Synthesis and Characterization of the Dimeric $[Mn(salen)(CO)]_2(ClO_4)_2$ [salen = *N,N'*-ethylenebis(salicylideneaminato)], a Carbonyl Complex of a Metal in the +3 Oxidation State

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The synthesis and characterization of $[Mn(salen)(CO)]_2(ClO_4)_2$ [salen = *N,N'*-ethylenebis(salicylideneaminato)], the first carbonyl complex of a first row transition metal in the +3 oxidation state, are reported; the formation of such a complex is critically dependent on the nature of the polymethylene chain in the Schiff's base ligand.

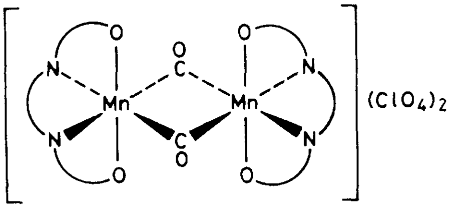
Carbon monoxide adducts of first-row transition metals in the +3 oxidation state have previously not been reported. We report here the synthesis and characterization of a manganese(III)–carbon monoxide adduct of empirical formula $[Mn(salen)(CO)]ClO_4$ [salen = *N,N'*-ethylenebis(salicylideneaminato)]. We have a particular interest in high-valent manganese complexes of Schiff's base ligands since we have evidence that they can aid the photodecomposition of water by visible light,[1] perhaps mimicking manganese-mediated water photolysis in the chloroplast during green plant photosynthesis.[2]

The complex $[Mn(salen)(CO)]ClO_4$ can be isolated in almost quantitative yield from the aerial oxidation of $[Mn^{II}(salen)(H_2O)_2]$ in an EtOH–MeOH (50:50) solution in the presence of perchlorate anions and sodium hydroxide.[3] Once formed, the complex appears to be indefinitely stable under a dinitrogen atmosphere, but decomposes to give $[Mn(salen)(H_2O)]ClO_4$ within 24 h in air.

The mull i.r. spectrum of $[Mn(salen)(CO)]ClO_4$ exhibits the usual bands assignable to co-ordination of the dianionic tetradentate Schiff's base[4] and, in addition, a medium-intensity slightly split band at 1710 cm^{-1}, assignable to $\nu(CO)$ of a bridging carbonyl group.[5] Further evidence of a bridging carbonyl species, and hence a dimeric structure, comes from the fast atom bombardment mass spectrum of the complex which exhibits a peak assignable to $\{[Mn(salen)(CO)]_2\}^+$ (698); other peaks of interest are assigned to $[Mn(salen)]^+$ (321), $[Mn(salen)(CO)]^+$ (349), and $[Mn(salen)(CO)_2]^+$ (377). The room temperature magnetic moment, $\mu_{eff} = 4.48\ \mu_B$ per Mn, is appreciably lower than expected for spin-only manganese(III), and may be explained through antiferromagnetic coupling through the bridging carbonyls. Additionally, the complete absence of an e.s.r. signal in the solid state at liquid dinitrogen temperature is consistent with the presence of manganese(III).

Attempts to remove the co-ordinated carbon monoxide by stirring the complex in a pyridine–iodine solution gave a gaseous product, which was identified as CO by g.c./mass spectroscopy after differentiation from the background N_2 peak. The source of the carbon monoxide in $[Mn(salen)(CO)]ClO_4$ is presumably carbonyl abstraction from the alcoholic solvents in the presence of a base, dioxygen, and a transition metal.[6]

In conclusion, we propose structure (**1**) for this complex.



(1)

We have investigated the reaction of other manganese(II) complexes [Mn(Base)(H_2O)$_2$] [Base = *N,N'*-methylene- or propylene-bis(salicylideneaminato)] under identical conditions. However, we only isolated the [Mn(Base)(H_2O)]ClO_4 complexes in almost quantitative yield and no trace of a carbonyl adduct was observed. The reaction to form [Mn(salen)-(CO)]ClO_4 appears to be highly specific for the ethylene Schiff's base.

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References

1 F. M. Ashmawy, C. A. McAuliffe, R. V. Parish, and J. Tames, unpublished results.
2 G. M. Chemiae, *Ann. Rev. Plant Physiol.*, 1968, **21**, 467; M. Calvin, *Science*, 1974, **184**, 375; M. Calvin and S. R. Cooper, *ibid.*, 1975, **185**, 4148.
3 J. Tames, Ph.D. Thesis, Manchester University, 1980.
4 J. R. Dilworth, C. A. McAuliffe, and B. J. Sayle, *J. Chem. Soc., Dalton Trans.*, 1977, 849.
5 F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' Wiley-Interscience, New York, 1980, p. 1072.
6 Ref. 5, p. 1298.