# Nitrosyl Complexes of Rhenium. Part 3.[1,2] Crystal and Molecular Structure of Tetraethylammonium Tetrachloronitrosyl(pyridine)rhenate(1−)

By **Gianfranco Ciani,* Domenico Giusto, Mario Manassero,** and **Mirella Sansoni,** Centro di Studio per la Sintesi e la Struttura dei Composti dei Metalli di Transizione nei Bassi Stati di Ossidazione del C.N.R., Istituto di Chimica Generale ed Inorganica dell'Università, via Venezian 21, 20133 Milano, Italy

The crystal and molecular structure of the title compound has been established by Patterson and Fourier methods based on three-dimensional $X$-ray counter data. The salt gives monoclinic crystals, space group $C2/c$, with unit-cell constants $a = 22.28(2)$, $b = 10.67(1)$, $c = 16.98(2)$ Å, $\beta = 94.15(8)°$, and $Z = 8$. The structure has been refined by least-squares methods to $R$ 0.030 for 2 697 independent reflections. The anion $[ReCl_4(NO)(py)]^-$ shows a distorted-octahedral geometry, with the four chlorine atoms lying in an equatorial plane and the other two ligands in axial directions. The Re–Cl bond lengths are in the range 2.353—2.379(2) Å. The nitrosyl group is linked linearly to the rhenium atom, as $[NO]^+$, with Re–N and N–O bonds of 1.749(6) and 1.171(9) Å. The Re–N(pyridine) bond distance [2.218(6) Å] is rather long, probably because of steric interactions involving the chlorine atoms and the *ortho*-hydrogen atoms of the pyridine.

CONTINUING our investigation on the reactivity of the anions $[Re(NO)X_5]^{2-}$ (X = Cl or Br) we have recently studied the reactions with various unidentate $N$-donor base ligands such as amines, pyridine (py), methylpyridines, and related species. Two kinds of products were obtained, namely the paramagnetic monosubstituted anions $[Re(NO)LX_4]^-$ and the diamagnetic trisubstituted compounds $[Re(NO)L_3X_2]$.[3] Our interest in the stereochemistry of these products, especially in order to obtain further data concerning the possible *trans* influence of the nitrosyl ligand (see ref. 1 and refs. therein) and the nature of the Re–N–O interaction, has prompted us to undertake $X$-ray analyses on members of the two families.

In this paper we report the complete results of the structure determination of the tetraethylammonium salt of the anion $[ReCl_4(NO)(py)]^-$, which are discussed also in comparison with the previously described solvent-containing anions $[ReBr_4(NO)L]^-$ (L = MeCN or EtOH).[1]

## EXPERIMENTAL

*Crystal Data.*—$C_{13}H_{25}Cl_4N_3ORe$, $M = 567.4$, Monoclinic, $a = 22.28(2)$, $b = 10.67(1)$, $c = 16.98(2)$ Å, $\beta = 94.15(8)°$, $U = 4\,026.3$ Å$^3$, $D_m = 1.85(2)$ (by flotation), $Z = 8$, $D_c = 1.87$ g cm$^{-3}$, $F(000) = 2\,200$, space group $Cc$ (no. 9) or $C2/c$ (no. 15), from systematic absences, Mo-$K_\alpha$ radiation, $\lambda = 0.710\,7$ Å, $\mu$(Mo-$K_\alpha$) = 69.1 cm$^{-1}$.

*Intensity Measurements.*—The crystal sample was an elongated polyhedron of dimensions 0.11 × 0.19 × 0.54 mm. The intensity measurements were carried out on a linear equi-inclination Pailred diffractometer by the ω-scan method, using graphite-monochromatized Mo-$K_\alpha$ radiation. The crystal was mounted along the axis of maximum elongation, $b$. Eleven levels of the reciprocal lattice, $h0l$—$h10l$, were collected within the limits $\mu \leqslant 19.46°$ and $2\theta \leqslant 52°$, corresponding to a total number of 3 871 reflections. No decay was observed during the data collection. The integrated intensities were corrected for Lorentz, polarization, and absorption effects. The transmission factors were calculated following the methods of refs. 4 and 5, and were found in the range 0.34—0.55. After removing all the reflections having $\sigma(I)/I > 0.25$, a final set of 2 697 independent data was used in the solution and refinement of the structure.

