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Synthesis and *X*-Ray Structure of μ-Carbonyl-bis-μ-hexafluoroisopropylidenamido-hexacarbonyldimanganese. An Analogue of Enneacarbonyldi-iron having Unsymmetrically Bridging Ligands

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Summary We report the synthesis of μ-carbonyl-bis-μ-hexafluoroisopropylidenamido-hexacarbonyldimanganese, a structural analogue of enneacarbonyldi-iron having unsymmetrically bridging ligands.

THERE is considerable current interest in the methylenamido-derivatives of transition metals. The CH_2=N group can behave either as a formally three-electron donor, in which it can take both terminal[1,2] and bridging[1,3] roles, or as a formally one-electron donor.[4,5] The hexafluoroisopropylidenamido ligand has previously been reported in the role of a terminal ligand,[5] and we now report the bridging mode of this ligand along with the first methylenamido-complexes of manganese.

$Me_3Sn{-}N{=}C(CF_3)_2$,[6] $Et_3Sn{-}N{=}C(CF_3)_2$, and $LiN{=}C(CF_3)_2$[6,7] each react with $[Mn(CO)_5Br]$ to form a binuclear complex which contains bridging methylenamido-ligands.

$$2[Mn(CO)_5Br] + 2M{-}N{=}C(CF_3)_2 \rightarrow [Mn_2\{(CF_3)_2C{=}N\}_2(CO)_7] + 3CO + 2MBr$$

$$(M = Me_3Sn,\ Et_3Sn,\ \text{and}\ Li)$$

The molecular geometry of $[Mn_2\{(CF_3)_2C{=}N\}_2(CO)_7]$ has been determined unambiguously by a single-crystal *X*-ray diffraction study.

Crystal data: $C_{13}F_{12}Mn_2N_2O_7$, $M = 634{\cdot}0$, monoclinic, space group $P2_1/c$ [C^5_{2h}; No. 14]; cell dimensions (at 20·6 °C): $a = 9{\cdot}298(5)$, $b = 26{\cdot}614(19)$, $c = 9{\cdot}543(8)$ Å, $\beta = 121{\cdot}00(5)°$, $U = 2022{\cdot}2$ Å^3, $D_m = 2{\cdot}06$, $D_c = 2{\cdot}08$ g cm^{-3}, $Z = 4$, μ(Mo-K_α) $= 14{\cdot}67$ cm^{-1}.

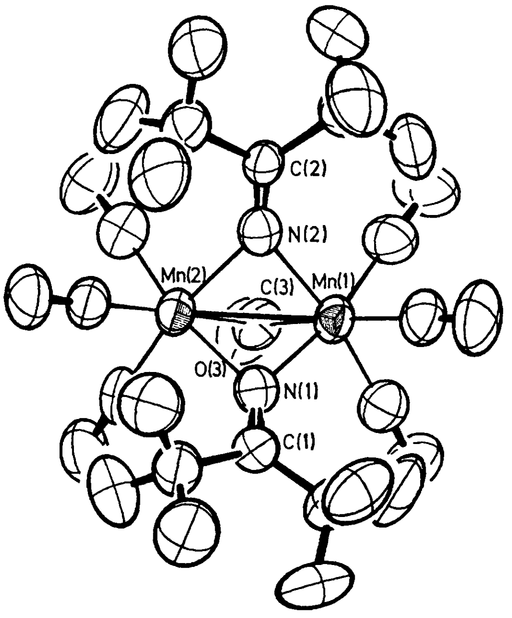

FIGURE. The molecular geometry of $[Mn_2\{(CF_3)_2C{=}N\}_2(CO)_7]$

Intensity data to $2\theta = 45°$ (Mo-K_α radiation) were collected with a Picker FACS-1 automated diffractometer and the structure was solved by Patterson, Fourier, and least-squares refinement techniques. All atoms have been accurately located, the final R-values being 10·9% for all 2630 reflections and 5·2% for the 1512 reflections for which $I > 3\sigma(I)$.

The molecular geometry, shown in the Figure, resembles that of enneacarbonyldi-iron[8] insofar as the complex is a member of the $(OC)_3M(\mu\text{-}X)_3M(CO)_3$ family. The two methylenamido-bridges presumably behave as formally three electron donors. This, along with the donation of two electrons from each carbonyl ligand, and a manganese–manganese bond [Mn(1)–Mn(2) = 2·518(2) Å], allows each metal atom to attain the appropriate 'noble-gas' configuration.

However, the molecule contains a unexpected feature in that the bridging carbonyl ligand is grossly unsymmetrical [Mn(1)–C(3) = 1·944(9), Mn(2)–C(3) = 2·173(9) Å; ∠Mn(1)–C(3)–O(3) = 151·0(8), ∠ Mn(2)–C(3)–O(3) = 133·8(7)°]. The unsymmetrical bridging carbonyl group is apparently balanced electronically by a smaller and opposing distortion of the μ-amido-ligands, *viz.*, Mn(1)–N(1) = 2·021(7) and Mn(1)–N(2) = 2·036(7) Å, *vs.* Mn(2)–N(1) = 1·999(7) and Mn(2)–N(2) = 1·972(7) Å. Angles at the nitrogen atoms are consistent with this interpretation, with those from Mn(1) [∠Mn(1)–N(1)–C(1) = 142·7(6)° and ∠Mn(1)–N(2)–C(2) = 141·8(6)°] being larger than those from Mn(2) [∠ Mn(2)–N(1)–C(1) = 139·7(6)° and ∠Mn(2)–N(2)–C(2) = 140·3(6)°]. Bridging angles are: ∠Mn(1)–N(1)–Mn(2) = 77·6(3), ∠Mn(1)–N(2)–Mn(2) = 77·9(3), and ∠Mn(1)–C(3)–Mn(2) = 75·2(3)°.

We note that 'grossly unsymmetrical' or 'semi-bridging' carbonyl groups have been reported previously.[9] However, in no previously reported case has the asymmetry of a bridging carbonyl group been compensated by a contrary asymmetry in another type of bridging ligand.

The unsymmetrical location of C(3)–O(3) is further reflected in the Mn–CO distances *trans* to it. Thus, Mn(1)–CO(*trans*) = 1·869(10) Å while Mn(2)–CO(*trans*) = 1·800(9) Å; also ∠C(3)–Mn(1)–CO(*trans*) = 169·7(4)° as opposed to ∠C(3)–Mn(2)–CO(*trans*) = 166·4(4)°. For comparison, we note that the remaining Mn–CO distances range from 1·789(10) to 1·833(10) Å.

Distances within the ligands are as expected, with N(1)–C(1) = 1·259(9) and N(2)–C(2) = 1·258(9) Å; the C(3)–O(3) bond length is 1·154(9) Å.

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