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# Chemical structure of the azidonitridotetracyanorhenate(V) ion

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## Abstract

The crystal structure of $Cs_2Na[ReN(N_3)(CN)_4]$ was determined by single-crystal X-ray diffraction and refined to $R=0.054$ using 1573 observed reflections. The yellow–orange crystals are orthorhombic, space group *Pnma*, with $a=15.772(3)$, $b=7.766(4)$, $c=10.456(3)$ Å and $Z=4$. The $[ReN(N_3)(CN)_4]^{3-}$ ion has a distorted octahedral geometry with the rhenium atom displaced by 0.34 Å towards the nitrido ligand from the plane formed by the carbon atoms of the four cyano ligands. Bond distances found: $Re–C_{av}=2.11(1)$, $Re{\equiv}N=1.65(2)$, Re–N(azido) = 2.36(2) Å.

## Introduction

The protonation and substitution behaviour of the *trans*-dioxotetracyano complexes of molybdenum(IV), tungsten(IV), rhenium(V) and technetium(V) are well established [1–15]. It was found that all of these complexes undergo two protonation reactions with the formation of the oxoaqua complex and that the aqua ligand in these complexes may be substituted by monodentate ligands. Kinetic results (such as observed linear free energy relationships [8, 13] as well as positive volume of activation [7]) indicated that these substitution reactions proceed via a dissociative activation.

The nitride ion ($N^{3-}$), like the isoelectronic oxide ion ($O^{2-}$), can function as a terminal ligand in transition metal complexes. The nitrido–aqua complex of rhenium(V) ($[ReN(H_2O)(CN)_4]^{2-}$) has recently been isolated as the tetraphenylarsonium salt and structurally characterized [16]. This crystal structure determination clearly showed a normal bonding mode for the cyano ligands. (It was claimed [17] that the cyano ligands in $K_2[ReN(CN)_4]\cdot H_2O$ are nitrogen bonded, that the Re–N–C moiety is bent and that there is no bonded ligand *trans* to the nitrido group, i.e. the rhenium atom is penta-coordinated.) The crystal structure of $(AsPh_4)_2[ReN(H_2O)(CN)_4]\cdot 5H_2O$ [16] also proved that the coordination site *trans* to the nitrido ligand is not vacant but that the nitridoaquatetracyano complex of rhenium(V) exists in the solid state and most probably also in aqueous solution. This structure determination clearly points to a very large *trans* influence of the nitrido ligand: the Re–$OH_2$ bond distance is 2.496(7) Å in comparison with 2.142(7) Å in $[ReO(H_2O)(CN)_4]^-$ [11] while the rhenium atom is displaced by 0.35 Å out of the plane formed by the four carbon atoms of the cyano ligands towards the terminal nitrido ligand. It is therefore expected that the nitrido–aqua complex should undergo substitution reactions similar to the oxo–aqua complexes of Mo(IV), W(IV), Re(V) and Tc(V). The title complex ($[ReN(N_3)(CN)_4]^{3-}$) has indeed been synthesized by means of the reaction

$$[ReN(H_2O)(CN)_4]^{2-}+N_3^- \rightleftharpoons [ReN(N_3)(CN)_4]^{3-}$$

just as in the case of the corresponding oxo–molybdenum(IV) complex [6]. The crystal structure of $Cs_2Na[ReN(N_3)(CN)_4]$ has been determined as part of a programme to investigate the substitution behaviour of complexes of the type $[ML(H_2O)(CN_4]^{m-}$ where M = Mo(IV), W(IV), Tc(V), Re(V); L = $O^{2-}$, $N^{3-}$.

## Experimental

$K_2[ReN(CN)_4]\cdot H_2O$ was prepared by the method of Johnson [18]. The azido complex was prepared as follows. 0.010 g (0.025 mmol) $K_2[ReN(CN)_4]\cdot H_2O$ was dissolved in 10 cm$^3$ water. 10 cm$^3$ of a solution containing 0.10 g (1.5 mmol) $NaN_3$ and 0.015 g (0.09 mmol) CsCl were added to the solution of $[ReN(CN)_4]^{2-}$. Well shaped yellow–orange crystals of $Cs_2Na[ReN(N_3)(CN)_4]$ suitable for X-ray analysis were obtained after 2 days of slow evaporation at room temperature. The yield was greater than 80%.

