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# Chemical Structure of Dicaesium Sodium Azidooxotetracyanomolybdate(IV)

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## Abstract

The structure of $Cs_2Na[MoO(CN)_4(N_3)]$ was determined by single-crystal X-ray diffraction methods from diffractometer data and refined to $R = 0.051$. The royal-blue crystals are orthorhombic, space group *Pnma*, with cell dimensions $a = 15.874$, $b = 7.875$, $c = 10.371$ Å, $Z = 4$. The $[MoO(CN)_4(N_3)]^{3-}$ ion is a distorted octahedron with the Mo atom displaced 0.28 Å towards oxygen from the plane containing four cyano groups. Bond distances found: $Mo{-}C_{av} = 2.17(1)$; $Mo{=}O = 1.70(1)$; Mo–N-(azido) = 2.29(2) Å. The azido chain is linear and bond at an angle of 121(1)° with Mo. The sodium ion has an octahedral environment, whilst caesium ions display distorted six- and nine-atom environments respectively.

## Introduction

The nature of the anionic species, when a bidentate ligand reacts with the *trans*-dioxotetracyanomolybdate(IV) ion in weakly alkaline solution (equilibrium 1):

$$[MoO_2(CN)_4]^{4-} + L{-}L + 2H^+ \rightleftharpoons [MoO(CN)_3(L{-}L)]^- + H_2O + CN^- \qquad (1)$$

was recently confirmed through structure determinations of $Na[MoO(CN)_3(phen)]\cdot 2phen$ [1] and $Na[MoO(CN)_3(phen)]\cdot 2phen\cdot CH_3OH\cdot H_2O$ [2]. Since the $[MoO_2(CN)_4]^{4-}$ ion exists in this form only in strong alkaline solution (>1 M) [3], it is rather the protonated forms $[MoO(OH)(CN)_4]^{3-}$ and $[MoO(H_2O)(CN)_4]^{2-}$ to be considered as the reactive species in (1). This supposition was confirmed in that no reaction occurred with 1,10-phenanthroline at $[OH^-] > 1$ M.

The existence of the protonated forms was duly established through structure determinations of $[Cr(en)_3][MoO(OH)(CN)_4]\cdot H_2O$, $[Pt(en)_2][MoO(H_2O)(CN)_4]\cdot 2H_2O$ [4] and $(Ph_4P)_2[MoO(H_2O)(CN)_4]\cdot 4H_2O$ [5]. These studies indicated a weak $Mo{-}OH_2$ bond (2.27–2.48 Å) as a result of the strong *trans* influence of the oxygen atom in the Mo=O bond. This ground state destabilization allows in principle substitution of the $H_2O$ molecule by stronger monodentate nucleophiles. The fact that a cyano ligand was also displaced from the parent ion in (1) raised the question in the course of our kinetic studies as to whether $H_2O$ (and/or $OH^-$) or $CN^-$ will be displaced first in a two–step mechanism involving a bidentate ligand such as 1,10-phenanthroline. The dissociative nature of labile cyano complexes in for example the reaction between $Ni(CN)_4^{2-}$ and ethylenediamine [6] emphasizes the importance of the M–CN bond strength. In addition it is also known that the Mo=O and Mo–C bond lengths in the Mo(IV) oxocyano complexes vary significantly, due to factors such as large resultant anionic charge in $[MoO_2(CN)_4]^{4-}$ ions [7] or distortional isomerization [5]. These, together with the total decomposition of the above complexes in weakly acidic media or in the presence of a $CN^-$ scavenger such as formaldehyde in weakly alkaline media, classify them as labile and make $CN^-$ substitution a viable concept. In order to elucidate this point we undertook a structure determination of an azido substituted product of the $[MoO_2(CN)_4]^{4-}$ ion.

## Experimental

### *Preparation of Complexes*

$NaK_3[MoO_2(CN)_4]\cdot 6H_2O$ was prepared from $K_4Mo(CN)_8\cdot 2H_2O$ by direct sunlight photolysis as reported previously [1]. The azido complex was prepared as follows: 3 M HCl was added dropwise to 7.0 ml 0.1 M $NaHCO_3$ containing 0.001 mol dissolved $NaK_3[MoO_2(CN)_4]\cdot 6H_2O$ until the pH was between 9.5 and 10. To this solution was added 0.04 mol $NaN_3$, stirred and heated to *ca.* 40 °C. A second solution, also at *ca.* 40 °C and containing 0.0024 mol CsCl in 2.0 ml 0.1 M $NaHCO_3$, was

