Ready, Reversible Conversion of a Quadruply Metal–metal Bonded Dinuclear Complex into a Mononuclear Complex

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The quadruply metal–metal bonded molybdenum(II) complex $[Mo_2L_2]$ (**1**) ($L = C_{22}H_{22}N_4{}^{2-}$) reacts with tetracyanoethylene (TCNE) to afford first the biradical compound $[(\mathbf{1})^{+\cdot}\,(\mathrm{TCNE})^{-\cdot}]$ and then, presumably *via* reaction with traces of water, the oxo-molybdenum(V) derivative $[MoOL][C_3(CN)_5]$ (**2**), the structure of which has been determined by *X*-ray diffraction [Mo–O 1.670(3) Å]; reduction of (**2**) with Na/Hg gives the dinuclear multiply metal–metal bonded radical anion $(\mathbf{1})^{-\cdot}$.

Several examples of the synthesis of triply- or quadruply-bonded dinuclear complexes from mononuclear precursors have been described,[1] but the inverse process, *i.e.*, the cleavage of triply- or quadruply-bonded dinuclear complexes into mononuclear species, is very rare if we exclude metathesis-like reactions[2] such as (1). This may be related, at least partially, to the high energy associated with M≡M and M≣M bonds, even if recent studies[3] have shown this energy to be much lower than previously estimated. Here we describe a chemical system which allows easy transformation of a dimolybdenum(II) complex with a quadruple metal–metal bond into a mononuclear molybdenum(V) compound which may then be reduced back to a multiply bonded dinuclear species.

$$[\mathrm{M}]\equiv[\mathrm{M}] + \mathrm{X}\equiv\mathrm{Y} \rightarrow [\mathrm{M}]\equiv\mathrm{X} + [\mathrm{M}]\equiv\mathrm{Y} \qquad (1)$$
$$(\mathrm{X} = \mathrm{Y} = \mathrm{C{-}R};\ \mathrm{X} = \mathrm{C{-}R},\ \mathrm{Y} = \mathrm{N})$$

We have previously described[4] the synthesis of the dimeric quadruply metal–metal bonded molybdenum complex $Mo_2(tmtaa)_2$ (**1**) [$tmtaa^{2-}$ = dibenzotetramethyltetra-aza-(14)annulene dianion, $C_{22}H_{22}N_4{}^{2-}$], its electrochemical and

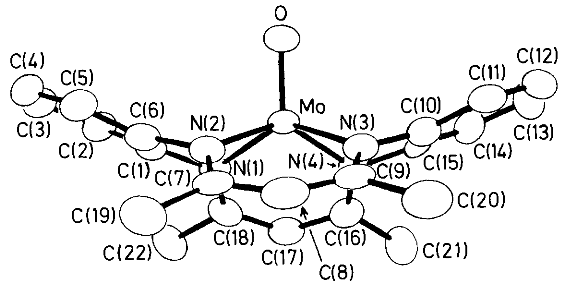


Figure 1. ORTEP drawing of (**2**). Selected bond distances and angles: Mo–O 1.670(3), Mo–N 2.034(4)—2.041(4) Å; O–Mo–N 110.1(2)—112.8(2)°. The $[C_3(CN)_5]^-$ anion displays similar features to those recently reported for the ferricinium derivative.[6]

chemical oxidation to the radical cation $[Mo_2(tmtaa)_2]^{+\cdot}$ ($\mathbf{1}^{+\cdot}$), and its electrochemical and chemical reduction to the radical anion $[Mo_2(tmtaa)_2]^{-\cdot}$ ($\mathbf{1}^{-\cdot}$). In contrast with the reaction we report here, no cleavage of the metal–metal bond was then observed.

Treatment at room temperature of a solution (toluene or acetonitrile) of (**1**) with one equiv. of the mild oxidising agent tetracyanoethylene (TCNE) results in a solution which gives two e.s.r. signals, one a 9-line multiplet characteristic of the radical anion $TCNE^{-\cdot}$ [g 2.0030; $A(14_N)$ 1.56 G (G = 10^{-4} T)][5] and the other the previously reported signal of ($\mathbf{1}^{+\cdot}$).[4] The signals are indicative of a single electron transfer from the molybdenum species to the organic substrate. At this stage crystallisation by concentration readily affords the biradical compound $[(\mathbf{1})^{+\cdot}\ (TCNE)^{-\cdot}]$ (ν_{CN} 2183, 2144 cm^{-1}) (see Scheme 1). However, if crystallisation is not induced, the intensities of the e.s.r. signals decrease with time and a new signal appears, indicative of the presence of an $S = \frac{1}{2}$ metal-centred radical (**2**) [g(iso) 1.9562; A_{iso} 34.7 G]. From an acetonitrile solution of (**1**) containing a four-fold excess of TCNE, (**2**) may be isolated in a pure state (70% yield) as a black powder after extraction and crystallisation from dichloromethane–pentane. An X-ray diffraction study† (Figure 1) revealed that (**2**) is a mononuclear molybdenum(v) compound containing the oxo-cation $[MoO(tmtaa)]^+$ (ν_{MoO} 950 cm^{-1}) and the pentacyanopropenide anion $[C_3(CN)_5]^-$ (ν_{CN} 2195 cm^{-1}). The presence of these two unexpected species clearly suggests the intervention of traces of water.‡

