

## The Preparation and Characterization of the Mixed Valence Complex Dianion $[\text{Mn}_3(\text{CO})_6(\mu_2\text{-NO}_2)_4(\mu_2\text{-ONO})_2]^{2-}$

Brian F. G. Johnson,\* Anke Sieker, Alexander J. Blake and Richard E. P. Winpenny

Department of Chemistry, The University of Edinburgh, West Mains Road, Edinburgh, Scotland EH9 3JJ

Treatment of  $\text{Mn}(\text{CO})_5\text{Cl}$  with trimethylamine *N*-oxide in  $\text{CH}_2\text{Cl}_2$  in the presence of  $[\text{PPN}]\text{NO}_2$  [ $\text{PPN}^+ = (\text{Ph}_3\text{P})_2\text{N}^+$ ] yields the new dianion  $[\text{Mn}_3(\text{CO})_6(\mu_2\text{-NO}_2)_4(\mu_2\text{-ONO})_2]^{2-}$ , which has been shown to contain a trinuclear  $\text{Mn}_3$  mixed valence unit linked by both nitro- and nitrito-bridges.

We are currently undertaking a reinvestigation of oxygen transfer reactions in a series of transition metal complexes in both solution and in the solid phase. In particular we are concerned with the O-atom transfer from bonded  $\text{NO}_x$  ligands ( $x = 1, 2$  and  $3$ ) to adjacent CO groups. In the course of these studies we have isolated and characterized an unusual mixed valence complex of manganese containing formally two  $[\text{Mn}^{\text{I}}(\text{CO})_3(\text{NO}_2)_3]^{2-}$  units coordinating through both  $\mu_2\text{-NO}_2$  and  $\mu_2\text{-ONO}$  linkages to a central  $\text{Mn}^{\text{II}}$  ion.

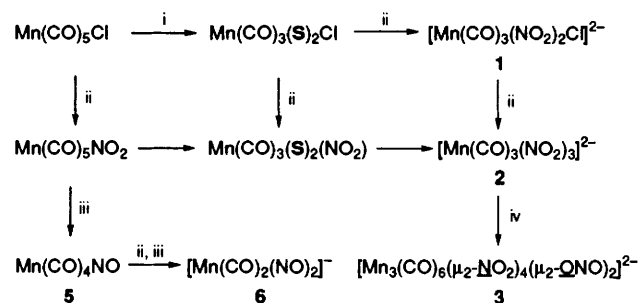
We have observed that the reaction of  $\text{Re}_2(\text{CO})_{10}$  with  $\text{Me}_3\text{NO}$  in  $\text{CH}_2\text{Cl}_2$  in the presence of  $[\text{PPN}]\text{NO}_2^\ddagger$  yields appreciable amounts of the anion  $[\text{Re}(\text{CO})_3(\text{NO}_2)_2\text{Cl}]^{2-}$  **4**. The formation of this anion led us to believe that initially either  $\text{Re}(\text{CO})_5\text{Cl}$  or some related species is generated, which then undergoes further reaction with  $\text{NO}_2^-$  to yield the observed derivative. On this basis the reaction of the readily accessible  $\text{Mn}(\text{CO})_5\text{Cl}$  with  $[\text{PPN}]\text{NO}_2$  under similar conditions was investigated.

The reaction is complex and, on the basis of IR spectroscopic evidence, appears to involve at least two highly reactive intermediates **1** and **2**, which over a period of several hours are converted to the final product  $[\text{Mn}_3(\text{CO})_6(\mu_2\text{-NO}_2)_4(\mu_2\text{-ONO})_2]^{2-}$  **3**. Although we have been unable to characterise **1** and **2** fully, the similarity of their IR spectra, and the close relationship these bear to that of  $[\text{Re}(\text{CO})_3(\text{NO}_2)_2\text{Cl}]^{2-}$ , led us to suspect that they are the anions  $[\text{Mn}(\text{CO})_3(\text{NO}_2)_2\text{Cl}]^{2-}$  **1** and  $[\text{Mn}(\text{CO})_3(\text{NO}_2)_3]^{2-}$  **2**. The reaction may then be envisaged as proceeding according to Scheme 1.