*Determination and Refinement of the Structure.*—The structure solution was based on a three-dimensional Patterson map, which showed the locations of the Re atoms. After a preliminary refinement of the rhenium parameters in the centrosymmetric space group $C2/c$, a successive difference-Fourier map showed all the remaining non-hydrogen atoms. The refinements were carried out successfully in the centrosymmetric space group, using block-diagonal least-squares methods. The cations were found to lie on two types of special positions. The one containing N(3) is placed on a crystallographic two-fold axis, coincident with a proper $C_2$ axis of the cation itself. The other cation, containing N(4), lies on an inversion centre, being disordered; the four C atoms directly bound to the nitrogen atom are doubled, giving rise approximately to a cube of half atoms, whereas the four external carbon atoms appear as two pairs correctly related by the inversion centre. All the non-hydrogen atoms of the anion were refined anisotropically, while the atoms of the cations were treated isotropically. The co-ordinates of the cationic hydrogen atoms were computed at the end of each cycle of refinement (C–H 1.08 Å, tetrahedral geometry) and their contribution to the structure factors was taken into account. Before completion of the refinement a difference-Fourier map revealed peaks in positions suitable for the pyridine hydrogen atoms. They were not refined but their contribution to the structure factors was also taken into account (assigning an overall thermal factor $B$ of 5.0 Å$^2$).

The final agreement indices $R$ and $R'$ $\{= [\Sigma w(F_o - k|F_c|)^2/\Sigma w F_o^2]^{\frac{1}{2}}\}$ were 0.030 and 0.038. The weighting scheme used was $w = 1/(A + BF_o + CF_o^2)$ where in the final cycles $A$, $B$, and $C$ had the values 7.9, −0.12, and 0.001 4, chosen on the basis of an analysis of $\Sigma w(F_o - k|F_c|)^2$. Atomic scattering factors were taken from ref. 6 for

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non-hydrogen atoms and from ref. 7 for hydrogen. The Re and Cl factors were corrected both for the real and imaginary part of the anomalous dispersion.[8] The final difference-Fourier map was rather flat, except for a peak of *ca.* 1.2 e Å$^{-3}$ in the vicinity of the Re atom.

TABLE 1

Final positional parameters ($\times$ 10$^4$)

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Re | 1 150(1) | 1 668(1) | 1 183(1) |
| Cl(1) | 2 165(1) | 1 017(2) | 1 415(1) |
| Cl(2) | 151(1) | 2 250(2) | 814(1) |
| Cl(3) | 1 475(1) | 3 716(2) | 886(1) |
| Cl(4) | 837(1) | −454(2) | 1 279(1) |
| N(1) | 1 091(3) | 2 034(6) | 2 179(3) |
| O | 1 059(3) | 2 293(7) | 2 845(3) |
| N(2) | 1 246(2) | 1 252(5) | −80(3) |
| C(1) | 1 743(3) | 1 600(8) | −424(4) |
| C(2) | 1 824(3) | 1 330(8) | −1 206(4) |
| C(3) | 1 383(3) | 719(8) | −1 651(4) |
| C(4) | 866(3) | 353(8) | −1 303(4) |
| C(5) | 819(3) | 632(7) | −518(4) |
| N(3) | 5 000 | 827(9) | 2 500 |
| C(31) | 4 462(5) | −38(14) | 2 428(7) |
| C(32) | 4 967(7) | 1 657(18) | 3 225(10) |
| C(33) | 3 858(6) | 694(15) | 2 280(8) |
| C(34) | 4 987(7) | 881(16) | 4 007(9) |
| N(4) | 2 500 | 2 500 | 5 000 |
| C(41) | 1 889(7) | 1 953(17) | 4 928(10) |
| C(42) | 2 678(9) | 3 209(21) | 4 334(12) |
| C(43) | 2 570(8) | 3 257(19) | 5 750(10) |
| C(44) | 2 916(8) | 1 289(18) | 5 167(10) |
| C(45) | 1 398(6) | 3 135(13) | 4 784(8) |
| C(46) | 2 618(6) | 2 421(15) | 3 523(8) |
| H(311) | 4 515 | −659 | 1 951 |
| H(312) | 4 455 | −558 | 2 959 |
| H(321) | 5 338 | 2 284 | 3 246 |
| H(322) | 4 561 | 2 175 | 3 163 |
| H(331) | 3 488 | 39 | 2 233 |
| H(332) | 3 804 | 1 326 | 2 767 |
| H(333) | 3 866 | 1 224 | 1 739 |
| H(341) | 4 962 | 1 510 | 4 502 |
| H(342) | 4 609 | 243 | 3 986 |
| H(343) | 5 401 | 355 | 4 072 |
| H(411) | 1 871 | 1 320 | 4 446 |
| H(412) | 1 829 | 1 455 | 5 456 |
| H(421) | 2 398 | 4 013 | 4 297 |
| H(422) | 3 129 | 3 487 | 4 477 |
| H(431) | 3 029 | 3 511 | 5 849 |
| H(432) | 2 305 | 4 078 | 5 670 |
| H(441) | 2 821 | 860 | 5 707 |
| H(442) | 2 850 | 633 | 4 701 |
| H(451) | 946 | 2 764 | 4 729 |
| H(452) | 1 445 | 3 768 | 5 281 |
| H(453) | 1 487 | 3 631 | 4 251 |
| H(461) | 2 757 | 2 998 | 3 047 |
| H(462) | 2 901 | 1 600 | 3 583 |
| H(463) | 2 155 | 2 137 | 3 399 |
| H(1) | 2 070 | 2 120 | −50 |
| H(2) | 2 150 | 1 620 | −1 470 |
| H(3) | 1 450 | 420 | −2 160 |
| H(4) | 530 | −290 | −1 650 |
| H(5) | 440 | 500 | −300 |

