

Molecular Structure of Tetraphenylphosphonium Tetracyanooxo(Hydrogen Cyanide- κ N)molybdate(IV) Pentahydrate: Novel Coordination of HCN to a Mo^{IV} Centre

Jaap P. Smit, Walter Purcell, Andreas Roodt* and Johann G. Leipoldt

Department of Chemistry, University of the Orange Free State, Bloemfontein 9300, South Africa

The crystal structure of $(\text{PPh}_4)_2[\text{MoO}(\text{NCH-}\kappa\text{N})(\text{CN})_4]\cdot 5\text{H}_2\text{O}$, displaying the first example of hydrogen cyanide coordinated to Mo^{IV} via the nitrogen atom, is described.

The chemistry of the $[\text{MO}_2(\text{CN})_4]^{(n+2)-}$ complexes, M=Mo^{IV}, W^{IV}, Re^V, Tc^V and Os^{VI} have been extensively studied during the last decade.¹⁻⁵ The dioxo complexes undergo protonation to form the $[\text{MO}(\text{OH})(\text{CN})_4]^{(n+1)-}$ and $[\text{MO}(\text{H}_2\text{O})(\text{CN})_4]^{n-}$ complexes, of which the aqua ligand can be substituted by monodentate^{3,4} (NCS⁻, F⁻, py and N₃⁻) and bidentate⁵ (2-picolinate, 2,2'-bipyridine) species. Upon substitution of the coordinated aqua ligand by CN⁻ ions, the well known $[\text{MO}(\text{CN})_5]^{(n+1)-}$,^{1,6} complexes (known for Mo^{IV}, W^{IV}, Tc^V and V^V), as important intermediates in the formation of the $[\text{M}(\text{CN})_6]^{4-}$ complex (known only for Mo^{IV}, W^{IV} and Nb^{III}), are formed.

We have recently⁷ shown by means of kinetic studies of the reaction between $[\text{MoO}(\text{H}_2\text{O})(\text{CN})_4]^{2-}$ and $[\text{WO}(\text{H}_2\text{O})(\text{CN})_4]^{2-}$ and cyanide ions that hydrogen cyanide also acts as a monodentate ligand in both these systems, as has been shown previously for other complexes,⁸ including $[\text{Ni}(\text{trien})]^{2+}$ and $[\text{Rh}(\text{TPPS})(\text{H}_2\text{O})_2]^{3+}$ [TPPS = tetrakis(4-sulfonatophenyl)porphyrin]. We consequently postulated the formation of the $[\text{Mo}(\text{NCH-}\kappa\text{N})(\text{CN})_4]^{2-}$ complex at pH values lower than the pK_{a1} value (=9.2) of HCN.

We have now succeeded in isolating this complex for the Mo^{IV} system as the tetraphenylphosphonium salt and report here, to our knowledge, the first X-ray crystallographic structural characterization of a complex containing hydrogen cyanide coordinated to a metal centre.†

K₃Na[MoO₂(CN)₄] \cdot 6H₂O (2.0 g, 4 mmol) and KCN (1.0 g, 18 mmol) was added to water (20 ml) and the pH was adjusted to 9.0 with concentrated H₂SO₄. To this solution was added 10 ml of an aqueous solution containing tetraphenylphosphonium chloride (0.2 g, 0.5 mmol). Blue crystals of $(\text{PPh}_4)_2[\text{MoO}(\text{NCH-}\kappa\text{N})(\text{CN})_4]\cdot 5\text{H}_2\text{O}$ 1‡ (yield 0.5 g, 13%) were obtained after 1–3 days.

Although we were unable to distinguish crystallographically by means of the temperature parameters between the positions of the carbon and the nitrogen atoms of the *trans* coordinated cyanide, or to determine the position of the hydrogen atom of the HCN ligand, the presence of the hydrogen cyanide ligand *trans* to the oxo is confirmed by the following. First, chemical analysis (for Na and K) revealed no cations other than the two PPh₄⁺ for each Mo^{IV} moiety present, pointing to the formation of the $[\text{MoO}(\text{NCH-}\kappa\text{N})(\text{CN})_4]^{2-}$ complex rather than the pentacyano complex,

