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The Crystal Structure of Tris-Cyclopentadienyldimanganese Trisnitrosyl; a Compound Containing Unsymmetrically Bonded Bridging Nitrosyl Groups

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As part of a systematic investigation of organometallic transition metal compounds containing nitrosyl groups as bridging ligands, we wish to report at this time the preliminary results of a three-dimensional single-crystal X-ray diffraction analysis of the long compound $(C_5H_5)_3Mn_2(NO)_3$.[1-4]

A major objective in these studies is to obtain a better understanding of the factors governing the symmetrical or unsymmetrical nature of nitrosyl groups when acting as bridging ligands.

X-ray data showed the dark-brown cubic-shaped crystals of $(C_5H_5)_3Mn_2(NO)_3$ to be orthorhombic with four binuclear molecules in the unit cell of dimensions: a = 18.201(3) Å, b = 10.802(2) Å, and c = 7.877(2) Å. The choice of the centrosymmetric space group P_{nma} (D_{2h}, No. 62), was supported by the results of the subsequent structure determination. A total of 3716 independent reflections having $2\theta_{MoK\alpha} < 71.0°$ were collected using Nb-filtered MoKα radiation and $\theta-2\theta$ scans on a Syntex P_1 Autodiffractometer. The 928 reflections having $2\theta_{MoK\alpha} < 43.0°$ and $I > \sigma(I)$ were used to solve and refine the structure using the heavy-atom technique and full matrix least squares. Unit weighted full-matrix least-squares refinement which employed anisotropic thermal parameters for the nonhydrogen atoms and isotropic thermal parameters for the hydrogen atoms resulted in a conventional R factor of 0.031.

The analysis shows that the crystal contains discrete binuclear $(h^5\text{-}C_5H_5)(NO)Mn(\mu\text{-}NO)_2Mn(h^1\text{-}C_5H_5)(h^5\text{-}C_5H_5)$ molecules with the *pentahapto*-bonded cyclopentadienyl rings in the *cis* configuration as shown in Fig. 1. The molecule possesses Cs-m symmetry with the two manganese atoms, the terminal nitrosyl group and one carbon atom (and its hydrogen atom) from each of the three cyclopentadienyl rings lying in a crystallographic mirror plane. Unlike the structure of $[(h^5\text{-}C_5H_5)(NO)Cr(\mu\text{-}NO)]_2$,[5] $(h^5\text{-}C_5H_5)(NO)Cr(\mu\text{-}NH_2)Cr(NO)(h^5\text{-}C_5H_5)$[6] and $[(h^5\text{-}C_5H_5)Fe(\mu\text{-}NO)]_2$,[7] which contain symmetrical bridging nitrosyl groups, this molecule possesses markedly unsymmetrical nitrosyl bridges very similar to those observed in the structure of $(h^5\text{-}C_5H_5)(NO_2)Mn(\mu\text{-}NO)_2Mn(NO)(h^5\text{-}C_5H_5)$.[4]

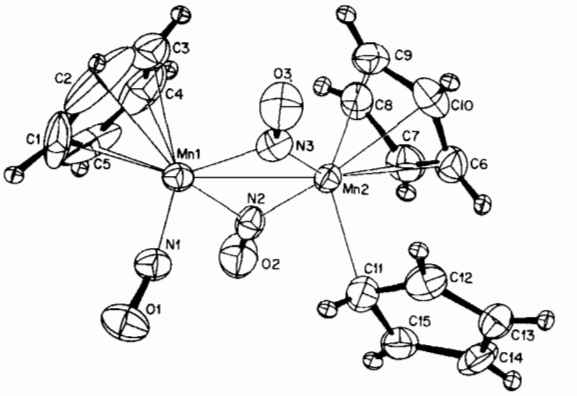

Figure 1. The molecular structure of triscyclopentadienyldimanganese trisnitrosyl.

The two manganese atoms of the complex are bonded to each other at a distance of 2.520(1) Å, and are bridged by two crystallographically equivalent nitrosyl ligands. The bridging Mn–N distances are of two distinct types having values of 1.944(3) Å and 1.752(3) Å for Mn1 and Mn2, respectively. The distance from the manganese atom to the nitrogen atom of the linear nitrosyl groups, Mn1–N1, is 1.656(5) Å. All three cyclopentadienyl rings are quite planar (maximum deviation of any carbon atom from its least-squares mean plane is 0.02 Å). The Mn–C, C–C, and C–H distances average 2.158(5) Å, 1.358(8) Å, and 0.87(5) Å respectively, for the *pentahapto*-bonded cyclopentadienyl rings. The *monohapto*-bonded cyclopentadienyl ring has two short C–C distances, 1.337(6) Å, thus indicating the existence of double bonds as expected, with the C–H bonds averaging 0.83(5) Å; the distance from the manganese atom to the bonded carbon in the *monohapto*-bonded cyclopentadienyl group, Mn2–C11, is 2.161(6) Å. The N–O bond lengths are 1.223(4) Å and 1.194(5) Å for bridging and terminal nitrosyl groups, respectively.

These bonding parameters suggest that a single (2-electron) bond exists between the two manganese atoms. Two of the cyclopentadienyl rings are bonded in the *pentahapto* fashion, and may be regarded as normal 5-electron donors; the third cyclopentadienyl ligand is of the *monohapto* type, being considered as a 1-electron donor. The terminal NO group on Mn1 is of the linear type which can, as usual, be treated as a 3-electron donor to the metal atom. Thus, not including the bridging NO groups, the manganese atoms Mn1 and Mn2 can be reckoned to have 16 and 14 electrons, respectively. They might be assigned formal oxidation numbers of +2 and 0, the shift of the nitrogen atom in the bridging nitrosyls toward the electron-deficient Mn2 atom is probably the result of its donating 2-electrons to Mn2 and only one to Mn1, thereby allowing each metal atom to achieve a filled valence shell configuration.

Acknowledgements

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