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TABLE 1. Summary of crystal data, data collection and structure refinement

| | |
|---|---|
| Compound | $Cs_2Na[ReN(N_3)(CN)_4]$ |
| Formula weight | 635.1 |
| Crystal system | orthorhombic |
| Space group | *Pnma* |
| $a$ (Å) | 15.772(3) |
| $b$ (Å) | 7.766(4) |
| $c$ (Å) | 10.456(3) |
| $Z$ | 4 |
| $D_{calc}$ (g cm$^{-3}$) | 3.29 |
| $\mu$ (Mo K$\alpha$) (cm$^{-1}$) | 156.9 |
| $F$(000) | 1104 |
| Crystal size (mm) | 0.15 × 0.10 × 0.075 |
| $T$ (K) | 298 |
| Scan type | $\omega$–$2\theta$ |
| Scan range | $0.59 + 0.34 \tan \theta$ |
| Index range | $0 \leqslant h \leqslant 10$, $0 \leqslant k \leqslant 14$, $0 \leqslant l \leqslant 22$ |
| No. unique reflections measured | 1861 |
| No. unique reflections observed, $I < 3\sigma(I)$ | 1573 |
| No. variables | 85 |
| $R$ | 0.054 |
| $R_w$ (unit weights) | 0.054 |

TABLE 2. Fractional coordinates (× 10$^4$) and equivalent isotropic thermal parameters (Å × 10$^3$) for $Cs_2Na[ReN(N_3)(CN)_4]$ with e.s.d.s. in parentheses

| | $x/a$ | $y/b$ | $z/c$ | $U_{eq}$[a] |
|---|---|---|---|---|
| Re | 1072.4(4) | 2500.0 | 2188.7(6) | 18.4(1) |
| Cs(1) | 3626(1) | 2500 | 5395(2) | 42 |
| Cs(2) | 3585(1) | 2400 | 10736(2) | 58 |
| Na | 1504(4) | 2500 | 8294(8) | 25(2) |
| C(1) | 1906(8) | 4364(17) | 2947(13) | 29(2) |
| C(2) | 107(8) | 4351(18) | 1959(14) | 31(3) |
| N(1) | 2367(9) | 5312(2) | 3371(16) | 53(4) |
| N(2) | −441(8) | 5285(19) | 1824(16) | 51(3) |
| N(3) | 616(11) | 2500 | 4338(17) | 53(6) |
| N(4) | 1128(11) | 2500 | 5151(18) | 54(6) |
| N(5) | 1601(13) | 2500 | 5971(2) | 155(20) |
| N(11) | 1417(10) | 2500 | 701(16) | 32(4) |

[a] $U_{eq} = \frac{1}{3}\Sigma_i \Sigma_j U_{ij} a_i^* a_j^* (\mathbf{a}_i \cdot \mathbf{a}_j)$.

### *Spectral data*

IR, KBr disc, cm$^{-1}$: $\nu$(Re≡N), 1074(vs); $\nu$(CN), 2124(vs); $\nu$(N–N), 2068(s).

### *Solution of the structure*

Complete crystal data and parameters for the data collection are reported in Table 1. The unit cell parameters were determined from a least-squares fit of 25 reflections with $17 < \theta < 20°$. The intensity measuring range was $3 < \theta < 30°$. An Enraf-Nonius CAD-4F diffractometer using graphite monochromated Mo K$\alpha$ radiation, $\lambda = 0.7107$ Å, was used for the data collection. The mean intensity of three standard reflections, measured every 3600 s of X-ray exposure, varied from the initial value by −11.3%. The intensity data were corrected for this effect. Empirical absorption corrections [19] were made with a minimum correction factor of 0.805 and maximum of 0.998. The intensities were also corrected for Lorentz and polarization effects.

The atomic scattering factors were obtained from ref. 20. The structure was solved by means of the Patterson and Fourier methods using SHELXS86 and subjected to anisotropic full-matrix least-squares refinement for all the atoms using SHELX76 [21]. The final atomic parameters are listed in Table 2.

## Results and discussion

A very interesting aspect of the structure of this nitrido complex is the fact that $Cs_2Na[ReN(N_3)(CN)_4]$ is isomorphous with $Cs_2Na[MoO(N_3)(CN)_4]$ [6] and $Cs_2Na(WO(N_3)(CN)_4]$ [7]. The packing pattern is thus also typically salt-like, the same as in the case of $Cs_2Na[MoO(N_3)(CN)_4]$ which has already been discussed in detail [6].

The most important bond lengths and angles within the complex are listed in Table 3. The numbering scheme of the atoms in the $[ReN(N_3)(CN)_4]^{3-}$ anion is shown in the perspective drawing, Fig. 1.

The rhenium atom is octahedrally coordinated to a nitrido ligand, an azido ligand *trans* to the nitrido ligand and four cyano ligands just as in the case of oxoazido complexes of Mo(IV) and W(IV) [6, 7]. The Re–C≡N bond distances and angles are normal compared to those of similar structural data mentioned in 'Introduction'. The Re≡N distance (1.65(2) Å) is suggestive of strong p$\pi$–d$\pi$ ligand-to-metal interaction and a large *trans* influence of the nitrido ligand. The rhenium atom is displaced by 0.34 Å out of the plane formed by the four carbon atoms of the cyano ligands. This out of plane distance (which is also an indicator of the relative metal–ligand bond strength and thus of the *trans* influence of the ligand) may be compared with that of 0.28 Å found in $[MoO(N_3)(CN)_4]^{3-}$ [6] and of 0.35 Å

