Molecular Structure of $[Mn^{III}L_2]^-$ $[H_2L$ = *N*-(3,5-Dichloro-2-hydroxybenzyl)glycine]: Evidence for a Pseudo-Jahn–Teller Compression

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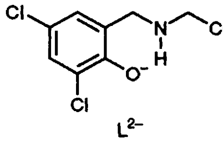
Reaction of 2 equivalents of the deprotonated ligand, L^{2-}, with manganese(II) under ambient conditions involves one-electron oxidation of the latter to afford the title complex; a single-crystal X-ray diffraction study of this heteroleptic complex has shown the Mn^{III} ion to be in a compressed rhombic octahedral environment in accordance with a pseudo-Jahn–Teller compression.

Over the past decade or so, there has been an upsurge in the exploration of the coordination chemistry of manganese not only because of the realisation that polynuclear manganese complexes[1] can potentially mimic the behaviour of the active sites of manganese-binding proteins, but also because of the recent emergence of manganese compounds possessing interesting structural, magnetic and spectroscopic features.[2] Our contribution focuses on the usual geometry shown by the mononuclear complex $[Mn^{III}L_2]^-$ $[H_2L$ = *N*-(3,5-dichloro-2-hydroxybenzyl)glycine] in the solid state. Commonly, the coordination sphere of high-spin Mn^{III} is characterised by pronounced axial elongation,[3] a structural feature attributed to the well-established Jahn–Teller effect. In this communication we show that the structure of $[Mn^{III}L_2]^-$ displays a pseudo-Jahn–Teller compression which is rare in mononuclear complexes of manganese(III) containing polydentate ligands.

Treatment of the deprotonated ligand, L^{2-}, with manganese(II) (2:1 molar ratio) under aerobic conditions produces the purple-tinged dark brown complex $[Mn^{III}L_2]^-$. The solid-state infrared spectrum† of this complex is similar to that of H_2L with the absorption bands occurring at lower energies, as expected. The electronic absorption spectrum† of $[Mn^{III}L_2]^-$ is consistent with a significantly distorted octahedral high-spin d^4 geometry.[4] Microanalysis† together with mass spectrometry† confirmed the formulation $[C_5H_{12}N][Mn^{III}L_2]$ ($[C_5H_{12}N]$ = piperidinium ion). Measurement of the molar conductivity in methanol gave $\Lambda_M = 85$ S cm^2 mol^{-1} which is concordant with a 1:1 electrolyte type.[5]

That the manganese ion in this complex is in a trivalent state is verified by the effective magnetic moment, $\mu_{eff} = 4.87\ \mu_B$ at 300 K, which compares favourably with the spin-only value for a spin-free d^4 configuration. Variable-temperature magnetic susceptibility data were recorded over the range 80–300 K. A plot of χ_M^{-1} *vs.* T showed correlation with the Curie–Weiss law: *viz.* $\chi_M = C/(T - \theta)$. The Weiss constant, $\theta \approx 4$ K, is indicative of a very weak ferromagnetic interaction. The effective magnetic moments, μ_{eff}, steadily decrease from 4.97 μ_B at 80 K to 4.87 μ_B at 300 K.

The molecular structure of the anionic complex $[Mn^{III}L_2]^-$, depicted in Fig. 1, has been determined by single-crystal X-ray crystallography.‡ The manganese(III) ion is coordinated to the two tridentate ligands in a distorted octahedral arrangement with the donor atoms—phenolate oxygen, amine nitrogen and carboxylate oxygen—of each ligand facially oriented. A conspicuous feature in the structure of $[Mn^{III}L_2]^-$ is axial compression of the Mn^{III} rhombically distorted octahedron. To our knowledge, $[Mn^{III}L_2]^-$ is the first example of a structurally characterised mononuclear manganese(III) complex showing a substantial pseudo-Jahn–Teller compression.



L^{2-}

Manganese(III) complexes which exhibit an axial compression are very scarce. Although Fackler and Avdeef[6] interpreted the structure of β-$[Mn(acac)_3]$ (acac = acetylacetonate) as being slightly tetragonally compressed, Day and co-workers[7] preferred to describe it as rhombically distorted with the three pairs of Mn–O bonds averaging 1.943, 1.985 and 2.016 Å. Incidentally, this [2 + 2 + 2] distortion is not unusual and has been reported for $LiMnAsO_4(OH)$[8] and MnF_3.[9] In addition, $[Mn^{III}L']\cdot3H_2O$ {H_3L' = $N[CH_2CH_2N{=}CHC_6H_3(5\text{-}Cl)(2\text{-}OH)]_3$}[10] has been shown to exhibit a [3 + 3] distortion in the solid state. The only structurally elucidated manganese(III) complex which clearly demonstrates a tetragonal compression is $[Mn^{III}_2(lac)_4(Hlac)]^{3-}$ (H_2lac = lactic acid),[11] but this is dinuclear.

The pseudo-Jahn–Teller compression occurs along the O(1B)–Mn(B)–O(1B″) axis since the axial Mn(B)–O(1B) bond distance [1.880(4) Å] is significantly shorter than the equatorial Mn(B)–O(2B) and Mn(B)–N(1B) bond distances [2.137(4) Å and 2.118(4) Å, respectively]. Although the angles O(2B)–Mn(B)–N(1B) [79.5(2)°] and O(2B)–Mn(B)–N(1B″) [100.5(2)°] vary considerably from the 90° angles of a square plane, the short axis is perpendicular to the MnN_2O_2-(carboxylate) plane as indicated by the slight deviations in the angles O(1B)–Mn(B)–N(1B), O(1B)–Mn(B)–N(1B″), O(1B)–Mn(B)–O(2B) and O(1B)–Mn(B)–O(2B″) [90.4(2), 89.6(2), 93.0(2) and 87.0(2)°, respectively] from the expected 90° angles. The Mn^{III} ion is at a crystallographic inversion centre.

