A new family of dimolybdenum compounds with cyanide and phosphine ligands

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Abstract

Reaction of Mo2Cl4(dpmm)2 with excess [n-Bu4N][CN] produces [Bu4N][Mo2III,III(CN)6(dpmm)2]·(CH3CN)·2(C6H6)·2(H2O)·2(C2H5CN) (I) the first example of an edge-sharing bioctahedral compound of Mo(II), that upon exposure to air oxidizes to the mixed valence analog [Bu4N][Mo2II,II(CN)6(dpmm)2]·2(CH3CN)·2(C6H6)·2(H2O) (2). ©2000 Elsevier Science S.A. All rights reserved.

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The use of transition metal cyanide compounds as building blocks for clusters and extended arrays is an active area of research [1,2]. One of our goals is to extend the field of cyanide chemistry to low valent metals that exhibit metal–metal bonding. Such compounds are scarce, with only a few examples having appeared in the literature to date [3–7]. These are K[Mo2(μ-CN)(CO)4(Cp)2], Mn2(μ-CN)H(CO)5(dpmm)2, [n-Bu4N]n[M2(μ-CN)n(OR)n] (n=1,2) (M=Mo or W), and [Rh2(μ-CN)(μ- CO)(CO)3(dpmm)3]ClO4 which contain one or two bridging cyanide ligands. Only two examples of M–M bonded compounds with terminal cyanides exist, viz., [n-Bu4N]2[Mo2(CN)6] and [Bu4N]2[Re2(CN)6(dpmm)2] prepared in our laboratories several years ago [7]. The octacyanodimolybdate anion constitutes the sole homoleptic dinuclear cyanide complex in the literature, and the dirhenium compound is the only cyanide complex of the edge-sharing biocahedral (ESBO) type. The discovery of these two unprecedented compounds prompted us to question whether other anionic M–M bonded ESBOs with cyanide ligands could be isolated. Neutral and cationic ESBO complexes are well established families of compounds [8,9] but prior to our results in the cyanide chemistry, anionic ESBOs were limited to one example, viz., [Re2Cl6(dpmm)2]− [10]. Herein we report the isolation of two new anionic ESBOs, [Mo2(CN)6(dpmm)2]2−/1−, from reactions of Mo2Cl4-

(dpmm)2 with excess cyanide. Although the pair exhibit similar molecular geometries, the bonding interactions between the Mo and the bridging cyanide ligands are quite different.

Upon mixing Mo2Cl4(dpmm)2 with excess [n- Bu4N][CN], an immediate reaction takes place to yield a dark red solution and red, air-sensitive microcrystals. IR, 1H and 31P NMR spectroscopies as well as single crystal X-ray diffraction methods were used to identify the product as [n-Bu4N]2[Mo2II,II(CN)6(dpmm)2]·2(CH3CN)·2(C6H6) (1). The molecular anion, depicted in Fig. 1, is isostructural with [Re2II,II(CN)6(dpmm)2]2−. The presence of two cyanide environments is confirmed by the IR spectrum which

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1 Crystallographic data for C32H42N6P2Mo2 (1): M=1601.71 monoclinc, a=27.505(6), b=18.824(4), c=23.108(5) Å, β=102.58(3)°, \(U=9909(3) Å^3\), \(T=173 \text{ K, space group C2/c (No. 15), Z=4,} \mu(\text{Mo-Ka})=0.368, 18233 \text{ reflections measured, 6568 unique} (R_{int}=0.1798), R=0.085, wR2=0.1357 (I>2\sigma), R1=0.2165, wR2=0.1749 (all data). The soft crystal diffracted poorly which led to refinement limitations. With the exceptions of C31 and C2, all non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were added in calculated positions. The high degree of thermal motion observed for the C3 and N3 atoms is attributed to librational disorder [13]. Based on the appearance of electron density maps of the region, it is unlikely that the bridging atoms are involved in a packing disorder of the molecule with two slightly different superimposed orientations of the ligand. Furthermore, the unreasonably short C3-N3 bond length of 1.028 Å is an expected consequence of libration. The presence of stronger π-interactions between the semi-bridging cyanides and the dimolybdenum core in 2 as evidenced by the side-on positioning of the triple bond leads to more rigid bonding and no apparent librational disorder.
exhibits two ν(CN) modes at 2094 and 2079 cm⁻¹ (terminal CN) and one at 1936 cm⁻¹ that is characteristic of the bridging mode [3–7].