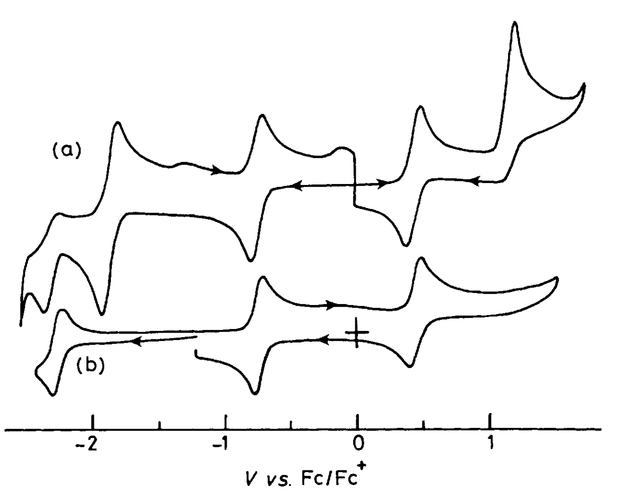
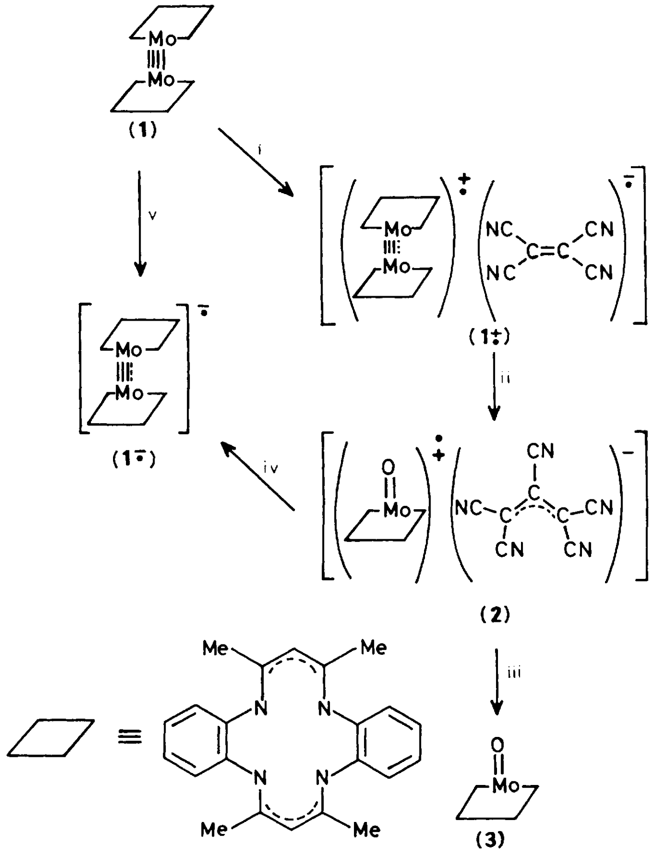


Figure 2. Cyclic voltammograms of (a) (**2**) and (b) (**3**). [In C_6H_5CN (0.1 M-Bu_4NPF_6), at 20 °C; scan rate 100 mV s^{-1}; potential *vs.* Fc/Fc^+.] The two processes observed for (**2**) at 1.17 and −1.81 V have been assigned to the $[C_3(CN)_5]^-$ unit by comparison with the c.v. of $[Et_4N][C_3(CN)_5]$.



Scheme 1. *Reagents:* i, TCNE in toluene or acetonitrile; ii, excess of TCNE in acetonitrile; iii, $Co(\eta-C_5H_5)_2$ in THF; iv, Na/Hg in THF; v, Na/Hg in toluene (see ref. 4).

The crystal structure determination shows that the molybdenum atom has a distorted square pyramidal co-ordination with an apical oxygen atom [Mo=O 1.670(3) Å] and the molybdenum displaced 0.737(1) Å above the N_4 co-ordination mean plane of the macrocycle.