The results of the refinements are reported in Table 1. Thermal factors and the final list of computed and observed structure-factor moduli are reported in Supplementary Publication No. SUP 22249 (8 pp.).* Calculations were carried out on a UNIVAC 1106 computer at the computing centre of Milan University, using local programs.

## DISCUSSION

The crystal packing consists of discrete $[NEt_4]^+$ cations and $[ReCl_4(NO)(py)]^-$ anions in the ratio 1 : 1. The cations lie on special positions: one half of them on inversion centres (being disordered) and the other half on two-fold crystallographic axes (coincident with proper $C_2$ axes of the cations). Both types have a transoid conformation of idealized $D_{2d}$ symmetry. A view of the packing down the *b* axis is shown in Figure 1.

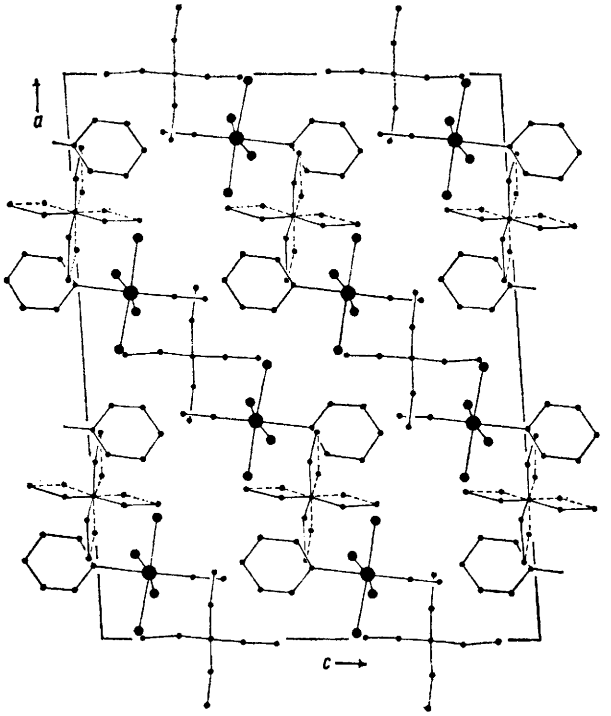

FIGURE 1 Projection of the structure down the *b* axis

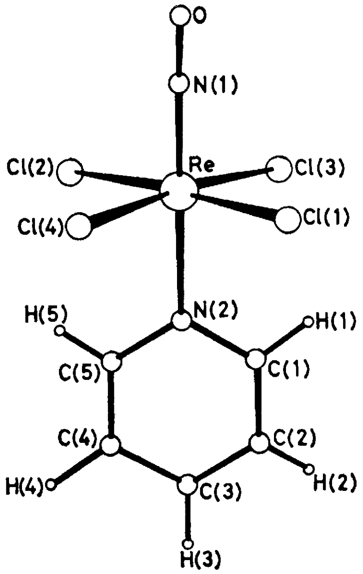

FIGURE 2 A view of the anion $[ReCl_4(NO)(py)]^-$

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

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The anion is illustrated in Figure 2. Interatomic distances and angles are reported in Table 2. The rhenium atom exhibits a distorted-octahedral co-ordination, with the nitrosyl group and the pyridine ligand in mutual *trans* positions. The plane of the pyridine ring nearly bisects the planes defined by Re, Cl(1), Cl(2), NO and, respectively, Re, Cl(3), Cl(4), NO (dihedral angles between the ' best planes ' of 43.4 and 46.7°). The idealized anion symmetry is therefore $C_{2v}$.

TABLE 2

Interatomic distances (Å) and angles (°) within the salt $[NEt_4][ReCl_4(NO)(py)]$

| | | | |
|---|---|---|---|
