A complete X-ray diffraction data set out to a 2θ limit of 105° (Cu Kα radiation) was collected and analyzed in the usual way.[10] The final R index on F_o for the 3514 intensities above background was 0.067. Although this structure analysis clearly established the basic geometry of the complex,[11] there were several unsatisfactory features of the structure. In particular, the molecule appeared to possess a noncrystallographic twofold axis in that there was disorder of the NO and Cl ligands and the Ru–SO_2 arrangement was also disordered. There were also difficulties in the location of the terminal carbon atoms of the diethyl ether solvate molecule. Hence, attention was directed at obtaining the desired compound as other than the diethyl ether solvate.

Chloronitrosyl(η^2-sulfur dioxide)bis(triphenylphosphine)ruthenium Dichloromethane Solvate. Powder of the solvate-free material was recrystallized from dichloromethane–pentane by vapor diffusion to yield the dichloromethane solvate as red-orange crystals. These crystals appear to undergo facile loss of solvent. Anal. Calcd for $RuCl(NO)(SO_2)(P(C_6H_5)_3)_2{\cdot}CH_2Cl_2$: C, 52.90; H, 3.84; N, 1.67. Found: C, 52.95; H, 4.05; N, 1.33. Infrared spectra (Nujol mulls) are similar to the spectra from benzene solution and show $\nu_{N=O}$ at 1754 cm^{-1}

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Table I. Crystal Data and Data Collection Procedures for $RuCl(NO)(\eta^2\text{-}SO_2)(PPh_3)_2\cdot CH_2Cl_2$

formula	$C_{37}H_{32}Cl_3NO_3P_2RuS$
formula wt	840.11
space group	C_i^1-$P\bar{1}$ (triclinic)
a	13.629 (2) Å
b	15.255 (3) Å
c	10.106 (2) Å
α	92.70 (1)°
β	104.41 (2)°
γ	65.48 (1)°
V	1848 Å^3
Z	2
ρ_{calcd}	1.498 g/cm^3
ρ_{obsd}	1.51 (1) g/cm^3
temp	22 °C
crystal shape	complex plate of approx dimensions 0.31 mm × 0.21 mm × 0.10 mm
crystal vol	0.0071 mm^3
radiation	Cu Kα (λ(Cu Kα_1) 1.540 562 Å) prefiltered through 1 mil thick Ni foil
linear absorp coeff (μ)	71.6 cm^{-1}
transmission factors	0.224–0.552
detector aperture	3.9 mm wide by 3.7 mm high, 30 cm from the crystal
takeoff angle	3.5°
scan speed	2.0° in 2θ/min
2θ limits	5.0–160.0°
bgd counts	10 s at each end of scan with rescan option
scan range	0.9° below Kα_1 to 0.8° above Kα_2
data collected	$\pm h$, $\pm k$, $l \leqslant 0$
p	0.04
unique data, $F_o^2 > 3\sigma(F_o^2)$	5379

and only one rather broad band at 1140–1155 cm^{-1} clearly assignable to SO_2 absorption. The high value of the NO absorption is consistent with a linear Ru–N–O linkage.[12]

Chloronitrosyl(η^2-sulfur dioxide-^{18}*O*)bis(triphenylphosphine)ruthenium. Approximately 0.3 mmol of $S^{18}O_2$ was condensed into an evacuated Schlenk tube containing a frozen solution of 0.05 mmol of freshly prepared $RuCl(NO)(PPh_3)_2$ dissolved in benzene. On warming, the green glass changed to a red-orange solution. Removal of solvent under vacuum afforded a yellow-orange powder whose IR spectrum showed a weak band at 864 ± 1 cm^{-1} which appears at 895 ± 5 cm^{-1} in the corresponding $S^{16}O_2$ spectrum. A possible shift in the band that occurs at 1140–1155 cm^{-1} in the $S^{16}O_2$ spectrum could not be detected, perhaps because this band overlaps with bands from phenyl modes.

Sulfur Dioxide-^{18}*O*. The $S^{18}O_2$ was produced simply by burning an excess of sulfur on an electrically heated nichrome wire in a sample tube containing $^{18}O_2$ and N_2. The $S^{18}O_2$ sample was separated from excess sulfur and from any residual $^{18}O_2$ by trap-to-trap condensation. The isotopic purity of the resultant sample was established from gas-phase IR spectra.