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TABLE I. Fractional Atomic Co-ordinates ($\times 10^4$) and Thermal Parameters ($\times 10^3$) with e.s.d.s in Parentheses.

| Atom | Point Symmetry | $x$ | $y$ | $z$ | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Mo | m | 1085.5(8) | 2500 | 2184(1) | 10.7(6) | 22.4(7) | 26.3(7) | – | –1.4(5) | – |
| C(1) | 1 | 1926(7) | 4383(15) | 2997(12) | 18(5) | 24(6) | 45(7) | 0(5) | 1(5) | 1(6) |
| C(2) | 1 | 93(7) | 4364(15) | 1953(12) | 20(5) | 23(6) | 49(7) | –2(5) | –1(5) | 4(6) |
| N(1) | 1 | 2386(7) | 5306(17) | 3437(13) | 30(6) | 51(8) | 80(9) | –17(6) | –1(6) | –18(7) |
| N(2) | 1 | –444(7) | 5284(16) | 1772(13) | 31(6) | 46(7) | 75(9) | 18(6) | –3(6) | 3(7) |
| N(3) | m | 624(9) | 2500 | 4274(15) | 13(7) | 84(13) | 33(8) | – | 5(7) | – |
| N(4) | m | 1105(9) | 2500 | 5152(14) | 10(7) | 140(19) | 20(8) | – | 9(7) | – |
| N(5) | m | 1558(12) | 2500 | 5988(18) | 20(10) | 520(70) | 20(10) | – | 0(8) | – |
| O | m | 1481(8) | 2500 | 658(12) | 20(7) | 69(10) | 37(7) | – | 0(6) | – |
| Na | m | 1501(4) | 2500 | 8365(6) | 15(3) | 29(3) | 32(3) | – | –0(2) | – |
| Cs(1) | m | 8614(1) | 2500 | 9559(1) | 32(1) | 47(1) | 49(1) | – | –0(1) | – |
| Cs(2) | m | 3596(1) | 2500 | 777(1) | 25(1) | 83(1) | 60(1) | – | –12(1) | – |

added to the first, covered with a thin plastic film and left for crystallization (16 h). Royal-blue, cube-like and excessively-twinned crystals (71% yield) of $Cs_2Na[MoO(CN)_4(N_3)]$ were obtained. Only a few needle–like crystals from the same batch proved suitable for X-ray analysis.

*Crystal Data*

$C_4N_7OCs_2NaMo$, molecular weight = 546.8, orthorhombic space group *Pnma*, $a = 15.874$, $b = 7.875$, $c = 10.371$ Å, $Z = 4$, $\mu$(Mo-K$\alpha$) = 64.6 cm$^{-1}$, measured density = 2.815 g cm$^{-3}$. Three-dimensional data were collected for $\theta$-values between 3 and 26° on a Philips PW1100 four circle single crystal X-ray diffractometer using graphite monochromated Mo-K$\alpha$ radiation ($\lambda$ = 0.7107 Å). A crystal with dimensions of 0.18 × 0.15 × 0.45 mm was used for the data collection. No decomposition was detectable during the data collection. A total of 1481 independent reflections were measured, of which 1345 with $I > 3\sigma(I)$ ($\sigma(I)$ based on counting statistics) were used in the structure refinement. Only Lorentz and polarization corrections were applied.

*Structure Determination*

Since there are only four formula units per unit cell, the molybdenum atoms must occupy the four-fold special position with site-symmetry m. The three-dimensional Patterson function showed, however, that all the heavy metal vector peaks occurred at P(U, 0, W) and P(U, ½, W), which indicated that the caesium atoms also occupied the same four-fold position. Distinction between these vector peaks was made on a trial-and-error basis, coupled with subsequent Fourier maps.

The final $R$ of 0.051 was obtained by a 5-cycle full-matrix least-squares refinement using anisotropic thermal parameters for all atoms. A final difference-Fourier map showed no relevant residues. Tabulated atomic scattering factors [8] were used and anomalous dispersion corrections [9] applied to molybdenum atoms. Calculations were performed with the X-ray 72 system of programs [10]. Final atomic co-ordinates are listed in Table I. A list of observed and calculated structure factors may be obtained from the authors.

