Nitrosyl Complexes of Rhenium. Crystal and Molecular Structures of the Tetraethylammonium Salts of Tetrabromo(ethanol)nitrosylrhenate(II) and of Acetonitriletetrabromonitrosylrhenate(II)

By **Gianfranco Ciani,* Domenico Giusto, Mario Manassero,** and **Mirella Sansoni,** Istituto di Chimica Generale ed Inorganica, Università degli Studi, via Venezian 21, Milano 20133, Italy

The crystal and molecular structures of the title compounds, $[NEt_4][Re(NO)Br_4(EtOH)]$ (I) and $[NEt_4][Re(NO)Br_4(MeCN)]$ (II), have been determined by the heavy-atom method from three-dimensional *X*-ray data collected by counter methods. Both compounds are orthorhombic. Compound (I) crystallizes in space group *Pbca*, $Z = 8$, with cell constants $a = 16.41(2)$, $b = 13.81(1)$, and $c = 16.91(2)$ Å; compound (II) is in space group $Pn2_1a$, $Z = 4$, with cell constants $a = 13.12(1)$, $b = 8.71(1)$, and $c = 17.25(2)$ Å. Least-squares refinements gave *R* 0.038 (I) and 0.030 (II), based on 837 and on 930 independent reflections. The anions display distorted octahedral geometry, with solvent molecules co-ordinated *trans* to nitrosyl groups. Mean Re–Br distances are 2.516 (I) and 2.511 Å (II). The nitrosyl groups are linked in an essentially linear manner, as NO^+ ligands. The Re–O(EtOH) [2.161(15) Å] and Re–N(MeCN) [2.153(11) Å] distances are longer than expected for single bonds, and this together with distortions of the octahedral geometry is discussed in comparison with the structures of similar compounds.

REACTION of the previously described pentahalogenonitrosyl compounds $[Re(NO)X_5]^{2-}$ ($X = Cl$ or Br) [1,2] with various common solvents produced a series of paramagnetic complexes $[Re^{II}(NO)X_4L]^-$, [3] in which L is *trans* to the nitrosyl group. For both classes of compound it was shown, on the basis of reactivity and chemical data, that the interaction between the rhenium atom and the ligand *trans* to nitrosyl is more labile than the other metal–ligand interactions.[2,3] In particular, the *trans*-Re–Cl bond in $[Re(NO)Cl_5]^{2-}$ was also considered to be weaker than the *cis*-metal–halogen bonds.[2] On the other hand, in the structure of the anion $[Ru(NO)Cl_5]^{2-}$ (refs. 4 and 5), Ru–Cl *trans* to NO was found to be shorter than the *cis* ones, and a similar shortening has been predicted for other octahedral compounds containing a σ-donor *trans* to a strong π-acceptor such as NO^+.

We have therefore undertaken the *X*-ray structure determinations of two members of the series $[Re(NO)X_4L]^-$, *i.e.* the tetraethylammonium salts of $[Re(NO)Br_4(EtOH)]^-$ (I) and of $[Re(NO)Br_4(MeCN)]^-$ (II), in order to ascertain that the solvent molecules belong definitely to the co-ordination sphere of the rhenium atoms, and to study the Re–L interactions. We also required information on the Re–NO bonding parameters.

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EXPERIMENTAL

Crystal Data.—(I), $C_{10}H_{26}Br_4N_2O_2Re$, $M = 711.8$, Orthorhombic, $a = 16.41(2)$, $b = 13.81(1)$, $c = 16.91(2)$ Å, $U = 3\,832$ Å^3, $D_m = 2.44(2)$ (by flotation), $Z = 8$, $D_c = 2.47$, $F(000) = 2\,648$. Space group *Pbca* (No. 61) from systematic absences. μ(Mo-K_α) = 154.8 cm^{-1}.

(II), $C_{10}H_{23}Br_4N_3ORe$, $M = 706.8$, Orthorhombic, $a = 13.12(1)$, $b = 8.71(1)$, $c = 17.25(2)$ Å, $U = 1\,971$ Å^3, $D_m = 2.36(2)$ (by flotation), $Z = 4$, $D_c = 2.38$, $F(000) = 1\,308$. Space group *Pnma* (No. 62) or $Pn2_1a$ [non-standard setting of $Pna2_1$ (No. 33)] from systematic absences. μ(Mo-K_α) = 151.1 cm^{-1}.