Crystallographic Study of $RuCl(NO)(\eta^2\text{-}SO_2)(PPh_3)_2\cdot CH_2Cl_2$. The specimen was sealed in a glass capillary in order to minimize solvent loss and decomposition. Preliminary film data failed to reveal any symmetry, other than the trivial center of symmetry, for this compound, and hence it was assigned to the triclinic system. On the basis of the setting angles of 15 manually centered reflections ($50 < 2\theta(\text{Cu K}\alpha_1) < 65°$), the reduced cell constants presented in Table I were obtained. The crystal chosen for data collection showed little mosaicity. Data were collected at room temperature on a Picker FACS-1 diffractometer using methods general in this laboratory.[10] Important features of the data collection are summarized in Table I.

The structure was solved in a facile manner, using procedures and computer programs described before.[10] Space group $P\bar{1}$ was assumed. The positions of the atoms in the inner coordination sphere were clear from a three-dimensional, origin-removed Patterson map. All nonhydrogen atoms were located on a subsequent difference Fourier map. Included in the final cycle of least-squares refinement were the contributions from hydrogen atoms placed at their calculated positions. The carbon atoms of the phenyl rings were constrained to the rigid-group approximation[13] with isotropic thermal motion, while all other atoms were allowed to vibrate anisotropically. The occupancy of the solvent molecule was also varied. This final refinement converged to values of R and R_w of 0.063 and 0.075, respectively, and to an error in an observation of unit weight of 2.00 electrons for the 182 variables and 5379 observations. The occupancy of the solvent molecule was found to be 0.94 (1), and hence the compound is the monosolvate. An analysis of $\sum w(|F_o| - |F_c|)^2$ as a function of $|F_o|$, setting angles, and Miller indices indicated no unusual trends.

Eighteen of the nineteen highest peaks (0.89–0.58 e/Å^3) in the final difference Fourier map are associated with the carbon atoms of the constrained phenyl rings. This suggests a slight inadequacy of the isotropic treatment of these atoms. But previous experience[14] has indicated that relaxation of this isotropic model, while reducing the R index and increasing the computational costs, does not significantly improve the definition of the chemically more interesting parts of a structure.

Final positional and thermal parameters are tabulated in Tables II and III. Root-mean-square amplitudes of vibration are given in Table IV.[15] In Table V the values of $10|F_o|$ and $10|F_c|$ for the reflections used in the refinement are given.[15]

Results and Discussion

The crystal structure of $RuCl(NO)(\eta^2\text{-}SO_2)(PPh_3)_2\cdot CH_2Cl_2$ consists of well-separated molecules of metal complex and solvent. A packing diagram is shown in Figure 1. All intermolecular contacts appear to be normal. Intramolecular distances and angles are given in Table VI.

The overall molecular structure of the metal complex is shown in Figure 2, while Figure 3 displays the inner coordination sphere and some important distances and angles. Rather than the anticipated square-pyramidal coordination about the Ru atom with either an axial, bent Ru–N–O linkage or an axial, bent Ru–SO_2 geometry, the coordination geometry actually found is that of a trigonal bipyramid with trans, axial

Table II. Positional and Thermal Parameters for the Nongroup Atoms of $RuCl(NO)(\eta^2\text{-}SO_2)(PPh_3)_2\cdot CH_2Cl_2$

ATOM	X[A]	Y	Z	B11[B]	B22	B33	B12	B13	B23
RU	0.084900(43)	0.188488(35)	0.165782(51)	5.50(4)	4.01(2)	8.08(5)	-2.01(2)	2.57(3)	-0.78(3)
S	0.04989(16)	0.05302(12)	0.18756(19)	8.01(16)	4.69(9)	12.13(22)	-2.81(10)	4.53(15)	-0.81(11)
P(1)	-0.09067(15)	0.29658(11)	0.21427(18)	6.69(15)	3.92(8)	10.46(20)	-2.27(9)	3.57(14)	-1.45(10)
P(2)	0.26397(14)	0.10048(11)	0.11293(16)	5.41(13)	4.30(8)	8.34(18)	-1.97(8)	2.20(12)	-0.18(9)
CL(1)	0.17944(17)	0.25207(14)	0.35567(20)	8.84(17)	6.78(12)	12.57(23)	-3.50(12)	1.88(16)	-2.97(13)
O(1)	0.11148(45)	0.08073(35)	0.31575(46)	11.62(54)	5.96(29)	9.77(54)	-3.76(34)	4.56(44)	-0.32(32)
O(2)	0.11836(47)	-0.03643(35)	0.13567(51)	11.80(56)	5.08(27)	13.65(66)	-3.13(32)	6.21(50)	-1.74(34)
N	0.03226(48)	0.23699(41)	-0.00264(58)	6.86(50)	5.36(34)	10.10(68)	-2.31(33)	3.58(47)	-1.18(38)
O(3)	0.00025(51)	0.26543(44)	-0.11256(61)	9.99(58)	7.97(41)	12.88(77)	-2.91(39)	2.40(55)	2.28(45)
C(1)	0.2894(18)	0.44707(68)	0.3641(14)	53.8(32)	7.23(43)	31.6(22)	-8.63(98)	17.5(22)	-3.60(77)
CL(2)	0.21952(42)	0.55062(44)	0.30409(59)	19.79(58)	19.35(59)	47.1(12)	-2.63(45)	7.71(66)	6.08(65)
CL(3)	0.40896(64)	0.42885(53)	0.47367(88)	35.9(11)	26.32(75)	71.3(19)	-8.18(69)	-18.5(11)	18.03(95)