## Results and Discussion

The packing pattern (Fig. 1) of $Cs_2Na[MoO(CN)_4(N_3)]$ is typical salt-like with the cations, molybdenum atoms, azide nitrogens and oxygen atoms situated in the mirror planes at y = ¼ and ¾. Alternating sodium and molybdenum atoms form a nearly linear chain along [001]. This chain is

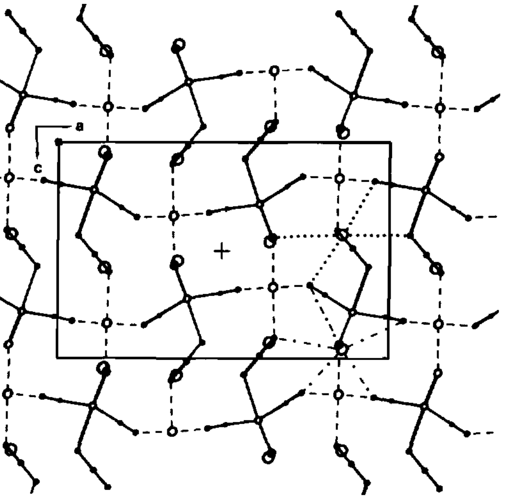

Fig. 1. Projection of the structure along [010]. Dashed lines: sodium contacts. Dotted lines: Cs(2) contacts. Dash–dotted lines: Cs(1) contacts.

further made up of alternating azido and oxo groups between these atoms, the non-linearity being the result of the bent Mo–azide bond, as well as neighbouring sodium and molybdenum atoms not sharing a common nitrogen atom of the azido group. Two similar zig-zag chains of the type Na···N≡C–Mo, each bisecting on neighbouring sodium and molybdenum atoms, form a two-dimensional network operating in the [100] and [010] directions. The net result is that each sodium ion serves as a link between six surrounding anions. These contacts are made up of one oxygen and five nitrogen atoms at the vertices of a near-perfect octahedron (Table II). Calculated shape characteristics [11] of this octahedron gave dihedral δ-angles varying between 69.3 and 71.4° and a twist angle $\phi_{av}$ = 59.4°, compared to theoretical values of 70.5 and 60° for the ideal octahedron respectively. It was further calculated that the sodium ion's out-of-plane distance, referring to the three 4-atom planes of this octahedron, varies between 0.029 and 0.036 Å.

TABLE II. Contact Distances (Å) for Cations with e.s.d.s in Parentheses.*

| | | | |
|---|---|---|---|
| Na····O$^{a}$ | 2.38(1) | Cs(2)····O | 3.36(1) |
| Na····N(1)$^{b}$ | 2.47(1) | Cs(2)····N(3)$^{j}$ | 3.22(1) |
| Na····N(1)$^{c}$ | 2.47(1) | Cs(2)····N(1)$^{k}$ | 3.36(1) |
| Na····N(2)$^{d}$ | 2.42(1) | Cs(2)····N(1)$^{l}$ | 3.36(1) |
| Na····N(2)$^{e}$ | 2.42(1) | Cs(2)····N(2)$^{j}$ | 3.69(1) |
| Na····N(5) | 2.47(2) | Cs(2)····N(2)$^{m}$ | 3.69(1) |
| | | | |
| Cs(1)····C(1)$^{f}$ | 3.71(1) | Cs(1)····C(2)$^{g}$ | 3.57(1) |
| Cs(1)····C(1)$^{g}$ | 3.71(1) | Cs(1)····C(2)$^{f}$ | 3.57(1) |
| Cs(1)····N(1)$^{f}$ | 3.89(1) | Cs(1)····N(2)$^{f}$ | 3.66(1) |
| Cs(1)····N(1)$^{g}$ | 3.89(1) | Cs(1)····N(2)$^{g}$ | 3.66(1) |
| Cs(1)····N(1)$^{h}$ | 3.61(1) | Cs(1)····N(2)$^{n}$ | 3.51(1) |
| Cs(1)····N(1)$^{i}$ | 3.61(1) | Cs(1)····N(2)$^{o}$ | 3.51(1) |
| | | Cs(1)····N(5)$^{h}$ | 3.31(2) |

*Symmetry codes for superscripts: $^{a}x, y, 1+z$. $^{b}\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}+z$. $^{c}\frac{1}{2}-x, 1-y, \frac{1}{2}+z$. $^{d}-x, 1-y, 1-z$. $^{e}-x, -\frac{1}{2}+y, 1-z$. $^{f}1-x, 1-y, 1-z$. $^{g}1-x, -\frac{1}{2}+y, 1-z$. $^{h}\frac{1}{2}+x, \frac{1}{2}-y, 1\frac{1}{2}-z$. $^{i}\frac{1}{2}+x, y, 1\frac{1}{2}-z$. $^{j}\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}-z$. $^{k}\frac{1}{2}-x, -\frac{1}{2}+y, -\frac{1}{2}+z$. $^{l}\frac{1}{2}-x, 1-y, -\frac{1}{2}+z$. $^{m}\frac{1}{2}+x, y, \frac{1}{2}-z$. $^{n}1+x, y, 1+z$. $^{o}1+x, \frac{1}{2}-y, 1+z$.

