# THE 8-QUINOLINOL AND 2-METHYL-8-QUINOLINOL COMPLEXES OF MANGANESE(III)

By A. R. Burns,* T. J. Cardwell,* and R. W. Cattrall*

Ray et al.[1] have prepared the complex tris(8-quinolinolato)manganese(III) by the reaction of tris(acetylacetonato)manganese(III) with 8-quinolinol in ethanol. They reported the complex as unsolvated, stable, shiny black crystals. We wish to report the preparation of the same complex with one mole of ethanol attached using two other methods: firstly, by the reaction of manganese(II) acetate with 8-quinolinol in ethanol solution which on standing oxidizes and precipitates the complex, and secondly, by the direct reaction of manganese(III) acetate with 8-quinolinol in ethanol solution which on standing also precipitates the complex as shiny black crystals. Using the latter method, solvates have also been prepared with several other alcohols, viz., methanol, propan-1-ol, butan-1-ol, pentan-1-ol, hexan-1-ol, and ethane-1,2-diol. The use of the branched-chain alcohols, propan-2-ol and 2-methylpropan-1-ol, however, yielded only the unsolvated complex.

We also wish to report the preparation of the complex tris(2-methyl-8-quinolinolato)manganese(III) which is precipitated in the unsolvated form as shiny black crystals by the direct reaction of manganese(III) acetate with 2-methyl-8-quinolinol in ethanol solution.

The ultraviolet and visible spectra and the magnetic moments of the complexes are indicative of high-spin octahedral manganese(III) complexes of 8-quinolinol and 2-methyl-8-quinolinol. However, we have observed one feature in the spectra which is different to that observed by Ray et al.[1] These workers have reported that the low energy absorption region of tris(8-quinolinolato)manganese(III) is unsymmetrical and they have suggested the possibility that the $^5T_{2g} \leftarrow {}^5E_g$ transition is located at about 19500 cm$^{-1}$. We do not observe this in the spectra of our complexes; however, we do observe a band in the region of 11000 cm$^{-1}$ for tris(8-quinolinolato)manganese(III) and a shoulder in the region of 14500 cm$^{-1}$ for tris(2-methyl-8-quinolinolato)manganese-(III). We have assigned these bands to the low energy $^5A_{1g} \leftarrow {}^5B_{1g}$ transition associated with a tetragonally distorted octahedral field.[2] The other two bands at higher energies expected in this case are obscured by the intense absorption bands associated with the ligand. The difference in the energies associated with the two low-energy transitions for the two complexes is interesting and may be related to an increased distortion (axial elongation) associated with the more sterically hindered 2-methyl-8-quinolinol compound. Thermogravimetric studies do indicate that

* Department of Chemistry, La Trobe University, Bundoora, Vic. 3083.

[2] Ray, M. M., Adhya, J. N., Biswas, D., and Poddar, S. N., Aust. J. Chem., 1966, 19, 1737.
[1] Davis, T. S., Fackler, J. P., and Weeks, M. J., Inorg. Chem., 1968, 7, 1994.

tris(8-quinolinolato)manganese(III) is more stable than tris(2-methyl-8-quinolinolato)-manganese(III).

Thermogravimetric and infrared spectral studies on the ethanol adduct of the 8-quinolinol complex are consistent with the presence of one mole of ethanol in the complex. It is interesting to note that during the thermal degradation of the ethanolated complex the mole of ethanol is lost at a relatively high temperature (160°).

Thermogravimetric study and the analysis for manganese of the adducts formed between tris(8-quinolinolato)manganese(III) and the other alcohols (Table 1) show that, for the smaller molecular size alcohols, 1 : 1 adducts are formed, and, for the larger alcohols, there appears to be a half a mole of alcohol per mole of complex. These results agree with those found by Umland and Adam[3] for similar adducts with tris(8-quinolinolato)chromium(III).

TABLE 1

THE COMPOSITIONS OF THE TRIS(8-QUINOLINOLATO)MANGANESE(III) ADDUCTS

| Solvent | Mn Found (%) | Mn Calc. (%) | Mole Ratio[a] Complex/Solvent | Temp. for Solvent Removal |
|---|---|---|---|---|
| Methanol | 10·6 | 10·6 | 1 : 1·03 | 160° |
| Ethanol | 10·6 | 10·3 | 1 : 1·03 | 160 |
| Propan-1-ol | 10·6 | 10·6 | 1 : 0·55 | 160 |
| Butan-1-ol | 10·6 | 10·5 | 1 : 0·56 | 210 |
| Pentan-1-ol | 10·4 | 10·3 | [b] | c. 210 |
| Hexan-1-ol | 10·2 | 10·2 | 1 : 0·54 | 210 |
| Ethane-1,2-diol | 10·0 | 10·0 | 1 : 0·89 | 210 |

[a] From thermogravimetric studies.

[b] Complex slowly decomposed at the temperature necessary to remove the solvent.

A recent crystal structure has been carried out by Folting et al.[4] on the methanol adduct of tris(8-quinolinolato)chromium(III). The results of this study have shown that the chromium is octahedrally coordinated by the three 8-quinolinol molecules which act as bidentate ligands. The structure is *trans* and is distorted. The methanol molecule is not coordinated to the chromium but is hydrogen-bonded to a *trans*-oxygen in one of the ligands. According to Folting et al.[4] the difficulty in removing methanol from the adduct is due to the trapping of two methanol molecules related to each other by a centre of symmetry, in a "cage-like" cavity formed by 8-quinolinol molecules from neighbouring complex molecules within the crystal. They point out that this cavity appears large enough to accommodate ethanol also. Preliminary studies by these workers indicate that the water and ethanol adducts of the chromium complex are isomorphous with the methanol adduct.