For both compounds cell dimensions were determined from precession photographs taken with Mo-K_α radiation ($\lambda = 0.7107$ Å).

Intensity Measurements.—Both intensity collections were performed on a PAILRED linear equi-inclination diffractometer by the ω scan method, by use of graphite-monochromatized Mo-K_α radiation.

The crystal of (I) was an irregular polyhedron of dimensions $0.11 \times 0.15 \times 0.33$ mm mounted along the axis of maximum elongation, *c*. 13 Levels of the reciprocal lattice, *hk*0—12, were collected within the sphere $2\theta \leqslant 50°$. The total number of collected reflections was 4 916.

The crystal of (II), a multifaced polyhedron of dimensions $0.13 \times 0.21 \times 0.40$ mm, was also mounted along the axis of maximum elongation, *b*. 9 Levels of the reciprocal lattice, *h*0—8*l*, were collected within the limit $2\theta \leqslant 53°$, corresponding to a total number of 4 090 reflections.

No decay was observed during the two data collections. Absorption corrections were computed by the method of Busing and Levy [6] with a sampling of 8^3 points within the crystals. Transmission factors were in the ranges 0.23—0.32 (I) and 0.13—0.23 (II). Integrated intensities were corrected for Lorentz and polarization factors, the latter being evaluated by taking into account the partial polarization of the incident beam.[7]

After removing all reflections having $\sigma(I)/I > 0.30$ a set of 1 526 reflections was obtained for compound (I), the number of independent reflections being 837. For (II) 1 742 reflections having $\sigma(I)/I \leqslant 0.25$ were selected, the independent reflections being 930.

Determination and Refinement of the Structures.—The solution of both structures was based on conventional Patterson and Fourier methods. Three-dimensional Patterson maps revealed the rhenium and bromine atom positions. Difference-Fourier syntheses, after preliminary refinements of the heavy atoms, showed the positions of all the remaining non-hydrogen atoms. The successive refinements of the structures were difficult because the location of the $ReBr_4$ moiety in the cell was such as to introduce supersymmetries in both cases. In (I) it became apparent, at this stage, that there was a pseudo-mirror plane at $z = 1/4$, approximately containing the Re, Br(1), and Br(4) atoms, the NO group, and the oxygen atom of the EtOH molecule, and relating the other two bromine atoms. This situation is responsible for the very low intensities observed for all *hkl* reflections with *h* odd and caused the presence, in the Fourier maps phased with the heavy atoms, of double images for the atoms lying outside the pseudo-plane. Refinements of the various possible models for the anion and the cation were carried out; the choice of the final structure model was based on the values of the agreement indices (especially with respect to the *h* odd reflections) and on consideration of bond distances and angles. Refinements were performed by full-matrix least-squares, the rhenium and bromine atoms being treated anisotropically and remaining atoms isotropically. The co-ordinates of the hydrogen atoms of all C_2H_5 groups were computed at the end of each cycle (C–H 1.08 Å; tetrahedral geometry) and their contribution to the structure factors was taken into account. The final agreement indices were: R 0.038 and R' 0.043 $\{R' = [\Sigma w(F_o - k|F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}}\}$.

The structure of (II) was first refined in the centrosymmetric space group *Pnma* with the anion lying in a special position on the symmetry plane at $y = 1/4$, which contained the Re, Br(2), and Br(3) atoms, the NO group, and the acetonitrile molecule, the other two bromine atoms being on opposite sides of the plane. The tetraethylammonium cation was located on the symmetry plane at $y = 3/4$, but appeared disordered: the four carbon atoms bonded to nitrogen were doubled by the mirror plane, approximately forming a cube of half-carbon atoms, whereas the four external carbon atoms appeared as two pairs correctly related by the plane. The agreement indices of the full-matrix refinements with the heavy atoms treated anisotropically were R 0.035 and R' 0.049. After discovery of some not too realistic bond parameters (N–O 0.98 Å), and in the hope of removing the disorder of the cation, we attempted refinement of the structure in the corresponding non-centrosymmetric space group $Pn2_1a$. Taking into account also the contribution of the imaginary part of the anomalous scattering for the Re and Br atoms [8] four refinements were carried out in order to choose the better tetraethylammonium model and to establish the absolute structure in relation to the polar axis. In all cases the agreement indices were found to be significantly [9] lower than for the centrosymmetric case and the model which gave the best agreement was assumed as the final one. At this stage the contribution to the structure factors of the ethyl hydrogen atoms was also taken into account.