Slow evaporation of an acetonitrile/benzene solution in air leads to the formation of green crystals of the one-electron oxidation product [n-Bu₄N][MoO₂²⁺(CN)₆(dpdm)₂] · 2(H₂O) · 2(CH₃CN) (2)³. An IR spectrum of the crystals exhibits two modes at 2108 and 1807 cm⁻¹. The lack of a second stretch in the higher energy region implies that the symmetric and anti-symmetric stretches for the four terminal cyanides are degenerate. The ¹H and ¹³C NMR spectra of the compound are broad, in accord with a MoO₂²⁺ mixed-valence species. An ORTEP representation of 2 is given in Fig. 2.

Fast-atom bombardment (FAB) mass spectrometry using both nitrobenzyl alcohol and glycerol matrices was conducted on 1 to investigate the possibility of incomplete cyanide/chloride metathesis. The mass spectra showed no evidence for the isotopic pattern characteristic of chlorine. Since 2 is made directly from 1 by oxidation in air, confirmation of the purity of 1 was taken to be sufficient for both compounds.

The molecular anions in the two compounds consist of trans-dppm ligands that bisect an equatorial plane containing two Mo atoms as well as four terminal and two bridging cyanide ligands. In 1, the bridging cyanides are coordinated through the C atom to the Mo–Mo unit in a slightly unsymmetrical fashion, whereas in 2 the bonding mode is best described as semi-bridging with a nearly linear Mo(1A)–C(3)–Mo(1) 2.474 Å bond and a side-on π interaction between C(3)N(3) and Mo(1). The different orientations of the bridging cyanide ligands in the two compounds is best appreciated by an inspection of the Mo1–C3–N3 angles which are 117.1(14)° and 86.2(3)° in 1 and 2 respectively. It is apparent from these structural differences and the bridging ν(CN) mode, which is lowered from 1936 cm⁻¹ in 1 to 1807 cm⁻¹ in 2, that oxidation of the MoO²⁺ core to MoO₅⁺ is accompanied by increased π-bonding from the bridging cyanides to the metal centers.

Although the data set for 1 is of a lower resolution than that of 2, a comparison of the metal–ligand bonding environments of the two compounds is nonetheless informative. According to the established MO bonding scheme for ESBO compounds, the electronic configurations of the MoO₂²⁺ and MoO₂²⁺,III compounds are σ²π²(δδ*)⁴ and σ²π²(δδ*)⁴ respectively [8, 9]. Since the δ and δ* orbitals are essentially non-bonding and may even be reversed in their energies, a bond order of approximately two would be predicted for both. The increase in the metal–metal bond length in the MoO₅⁺ versus the MoO₄⁺ compound (2,8299(10) Å versus 2,7092(2) Å) (see Fig. 3) can be attributed to the donation of electron density from the π orbitals of the side-on bridging cyanide to the π* LUMO of the Mo–Mo bond. For example, if d₄ is taken to be the d-orbital involved in metal–metal π-bonding.

Fig. 1. ORTEP representation of [n-Bu₄N][MoO₂²⁺(CN)₆(dpdm)₂] with selected bond distances (Å) and angles (°): Mo1–Mo1(A) 2.709(2), Mo1–C1 2.167(13), Mo1–C2 2.186(11), Mo1–C3 2.199(12), Mo1–C3(A) 2.077(12), C1–N1 1.162(12), C2–N2 1.132(11), C3–N3 1.082(12), Mo1–P1 2.474(3), Mo1–P2 2.470(3), C2–Mo1–C1 87.1(4), C3–Mo1–C1 163.5(4), C3–Mo1–C2 83.0(4), N3–C3–Mo1 117.1(14), N3–C3–Mo1(A) 162.8(14), P1–Mo1–P2 172.85(10). Hydrogen atoms were omitted for the sake of clarity.

Fig. 2. ORTEP representation of [n-Bu₄N][MoO₂²⁺(CN)₆(dpdm)₂] with selected bond distances (Å) and angles (°): Mo1–Mo1(A) 2.8299(10), Mo1–C1 2.181(5), Mo1–C2 2.155(4), Mo1–C3 2.252(3), Mo1–C3(A) 2.032(4), C1–N1 1.153(6), C2–N2 1.151(5), C3–N3 1.161(5), Mo1–P1 2.5423(11), Mo1–P2 2.5370(11), C2–Mo1–C1 78.47(16), C3–Mo1–C1 157.64(15), C3–Mo1–C2 80.75(15), N3–C3–Mo1 86.2(3), N3–C3–Mo1(A) 168.2(3), P1–Mo1–P2 174.31(3). Hydrogen atoms were omitted for the sake of clarity.

