

The Structures of the Methanol and Hexanol Adducts of Tris(quinolin-8-olato)manganese(III)

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Abstract

X-ray analyses of monoclinic crystals of the methanol and hexanol adducts of tris(8-quinolinolato)-manganese(III) respectively have established their structure. The crystals are isomorphous and belong to the space group $P2_1/n$ with $Z = 4$. The cell parameters are $a = 10.847$, $b = 13.201$, $c = 17.285$ Å, $\beta = 97.56^\circ$ (methanol) and $a = 11.201$, $b = 13.342$, $c = 17.200$ Å, $\beta = 97.09^\circ$ (hexanol). The methanol structure contains one alcohol molecule per asymmetric unit whereas in the hexanol structure there is only half an alcohol molecule. The hexanol is therefore disordered, with the centre of the central C-C bond lying at the crystallographic centre of symmetry. The configuration of the tris-chelate is *meridional*.

The preparation of alcohol solvates of tris(8-quinolinolato)manganese(III) has been reported by Burns *et al.*¹ The formation of these solvates has been restricted to those with straight-chain alcohols, namely the homologues methanol to hexan-1-ol and ethane-1,2-diol. A thermogravimetric study in conjunction with chemical analysis also reported by these authors has shown that the smaller alcohol molecules, methanol and ethanol, form 1:1 adducts, whereas for the larger propan-1-ol, butan-1-ol and hexan-1-ol molecules there was half a mole of alcohol per mole of complex. In addition, thermal studies have shown that it is difficult to remove the alcohol molecule from the complex. These results agree with those of Umland and Adam² for similar adducts of tris(quinolin-8-olato)chromium(III). An X-ray structure analysis of the methanol adduct of the latter by Folting *et al.*³ has shown that the chromium is octahedrally coordinated to the three quinolin-8-ol molecules which act as bidentate ligands and the structure is *meridional* and distorted. Two methanol molecules related by a centre of symmetry were situated in a 'cage-like' cavity formed by quinolin-8-ol groups from adjacent complex molecules within the crystal. This cavity was large enough to accommodate two ethanol molecules and subsequently Folting *et al.* found that the ethanol and methanol adducts of the chromium complex were isomorphous. Although it was thought that the methanol and ethanol adducts of the manganese complex were isomorphous with the chromium analogues, in the case of the adducts formed by the larger alcohols the 'cage-like' cavity in the crystal was only large enough to accommodate one alcohol molecule. As the large alcohol

¹ Burns, A. R., Cardwell, T. J., and Catrall, R. W., *Aust. J. Chem.*, 1971, 24, 661.

² Umland, F., and Adam, K., *Z. Anorg. Allg. Chem.*, 1965, 341, 388; Umland, F., Gudmundson, G. H., and Adam, K., *Naturwissenschaften*, 1961, 48, 49.

³ Folting, K., Cox, M. M., Moore, J. W., and Merritt, L. L., *Chem. Commun.*, 1968, 1170.

molecules do not possess a centre of symmetry, it was of interest to determine their mode of packing in the crystal of the solvated complex. We have carried out X-ray structure analyses of the methanol and hexanol adducts of tris(quinolin-8-olato)manganese(III) and now wish to report these results.

Both compounds crystallize in the monoclinic space group $P2_1/n$ with four molecules in the unit cell. For the methanol adduct, the unit cell dimensions are $a = 10.847(3)$, $b = 13.201(4)$, $c = 17.285(5)$ Å, $\beta = 97.56(5)^\circ$, the asymmetric unit being $\text{Mn}(\text{C}_9\text{H}_5\text{NO})_3, \text{CH}_3\text{OH}$. For the hexanol adduct, $a = 11.201(4)$, $b = 13.342(4)$, $c = 17.200(5)$ Å, $\beta = 95.09(6)^\circ$, and the asymmetric unit is $\text{Mn}(\text{C}_9\text{H}_5\text{NO})_3, \frac{1}{2}\text{C}_6\text{H}_{13}\text{OH}$. Intensity data measured with Cu K α radiation and estimated visually from Weissenberg film were used to solve the structure of the methanol adduct. For its refinement, data to 1.14 Å were remeasured on a four-circle

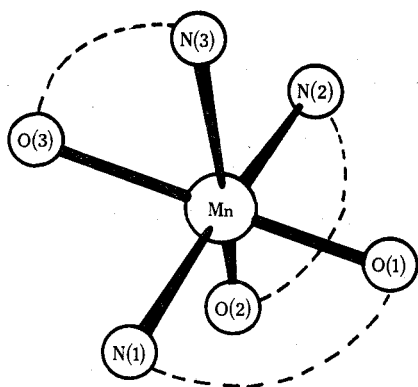


Fig. 1. Configuration of tris(quinolin-8-olato)manganese(III).