In the full-matrix refinements the y co-ordinates of the NO atoms were widely oscillating about the value $y = 1/4$ and the calculated N–O bond distance was found to be short, with values of *ca*. 1.00 Å, a situation arising from the fact that the group lies approximately on the pseudo-mirror plane. Attempts to overcome the difficulties with the use of disordered models led to divergence. In order to get convergence for the NO atoms the final least-squares cycles were carried out with a two-block matrix, one containing the NO and the other all the remaining parameters. The final agreement values were R 0.030 and R' 0.035.

Attempts to refine the anion light atoms with anisotropic thermal parameters led in both structures to non-positive-definite matrices for some of the atoms lying nearest to the pseudo-planes.

The weighting scheme used in the refinements of both structures was $w = 1/(A + BF_o + CF_o^2)$ where A, B, and C were chosen on the basis of an analysis of $\Sigma w\Delta^2$ and had the following values in the final cycles: 274.4, -2.07, and 0.0048 (I), and 29.5, -0.58, and 0.0034 (II).

Atomic scattering factors were taken from ref. 10 for non-hydrogen atoms and from ref. 11 for hydrogen, the real

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TABLE 1

Positional and thermal parameters [a] (× 10^4) for (I)

(*a*) Anisotropic

Atom	x	y	z	b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}
Re	1 670(1)	579(1)	2 543(1)	20(1)	0(1)	3(1)	30(1)	2(2)	21(1)
Br(1)	2 878(1)	1 713(1)	2 470(3)	28(1)	−20(1)	−7(4)	48(1)	1(6)	34(1)
Br(2)	1 672(1)	476(2)	1 054(1)	35(1)	−4(2)	−4(2)	50(1)	−4(2)	24(1)
Br(3)	1 819(1)	548(2)	4 015(2)	37(1)	−18(2)	−5(1)	53(1)	0(2)	24(1)
Br(4)	645(1)	−768(1)	2 630(2)	30(1)	−25(1)	3(2)	49(1)	−12(3)	32(1)

(*b*) Isotropic

Atom	x	y	z	B/Å^2	Atom	x	y	z	B/Å^2
N(1)	957(9)	1 493(10)	2 591(17)	2.1(3)	C(4)	4 488(16)	3 054(21)	−783(19)	3.4(6)
O(1)	421(9)	2 064(10)	2 505(19)	4.0(3)	C(5)	4 643(16)	3 104(20)	721(19)	3.4(5)
O(2)	2 474(9)	−659(11)	2 506(17)	3.7(3)	C(6)	4 526(14)	1 543(17)	−26(17)	2.5(4)
C(1)	3 347(14)	−760(15)	2 288(15)	2.9(4)	C(7)	2 807(19)	2 117(24)	−412(23)	4.9(7)
C(2)	3 418(19)	−1 279(21)	1 534(21)	3.9(6)	C(8)	4 257(16)	4 134(20)	−843(19)	3.3(5)
N(2)	4 257(8)	2 615(15)	21(17)	2.1(3)	C(9)	5 549(19)	3 164(25)	691(22)	4.7(7)
C(3)	3 331(13)	2 650(16)	178(15)	2.3(4)	C(10)	4 355(17)	941(22)	739(21)	3.9(6)

(*c*) Hydrogen atoms [c,d]

Atom	x	y	z	Atom	x	y	z
H(11)	3 618	−50	2 230	H(71)	2 175	2 189	−247
H(12)	3 663	−1 160	2 744	H(72)	2 900	2 422	−993
H(21)	4 054	−1 350	1 378	H(73)	2 975	1 361	−417
H(22)	3 149	−1 989	1 592	H(81)	4 431	4 409	−1 417
H(23)	3 104	−879	1 078	H(82)	3 607	4 214	−766
H(31)	3 203	2 334	748	H(83)	4 571	4 537	−388
H(32)	3 128	3 394	172	H(91)	5 771	3 525	1 216
H(41)	5 138	2 993	−869	H(92)	5 802	2 443	662
H(42)	4 175	2 670	−1 248	H(93)	5 732	3 568	174
H(51)	4 421	3 839	766	H(101)	4 561	206	654
H(52)	4 490	2 713	1 254	H(102)	4 677	1 261	1 231
H(61)	4 207	1 189	−503	H(103)	3 709	942	860
H(62)	5 174	1 508	−132				

