

THE CRYSTAL STRUCTURE OF (AsPh₄)₂[Re(NO)(H₂O)(CN)₄] · 5H₂O

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Abstract—The crystal structure of (AsPh₄)₂[Re(NO)(H₂O)(CN)₄] · 5H₂O has been determined from three-dimensional X-ray diffraction data. The [Re(NO)(H₂O)(CN)₄]²⁻ ion has a distorted octahedral geometry with the following bond distances: Re—NO = 1.732(7), Re—OH₂ = 2.165(5) and Re—CN_{av} = 2.09 Å. The NO group bond is at 178.4(7)° to the rhenium atom and N—O = 1.181(8) Å. The rhenium atom is displaced by 0.17 Å out of the plane formed by the four carbon atoms of the cyano ligands towards the nitrosyl ligand.

Transition metal nitrosyl complexes have recently received considerable attention due to their possible uses in pollutant control (reduction of NO in exhaust fumes emitted by internal combustion engines) and the production of organo-nitrogen compounds from nitric acid assisted by transition metal catalysts.¹⁻³

One of the most important aspects of transition metal nitrosyl complexes is the bonding nature of the nitric oxide in these type of complexes. The three principal metal to nitrogen interactions are: (i) linear M—N—O groups; (ii) bent M—N—O groups; and (iii) bridging NO groups.³ The first X-ray structure which unequivocally proved the existence of bent NO groups was done by Ibers in 1968.⁴ His results have shown that the metal-nitrosyl bond angle in the [IrCl(CO)(NO)(PPh₃)₂]⁺ cation can be as small as 124°. Structural results in recent years have revealed that a large percentage of nitrosyl transition complexes have linear M—NO orientations and that a variety of angles, between 170° and 120°, are observed for those complexes which have bent M—NO groups. It is now customary to regard linear metal-nitrosyl bonds as derived from NO⁺ and bent (120°) from NO⁻. In spite of numer-

ous efforts to predict the bonding mode of the nitrosyl in different complexes using $\nu(\text{NO})$ and available structural results, no reliable method has yet been formulated.⁵⁻⁷

Cyano nitrosyl complexes of general formula [M(NO)(CN)₅]ⁿ⁻ have been reported for vanadium(I),⁸ chromium(I),⁹ manganese(I),¹⁰ molybdenum(0)¹¹ and rhenium(I).¹² A number of these complexes have been crystallographically characterized¹³⁻¹⁵ and all these cyano complexes have, without exception, linear M—N—O groups, i.e. NO⁺ ligands (see above).

Our interest in cyano nitrosyl complexes stems from our continuous research on the influence of terminal ligands on the physical and chemical properties of transition metal complexes. The influence of both the oxo (O²⁻) and nitrido (N³⁻) ligands on the substitution behaviour of [ML(H₂O)(CN)₄]ⁿ⁻ type of complexes have been kinetically and structurally investigated.¹⁶⁻¹⁹ Recently we turned our attention to nitrosyl as a terminal ligand and decided to prepare the [Re(NO)(H₂O)(CN)₄]²⁻ complex in order to determine the influence of this terminal group on the substitution behaviour of these type of complexes. We have succeeded in isolating the [Re(NO)(H₂O)(CN)₄]²⁻ ion and hereby report the X-ray crystal structure determination of (AsPh₄)₂[Re(NO)(H₂O)(CN)₄] · 5H₂O.

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EXPERIMENTAL

Synthesis

$K_2[Re(NO)(H_2O)(CN)_4]$ was successfully prepared by using a slight variation to the method described by Bhattacharyya and Roy.¹⁹ Instead of using excess cyanide we only introduced a 1:4 Re:CN ratio which enabled us to isolate the $K_2[Re(NO)(H_2O)(CN)_4]$ complex (hygroscopic salt). $(AsPh_4)_2[Re(NO)(H_2O)(CN)_4] \cdot 5H_2O$ was obtained by preparing concentrated $K_2[Re(NO)(H_2O)(CN)_4]$ in water and adding this solution to an ethanol-water solution containing $AsPh_4Cl$. Green-yellow crystals suitable for data collection were obtained after *ca* 30 h (yield 60%).