$[\text{MoO}(\text{CN})_5]^{3-}$. Secondly, the value of the Mo=O stretching frequency in this complex (940 cm⁻¹) is much larger than the $\nu_{\text{Mo=O}}$ value of 920 cm⁻¹ for the $[\text{MoO}(\text{CN})_5]^{3-}$ complex, suggesting a much weaker bonding ligand (HCN) than a cyano moiety *trans* to the oxo ligand. It is interesting to note that the $\nu_{\text{Mo=O}}$ value in this complex is intermediate between the 915 cm⁻¹ of $[\text{MoO}(\text{OH})(\text{CN})_4]^{3-}$ and the 980 cm⁻¹ for $[\text{MoO}(\text{H}_2\text{O})(\text{CN})_4]^{2-}$ as one would expect from the relative donicities of these ligands (OH⁻, NCH and H₂O) *trans* to the oxo. Attempted confirmation of the HCN presence by introduction of D₂O in the system proved unsuccessful since the HCN/DCN stretches are overshadowed by the other four coordinated cyano ligands and their corresponding interaction with the H₂O/D₂O that crystallises out in the unit cell. A tendency of broadening towards higher wavenumber was all that was observed. Thirdly, the bond distances obtained in this structure determination suggests that the ligand coordinated *trans* to the oxo is a HCN molecule since the bond distance of 2.435(14) Å is significantly longer than that found in $[\text{MoO}(\text{CN})_5]^{3-}$ [$\text{Mo-C}_{\text{trans}} = 2.373(6)$ Å]. This structure determination can also be compared with that of $[(\text{PPh}_3)_2\text{N}]_2[\text{MoO}(\text{NCMe-}\kappa\text{N})(\text{CN})_4]^{6b}$ showing the similarity in coordination in HCN (*via* the nitrogen atom) as compared

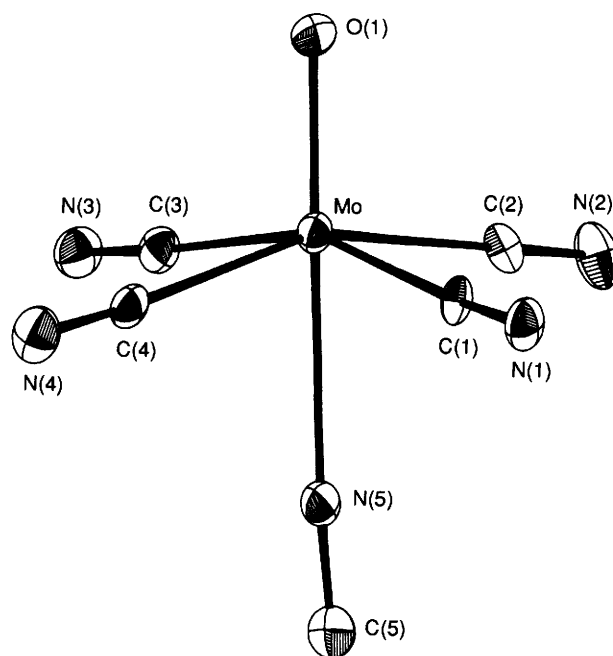


Fig. 1 Molecular structure of the $[\text{MoO}(\text{NCH-}\kappa\text{N})(\text{CN})_4]^{2-}$ anion showing the atom labelling. Selected interatomic distances (Å) and angles (°) are as follows: Mo–O(1) 1.655(9), Mo–C(1) 2.142(9), Mo–C(2) 2.134(13), Mo–C(3) 2.14(2), Mo–C(4) 2.125(12), Mo–N(5) 2.435(14), C(1)–N(1) 1.121(13), C(2)–N(2) 1.12(2), C(3)–N(3) 1.18(2), C(4)–N(4) 1.15(2), C(5)–N(5) 1.14(2); C(1)–Mo–C(3) 160.2(6), C(2)–Mo–C(4) 159.5(5), O(1)–Mo–C(1) 101.2(4), N(5)–Mo–C(2) 76.9(5), N(5)–Mo–C(4) 83.1(5), O(1)–Mo–N(5) 172.3(4), Mo–N(5)–C(5) 172.2(12), Mo–C(2)–N(2) 176.0(12), Mo–C(3)–N(3) 176.2(14); displacement of Mo^{IV} atom towards the oxo ligand from the plane formed by the four cyano carbon atoms is 0.37(1) Å.

† Crystal data: blue crystal, loses solvent within an hour at 30 °C, stable in refrigerator for up to 4 weeks (0.25 × 0.25 × 0.25 mm), grown from aqueous CN⁻/HCN solution at pH ca. 9, covered immediately after isolation with a thin layer of Canada balsam. C₅₃H₅₁N₅O₆P₂Mo, M = 1011.9, monoclinic, P2₁/n, a = 15.533(14), b = 19.935(3), c = 16.684(5) Å; β = 100.91(5)°; V = 5072.8(6) Å³, Z = 4, D_c = 1.325 g cm⁻³. Data were collected at 22 °C [2590 I > 3σ(I)] on an Enraf-Nonius CAD4F Diffractometer using Mo-Kα radiation (λ = 0.71069 Å); 2θ_{max} = 50°. The structure was solved by Patterson and successive Fourier methods and refined to R = 5.65 and R_w = 6.09% (unit weights) using SHELX76 (G. M. Sheldrick, SHELX76, Program for crystal structure determination, University of Cambridge, England, 1976). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

‡ Data for 1: IR (KBr) ν(Mo=O) 940; ν(C≡N) 2086 cm⁻¹; (Found: Na < 0.3, K < 0.05%; Na or K complex would require Na, 2.27 or K, 3.8%).

with acetonitrile (NCMe), with a Mo–NCMe bond distance of 2.500(7) Å. This is in agreement with the fact that a hydride is a stronger electron donor than a methyl group, resulting in the nitrogen atom of the HCN being a better electron donor than the NCMe nitrogen atom.