[a] The estimated standard deviation, in the last significant digit, is in parentheses here and in succeeding Tables. [b] The anisotropic temperature factors are given by exp $-(h^2b_{11} + k^2b_{22} + l^2b_{33} + hkb_{12} + hlb_{13} + klb_{23})$. [c] The hydrogen atoms are labelled **H(*ij*)** where *i* is the number of the carbon atom to which they are bonded. [d] The hydrogen atoms were all assigned an isotropic thermal factor of 4.0 Å^2.

TABLE 2 [a]

Positional and thermal parameters (× 10^4) for (II)

(*a*) Anisotropic

Atom	x	y	z	b_{11}	b_{12}	b_{13}	b_{22}	b_{23}	b_{33}
Re	−1 767(1)	−2 500	−914(1)	55(1)	−12(6)	0(1)	139(1)	−6(4)	26(1)
Br(1)	−1 621(2)	−5 373(3)	−952(1)	129(2)	4(4)	25(3)	156(3)	82(3)	52(1)
Br(2)	−1 570(1)	−2 456(7)	−2 366(1)	98(1)	−50(13)	−7(1)	176(2)	49(5)	27(1)
Br(3)	−1 633(1)	−2 572(9)	533(1)	79(1)	−35(13)	1(1)	336(4)	−14(9)	29(1)
Br(4)	−1 649(2)	376(2)	−934(1)	96(1)	−51(4)	−12(3)	131(3)	−6(4)	62(1)

(*b*) Isotropic

Atom	x	y	z	B/Å^2	Atom	x	y	z	B/Å^2
N(1)	−3 117(8)	−2 493(74)	−915(7)	3.9(2)	C(4)	−4 837(16)	1 560(27)	−1 034(12)	4.8(4)
O(1)	−3 874(7)	−2 455(65)	−924(6)	4.5(2)	C(5)	−3 955(16)	3 497(29)	−1 781(12)	4.7(4)
N(2)	−132(8)	−2 289(27)	−882(7)	3.8(2)	C(6)	−5 886(18)	3 528(31)	−1 727(13)	5.4(5)
C(1)	721(9)	−2 232(24)	−874(9)	3.2(2)	C(7)	−4 202(17)	425(28)	−2 601(13)	5.3(4)
C(2)	1 834(13)	−2 155(26)	−849(10)	5.2(3)	C(8)	−5 783(22)	236(41)	−1 049(17)	7.6(7)
N(3)	−4 929(8)	2 658(36)	−1 766(5)	3.0(2)	C(9)	−3 880(19)	4 642(31)	−2 430(15)	5.9(5)
C(3)	−5 027(18)	1 661(29)	−2 512(13)	5.3(5)	C(10)	−5 844(16)	4 549(29)	−982(13)	5.1(4)

(*c*) Hydrogen atoms

Atom	x	y	z	Atom	x	y	z
H(31)	−5 751	1 075	−2 510	H(73)	−4 235	−351	−2 114
H(32)	−4 977	2 391	−3 017	H(81)	−5 714	−503	−549
H(41)	−4 109	981	−1 045	H(82)	−6 512	811	−1 035
H(42)	−4 896	2 234	−510	H(83)	−5 725	−441	−1 570
H(51)	−3 860	4 119	−1 244	H(91)	−3 149	5 212	−2 404
H(52)	−3 335	2 693	−1 850	H(92)	−3 955	4 057	−2 978
H(61)	−5 958	4 236	−2 238	H(93)	−4 480	5 483	−2 372
H(62)	−6 520	2 740	−1 697	H(101)	−6 538	5 208	−935
H(71)	−4 328	−205	−3 131	H(102)	−5 762	3 826	−477
H(72)	−3 460	964	−2 620	H(103)	−5 201	5 321	−1 018

[a] See footnotes to Table 1.

and imaginary parts of the anomalous dispersion being also taken into account for the heavy atoms.[8]

Final difference-Fourier maps did not show peaks exceeding 1.0 eÅ^{-3} for (I) and 0.8 eÅ^{-3} for (II).