[A] ESTIMATED STANDARD DEVIATIONS IN THE LEAST SIGNIFICANT FIGURE(S) ARE GIVEN IN PARENTHESES IN THIS AND ALL SUBSEQUENT TABLES. [B] THE FORM OF THE ANISOTROPIC THERMAL ELLIPSOID IS: $EXP[-(B11H^2+B22K^2+B33L^2+2B12HK+2B13HL+2B23KL)]$. THE QUANTITIES GIVEN IN THE TABLE ARE THE THERMAL COEFFICIENTS X 10^3.

Table III. Derived Parameters for the Rigid Group Atoms of $RuCl(NO)(\eta^2\text{-}SO_2)(PPh_3)_2\cdot CH_2Cl_2$

ATOM	X	Y	Z	B,A^2	ATCM	X	Y	Z	B,A^2
C(11)	-0.12915(43)	0.25888(37)	0.35384(45)	3.64(13)	C(41)	0.34033(36)	0.17521(32)	0.12433(48)	3.52(11)
C(12)	-0.23803(38)	0.26957(40)	0.33993(47)	5.21(18)	C(42)	0.45635(36)	0.13610(26)	0.16832(48)	3.96(12)
C(13)	-0.26547(37)	0.23758(46)	0.44678(63)	6.50(20)	C(43)	0.51295(30)	0.19337(38)	0.16295(56)	5.38(18)
C(14)	-0.18402(52)	0.19490(44)	0.56755(52)	6.32(22)	C(44)	0.45353(46)	0.28975(36)	0.11359(60)	6.06(18)
C(15)	-0.07513(45)	0.18422(41)	0.58146(44)	6.32(20)	C(45)	0.33750(46)	0.32886(26)	0.06960(60)	6.82(21)
C(16)	-0.04770(33)	0.21621(40)	0.47461(55)	5.18(16)	C(46)	0.28090(30)	0.27159(34)	0.07497(55)	5.54(20)
C(21)	-0.20980(34)	0.31979(33)	0.06732(40)	3.52(11)	C(51)	-0.24925(38)	-0.06825(31)	0.06549(33)	3.23(11)
C(22)	-0.21289(36)	0.24272(26)	-0.01088(48)	4.25(14)	C(52)	-0.28092(39)	-0.10955(31)	0.15832(46)	4.51(14)
C(23)	-0.30395(45)	0.25694(33)	-0.12152(47)	5.11(16)	C(53)	-0.26397(44)	-0.08666(35)	0.29500(42)	4.88(16)
C(24)	-0.39191(37)	0.34825(40)	-0.15397(47)	6.03(20)	C(54)	-0.21536(44)	-0.02246(36)	0.33885(33)	4.51(14)
C(25)	-0.38882(38)	0.42532(30)	-0.07578(56)	6.28(19)	C(55)	-0.18370(40)	0.01884(32)	0.24602(45)	4.78(14)
C(26)	-0.29776(44)	0.41110(28)	0.03487(49)	4.96(16)	C(56)	-0.20064(40)	-0.00405(31)	0.10935(41)	3.97(13)
C(31)	-0.09310(49)	0.41485(35)	0.25166(61)	4.12(14)	C(61)	0.36191(36)	-0.00903(28)	0.21734(43)	3.56(11)
C(32)	-0.05415(51)	0.45588(42)	0.16758(54)	5.56(18)	C(62)	0.36879(41)	-0.01062(31)	0.35732(47)	4.78(16)
C(33)	-0.05619(57)	0.54743(45)	0.19074(71)	6.55(25)	C(63)	0.44705(47)	-0.09141(39)	0.44227(35)	5.99(18)
C(34)	-0.09718(65)	0.59794(37)	0.29798(82)	8.05(27)	C(64)	0.51843(40)	-0.17060(32)	0.38723(50)	5.65(18)
C(35)	-0.13613(70)	0.55690(53)	0.38206(72)	12.17(43)	C(65)	0.51155(41)	-0.16902(30)	0.24725(53)	5.13(18)
C(36)	-0.13409(61)	0.46536(54)	0.35890(65)	9.59(36)	C(66)	0.43329(42)	-0.08823(35)	0.16230(37)	4.32(14)