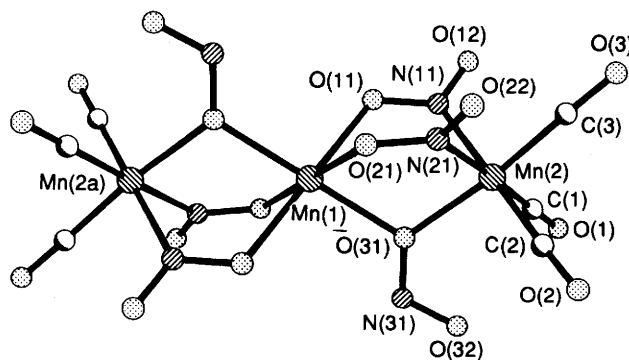
The  $\text{PPN}^+$  salt of **3** has been fully characterized by the usual analytical and spectroscopic methods and the molecular and crystallographic structure $^\ddagger$  was established from single crystals grown from acetone-diethyl ether (see Fig. 1). The dianion contains a centrosymmetric array of three manganese atoms. The central Mn atom  $[\text{Mn}(1)]$  lies on an inversion centre, and

is bound to six oxygen donors from  $\text{NO}_2^-$  ligands. The coordination geometry shows a trigonal elongation from octahedral, with the angles between the three crystallographically unique oxygen atoms reduced to  $80.62(14)$ ,  $81.56(14)$  and  $85.13(14)^\circ$ . The second metal atom in the asymmetric unit  $[\text{Mn}(2)]$  is bonded to three carbonyls, two nitrogen atoms from bridging  $\text{NO}_2^-$  ligands, and a  $\mu_2$ -oxygen  $[\text{O}(31)]$  from a third  $\text{NO}_2^-$ . The coordination geometry of  $\text{Mn}(2)$  is only slightly distorted from octahedral. There are two different bridging modes of  $\text{NO}_2^-$  units in the molecule: one involving both nitrogen and oxygen atoms [*e.g.*  $\text{N}(11)$ ,  $\text{O}(11)$  and  $\text{N}(21)$ ,  $\text{O}(21)$ ], and the second using only the oxygen  $[\text{O}(31)]$ . The IR spectrum of **3** in the solid state is totally consistent with the established molecular structure. Thus, three strong  $\nu(\text{CO})$  bands are observed at  $2034$ ,  $1954$  and  $1926\text{ cm}^{-1}$  (in Nujol) together with absorptions which may be readily assigned to both bridging nitro ( $-\text{NO}_2$ ) and nitrito ( $-\text{ONO}$ ) groups. Such bridging ligands have been observed previously.<sup>1-3</sup>

The formation of **3** is of interest. It would appear that the dianion  $[\text{Mn}(\text{CO})_3(\text{NO}_2)_3]^{2-}$  **2** is able to function as a tridentate ligand coordinating through three O atoms from each separate coordinated  $\text{NO}_2$  ligand. The difference in coordination mode of the three  $\text{NO}_2$  groups is difficult to understand but it is not unique, and has been seen previously in derivatives of  $\text{Ni}^{\text{II}}$ , which are clearly related to **3**.<sup>1</sup>



**Scheme 1** The reaction of  $\text{Mn}(\text{CO})_5\text{Cl}$  to produce **3**, **5** and **6**: i,  $\text{Me}_3\text{NO}$  (2 equiv.) in  $\text{CH}_2\text{Cl}_2$ ; ii,  $[\text{PPN}]\text{NO}_2$ ; iii, O atom transfer from  $\text{NO}_2$  to CO; iv, reaction with  $\text{Mn}^{\text{II}}$  ( $\text{S}$  = solvent)



**Fig. 1** The anion **3**. Selected bond lengths:  $\text{Mn}(1)\text{-O}(11)$  2.180(4),  $\text{Mn}(1)\text{-O}(21)$  2.159(4),  $\text{Mn}(1)\text{-O}(31)$  2.129(4),  $\text{Mn}(2)\text{-N}(11)$  2.044(4),  $\text{Mn}(2)\text{-N}(21)$  2.040(4),  $\text{Mn}(2)\text{-O}(31)$  2.032(4),  $\text{Mn}(2)\text{-C}(1)$  1.832(6),  $\text{Mn}(2)\text{-C}(2)$  1.809(6),  $\text{Mn}(2)\text{-C}(3)$  1.798(6) Å.