The results of the refinements are reported in Tables 1 and 2. Final lists of observed and calculated structure factors moduli are given in Supplementary Publication No. SUP 21396 (3 pp., 1 microfiche).*

Computations.—All computations were performed on a UNIVAC 1106 computer. For absorption correction a local programme was used, in which the directions of primary and diffracted beams were evaluated as described elsewhere.[12] Counter data reduction and statistical analysis for weighting schemes were based upon Fortan programmes by Sansoni. In addition, local versions of entries No. 7528, 7531, 7532, and 7535 in the 1966 ' International World List of Crystallographic Programs ' were used for Fourier analysis, structure-factor, and least-squares calculations; Johnson's ORTEP was used for thermal ellipsoid plotting, and a programme by Domenicano and Vaciago for computation of the molecular parameters.

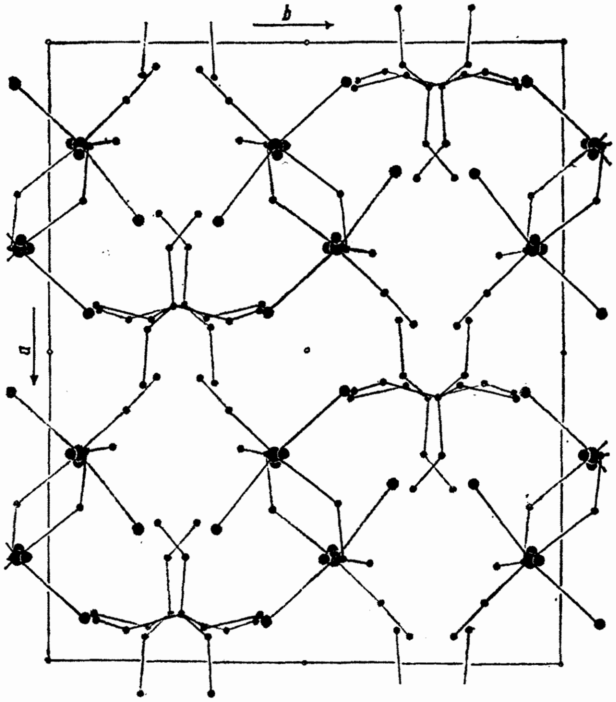

FIGURE 1 Projection of the structure of $[NEt_4][Re(NO)Br_4(EtOH)]$, compound (I), down the *c* axis

DESCRIPTION OF THE STRUCTURES AND DISCUSSION

The crystal structures of compounds (I) and (II) are illustrated in Figures 1 and 2, and consist of the packings of discrete $[NEt_4]^+$ cations and $[Re(NO)Br_4(EtOH)]^-$ and $[Re(NO)Br_4(MeCN)]^-$ anions, respectively. All non-bonded intermolecular contacts are normal van der Waals contacts.

The geometries of the anions are shown in Figure 3 and bonding parameters are reported in Table 3 for (I) and in Table 4 for (II). Both anions display distorted octahedral co-ordination geometries, with the four bromine atoms lying on an equatorial plane and the nitrosyl group and the solvent molecule in axial direction. All the Re–Br distances are similar and their means [2.516 (I) and 2.511 Å (II)] can be compared with the corresponding mean values in $[ReOBr_4(H_2O)]^-$ (2.51 Å)[13], $[ReOBr_4(MeCN)]^-$ (2.48 Å),[14] and $[ReBr_6]^{2-}$ (2.51 Å).[15] The rhenium atoms do not lie in the ' best planes ' defined by the bromine atoms but are displaced in the direction of the NO group by 0.18 Å for (I) and

