

Molecular Structure of an unusual Binuclear Manganese Complex with Highly Unsymmetrical Nitrosyl Bridges

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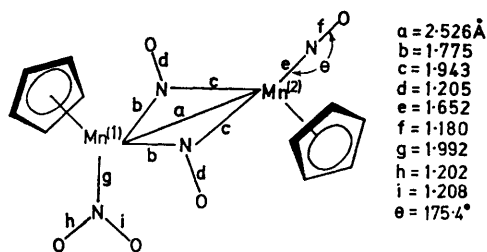
Summary The molecular structure of a new compound, $(h^5\text{-C}_5\text{H}_5)(\text{NO}_2)\text{Mn}^{(1)}(\mu\text{-NO})_2\text{Mn}^{(2)}(\text{NO})(h^5\text{-C}_5\text{H}_5)$, has been determined by X-ray crystallography, in which the most striking feature is the presence of highly unsymmetrical NO bridges: N-Mn⁽¹⁾ = 1.775(4) Å; N-Mn⁽²⁾ = 1.943(4) Å;

a probable structure for $(\text{C}_5\text{H}_5)_3\text{Mn}_2(\text{NO})_3$ can be inferred from the structure here reported.

IN the course of a study of the long known, but still incompletely characterized compound,¹⁻³ $(\text{C}_5\text{H}_5)_3\text{Mn}_2(\text{NO})_3$ (**1**), we

obtained a small yield of a compound of empirical formula $C_{10}H_{10}N_4O_5Mn_2$ (**2**). The identity and structure of (**2**), which readily afforded well formed crystals, has been established by a single-crystal *X*-ray structural study.

The compound crystallizes in the monoclinic space group $P2_1/c$: $a = 7.013(3)$, $b = 12.453(1)$, $c = 16.246(10)$ Å, $\beta = 110^\circ 00' \pm 6'$; $D_m = 1.89$, $D_c = 1.88$ g cm $^{-3}$; $Z = 4$. The structure was solved from Patterson and electron density maps and refined by least-squares methods to final unweighted and weighted residuals of 8.9 and 5.6% respectively, by using 2719 independent, non-zero reflections collected on a General Electric XRD-5 manual diffractometer, using θ - 2θ scans and niobium-filtered Mo- K_α radiation.



FIGURE

The structure is shown in the Figure, which gives some of the more interesting dimensions. All e.s.d.'s are less than 0.01 Å. Both $Mn(C_5H_5)$ groups have essentially C_{5v} local symmetry and may be regarded as ordinary $(h^5-C_5H_5)M$ groups. The terminal NO group on $Mn^{(2)}$ is of the linear

type which can, as usual, be treated as a 3-electron donor to the metal atom. The nitro-group bound to $Mn^{(1)}$ has the normal appearance of such a ligand and can be considered as a neutral, 1-electron donor. The $Mn^{(1)}-Mn^{(2)}$ distance implies the probable presence of a single (2-electron) bond. Thus, not including the bridging nitrosyl groups, the manganese atoms, $Mn^{(1)}$ and $Mn^{(2)}$, can be reckoned to have 14 and 16 electrons, respectively. They might be assigned formal oxidation numbers of +2 and 0, respectively.

The nitrosyl bridges are markedly unsymmetrical. This could be accounted for by assuming that each one donates two electrons to $Mn^{(1)}$ but only one electron to $Mn^{(2)}$, thus allowing each manganese atom to achieve a filled valence shell configuration.

While bridging NO groups have long been considered, on indirect evidence, to exist, there is prior direct *X*-ray evidence for them only in $(h^5-C_5H_5)_3Mn(NO)_4$ ⁴ (which contains a triply bridging nitrosyl as well as three double-bridging ones) and in $(h^5-C_5H_5)(NO)Cr(\mu-NO)(\mu-NH_2)Cr(NO)(h^5-C_5H_5)$.⁵ Only in the second case were accurate structural parameters determined and the bridge system $Cr(\mu-NO)Cr$ was found to be symmetrical.

We suggest that $(C_5H_5)_3Mn_2(NO)_3$, the structure of which has been the subject of much speculation,¹⁻³ may have a structure similar to that reported here except that for the replacement by a $(h^1-C_5H_5)$ group of the NO_2 group on $Mn^{(1)}$. Research is in progress to elucidate the structure of this and related compounds.

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