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† *Crystal data* for (**2**): $C_{22}H_{22}MoON_4.C_8N_5.CH_2Cl_2$, M = 703.4, triclinic, a = 9.057(5), b = 12.327(4), c = 14.939(5) Å, α = 103.69(7), β = 102.54(9), γ = 96.31(8)°, U = 1558(2) $Å^3$, space group $P\bar{1}$, Z = 2, D_c = 1.50 g cm^{-3}, Mo-K_α radiation, λ = 0.71069 Å, μ(Mo-K_α) = 6.22 cm^{-1}, $F(000)$ = 710, T = 296 K; R = 0.048, R_w = 0.043 for 3168 observed [$I > \sigma(I)$] diffractometer reflections out of 4213 measured (h 0 − 13, k 0 ± 14, l 0 ± 15, $2\theta < 55°$). The molybdenum atom was located by the Patterson method and all non-hydrogen atoms were located from difference Fourier maps. All atoms were refined first isotropically (R = 0.094) and then anisotropically (R = 0.057). At this stage, all hydrogen atoms were located in difference maps (0.59 − 0.30 e $Å^{-3}$) and refined with an overall isotropic temperature factor. The final cycles of full-matrix least-squares refinement (468 parameters refined) gave R = 0.048, R_w = 0.043, S_w = 1.5, Δe = 0.40 e $Å^{-3}$. The remaining difference Fourier map was featureless.

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

‡ $[C_3(CN)_5]^-$ has been previously shown to arise from hydrolysis of TCNE in the presence of a base B according to $2C_2(CN)_4 + B + 2H_2O \rightarrow BH^+ + [C_3(CN)_5]^- + CO_2 + 3HCN$; see ref. 7.

Cyclic voltammetry (c.v.) of (**2**) in benzonitrile (0.1 M-Bu_4NPF_6 as supporting electrolyte; scan rate 100 mV s^{-1}) shows five redox processes (Figure 2). Separate c.v. study of $[Et_4N][C_3(CN)_5]$ indicates that two of the processes are associated with the $[C_3(CN)_5]^-$ anion, the other three with the molybdenum cation. In the anodic sense, a reversible one-electron process is observed at $E_{\frac{1}{2}} = 0.44$ V (*vs*. Fc/Fc^+). In the cathodic sense, while the second reduction at $E_{\frac{1}{2}} = -2.22$ V is only quasi-reversible, the first at $E_{\frac{1}{2}} = -0.73$ V is associated with a chemically and electrochemically reversible one-electron step. It may thus be expected that both oxidation and reduction of (**2**) can be achieved chemically. However, only chemical reductions have been observed; attempts to oxidise (**2**) with $[(BrC_6H_4)_3N][SbCl_6]$ in tetrahydrofuran (THF) gave no tractable compounds.

Reduction of (**2**) with cobaltocene is realised in THF at room temperature, quantitatively yielding (**3**) and the cobalticinium derivative $[Co(\eta\text{-}C_5H_5)_2][C_3(CN)_5]$. The product (**3**) ($\nu_{MoO}$ 940 cm^{-1}) is a very air-sensitive diamagnetic compound which has been firmly characterised by its cyclic voltammogram and n.m.r. data§ as the oxomolybdenum(IV) complex illustrated (Scheme 1).

Treatment of (**2**) with an excess of Na/Hg in THF at room temperature affords a paramagnetic species which, by comparison of its e.s.r. spectrum with that of an authentic sample, has been shown to be the previously reported[4] dinuclear radical anion $[Mo_2(tmtaa)_2]^{\cdot-}$ ($\mathbf{1}^{\cdot-}$).

The oxomolybdenum(V) cation of (**2**) and the oxomolybdenum(IV) molecular complex (**3**) are the first reported oxo-complexes of molybdenum with the $tmtaa^{2-}$ ligand. They each have analogues in porphyrin chemistry[8] but, to our knowledge, no straightforward formation of triply or quadruply metal–metal bonded dinuclear complexes from mononuclear oxo-complexes has been reported for that system.[9] Therefore, although the mechanisms of the transformations of (**1**) into (**2**) and of (**2**) into ($\mathbf{1}^{\cdot-}$) are not yet elucidated, the reactions described here open up a new and interesting area of redox chemistry of molybdenum complexes.

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§ *N.m.r. data* for (**3**): (CD_2Cl_2) δ 2.11 (12 H, s, CH_3), 4.90 (2 H, s, CH), 6.98 (8 H, s, C_6H_4).

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