RIGID GROUP PARAMETERS

GROUP	X_C^A	Y_C	Z_C	$CELTA^B$	EPSILCN	ETA
GRP 11	-0.15658(33)	0.22689(25)	0.46070(38)	-1.4840(37)	-2.8199(32)	-2.0659(36)
GRP 12	-0.30086(29)	0.33402(25)	-0.04333(34)	0.4578(32)	-2.8358(30)	0.6756(32)
GRP 13	-0.09514(35)	0.50639(32)	0.27482(47)	1.9645(95)	-2.0151(46)	-2.7295(96)
GRP 21	0.39693(30)	0.23248(24)	0.11896(33)	1.0822(29)	2.9782(33)	2.9727(38)
GRP 22	-0.23231(25)	-0.04535(21)	0.20217(31)	-0.4324(32)	2.8279(24)	-1.5889(31)
GRP 23	0.44017(27)	-0.08982(24)	0.30229(35)	-2.3246(79)	2.0256(27)	-1.5440(76)

[A] X_C, Y_C, AND Z_C ARE THE FRACTIONAL COCRCINATES OF THE ORIGIN OF THE RIGID GROUP. [B] THE RIGIO GROUP ORIENTATION ANGLES DELTA, EPSILON, AND ETA(RADIANS) HAVE BEEN CEFINED PREVICUSLY: S.J. LA PLACA AND J.A. IBERS, ACTA CRYSTALLCGR., 18, 511(1965).

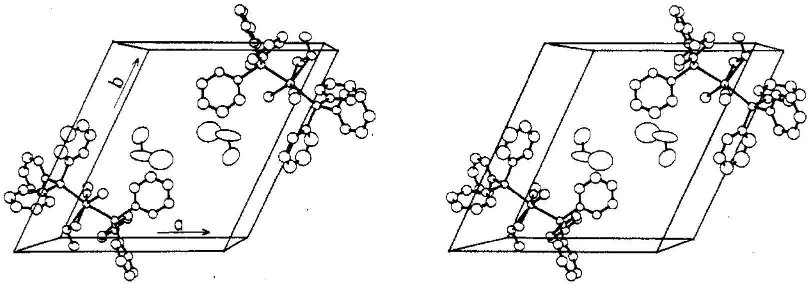

Figure 1. Stereoview of a unit cell of $RuCl(NO)(\eta^2\text{-}SO_2)(PPh_3)_2\cdot CH_2Cl_2$. The axes are as indicated with *c* coming up out of the plane of the paper. The vibrational ellipsoids are drawn at the 40% probability level. Hydrogen atoms have been omitted.

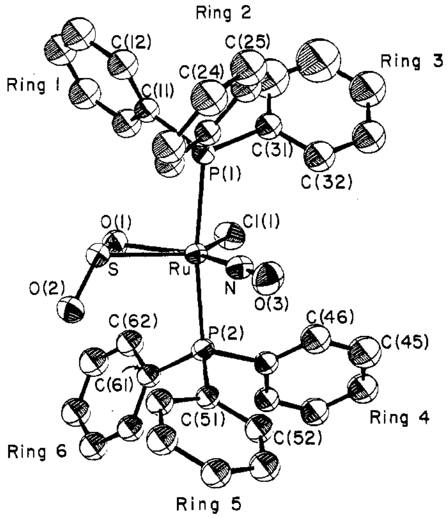

Figure 2. Perspective view showing all nonhydrogen atoms of the $RuCl(NO)(\eta^2\text{-}SO_2)(PPh_3)_2$ molecule and indicating the numbering scheme used. The vibrational ellipsoids are drawn at the 40% level.