TABLE 3. Interatomic bond distances (Å) and angles (°) in the $[ReN(N_3)(CN)_4]^{3-}$ anion

| | | | |
|---|---|---|---|
| Re–C(1) | 2.110(13) | Re–C(2) | 2.108(12) |
| Re–N(3) | 2.36(2) | Re–N(11) | 1.65(2) |
| C(1)–N(1) | 1.13(2) | C(2)–N(2) | 1.14(2) |
| N(3)–N(4) | 1.17(2) | N(4)–N(5) | 1.14(3) |
| C(1)–Re–C(2) | 91.4(5) | C(1)–Re–N(3) | 80.4(5) |
| C(2)–Re–N(3) | 83.6(5) | C(1)–Re–N(11) | 98.6(5) |
| C(2)–Re–N(11) | 97.5(5) | N(3)–Re–N(11) | 178.5(7) |
| Re–C(1)–N(1) | 177.5(13) | C(1)–Re–C(1) | 86.6(7) |
| Re–C(2)–N(2) | 176.6(13) | C(2)–Re–C(2) | 86.0(7) |
| Re–N(3)–N(4) | 118.7(14) | N(3)–N(4)–N(5) | 177.5(23) |

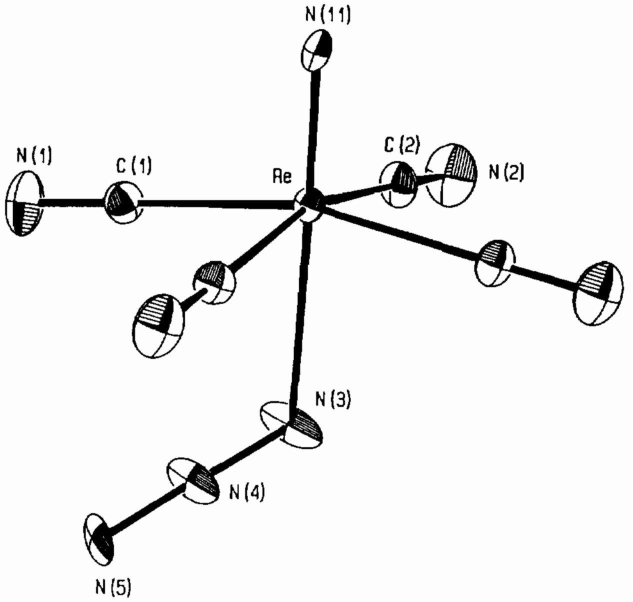

Fig. 1. Perspective view of the $[ReN(N_3)(CN)_4]^{3-}$ ion with atomic labelling scheme.

found in $[ReN(H_2O)(CN)_4]^{2-}$ [16]. The rhenium atom, being displaced towards the nitrido ligand along the N≡Re–N(3) axis, forces the *cis*-bonded cyano ligands and the N(3) atom closer together. The average N(3)–Re–C bond angle is 82.0°.

The Re–N(3) bond distance (2.36(2) Å) is slightly longer than the corresponding bond distance in $[MoO(N_3)(CN)_4]^{3-}$ (2.29(2) Å) [6] in agreement with the larger *trans* influence of the nitrido ligand compared to that of the oxo ligand. This is not surprising in view of the fact that the nitrido ligand is one of the strongest $\pi$-electron donors known. This large *trans* influence of the nitrido ligand (compared to that of the oxo ligand) is especially noted when comparing the Re–$OH_2$ bond distances in $[ReN(H_2O)(CN)_4]^{2-}$ (2.496(7) Å) [16] and $[ReO(H_2O)(CN)_4]^{-}$ (2.142(7) Å) [11]. The Re–N(3)–N(4) angle is in agreement with a $sp^2$ hybridization for N(3) and this together with the near equal N–N distances within the azido ligand suggests small $\pi$-interaction with the rhenium atom [22]. The relative high thermal parameter for N(5) is not unexpected since this atom is at the end of the Re–N–N–N chain. The azido chain is linear within experimental error as found in $[MoO(N_3)(CN)_4]^{3-}$ [6] and $[MoN(N_3)(Ph_2P(CH_2)_2PPh_2)_2]$ [23].

This structure determination has proved that the aqua ligand *trans* to the nitrido ligand in $[ReN(H_2O)(CN)_4]^{2-}$ may be substituted by monodentate ligands and that only the aqua ligand is substituted even in the presence of a large excess of the incoming ligand. In view of the large *trans* influence of the nitrido ligand one would also anticipate a dissociative reaction mode as we observed for the substitution reactions of $[MoO(H_2O)(CN)_4]^{2-}$ [4, 5], $[WO(H_2O)(CN)_4]^{2-}$ [7–9] and $[ReO(H_2O)(CN)_4]^{1-}$ [12, 13]. A kinetic study of the substitution reactions of $[ReN(H_2O)(CN)_4]^{2-}$ is currently underway.

## Supplementary material

Tables of a complete list of bond lengths and bond angles, anisotropic thermal parameters and of observed and calculated structure factors are available on request from the authors.

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