Spectral data: $\nu(CN)$, 2080; $\nu(NO)$, 1677 cm^{-1} ; $\lambda_{max} = 490$ nm.

The tetraphenylphosphonium salt of $[Re(NO)(H_2O)(CN)_4]^{2-}$ was isolated and analysed before crystals of the title complex, suitable for a structure determination, were obtained.

Analysis for $ReC_{52}H_{52}N_5O_7P_2 \cdot ((PPh_4)_2[Re(NO)(H_2O)(CN)_4] \cdot 5H_2O)$; found (calc. data): Re, 17.7 (16.8); C, 56.2 (56.4); H, 4.6 (4.7); N, 6.6 (6.3); O, 9.1 (10.1); P, 5.8 (5.6)%. The disparity in the rhenium and oxygen analyses are attributed to $KReO_4$ impurity.

Crystal data

$(AsPh_4)_2[Re(NO)(H_2O)(CN)_4] \cdot 5H_2O$, $M_r = 1194.96$ crystallizes in the triclinic space group P_1 with cell dimensions $a = 13.642(2)$, $b = 13.905(2)$, $c = 16.557(5)$ Å, $\alpha = 109.70(2)$, $\beta = 89.80(2)$, $\gamma = 117.37(2)^\circ$, $V = 2582(1)$ Å³, $Z = 2$, $D_{exp} = 1.53$ g cm^{-3} and $\mu(Mo-K\alpha) = 3.68$ mm⁻¹. The three-dimensional intensity data were collected on an Enraf-Nonius CAD-4 diffractometer (Nb-filter) using Mo- $K\alpha$ radiation ($\lambda = 0.7107$ Å). A crystal with dimensions $0.24 \times 0.40 \times 0.50$ mm was used for data collection. Eleven per cent decomposition of the crystal was observed during the data collection probably due to loss of some of the large number of lattice water molecules present in the structure. A total of 4898 independent reflections were measured of which all were considered as observed [$I > 3\sigma(I)$]. Lorentz, polarization and absorption corrections were applied. The structure was solved by means of the Patterson and Fourier methods. The final R was 0.045 using all the observed reflections, and refinement of all the non-hydrogen atoms anisotropically. The hydrogen atom positions were calculated as 'riding' on the adjacent carbon atom [$d(C-H) = 0.93$ Å] and refined with an overall isotropic thermal parameter. Atomic scattering factors

were obtained from Cromer and Mann.²⁰ The SHELXS86²¹ and SHELXL93²² programs were used for all the calculations. A final difference Fourier showed no sign of disorder and a residual peak of $2.8 e \text{ \AA}^{-3}$ was observed within 1 Å of the heavy atom.

RESULTS AND DISCUSSION

The most important bond lengths and angles are reported in Table 1. The numbering scheme of the $[Re(NO)(H_2O)(CN)_4]^{2-}$ anion is shown in Fig. 1.

The Re atom is octahedrally surrounded by the nitrosyl, an aqua ligand *trans* to the nitrosyl and four cyano groups *cis* to the nitrosyl group. The average C≡N bond lengths of 1.15 Å compares favourably with those found in other rhenium cyano complexes with rhenium in the +5 oxidation state. All the Re—C—N moieties are linear within experimental error. The Re—NO bond distance of

Table 1. Selected bond lengths (Å) and angles (°) for the $[Re(NO)(H_2O)(CN)_4]^{2-}$ ion with standard deviations in parentheses