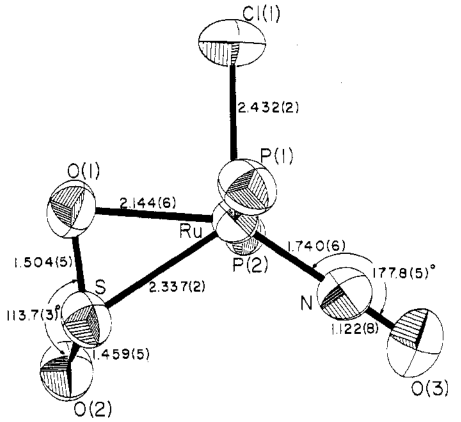

Figure 3. Inner coordination sphere for $RuCl(NO)(\eta^2\text{-}SO_2)(PPh_3)_2$, with relevant bond lengths and angles shown. The vibration ellipsoids are drawn at the 50% probability level.

phosphine groups and with the equatorial ligands being Cl, a linear NO, and η^2-SO_2 bound through atoms S and O(1). The basal plane contains atoms Ru, S, Cl(1), O(1), N, and

Table VI. Selected Distances (Å) and Angles (deg) in $RuCl(NO)(\eta^2\text{-}SO_2)(PPh_3)_2\cdot CH_2Cl_2$

Bond Distances

Ru–P(1)	2.433 (2)	P(1)–C(11)	1.814 (6)
Ru–P(2)	2.430 (2)	P(1)–C(21)	1.827 (4)
Ru–Cl(1)	2.432 (2)	P(1)–C(31)	1.814 (6)
Ru–S	2.337 (2)	P(2)–C(41)	1.819 (6)
Ru–N	1.740 (6)	P(2)–C(51)	1.831 (4)
Ru–O(1)	2.144 (6)	P(2)–C(61)	1.817 (4)
S–O(1)	1.504 (5)	N–O(3)	1.122 (8)
S–O(2)	1.459 (5)	C(1)–Cl(2)	1.52 (1)
		C(1)–Cl(3)	1.65 (2)

Bond Angles

P(1)–Ru–P(2)	172.09 (6)	Ru–S–O(1)	63.6 (2)
P(1)–Ru–Cl(1)	88.16 (7)	Ru–S–O(2)	117.6 (2)
P(2)–Ru–Cl(1)	87.74 (7)	O(1)–S–O(2)	113.7 (3)
P(1)–Ru–N	89.1 (2)	Ru–P(1)–C(11)	117.2 (2)
P(2)–Ru–N	87.8 (2)	Ru–P(1)–C(21)	112.5 (2)
P(1)–Ru–S	92.15 (6)	Ru–P(1)–C(31)	111.0 (2)
P(2)–Ru–S	95.76 (6)	Ru–P(2)–C(41)	111.6 (2)
P(1)–Ru–O(1)	91.9 (1)	Ru–P(2)–C(51)	112.3 (2)
P(2)–Ru–O(1)	94.4 (1)	Ru–P(2)–C(61)	117.9 (2)
Cl(1)–Ru–S	123.79 (7)	C(11)–P(1)–C(21)	104.4 (3)
Cl(1)–Ru–O(1)	84.9 (1)	C(11)–P(1)–C(31)	106.2 (3)
Cl(1)–Ru–N	125.6 (2)	C(21)–P(1)–C(31)	104.5 (2)
N–Ru–S	110.6 (2)	C(41)–P(2)–C(51)	102.3 (3)
N–Ru–O(1)	149.5 (2)	C(41)–P(2)–C(61)	104.8 (2)
S–Ru–O(1)	38.9 (1)	C(51)–P(2)–C(61)	106.6 (2)
Ru–N–O(3)	177.8 (5)	Cl(2)–C(1)–Cl(3)	115.1 (12)

Torsion Angles

Ru–P(1)–C(11)–C(12)	−136.6 (4)
Ru–P(1)–C(21)–C(26)	−140.7 (4)
Ru–P(1)–C(31)–C(36)	−136.8 (5)
C(11)–P(1)–P(2)–C(61)	−2.2 (3)
C(21)–P(1)–P(2)–C(51)	1.3 (3)
Ru–P(2)–C(41)–C(42)	146.4 (4)
Ru–P(2)–C(51)–C(52)	112.4 (3)
Ru–P(2)–C(61)–C(66)	145.3 (4)
C(31)–P(1)–P(2)–C(41)	−1.1 (3)

Interplanar Angle

Plane 1 (Ru,S,O(1))–Plane 2 (S,O(1),O(2))	110.3 (3)

Table VII. Comparison of Distances and Angles for the Two Examples of $M(\eta^2\text{-}SO_2)$ Coordination

	$Rh(NO)(\eta^2\text{-}SO_2)(PPh_3)_2$ [a]	$RuCl(NO)(\eta^2\text{-}SO_2)(PPh_3)_2$ [b]
Bond Distances, Å		
M–S	2.326 (2)	2.337 (2)
M–O(1)[c]	2.342 (5)	2.144 (6)
S–O(1)	1.493 (5)	1.504 (5)
S–O(2)	1.430 (5)	1.459 (5)
Bond Angles, Deg		
O(1)–M–S	37.3 (1)	38.9 (1)
M–S–O(1)	71.9 (2)	63.6 (2)
M–S–O(2)	106.4 (2)	117.6 (2)
O(1)–S–O(2)	115.1 (4)	113.7 (3)
Interplanar Angles, Deg		
M–S–O(1)/S–O(1)–O(2)	100.3 (3)	110.3 (3)