The remaining holes in the stacking pattern are filled with caesium ions, of which the neighbouring contacts are less regularly orientated compared to that of the sodium ion. Both Cs(1) and Cs(2) are more or less tetrahedrally surrounded by four molybdenum atoms. The Cs(2) ion has an octahedral environment consisting of one oxygen and five ntirogen atoms (Table II). This octahedron is elongated along an axis extending roughly through the midpoints of triangular planes N(1), N(1)′, O and N(2), N(2)′, N(3), which are tilted at 4.8° relative to each other. The caesium ions are also at 2.72 and 2.67 Å from the latter planes respectively compared to the remaining six caesium-plane distances, ranging between 1.48 and 1.65 Å. This distortion is further emphasized in that the δ-angles involving edges common to each of the above-mentioned two planes are large (75.4–85.5°) compared to remaining δ's between 57.3 and 69.9°.

The Cs(1) ion's environment involves one azido and eight cyano nitrogens in the form of a monocapped cube. The average Cs(1)···N contacts (3.63 Å) are 0.17 Å longer than those of Cs(2), but both distances show a large spread as a result of an ineffective packing pattern. It is for this reason that Cs(2)···(C) distances were also included in Table II, which are comparable to those of $Cs_4[U(NCS)_8]$ [12] where the cation made short contacts with all three types of atoms in the pseudo-halogen chains. The average Cs···N contacts for this structure are also comparable with those of $Cs_3[Mo(CN)_8]\cdot 2H_2O$ [13] (3.35 Å), $Cs[I(ICN)_2]$ [14] (3.2, 3.55 Å), $Cs_2[TCNQ]_3$ (TCNQ = 7,7,8,8-tetracyanoquinodimethane) [15] (3.07–3.49 Å) and $Cs_3[UO_2(NCS)_5]$ [16] (3.44–3.73 Å).

The relevant data pertaining to the $[MoO(CN)_4(N_3)]^{3-}$ ion are given in Table III. The Mo–C≡N bond distances and angles are normal compared to those of similar structural data mentioned in the Introduction. The Mo=O distance (1.70(1) Å) is also of the expected magnitude and is suggestive of strong pπ–dπ ligand-to-metal interaction. The Mo–N(3) bond is comparable to the 2.20(2) Å for $[Mo^{IV}(N)(N_3)(Ph_2P(CH_2)_2PPh_2)_2]$ [17] as well as 2.21(1) and 2.24(1) Å in the azido-bridged $[Mo_2{}^{V}O_2(\mu\text{-}N_3)\{S(CH_2)_3S\}_3]^-$ ion [18]. The Mo–N(3)–N(4) angle confirms the $sp^2$ hybridized character of the N(3) atom and this, together with near equal N–N distances in the azido chain, suggests small π-interaction [19] with the Mo atom.

TABLE III. Bond Distances (Å) and Bond Angles (°) with e.s.d.s in Parentheses.[a]

| | | | |
|---|---|---|---|
| Mo–O | 1.70(1) | C(1)–N(1) | 1.13(2) |
| Mo–C(1) | 2.17(1) | C(2)–N(2) | 1.13(2) |
| Mo–C(2) | 2.17(1) | N(3)–N(4) | 1.19(2) |
| Mo–N(3) | 2.29(2) | N(4)–N(5) | 1.13(2) |
| | | | |
| Mo–C(1)–N(1) | 177(1) | Mo–N(3)–N(4) | 121(1) |
| Mo–C(2)–N(2) | 176(1) | N(3)–N(4)–N(5) | 180(2) |
| N(3)–Mo–C(1) | 80.1(4) | O–Mo–C(1) | 97.7(4) |
| N(3)–Mo–C(2) | 82.7(4) | O–Mo–C(2) | 99.5(5) |
| C(1)–Mo–C(2)′ | 162.8(5) | C(1)–Mo–C(2) | 91.6(4) |
| O–Mo–N(3) | 177.0(6) | C(1)–Mo–C(1)′ | 86.4(4) |
| C(1)′–C(1)–C(2) | 89.7(4) | C(2)–Mo–C(2)′ | 85.3(4) |
| C(1)–C(2)–C(2)′ | 90.3(4) | | |

[a] Superscripts denote mirror reflected atoms.