It seems certain in view of the above discussion that the methanol and ethanol adducts of tris(8-quinolinolato)manganese(III) are isomorphous with the chromium compound. The structures are probably *trans* and distorted (accounting for the tetragonal distortion observed in the electronic spectrum). The alcohol molecules in the adducts are difficult to remove and this is accounted for in terms of the suggestion

[3] Umland, F., and Adam, K., Z. anorg. allg. Chem., 1965, **341**, 308; Umland, F., Gudmundsson, G. H., and Adam, K., Naturwissenschaften, 1961, **48**, 49.

[4] Folting, K., Cox, M. M., Moore, J. W., and Merritt, L. L., Chem. Commun., 1968, 1170.

above of Folting *et al.*[4] It also appears certain that, in the case of the adducts formed with the larger alcohols, the "cage-like" cavity in the crystal structure is only large enough to accommodate one alcohol molecule. The fact that it is impossible to prepare adducts using propan-2-ol and 2-methylpropan-1-ol is very likely due to the inability of the more bulky branched-chain alcohol molecule to fit into the cavity formed by the 8-quinolinol molecules.

Prior to the work of Folting *et al.*,[4] it had been suggested[3] that it was the *cis* form of tris(8-quinolinolato)chromium(III) which formed a methanol adduct whereas the *trans* form did not. However, Folting *et al.*[4] point out that this suggestion is not correct and that it is, in fact, the *trans* form of tris(8-quinolinolato) metal(III) complexes which forms an adduct.

Ray *et al.*[1] have not reported obtaining the tris(8-quinolinolato)manganese(III) as the ethanol adduct using their method of preparation [starting from the symmetrical tris(acetylacetonato)manganese(III) in ethanol solution]. This poses the question whether they actually prepared the *cis* form of the compound. We have repeated their preparation and have only been able to obtain an ethanol adduct, suggesting that the complex is most likely the *trans* isomer.

## Experimental

### *Tris(8-quinolinolato)manganese(III)*

This compound was prepared by a different procedure to that used by Ray *et al.*[1] Manganese(II) acetate tetrahydrate ($4 \times 10^{-3}$ mol) and 8-quinolinol ($12 \times 10^{-3}$ mol) each in 100 ml of dry ethanol were mixed to give initially a clear yellow solution. On standing, the yellow solution changed to a dark brown colour and shiny black crystals were precipitated overnight. The complex, which was found to have 1 mol. propn. of ethanol attached, was washed with dry ethanol and dried in vacuum at 25°. This monoethanolated complex could also be prepared by mixing solutions of manganese(III) acetate dihydrate ($3 \cdot 7 \times 10^{-3}$ mol) and 8-quinolinol ($11 \cdot 2 \times 10^{-3}$ mol) in 50 ml of ethanol respectively. The resultant solution yielded shiny black crystals on standing overnight (Found: C, 65·6; H, 4·5; Mn, 10·6; N, 8·0; $\mu_{eff} = 4 \cdot 8$ B.M. Calc. for $C_{27}H_{18}MnN_3O_3,C_2H_5OH$: C, 65·3; H, 4·5; Mn, 10·3; N, 7·9%).

The monoethanolated complex was converted into the unsolvated form by heating at 180° for 1 hr. This unsolvated complex could also be prepared by mixing stoicheiometric amounts of manganese(III) acetate dihydrate and 8-quinolinol in 2-methylpropan-1-ol (Found: C, 66·6; H, 3·9; Mn, 11·7; N, 8·4; $\mu_{eff} = 5 \cdot 0$ B.M. Calc. for $C_{27}H_{18}MnN_3O_3$: C, 66·6; H, 3·7; Mn, 11·3; N, 8·6%).

The adducts with the other alcohols were all prepared, as above, using the manganese(III) acetate method and the appropriate solvent. The compositions of these adducts (Table 1) were obtained from the analyses for manganese and from the weight losses associated with the removal of solvent from the adduct in the thermogravimetric studies.

### *Tris(2-methyl-8-quinolinolato)manganese(III)*

This compound was prepared by mixing solutions of stoicheiometric amounts of manganese(III) acetate dihydrate ($3 \cdot 7 \times 10^{-3}$ mol) and 2-methyl-8-quinolinol ($11 \cdot 2 \times 10^{-3}$ mol) in 100 ml ethanol respectively. Small, shiny, black crystals were obtained after standing for 2–3 days and were washed in ethanol and dried in vacuum at 25° (Found: C, 66·9; H, 4·7; Mn, 10·6; N, 7·8; $\mu_{eff} = 5 \cdot 0$ B.M. Calc. for $C_{30}H_{24}MnN_3O_3$: C, 68·0; H, 4·6; Mn, 10·4; N, 7·9%).

It was not possible to prepare the latter complex using manganese(II) acetate tetrahydrate.

### Analyses and Thermogravimetric Studies

Analyses for manganese were obtained using atomic absorption spectrophotometry. Microanalyses were carried out by the Australian Microanalytical Service, Melbourne.

Thermogravimetric studies were carried out using a Stanton TR-01 thermobalance.