[a] Reference 16. [b] Present work. [c] In both compounds O(1) refers to the oxygen atom which is bound to the metal. This differs from the notation of Ryan and Moody.[16]

O(3) and none of these atoms deviates from the best weighted least-squares plane by more than 0.021 (5) Å. Atom O(2) is 1.24 Å from this plane. The η^2 mode of bonding of SO_2 to a transition metal has been observed[16] only once before in $Rh(NO)(\eta^2\text{-}SO_2)(PPh_3)_2$. Comparisons will be made primarily between these two structures, although if one considers the SO_2 ligand as occupying a single coordination site, then the Rh complex is four-coordinate and tetrahedral and the Ru complex is five-coordinate and trigonal bipyramidal. Nevertheless, since the Rh–N–O geometry is distinctly bent, one could consider it to be formally a $Rh^+\text{–}NO^-$ system isoelectronic with the present $Ru^0Cl^-NO^+$ system.

Table VII compares the various distances and angles relevant to SO_2 coordination in these two compounds. Despite a different metal and different coordination number, the M–S distances are essentially the same. But the Mo–O(1) distances are markedly different. In the Rh complex the Rh–O distance of 2.342 (5) Å is far longer than a Rh–O single-bond distance exemplified by those of 2.079 (7) and 2.091 (8) Å in $Rh(NO)(SO_4)(PPh_3)_2$.[17] One could consider the SO_2 bonding in $Rh(NO)(SO_2)(PPh_3)_2$ as tending toward the more usual S-bonded pyramidal SO_2 arrangement. In the present Ru complex there is no such tendency. The Ru–O bonded distance of 2.144 (6) Å is near to the presumed Ru–O single-bond distances of 2.079 (7) Å in $RuCl(NO)(SO_4)(PPh_3)_2$[18] and of 2.111 (5) Å in $Ru(SO_4)(CO)_2(PPh_3)_2$.[19]

Previously[16] this S,O-bonded geometry for SO_2 has been compared with related η^2 arrangements observed for $Ni\text{–}CO_2$ in $Ni(CO_2)(PCy_3)_2$[20] (Cy = cyclohexyl) and for $Pt\text{–}CS_2$ in $Pt(CS_2)(PPh_3)_2$.[21] Yet it is important to note that in these former structures the $\eta^2\text{-}CO_2$ and $\eta^2\text{-}CS_2$ ligands are coplanar with the metal, whereas in the two instances of $\eta^2\text{-}SO_2$ coordination this is not the case. The dihedral angle between M, S, and O(1) and S, O(1), and O(2) is 110.3 (3)° in the present structure and 100.3 (3)° in $Rh(NO)(\eta^2\text{-}SO_2)(PPh_3)_2$.[16]

In view of the multiple modes of coordination of SO_2 in transition-metal complexes, can one differentiate among these using spectroscopic techniques? Such differentiation would aid markedly in the selection of compounds for structural study, as it has in the nitrosyl and aryldiazo[22] fields. Kubas[23] indicates that in general if the $M\text{–}SO_2$ geometry is bent, the S=O stretching frequencies occur near 1200 and 1050 cm^{-1}, while if the $M\text{–}SO_2$ geometry is planar, these frequencies occur near 1300 and 1100 cm^{-1}. (The antisymmetric and symmetric stretching frequencies in SO_2 are at 1340 and 1150 cm^{-1},[24] while those in $Pt(CH_3)(PPh_3)_2I\text{–}SO_2$, in which there is a very weak I–S interaction, occur at 1322 and 1138 cm^{-1}.[25]) In $Rh(NO)(\eta^2\text{-}SO_2)(PPh_3)_2$ bands attributed to SO_2 are found at 1138 and 948 cm^{-1}.[16] Thus, there may be reasonable spectroscopic criteria for distinguishing the various modes of attachment of SO_2 to metal systems. But there are also difficulties. Whereas the band at 948 cm^{-1} is very strong in $Rh(NO)(\eta^2\text{-}SO_2)(PPh_3)_2$, there is only a very weak band in this region (895 cm^{-1}) in $RuCl(NO)(\eta^2\text{-}SO_2)(PPh_3)_2$. In order to establish that this band indeed arises from the presence of $\eta^2\text{-}SO_2$, the spectrum of the corresponding $S^{18}O_2$ compound was obtained. This spectrum shows only one shifted band, a weak band at 864 ± 1 cm^{-1}, which corresponds to the 895 ± 5 cm^{-1} band in the $S^{16}O_2$ spectrum shifted by about the amount predicted on the basis of a simple-harmonic-oscillator approximation. No other bands are shifted on isotopic substitution, although the band at 1140–1155 cm^{-1}, which from the spectral analysis of $Rh(NO)(\eta^2\text{-}SO_2)(PPh_3)_2$ was assigned to the presence of SO_2, partly overlaps with bands arising from phenyl modes. It thus appears that a low-frequency band (890–950 cm^{-1}) may be useful as an indication of the presence of S,O-bonded SO_2. However, in view of the great differences in intensity of this band in the two compounds known to exhibit this mode of coordination, considerable care must be exercised in searching the indicated region of the spectrum. Failure to find this band is presumably the cause of the incorrect structural assignment[16] for $RuCl(NO)(SO_2)(PPh_3)_2$ made previously from infrared spectral results.

