The Crystal Structure of an Octahedral High-spin Mn$^{\text{III}}$ Complex, Acetylacetonatobis-(*N*-phenylaminotroponiminato)manganese(III)

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Summary The crystal structure of acetylacetonatobis-(*N*-phenylaminotroponiminato)manganese(III) has revealed the first distorted octahedral complex of high-spin Mn$^{\text{III}}$ and has suggested empirical rules for predicting the final configurations of octahedral Cu$^{\text{II}}$ and Mn$^{\text{III}}$ compounds.

THE d_{z^2} and $d_{x^2-y^2}$ orbitals in a metal ion are degenerate in an octahedral field; however, the presence of non-equivalent ligands may remove the degeneracy. The resulting distorted octahedral configuration (erroneously called a Jahn–Teller distortion) will have either two short and four bonds or four short and two bonds. A number of examples of the latter configuration are known for Cu$^{\text{II}}$, a d^9 system; however, no examples of either type are known for high spin Mn$^{\text{III}}$, a d^4 system. In fact, the only structural study of a high-spin Mn$^{\text{III}}$ complex, tris(acetylacetonato)-manganese(III),[1] suggests that an angular distortion (rather than a change in bond lengths) is used to remove the degeneracy. A study of acetylacetonatobis-(*N*-phenylaminotroponiminato)manganese(III) has revealed the first example of a distorted octahedral configuration for a high-spin manganese(III) complex. Our results together with other recent studies[2–4] have suggested some empirical rules for predicting the final configuration of Mn$^{\text{III}}$ and Cu$^{\text{II}}$ complex ions.

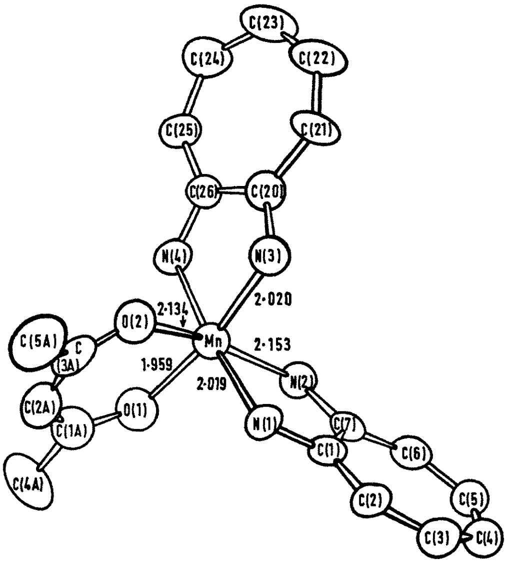

FIGURE. *The configuration and atomic numbering in acetylacetonatobis-*(N-*phenylaminotroponiminato*)*manganese*(III). *The atoms are drawn as boundary ellipsoids to illustrate the thermal motion. Bond lengths in* Å: *all* ±0·005 Å.

Crystal data: $\text{MnC}_{43}\text{H}_{37}\text{N}_4\text{O}_2$, dark black monoclinic crystals, $a = 11{\cdot}00(1)$, $b = 20{\cdot}25(1)$, $c = 16{\cdot}50(1)$,Å, $\beta = 102{\cdot}2(1)°$, $D_m = 1{\cdot}30$, $D_c = 1{\cdot}29$ g/cm^3, $Z = 4$; space group $P2_1/n$ (No. 14).

The 4096 observed reflections measured using Cu-K_α radiation were used in the analysis. The structure was refined by least-squares methods, all atoms with anisotropic thermal parameters, to an R, the usual residual, of 0·073. The location of the hydrogen atoms and further refinement is continuing.

The co-ordination about the Mn atom (Figure) is the four short–two long distortion observed in Cu$^{\text{II}}$ complexes. The difference of about 0·13 to 0·17 Å between the long and short bonds is less than that observed[4] in the d^9 case. A comparison of (acac)Mn(pati)$_2$† with (hfacac)$_2$Cu(bipy)[4] shows that the distortion involves the poorest donor atoms in each molecule. This principle explains the unusual two short-four long configuration observed in the bis(diethylenetriamine)copper(II) cation.[5]

A comparison of (acac)Mn(pati) with (acac)$_3$Mn [1] illustrates two other points. The average Mn–O bond distance in (acac)$_3$Mn is 1·894 Å and all the Mn–O bonds are equivalent. The Mn–O distance in (acac)Mn(pati)$_2$ is 1·959 Å which is significantly longer than in (acac)$_3$Mn. These changes in Mn–O bond distances may be due to the nitrogen ligands in the molecule; however, additional structural data are required before a definitive decision can be made. The absence of a bond distortion in (acac)$_3$Mn suggests that symmetrical tris-chelates may remove the degeneracy of the d_{z^2} and $d_{x^2-y^2}$ levels by an angular distortion rather than a bond lengthening.

In conclusion, it appears that for bond distortions to occur in octahedral Cu$^{\text{II}}$ or high-spin Mn$^{\text{III}}$ with tris-chelates, at least one dissimilar atom must be present. The resulting configuration will have the poorest donor atom furthest away from the metal ion, a hypothesis which is reasonable on electrostatic grounds.

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† Abbreviations: acac is acetylacetonato, pati is *N*-phenylaminotroponiminato, hfacac is hexafluoroacetylacetonato and bipy is 2,2′-bipyridyl.

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