Table 1. Some bond lengths and angles of both the complex structures together with their estimated deviations

Bond lengths (Å)	Methanol adduct	Hexanol adduct	Bond angles (degrees)	Methanol adduct	Hexanol adduct
Mn–N(1)	2.241(8)	2.224(6)	O(1)–Mn–N(2)	92.3(3)	93.8(2)
Mn–N(2)	2.266(8)	2.263(5)	O(1)–Mn–N(3)	90.2(3)	90.2(2)
Mn–N(3)	2.058(8)	2.057(6)	O(1)–Mn–O(2)	95.5(3)	95.5(2)
Mn–O(1)	1.916(7)	1.907(5)	O(2)–Mn–O(3)	92.9(3)	93.1(2)
Mn–O(2)	1.924(7)	1.915(5)	O(2)–Mn–N(1)	93.0(3)	94.5(2)
Mn–O(3)	1.905(7)	1.922(5)	O(3)–Mn–N(1)	95.0(3)	93.0(2)
C–N(mean)	1.35(1)	1.35(1)	O(3)–Mn–N(2)	94.0(3)	94.2(2)
C–C(mean)	1.41(2)	1.41(1)	N(3)–Mn–N(1)	94.5(3)	95.1(2)
C–O(mean)	1.35(1)	1.34(1)	N(3)–Mn–N(2)	93.7(3)	91.6(2)

diffractometer. Intensity data for the hexanol adduct to 0.91 Å were measured with Mo K α radiation on a four-circle diffractometer. Both structures were solved by the heavy-atom method and refined by difference and block diagonal least-squares procedures. Atoms of the metal complex were given anisotropic temperature factors and the alcohol atoms given isotropic ones. A conventional R of 0.079 for the 1536 observed terms of the methanol structure and an R of 0.073 for the 2509 observed terms of the hexanol were attained. The dimensions of the metal coordination sphere are given in Table 1 while the numbering of the atoms appears in the Fig. 1.

The structure of the methanol adduct is most likely isomorphic with the chromium analogue.* As expected, the manganese is octahedrally coordinated to the oxygen and nitrogen atoms of each quinolin-8-ol group, the octahedron is distorted, the complex is in the *meridional* configuration and the methanol molecule is hydrogen bonded to a *meridional* oxygen, O(1) (see Fig. 1) the O(1)···OH(methanol) distance being 2.79 Å. Two methanol molecules related by the crystallographic centre of symmetry lie in the 'cage-like' cavity as described previously, and the intermolecular distance between these two molecules C(MeOH)···C'(MeOH) is 4.93 Å. The compound is a racemate.

The structure of the hexanol adduct is isomorphic with the methanol adduct. In this instance, instead of two alcohol molecules related by a centre of symmetry being accommodated in the cavity, there is one disordered hexanol molecule. The crystallographically imposed symmetry requires that the molecule lies with the mid-point of its central C–C bond at the centre of symmetry and that it adopts two orientations in the unit cell. This results in the sites of three carbon atoms of the hexanol molecule comprising the asymmetric unit being fully occupied, whereas the oxygen atom site is only one half occupied. Similar instances of disorder have also been noted in the crystal structures of azulene⁴ and *p*-chloronitrobenzene.⁵ The O(1)···OH(hexanol) distance is 2.91 Å.

Acknowledgments

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* To date no detailed description of this structure has been reported.

⁴ Robertson, J. M., Shearer, H. M. M., Sim, G. A., and Watson, D. G., *Acta Crystallogr.*, 1962, **15**, 1.

⁵ Mak, T. C. W., and Trotter, J., *Acta Crystallogr.*, 1962, **15**, 1078.