Although there have been attempts to understand in molecular orbital terms the modes of attachment of SO_2 to transition metals, these have not been markedly useful for the prediction of geometries. Thus, the prediction[5] that a d^8 complex should exhibit a bent $M\text{–}SO_2$ geometry (in consonance with the structural results on the two known examples[1,6]) was followed almost immediately by the discovery[26] of a d^8 complex with a planar $M-SO_2$ geometry and concomitant rationalization of the result in molecular orbital terms. But there is no anticipation on theoretical grounds for the η^2 mode of coordination of SO_2 to be found in the literature nor has there yet appeared an ex post facto rationalization.

It may be that as the number of structurally characterized SO_2 complexes increases, our ability to predict geometries will also improve. It clearly is an interesting question whether the η^2 mode of bonding of SO_2 will remain rare or whether the two known structures are the forerunners of a large class of compounds. The bent mode of bonding of NO to transition metals was novel in 1968[2] and is now probably as common as the linear mode.

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Registry No. $RuCl(NO)(\eta^2\text{-}SO_2)(P(C_6H_5)_3)_2\cdot CH_2Cl$, 66701-48-2.

Supplementary Material Available: Root-mean-square amplitudes of vibration (Table IV) and a listing of structure amplitudes (Table V) (38 pages). Ordering information is given on any current masthead page.

References and Notes

(1) S. J. La Placa and J. A. Ibers, *Inorg. Chem.*, **5**, 405 (1966).
(2) D. J. Hodgson, N. C. Payne, J. A. McGinnety, R. G. Pearson, and J. A. Ibers, *J. Am. Chem. Soc.*, **90**, 4486 (1968).
(3) D. J. Hodgson and J. A. Ibers, *Inorg. Chem.*, **7**, 2345 (1968); **8**, 1282 (1969).
(4) B. A. Frenz and J. A. Ibers, *MTP Int. Rev. Sci.: Phys. Chem., Ser. One*, **11**, 33 (1972); R. Eisenberg and C. D. Meyer, *Acc. Chem. Res.*, **8**, 26 (1975).
(5) R. R. Ryan and P. G. Eller, *Inorg. Chem.*, **15**, 494 (1976).
(6) K. W. Muir and J. A. Ibers, *Inorg. Chem.*, **8**, 1921 (1969).
(7) M. H. B. Stiddard and R. E. Townsend, *Chem. Commun.*, 1372 (1969).
(8) M. B. Fairy and R. J. Irving, *J. Chem. Soc. A*, 475 (1966).
(9) K. R. Laing and W. R. Roper, *Chem. Commun.*, 1556 (1968).
(10) See, for example, J. M. Waters and J. A Ibers, *Inorg. Chem.*, **16**, 3273 (1977).
(11) R. D. Wilson and J. A. Ibers, Abstract J-9, American Crystallographic Association Meeting, East Lansing, Mich., Aug 7–12, 1977.
(12) B. L. Haymore and J. A. Ibers, *Inorg. Chem.*, **14**, 3060 (1975).
(13) S. J. La Placa and J. A. Ibers, *Acta Crystallogr.*, **18**, 511 (1965).
(14) L. D. Brown and J. A. Ibers, *Inorg. Chem.*, **15**, 2788 (1976).
(15) Supplementary material.
(16) D. C. Moody and R. R Ryan, *J. Chem. Soc., Chem. Commun.*, 503 (1976); *Inorg. Chem.*, **16**, 2473 (1977).
(17) B. C. Lucas, D. C. Moody, and R. R. Ryan, *Cryst. Struct. Commun.*, **6**, 57 (1977).
(18) J. Reed, S. L. Soled, and R. Eisenberg, *Inorg. Chem.*, **13**, 3001 (1974).
(19) D. C. Moody and R. R Ryan, *Cryst. Struct. Commun.*, **5**, 145 (1976).
(20) M. Aresta, C. F. Nobile, V. G. Albano, E. Forni, and M. Manassera, *J. Chem. Soc., Chem. Commun.*, 636 (1975).
(21) R. Mason and A. I. M. Rae, *J. Chem. Soc. A*, 1767 (1970).
(22) M. Cowie, B. L. Haymore, and J. A. Ibers, *J. Am. Chem. Soc.*, **98**, 7608 (1976).
(23) G. J. Kubas, Abstracts, 172nd National Meeting of the American Chemical Society, San Francisco, Calif., Sept 3, 1976, No. 240.
(24) E. R. Lippincott and F. E. Welsh, *Spectrochim. Acta*, **17**, 123 (1961).
(25) M. R. Snow and J. A. Ibers, *Inorg. Chem.*, **12**, 224 (1973).
(26) R. R. Ryan, P. G. Eller, and G. J. Kubas, *Inorg. Chem.*, **15**, 797 (1976).