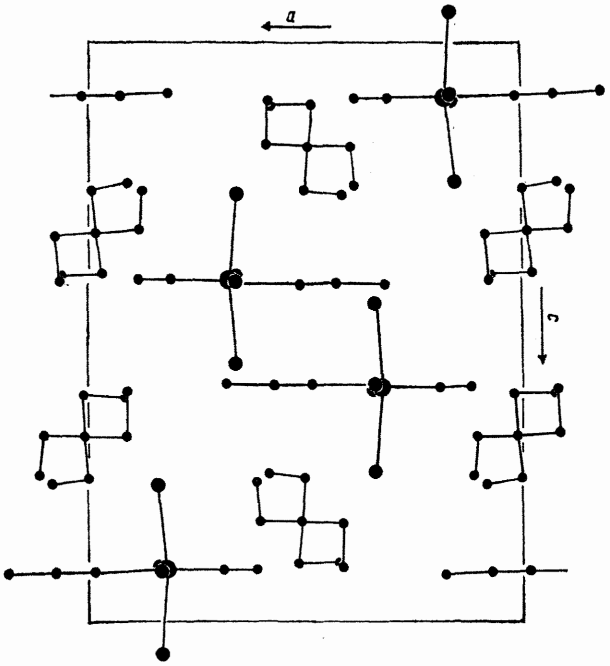

FIGURE 2 Projection of the structure of $[NEt_4][Re(NO)Br_4(MeCN)]$, compound (II), down the *b* axis

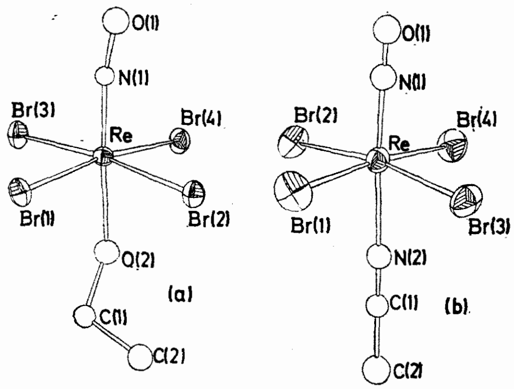

FIGURE 3 ORTEP drawings of the anions (a) (I) and (b) (II); thermal ellipsoids at 30% probability

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* See Notice to Authors No. 7, in *J.C.S. Dalton*, 1974, Index issue (items less than 10 pp. are supplied as a full-size copies).

[12] G. Ciani, M. Manassero, and M. Sansoni, *J. Appl. Cryst.*, 1971, **4**, 173.

[13] F. A. Cotton and S. J. Lippard, *Inorg. Chem.*, 1965, **4**, 1621.

[14] F. A. Cotton and S. J. Lippard, *Inorg. Chem.*, 1966, **5**, 416.

[15] F. A. Cotton and S. J. Lippard, *Inorg. Chem.*, 1965, **4**, 59.

0.19 Å for (II). This distortion is also indicated by the means of the (ON)–Re–Br apical angles [94.1° (I), and 94.5° (II)]. The *cis*-Br–Re–Br angles are all close to 90° and an idealized C_{4v} symmetry can be assigned to the rhenium co-ordination polyhedron.

TABLE 3

Selected interatomic distances (Å) and angles (°) in (I)

Re–Br(1)	2.529(2)	Br(1)–Re–Br(2)	89.1(2)
Re–Br(2)	2.521(3)	Br(1)–Re–Br(3)	89.0(2)
Re–Br(3)	2.502(4)	Br(2)–Re–Br(4)	91.0(1)
Re–Br(4)	2.512(2)	Br(3)–Re–Br(4)	89.7(1)
Re–N(1)	1.723(15)	Br(1)–Re–Br(4)	170.4(1)
Re–O(2)	2.161(15)	Br(2)–Re–Br(3)	173.0(1)
N(1)–O(1)	1.19(2)	Br(1)–Re–N(1)	94.6(5)
O(2)–C(1)	1.49(3)	Br(2)–Re–N(1)	95.1(1.0)
C(1)–C(2)	1.47(4)	Br(3)–Re–N(1)	91.8(1.0)
Br · · · Br(*cis*) *	3.549	Br(4)–Re–N(1)	94.9(5)
Br · · · N(1) *	3.15	Br(1)–Re–O(2)	90.6(4)
Br · · · O(2) *	3.19	Br(2)–Re–O(2)	85.7(8)
Br(1) · · · H(11)	2.75	Br(3)–Re–O(2)	87.5(8)
N(2)–C(3)	1.54(3)	Br(4)–Re–O(2)	79.9(4)
N(2)–C(4)	1.54(4)	Re–N(1)–O(1)	169(3)
N(2)–C(5)	1.50(4)	Re–O(2)–C(1)	132.1(1.3)
N(2)–C(6)	1.55(3)	N(1)–Re–O(2)	174.7(7)
C(3)–C(7)	1.51(4)	O(2)–C(1)–C(2)	110(2)
C(4)–C(8)	1.54(4)	N(2)–C–C *	114
C(5)–C(9)	1.49(4)	C–N(2)–C *	109
C(6)–C(10)	1.56(5)		