The $[MoO(CN)_4(N_3)]^{3-}$ ion has distorted octahedral geometry with the Mo atom being pulled out of the plane containing the four cyano groups towards the oxygen atom (Fig. 1). The out-of-plane distances for the Mo atom were calculated as 0.28, 0.009 and 0.01 Å for the C(1)C(2)C(2)'C(1)', C(2)OC(1)'N(3) and C(2)'OC(1)N(3) planes respectively (superscripts denote mirror-reflected atoms). This displacement correlated well with those found for the $[MoO(CN)_3(phen)]^-$ ion [1, 2] and seems to be a frequently occurring phenomenon for octahedrally co-ordinated transition metal ions containing one strongly $\pi$-bonded nitrido [20] or oxo ligand on the axis normal to the plane containing the *cis*-bonded ligands. This distortion of the octahedral environment is shown by a large *trans* influence of the $\pi$-bonded ligand as well as mutual non-bonded repulsions between remaining *trans-* and *cis*-bonded ligands. The Mo–N(3) azido bond distance, as well as the relevant ones cited above, is longer than usual, due to this strong *trans* influence if compared for example with a *cis*-bonded $Mo^{VI}$–N azido distance of 2.04 Å in the square pyramidal configuration of $[Mo(N)(N_3)_3(py)]$ [21]. We suggest that the latter configuration and co-ordination number, compared to the sterically more favourable trigonal pyramidal geometry, is due to the strong *trans* influence of the nitrido ligand [20]. A similar but smaller effect, and without loss of the sixth ligand *trans* to the Mo=O bond, is observable in the structural data of Mo(IV) cyano complexes containing one multiple bonded oxygen atom which has a smaller *trans* influence than does the nitrido ligand. The Mo atom, being displaced towards oxygen along the O=Mo–N(3) axis, forces the *cis*-bonded and N(3) atoms closer together and thus enlarges the O–Mo–C angles towards a square pyramidal type. Averaged angles of *cis*-bonded ligands to the respective Mo=O bonds are as follows: $[MoO(CN)_3(phen)]^-$, 99 [1] and 100.6° [20]; $[MoO(CN)_5]^{3-}$, 100.2°; $[MoO(OH_2)(CN)_4]^{2-}$, 99.8 and 100.3° [5]; $MoO(CN)_4(N_3)]^{3-}$, 98.6°.

These values, if compared to 90.0° in the $[MoO_2(CN)_4]^{4-}$ ion [7] containing two *trans*-orientated and equally donating $\pi$-bonding oxo ligands, emphasize the effect which only one $\pi$-bonded oxo group exerts on the final geometry of the anion.

Non-bonded repulsions, similar to those found for the $[MoO(CN)_3(phen)]^-$ ion [1, 2], is also detectable for the present anion. Taking the N(3)–Mo=O bond axis as linear (Table III) it is evident that the C(1)···C(2) = 3.11(2), C(1)···C(1)' = 2.97(2), C(2)···C(2)' = 2.94(2), C(1)···N(3) = 2.87(2) and C(2)···N(3) = 2.94(2) Å distances are representative of repulsion interactions on the basis of Van der Waals radii of 1.6 Å for carbon in covalent cyanides [22] and 1.5 Å for nitrogen.

This structure determination proved that monodentate substitution on the protonated forms of the dioxotetracyanomolybdate(IV) ion proceeded through a position *trans* to the oxo group, which must involve displacement of an aquo or hydroxo group. For the case of the $[MoO(CN)_3(phen)]^-$ ion, it can thus be assumed that initial attack of the phen ligand involved substitution in the same *trans* position followed by $CN^-$ displacement during ring closure. The structural data on these substitution products also point to a labile character for this bond due to the *trans* influence of the oxo group and ligand–ligand repulsions. The stability of the substitution product is thus dependent on the electronic control the oxo group has on the electron density along the O=Mo–L axis, as well as steric factors operating in conjunction with it. The blue or green distortional isomers, reported for $[MoOCl_2(PMe_2Ph)_3]$, $[MoOCl_2(PEt_2Ph)_3]$ [23] and $[MoO(OH_2)(CN)_4]^{2-}$ or $[MoO(CN)_5]^{3-}$ ions [5], illustrate this principle.

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