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Crystal and Molecular Structure of the Decacoordinate Compound ((Hydroxyethyl)ethylenediaminetriacetato)diaquolanthanum(III) Trihydrate

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The crystal and molecular structure of the trihydrate of ((hydroxyethyl)ethylenediaminetriacetato)diaquolanthanum(III), $La[(O_2CCH_2)_2NCH_2CH_2N(CH_2CH_2OH)(CH_2CO_2)(H_2O)_2]\cdot 3H_2O$ (triclinic, $P\bar{1}$, $a = 9.476$ (2) Å, $b = 10.947$ (3) Å, $c = 9.391$ (2) Å, $\alpha = 108.18$ (2)°, $\beta = 104.66$ (3)°, $\gamma = 79.31$ (3)°, $Z = 2$, Mo Kα radiation), has been determined by three-dimensional X-ray analysis. The structure was solved by conventional Patterson and Fourier techniques and refined by a full-matrix least-squares procedure to a final conventional discrepancy factor, $R = \sum||F_o| - |F_c||/\sum|F_o|$, of 6.4% for 1637 observed reflections ($F_o > 2\sigma_{F_o}$). This molecule crystallizes as a dimer, utilizing the crystallographic center of symmetry. The eight coordination sites satisfied by (hydroxyethyl)ethylenediaminetriacetate include five solely from one group—including one from the oxygen of the hydroxyethyl group—two by a sharing of a carboxymethyl oxygen between the two lanthanum atoms, and one from the carboxymethyl oxygen from the ligand primarily coordinated to the other lanthanum atom. The lanthanum cations are decacoordinate, with a geometry approximating the bicapped square antiprism.

Introduction

Powell and Burkholder have demonstrated that the Gd–Eu and Eu–Sm separation factors in cation-exchange elution with ammonium ethylenediaminetetraacetate (EDTA) can be augmented by increasing the temperature from 25 to 92 °C and have shown that similar enhancements should occur in the cases of Ho–Dy and Dy–Tb pairs when (hydroxyethyl)ethylenediaminetriacetate (HEDTA) is the eluent.[1] The stabilities of the four heaviest HEDTA chelate species (Tm–Lu) are not affected by this increase in temperature, whereas the stabilities of the remaining lanthanide HEDTA species vary significantly with temperature. This difference may be explained by the assumption that the HEDTA ligand always forms pentadentate bonds to the four smaller lanthanides (Lu^{3+} through Eu^{3+}) and hexadentate bonds to those lanthanides larger than Eu^{3+} at temperatures approaching 0 °C, with the remaining coordination sites being occupied by water molecules.

There have been numerous articles recently on compounds exhibiting large coordination numbers, and considerable controversy has arisen over the preferred geometry in cases of high coordination numbers. Thus, the crystal structure determination of LaHEDTA was undertaken in order to provide further information on the coordination of the HEDTA ligand to the lighter lanthanides and the geometry of the resulting complex.

Experimental Section

Crystal Data. Well-formed white rhombohedral crystals of LaHEDTA were supplied by J. E. Powell of this laboratory and were used without further purification. A crystal of approximate dimensions 0.4 × 0.4 × 0.2 mm was mounted on a glass fiber. Preliminary precession photographs indicated that the compound crystallized in

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