$^\ddagger$   $\text{PPN} = (\text{Ph}_3\text{P})_2\text{N}^+$ .

$^\ddagger$  Crystal data for  $\text{C}_{78}\text{H}_{60}\text{N}_8\text{O}_{18}\text{P}_4\text{Mn}_3$  **3**:  $M = 1686$ , triclinic, space group  $P\bar{1}$ ,  $a = 10.705(7)$ ,  $b = 12.886(7)$ ,  $c = 15.924(8)$  Å,  $\alpha = 71.22(5)$ ,  $\beta = 79.24(3)$ ,  $\gamma = 83.67(3)^\circ$ ,  $V = 2040$  Å<sup>3</sup> [from 2θ values of 19 reflections measured at  $\pm\omega$  ( $25 \leq 2\theta \leq 30^\circ$ ),  $\lambda = 0.71073$  Å],  $Z = 1$ ,  $D_c = 1.372$  g cm<sup>-3</sup>,  $T = 150$  K, yellow lath,  $\mu = 0.584$  mm<sup>-1</sup>.

Crystal data for  $\text{C}_{15}\text{H}_{33}\text{N}_5\text{O}_7\text{Cl}_5\text{Re}$  **4**:  $M = 758.9$ , monoclinic, space group  $P2_1/a$ ,  $a = 12.2591(15)$ ,  $b = 23.712(4)$ ,  $c = 9.8119(13)$  Å,  $\beta = 90.055(13)^\circ$ ,  $V = 2852$  Å<sup>3</sup>, [from 2θ values of 104 reflections measured at  $\pm\omega$  ( $30 \leq 2\theta \leq 32^\circ$ ),  $\lambda = 0.71073$  Å],  $Z = 4$ ,  $D_c = 1.77$  g cm<sup>-3</sup>,  $T = 150$  K, brown-orange tablet,  $\mu = 4.83$  mm<sup>-1</sup>.

Data collection and processing: Stoë Stadi-4 four-circle diffractometer, graphite-monochromated Mo-K $\alpha$  X-radiation,  $\omega$ -2θ scans. Structure **3** was solved by direct methods; **4** was solved by the heavy atom method and the data were corrected for absorption. In both cases the non-hydrogen atoms were refined anisotropically to give: for **3**  $R = 0.0604$  ( $R_w = 0.0820$ ) for 4078 independent observed reflections [ $2\theta \leq 45^\circ$ ,  $F > 4\sigma(F)$ ]; for **4**,  $R = 0.0482$  ( $R_w = 0.0643$ ) for 3385 independent observed reflections [ $2\theta \leq 45^\circ$ ,  $F > 4\sigma(F)$ ]. For structure solution SHELXS-86 (G. M. Sheldrick, University of Göttingen, Germany, 1986) and for refinement SHELX-76 (G. M. Sheldrick, University of Cambridge, England, 1976) were used. Complex **3** contained a half-occupied, disordered molecule of diethyl ether, the atoms of which were refined isotropically.

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.

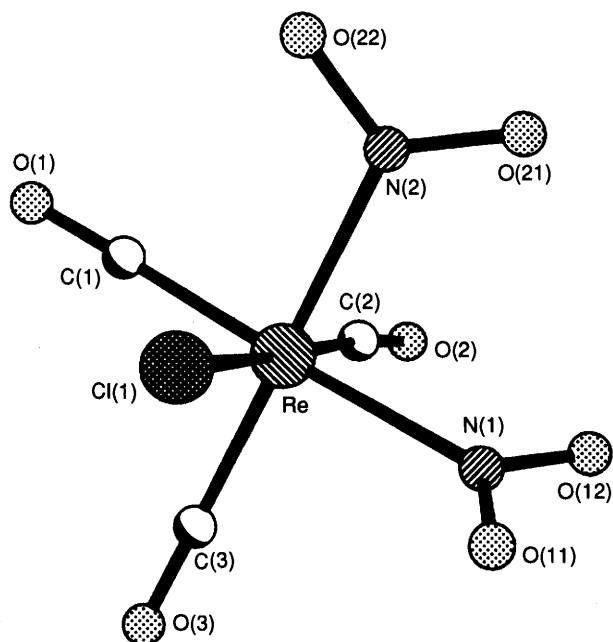


Fig. 2 The anion 4. Selected bond lengths: Re–Cl(1) 2.4881(5), Re–C(1) 1.921(13), Re–C(2) 1.908(13), Re–C(3) 1.906(12), Re–N(1) 2.243(11), Re–N(2) 2.208(11), N(1)–O(11) 1.099(17), N(1)–O(12) 1.208(18), N(2)–O(21) 1.187(16), N(2)–O(22) 1.234(17) Å.