* Mean.

TABLE 4

Selected interatomic distances (Å) and angles (°) in (II)

Re–Br(1)	2.511(3)	Br(1)–Re–Br(2)	88.9(2)
Re–Br(2)	2.519(2)	Br(1)–Re–Br(3)	89.8(2)
Re–Br(3)	2.505(2)	Br(2)–Re–Br(4)	88.0(2)
Re–Br(4)	2.510(2)	Br(3)–Re–Br(4)	92.0(2)
Re–N(1)	1.771(11)	Br(1)–Re–Br(4)	171.7(1)
Re–N(2)	2.153(11)	Br(2)–Re–Br(3)	170.1(1)
N(1)–O(1)	0.99(2)	Br(1)–Re–N(1)	95(2)
N(2)–C(1)	1.12(2)	Br(2)–Re–N(1)	95.8(4)
C(1)–C(2)	1.46(2)	Br(3)–Re–N(1)	94.1(4)
Br · · · Br(*cis*) *	3.540	Br(4)–Re–N(1)	93(2)
Br · · · N(1) *	3.18	Br(1)–Re–N(2)	90.6(6)
Br · · · N(2) *	3.18	Br(2)–Re–N(2)	85.5(3)
N(3)–C(3)	1.56(3)	Br(3)–Re–N(2)	84.6(3)
N(3)–C(4)	1.59(3)	Br(4)–Re–N(2)	81.6(6)
N(3)–C(5)	1.47(3)	Re–N(1)–O(1)	178(6)
N(3)–C(6)	1.47(3)	Re–N(2)–C(1)	177(2)
C(3)–C(7)	1.53(4)	N(1)–Re–N(2)	175(2)
C(4)–C(8)	1.69(4)	N(2)–C(1)–C(2)	179(2)
C(5)–C(9)	1.50(4)	N(3)–C–C *	112
C(6)–C(10)	1.56(4)	C–N(3)–C *	109

* Mean.

The Re–N(1) [1.723(15) and 1.771(11) Å] and N(1)–O(1) bond lengths in (I) [1.19(2) Å] are in the range found for corresponding interactions in a number of second- and third-row transition-metal nitrosyls. The N(1)–O(1) bond length in compound (II) [0.99(2) Å] is very short, probably as a consequence of some disorder, which it was not possible to resolve (see Experimental section). The Re–N–O interaction is slightly bent in (I) [169(3)°] and the short N–O distance in (II) may be interpreted as an indication of the presence of similar bending in this compound too. The extent of the bendings, however, and the uncertainties in the values, are such that, for both compounds, we may consider the Re–N–O interactions as being essentially linear, and therefore indicating the presence of NO^+ ligands. Similar moderate bendings have been found in other octahedral complexes containing one NO^+ or an isoelectronic $ArN_2{}^+$ ligand, *e.g.* in $[Ru(NO)(NH_3)_5]^{3+}$ [172.8(9)°],[16] $[Ru(NO)(NH_3)_4(OH)]^{2+}$ [173.8(3)],[16] and $[RuCl_3(p\text{-}N_2C_6H_4Me)(PPh_3)_2]$ [171.2(9)°].[17] A linear M–N–O interaction for an octahedral d^5 metal-atom complex of C_{4v} symmetry agrees with the predictions based on MO diagrams (see refs. 2 and 18 and refs. therein). Following the scheme suggested for the isoelectronic anion $[Re(NO)Cl_5]^{2-}$ we have an $e^4b_1{}^1$ ground-state,[2] in agreement with the magnetic behaviour of these compounds.