| (*a*) Anion | | | |
| Re–Cl(1) | 2.371(2) | C(2)–C(3) | 1.36(1) |
| Re–Cl(2) | 2.353(2) | C(3)–C(4) | 1.39(1) |
| Re–Cl(3) | 2.368(2) | C(4)–C(5) | 1.38(1) |
| Re–Cl(4) | 2.379(2) | Cl · · · Cl(*cis*) * | 3.342 |
| Re–N(1) | 1.749(6) | N(1) · · · Cl * | 3.03 |
| Re · · · O | 2.920(6) | N(2) · · · Cl * | 3.14 |
| Re–N(2) | 2.218(6) | Cl(1) · · · C(1) | 3.257(8) |
| N(1)–O | 1.171(9) | Cl(3) · · · C(1) | 3.255(9) |
| N(2)–C(1) | 1.34(1) | Cl(2) · · · C(5) | 3.288(8) |
| N(2)–C(5) | 1.34(1) | Cl(4) · · · C(5) | 3.264(8) |
| C(1)–C(2) | 1.38(1) | | |
| C–H(py) | 0.93—1.15 (av. 1.01) | | |
| Cl(1)–Re–Cl(3) | 90.2(1) | N(2)–Re–Cl(1) | 86.8(2) |
| Cl(1)–Re–Cl(4) | 89.4(1) | N(2)–Re–Cl(2) | 87.2(2) |
| Cl(2)–Re–Cl(3) | 89.9(1) | N(2)–Re–Cl(3) | 85.7(2) |
| Cl(2)–Re–Cl(4) | 89.6(1) | N(2)–Re–Cl(4) | 85.7(2) |
| Cl(1)–Re–Cl(2) | 174.0(1) | Re–N(2)–C(1) | 120.5(5) |
| Cl(3)–Re–Cl(4) | 171.4(1) | Re–N(2)–C(5) | 121.4(5) |
| Re–N(1)–O | 178.9(7) | C(1)–N(2)–C(5) | 118.1(6) |
| N(1)–Re–N(2) | 178.2(3) | N(2)–C(1)–C(2) | 122.0(7) |
| Re–N(2) · · · C(3) | 179.2(3) | C(1)–C(2)–C(3) | 119.5(8) |
| N(1)–Re–Cl(1) | 92.4(2) | C(2)–C(3)–C(4) | 119.1(7) |
| N(1)–Re–Cl(2) | 93.6(2) | C(3)–C(4)–C(5) | 118.4(7) |
| N(1)–Re–Cl(3) | 92.6(2) | C(4)–C(5)–N(2) | 122.9(7) |
| N(1)–Re–Cl(4) | 96.0(2) | | |
| (*b*) Cations | | | |
| N(3)–C(31) | 1.51(1) | N(4)–C(43) | 1.51(2) |
| N(3)–C(32) | 1.52(2) | N(4)–C(44) | 1.60(2) |
| C(31)–C(33) | 1.56(2) | C(41)–C(45) | 1.68(2) |
| C(32)–C(34) | 1.56(2) | C(42)–C(46) | 1.61(3) |
| N(4)–C(41) | 1.48(2) | C(43)–C(46′) | 1.52(2) |
| N(4)–C(42) | 1.44(2) | C(44)–C(45′) | 1.64(2) |
| C–N(3)–C * | 109 | C–N(4)–C * | 109 |
| N(3)–C–C * | 112 | N(4)–C–C * | 110 |

* Mean value.