Nitrito-groups are often observed in the initial stages of the formation of nitro complexes.

The isolation of 3 serves to emphasise that complexes such as 1 and 2 are well able to function as ligand groupings and that 3 may be regarded formally as an octahedrally coordinated complex of  $Mn^{II}$  bonded to two tridentate  $[Mn(CO)_3(NO_2)_3]^{2-}$  ligands. Dianion 3 resembles the nickel(II) derivatives first reported by Goodgame and coworkers.<sup>1</sup> In related studies we have found that in the crystal structure of  $K_3[Co(NO_2)_6]$  the  $K^+$  cation is effectively solvated by  $[Co(NO_2)_6]^{3-}$  anions and is surrounded by a quasi-icosahedral arrangement of O atoms from adjacent  $NO_2$  groups.<sup>4</sup>

The molecular structure of the anion  $[Re(CO)_3(NO_2)_2Cl]^{2-}$  4, which has been established from single X-ray diffraction experiments, is shown in Fig. 2. In this case both  $NO_2^-$  ligands are bonded through the N atom. Preliminary studies would indicate that the chemistry of the corresponding rhenium compounds parallels that observed for manganese. Although mixed  $NO_2^-/CO$  complexes have been discussed in the literature,<sup>5</sup> 4 appears to be one of the first crystallographically characterised mononuclear complexes which contain both ligands. A highly unusual trinuclear complex of the formula  $Re_3(CO)_{14}(NO_2)$  containing both  $NO_2^-$  and CO has been isolated by Ziegler and coworkers.<sup>6</sup>

The carbonyl nitrosyl species  $Mn(CO)_4(NO)$  5 and  $[Mn(CO)_2(NO)_2]^-$  6 may also be prepared via a route similar to that we have described above. In this case the reaction probably follows the alternative pathway outlined below in which  $Mn(CO)_5(NO_2)$  produced initially from the reaction of  $Mn(CO)_5Cl$  with  $NO_2^-$  undergoes O-transfer to produce  $Mn(CO)_4(NO)$  and  $CO_2$ . The neutral nitrosyl carbonyl then probably reacts further with  $NO_2^-$  to produce first the anion  $[Mn(NO)(CO)_3(NO_2)]^-$  which, after oxygen transfer, gives the observed anionic product  $[Mn(CO)_2(NO)_2]^-$  and  $CO_2$ . Significantly, the monoanion  $[Mn(CO)_2(NO)_2]^-$  readily undergoes reaction with  $O_2$  to regenerate nitro-complexes.

We thank the Verband der Chemischen Industrie for a Kekule scholarship to A. S. and the University of Edinburgh for support.

Received, 7th May 1993; Com. 3/02623J

## References

- 1 D. M. L. Goodgame, M. A. Hitchman, D. F. Marsham, P. Phavanantha and D. Rogers, *Chem. Commun.*, 1969, 1383.
- 2 U. Thewalt and R. E. Marsh, *Inorg. Chem.*, 1970, **9**, 1604.
- 3 D. M. L. Goodgame, M. A. Hitchman and D. F. Marsham, *J. Chem. Soc. A*, 1971, 259.
- 4 B. F. G. Johnson, E. Parisini and Y. V. Roberts, to be published.
- 5 K. R. Grundy, K. R. Laing and W. R. Roper, *J. Chem. Soc., Chem. Commun.*, 1970, 1500; D. T. Doughty, R. P. Stewart, Jr., and G. Gordon, *J. Am. Chem. Soc.*, 1981, **103**, 3388.
- 6 F. Oberdorfer, B. Balbach and M. L. Ziegler, *Z. Naturforsch., Teil B*, 1982, **37**, 157.