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² Crystallographic data for C₅H₅N₃P₂O₂Mo₂: M = 1359.25, monoclinic, a = 27.353(6), b = 10.741(2), c = 26.149(5) Å, β = 107.50(3)°, U = 7327(3) Å², T = 173 K, space group C2/c (No. 15), Z = 4, μ(Mo-Kα) = 0.481, 22662 reflections measured, 8462 unique (R_int = 0.0948), R1 = 0.0602, wR2 = 0.1166 (7 > 2σ), R1 = 0.0995, wR2 = 0.1311 (all data). All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were located from the difference map and refined isotropically. The O1–H1WA and O1–H1WB distances were restrained to reasonable values.
formation, the donation of electron density into the $\pi^*$ MO would occur from a $\pi$-interaction with the p$_y$ bonding MO of the CN triple bond.

The spatial arrangement of the terminal cyanides is such that interactions with Lewis acids to form larger assemblies should be possible. An especially interesting direction for this chemistry is the use of the paramagnetic $\text{Mo}_2^{\text{II,III}}$ compound as a building block in reactions with first row transition metals 11,12. A reaction of trans-[Ni(en)(MeCN)$_2$]$_2^{2+}$ with [n-Bu$_4$N][Mo$_2^{\text{II,III}}$(CN)$_6$(dppm)$_2$] has been carried out, and the resulting product contains both the Mo and Ni units as judged by IR spectroscopy. Details of this chemistry will be reported in due course.

Experimental

Syntheses

All manipulations were carried out under an inert atmosphere using standard Schlenk-line techniques. [n-Bu$_4$N]$_2$[Mo$_2^{\text{II,III}}$(CN)$_6$(dppm)$_2$] was prepared by combining dichloromethane solutions of Mo$_2$Cl$_4$(dppm)$_2$ (0.100 g, 0.091 mmol) and [n-Bu$_4$N]$_2$[CN] (0.146 g, 0.544 mmol). Upon mixing, a dark red solution and a dark red microcrystalline solid were obtained. The solution was concentrated to $\sim$5 ml and the product was collected by filtration and washed with dichloromethane (3 $\times$ 5 ml). Yield after drying was 65%. X-ray quality single crystals of [n-Bu$_4$N]$_2$[Mo$_2^{\text{II,III}}$(CN)$_6$(dppm)$_2$]$\cdot$2(CH$_3$CN)$\cdot$2(C$_6$H$_5$)$_2$ (1) were grown by diffusion of benzene into an acetonitrile solution of the compound in a flame sealed thin tube. Exposure of the solution to air resulted in the growth of green crystals of [n-Bu$_4$N][Mo$_2^{\text{II,III}}$(CN)$_6$(dppm)$_2$]$\cdot$2(H$_2$O)$\cdot$2(CH$_3$CN).

Spectroscopic data

[n-Bu$_4$N]$_2$[Mo$_2^{\text{II,III}}$(CN)$_6$(dppm)$_2$]$\cdot$2(CH$_3$CN)$\cdot$2(C$_6$H$_5$)$_2$ (1), $^1$H NMR: $\delta$ 4.08, phenyl multiplets $\delta$ 7.60 and 6.96; [$^1$H]$_3$P NMR: $\delta$ 25.47; $\nu$$_{CN}$: 2094, 2080, and 1936 cm$^{-1}$; UV--Vis (CH$_3$CN): $\lambda_{max}$ (nm) ($\epsilon$ (M$^{-1}$ cm$^{-1}$)) 553 (1.9 $\times$ 10$^4$) 333 (3.4 $\times$ 10$^4$), [n-Bu$_4$N][Mo$_2^{\text{II,III}}$(CN)$_6$(dppm)$_2$]$\cdot$2(H$_2$O)$\cdot$2(CH$_3$CN) (2): $\nu$$_{CN}$: 2108 and 1807 cm$^{-1}$.

Supplementary material

Further details of the X-ray crystallography, structural results, and electron density mapping studies are available on request from author K.R.D.

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References