The two PPh_4^+ cations show the normal expected geometry.

This rare X-ray crystallographic verification of a nitrogen coordinated HCN confirms the active participation of hydrogen cyanide in these systems and is an important point worth noting in future research on similar complexes.

Financial support from the South African FRD and the Research Fund of the University of the Orange Free State is gratefully acknowledged.

Received, 11th May 1993; Com. 3/02685J

References

- 1 J. G. Leipoldt, S. S. Basson and A. Roodt, in *Advances in Inorganic Chemistry*, ed. A. G. Sykes, vol. 40, 1993, Academic Press, Talahassee, in the press; J. G. Leipoldt, S. S. Basson, A. Roodt and W. Purcell, *Polyhedron*, 1992, **11**, 2277.
- 2 A. Roodt, J. G. Leipoldt, S. S. Basson and I. M. Potgieter, *Transition Met. Chem.*, 1990, **15**, 439; W. Purcell, A. Roodt, S. S. Basson and J. G. Leipoldt, *Transition Met. Chem.*, 1987, **12**, 209.
- 3 A. Roodt, J. G. Leipoldt, E. A. Deutsch and J. C. Sullivan, *Inorg. Chem.*, 1992, **31**, 1080; A. Roodt, J. G. Leipoldt, S. S. Basson and I. M. Potgieter, *Transition Met. Chem.*, 1988, **13**, 336; J. G. Leipoldt, R. van Eldik, S. S. Basson and A. Roodt, *Inorg. Chem.*, 1986, **14**, 57.
- 4 W. Purcell, A. Roodt and J. G. Leipoldt, *Transition Met. Chem.*, 1991, **17**, 339; J. G. Leipoldt, S. S. Basson, A. Roodt and I. M. Potgieter, *S. Afr. Jour. Chem.*, 1987, **39**, 179; A. Roodt, J. G. Leipoldt, L. Helm and A. E. Merbach, *Inorg. Chem.*, 1992, **31**, 2864.
- 5 S. S. Basson, J. G. Leipoldt and I. M. Potgieter, *Inorg. Chim. Acta*, 1984, **87**, 57; I. M. Potgieter, S. S. Basson, A. Roodt and J. G. Leipoldt, *Inorg. Chem.*, 1987, **26**, 57; A. Samotus, A. Kanas, W. Glug, J. Szklarzewicz and J. Burgess, *Transition Met. Chem.*, 1991, **16**, 614; J. G. Leipoldt, S. S. Basson, A. Roodt and I. M. Potgieter, *Transition Met. Chem.*, 1986, **11**, 323; J. Szklarzewicz, A. Samotus, N. W. Alcock and M. Moll, *J. Chem. Soc., Dalton Trans.*, 1990, 2959; A. Roodt, S. S. Basson and J. G. Leipoldt, *Polyhedron*, submitted.
- 6 (a) K. Wieghardt, G. Backes-Dahman, W. Holzbach, W. J. Swiridoff and J. Weiss, *Z. Anorg. Allg. Chem.*, 1983, **499**, 44; (b) H. Arzoumanian, M. Pierrot, F. Ridouane and J. Sanchez, *Transition Met. Chem.*, 1991, **16**, 422.
- 7 J. P. Smit, W. Purcell, A. Roodt and J. G. Leipoldt, *Polyhedron*, in the press; J. P. Smit, A. Roodt, W. Purcell and J. G. Leipoldt, *J. Chem. Soc., Dalton Trans.*, submitted.
- 8 G. B. Kolski and D. W. Margerum, *Inorg. Chem.*, 1968, **7**, 2230; G. B. Kolski and D. W. Margerum, *Inorg. Chem.*, 1969, **8**, 1125; P. Hambright and R. Langley, *Inorg. Chim. Acta*, 1987, **137**, 209; W. W. Reenstra and W. P. Jencks, *J. Am. Chem. Soc.*, 1979, **101**, 5780; E. Billo, *Inorg. Chem.*, 1973, **12**, 2783; D. Margerum, G. Caley, D. Weatherburn and D. Pagenkopf, in *Coordination Chemistry*, ed., A. E. Martell, ACS Monograph 174, Washington DC, 1978, ch. 1.