Re(1)—N(5)	1.732(7)
Re(1)—C(3)	2.071(12)
Re(1)—C(1)	2.080(14)
Re(1)—C(2)	2.105(8)
Re(1)—C(4)	2.106(8)
Re(1)—O(2)	2.165(5)
O(1)—N(5)	1.181(8)
C(3)—N(3)	1.171(11)
C(1)—N(1)	1.129(13)
N(2)—C(2)	1.138(10)
C(4)—N(4)	1.158(9)
N(5)—Re(1)—C(3)	93.6(4)
N(5)—Re(1)—C(1)	97.2(3)
C(3)—Re(1)—C(1)	169.2(3)
N(5)—Re(1)—C(2)	94.1(3)
C(3)—Re(1)—C(2)	90.8(4)
C(1)—Re(1)—C(2)	89.1(4)
N(5)—Re(1)—C(4)	93.5(3)
C(3)—Re(1)—C(4)	90.0(4)
C(1)—Re(1)—C(4)	88.7(4)
C(2)—Re(1)—C(4)	172.3(3)
N(5)—Re(1)—O(2)	178.0(3)
C(3)—Re(1)—O(2)	84.5(3)
C(1)—Re(1)—O(2)	84.7(3)
C(2)—Re(1)—O(2)	86.4(3)
C(4)—Re(1)—O(2)	86.0(3)
N(3)—C(3)—Re(1)	179.3(8)
N(1)—C(1)—Re(1)	176.7(9)
N(4)—C(4)—Re(1)	175.6(7)
O(1)—N(5)—Re(1)	178.4(7)
N(2)—C(2)—Re(1)	176.5(7)

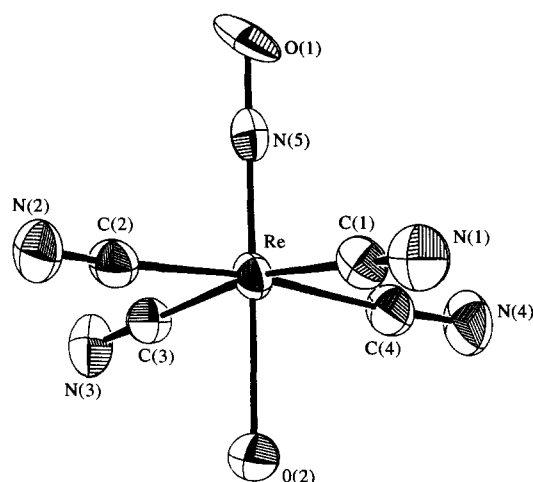


Fig. 1. Perspective drawing and numbering scheme of the $[\text{Re}(\text{NO})(\text{H}_2\text{O})(\text{CN})_4]^{2-}$ ion.

1.732(7) Å is in good agreement with the 1.71 and 1.66 Å which were found in $[\text{Cr}(\text{NO})(\text{CN})_5]^{3-}$ (ref. 14) and $[\text{Mn}(\text{NO})(\text{CN})_5]^{3-}$ (ref. 15), respectively. The N—O bond distance of 1.181(8) Å is in excellent agreement with those found in other nitrosyl complexes³ while the linear Re—N—O orientation [178.4(7)°] corresponds to metal nitrosyl angles obtained in other nitrosyl cyano complexes.^{14,15} The Re—OH₂ bond distance of 2.165(5) Å agrees well with the 2.142(7) Å of the corresponding bond in $[\text{ReO}(\text{H}_2\text{O})(\text{CN})_4]^-$ (ref. 23) suggesting that the *trans* influence of the oxo and the nitrosyl groups are comparable. The *trans* influence of the nitrosyl group is also evident from the mode of distortion from the regular octahedral geometry of the $[\text{Re}(\text{NO})(\text{H}_2\text{O})(\text{CN})_4]^{2-}$ ion. The rhenium atom is displaced by 0.17 Å out of the plane formed by the carbon atoms of the four cyano groups towards the nitrosyl group and corresponds well with the 0.16 Å which were observed in $[\text{Mo}(\text{NO})(\text{CN})_5]^{3-}$ (ref. 11).

The AsPh_4^+ cations are tetrahedral with the C—As—C angles ranging from 107.6 to 111.5°. The average As—C bond length of 1.91 Å is in good agreement with those found in other complexes^{24,25} while the C—C bonds are considered to be normal.

The isolation and characterization of the $[\text{Re}(\text{NO})(\text{H}_2\text{O})(\text{CN})_4]^{2-}$ ion confirms the existence of the aqua complex under certain conditions and opens up the possibility of performing substitution reactions on this complex. It also opens up the possibility of isolating the corresponding complex for other nitrosyl transition metal complexes to enable a comparative study on these complexes to be carried out.

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