The solvent molecules, EtOH and MeCN, are found to be definitely co-ordinated to the rhenium atoms by single σ bonds. The Re–O(EtOH) and Re–N(MeCN) bond distances [2.161(15) and 2.153(11) Å] are *ca.* 0.1 Å longer than expected {see *e.g.* 2.05(3) Å for Re–N in $[ReCl_3(MeCN)(PPh_3)_2]$ (ref. 19)}. By comparison the Re–O and Re–N single-bond lengths obtained from the sums of the relevant covalent radii [20] are 2.03 and 2.07 Å.

The co-ordination of the ethanol molecule in (I) is influenced by intramolecular contacts: the Re–O(2)–C(1) angle [132.1(1.3)°] is very probably determined by the necessity for minimizing the non-bonded contacts between the bromine and the hydrogen atoms of the ethanol. Data for co-ordinated alcohol molecules are scarce: M–O–C 121.9(1.1)° is reported for a bonded methanol molecule in a uranium complex.[21] In ethoxo-complexes the M–O–C angles are generally larger than in the present case {*e.g.* 149° in $[NbOCl_2(EtO)(bipy)]$ [22] and 165.5° in $Ti_2Cl_4(EtO)_4$ [23]}, the difference being due to the fact that the hydrogen atom bonded to oxygen prevents an excessive enlargement of the angle through non-bonded contacts.

The MeCN molecule is co-ordinated in an essentially linear manner, with Re–N(2)–C(1)177(2)°. Non-linear metal–acetonitrile linkages have been found: in two copper complexes (Cu–N–C 165 and 159°), where the fact was ascribed to the partial use of sp^2 hybrid orbitals by the nitrogen,[24] and in $[ReOBr_4(CH_3CN)]^-$ [170(4)° ref. 14]. The present value is very similar to that reported (175°) for $[ReCl_3(MeCN)(PPh_3)_2]$;[19] it seems probable that an important role in determining this angle is also played by intra- and inter-molecular contacts. Bonding parameters within the solvent molecules are normal.

Some further comments on the rhenium–solvent

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interactions are required. As mentioned earlier, in the structure of $[NH_4]_2[Ru(NO)Cl_5]$ the axial Ru–Cl distance was slightly but significantly shorter [2.357(1) Å] than the equatorial ones (mean 2.376 Å).[4] It was suggested that the shortening was due to the strong π-acceptor and poor σ-donor capability of NO^+ so that the axial Cl^- competes successfully with it for σ electrons. It was further suggested that a similar shortening would be found in other octahedral complexes containing a σ-donor and a π-acceptor ligands mutually *trans*, such as $[Ru(NO)(NO_2)_4(OH)]^{2-}$ (ref. 25) and $[Ru(NO)(NH_3)_4(OH)]^{2+}$ (ref. 16). However, in both (I) and (II), we have found rather long M–L(ax) bond lengths. If the lengthenings are true (the accuracy of our results may not be too high for reasons already cited in the Experimental section), they are probably due to intramolecular steric effects: as pointed out for $[OsNCl_5]^{2-}$ (ref. 26), the multiply bonded ligand forces away the equatorial ones, causing a displacement of the metal from the basal plane and lengthening of the M–L(ax) bond in order to minimize L(ax) $\cdots$ L(eq) repulsions. Compounds (I) and (II exhibit average apical angles more than 2° larger than for $[Ru(NO)Cl_5]^{2-}$ (92.0°),[4] owing to the presence of the bulkier bromine atoms. The rhenium–solvent bonds are therefore weakened, so that the N(1) $\cdots$ L(eq) become very similar to the L(ax) $\cdots$ L(eq) contacts. [3.15 and 3.19 Å in (I), and 3.18 and 3.18 Å in (II)]. These contact values are also comparable with the corresponding ones in $[ReOBr_4(H_2O)]^-$ (3.24 and 3.17 Å), and $[ReOBr_4(MeCN)]^-$ (3.22 and 3.14 Å), in which the more strongly bonded oxo-ligand causes a large weakening of the rhenium–solvent interactions, Re–O(H_2O) 2.32(4),[13] and Re–N(MeCN) 2.31(6) Å.[14]

We thank the Italian Consiglio Nazionale delle Ricerche for financial support.

[4/2562 *Received, 9th December*, 1974]

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