The rhenium atom is significantly displaced (0.15 Å) out of the ' best plane ' of the chlorine atoms toward the nitrosyl ligand, as is also indicated by the value of the mean apical angle (ON)–Re–Cl (93.6°). This angle is somewhat larger than the mean apical (ON)–M–Cl angles in $[RuCl_5(NO)]^{2-}$ (92.0°)[9] and in $[IrCl_5(NO)]^-$ (92.1°),[10] but the average values of the (ON) · · · Cl non-bonding contacts are comparable in the three cases. The Re–Cl distances in the present compound are similar, falling in the range 2.353—2.379(2) Å (mean 2.368 Å). A variety of Re–Cl bond lengths is reported in the literature which cover a rather large range, depending on the metal oxidation state and on intramolecular interactions. Our mean value is, in particular, comparable with those found in $[Re_2Cl_4(PEt_3)_4]$ [2.36(4) Å][11] and in $[ReCl_3(NCMe)(PPh_3)_2]$ (mean 2.37 Å).[12]

The Re–N–O interaction is linear, as expected for this $d^5$ octahedral compound, the nitrosyl group being bound as $[NO]^+$. The Re–N(1) and N(1)–O distances have values similar to those found in $[ReBr_4(NO)(HOEt)]^-$ [1.723(15), 1.19(2) Å][1] and in $[ReCl_2(NO)(PMePh_2)_3]$ [1.775(10), 1.182(14) Å].[13] The Re–N(2) bond length [2.218(6) Å] is long when compared with the value obtained from the sum of the relevant covalent radii (2.08 Å).[14] The only known structure containing rhenium–pyridine bonds is that of $[ReO_2(py)_4]^+$, with a mean Re–N distance of 2.14 Å.[15] Other examples of rather long Re–N single σ bonds are those found in $[ReBr_4(NO)(NCMe)]^-$ [Re–N(NCMe) 2.153(11) Å],[1] in $[ReO_2(en)_2]^+$ (en = ethylenediamine) (mean Re–N 2.16 Å),[16] in $[Re_2Cl_4O_3(en)_2]$ (mean Re–N 2.18 Å),[17] and in $[ReCl_2(NH_3)(N_2HPh)(PMe_2Ph)_2]^+$ [Re–N(NH$_3$) 2.200(13) Å].[18] A Re–N bond length longer than that of the present structure was found only in $[ReBr_4O(NCMe)]^-$ [2.31(6) Å].[19]

We have already made some comments in ref. 1 concerning the *trans* influence of the $[NO]^+$ ligand. Further structural data have been obtained since then, namely for $[IrCl_5(NO)]^-$ and $[IrBr_5(NO)]^-$,[10] which seem to support the original suggestion by Veal and Hodgson[9] {from the structure of $[RuCl_5(NO)]^{2-}$} that when the good π-acceptor but poor σ-donor ligand $[NO]^+$ is *trans* to a good σ-donor X ligand a short M–X bond is to be expected. However, various other factors must be taken into account, such as the metal oxidation state, and, mainly, the presence of intramolecular steric interactions, which may have some lengthening effect on the M–X bond as in the case of the anions[1] $[ReBr_4(NO)(NCMe)]^-$ and $[ReBr_4(NO)(HOEt)]^-$. In the present structure the Re–N(py) bond is long, very probably as a consequence of the non-bonding contacts involving the equatorial chlorine atoms and the pyridine C and H atoms in *ortho* positions. The mean values of the closest Cl · · · C and Cl · · · H interactions (3.27 and

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2.80 Å) are significantly shorter than the sum of the relevant van der Waals radii.[14]

Finally, the atoms of the pyridine ring are approximately co-planar, with displacements out of the ' best plane ' (neglecting the H atoms) less than 0.01 Å. The mean N–C and C–C bond distances (1.34 and 1.38 Å) are normal.

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