The nature of the ligand, L^{2-}, prevents the Mn^{III} ion in the $[Mn^{III}L_2]^-$ complex from adopting a rigorous Jahn–Teller distortion. However, from the crystallographic data it is

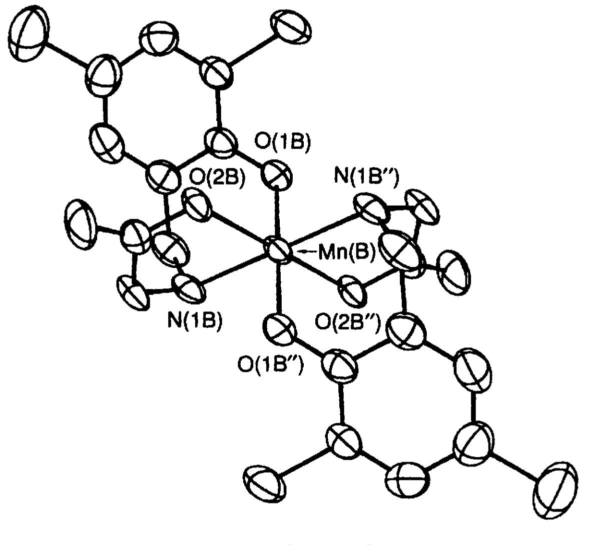


Fig. 1 Molecular structure of the $[Mn^{III}L_2]^-$ anion showing the 50% thermal ellipsoids and the atom-labelling scheme. Only one of the two independent molecules in the crystallographic asymmetric unit is shown. Relevant interatomic distances and angles are discussed in the text.

observed that there are misdirected interactions in the *xy*-plane and these will result in a lowering of the energy of the $d_{x^2-y^2}$ orbital and allow more electron delocalisation into the *xy*-plane. This enables the complex to initiate a strong interaction between the basic phenolate oxygen atoms and the d_{z^2} orbital with some transference of charge to the metal. The complex thus has a $d_{x^2-y^2}$ ground state with short bonds along the *z*-axis and longer bonds in the *xy*-plane.

Preference for a distortion involving equatorial elongation is probably enhanced by the flexibility of the polydentate ligand. This might explain, in part, why axially compressed Schiff-base complexes of manganese(III) are non-existent. Weak bonding of Mn^{III} to the equatorial donor atoms is also expected to promote the distortion in question and, indeed, examples of Mn^{III}–N(amine)[12] and Mn^{III}–O(carboxylate)[13] elongations abound in the literature. In an attempt to probe the factors which dictate the type of tetragonal distortion to be undergone by a given high-spin manganese(III) complex, we are extending this work to other *N*-(2-hydroxybenzyl)glycine derivatives and related ligands.

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Footnotes

† *Physical and Spectroscopic Data* for $[C_5H_{12}N][Mn^{III}L_2]$: Crystals of good quality were grown from MeOH–EtOH (1 : 1) at room temp. and used fresh for all measurements. Selected IR data (KBr disc): 3154 (br), 1596 cm^{-1}. Electronic absorption spectrum (MeOH), λ_{max} (ε_{max}/$dm^3\ mol^{-1}\ cm^{-1}$) 294 (11040), 352 (4970), 491 (1590), 600 (1270). Satisfactory elemental analytical data were obtained for C, H and N. Negative-ion liquid secondary ionisation mass spectrum (3-nitrobenzyl alcohol matrix): P^- at *m/z* 549 (calc. for $[^{12}C_{18}{}^{1}H_{14}{}^{35}Cl_4{}^{55}Mn^{14}N_2{}^{16}O_6]^-$ *m/z* 549). μ_{eff} (300 K) = 4.87 μ_B. M.p. = 206 °C (decomp.).

‡ *Crystal data* for $[C_5H_{12}N][Mn^{III}L_2]$: $C_{23}H_{26}Cl_4MnN_3O_6$: M_r = 637.2, triclinic, space group $P\bar{1}$, a = 11.739(5), b = 12.279(6), c = 9.906(5) Å, α = 98.97(5), β = 95.56(4), γ = 101.02(5)°, U = 1372.5 $Å^3$, Z = 2, T = 298 K, D_c = 1.54 g cm^{-3}, $F(000)$ = 652, μ (Mo-Kα) = 8.96 cm^{-1}. The block-shaped purple-tinged dark brown crystal (dimensions, 0.57 × 0.50 × 0.18 mm) was mounted in a Lindemann glass capillary and the intensity data were recorded on an Enraf-Nonius CAD-4 diffractometer equipped with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Of the 3811 unique reflections collected in the range $2.0 \leqslant 2\theta \leqslant 46.0°$, 3118 with $I \geqslant 3.0\sigma(I)$ were regarded as observed and used in subsequent refinements. Absorption correction was performed by using ψ-scan data. The structure was solved by direct methods and refined by full-matrix least-squares analysis. Hydrogen atoms were placed at fixed, calculated positions. Refinement converged with R = 0.048 and R_w = 0.058 (*Moien Crystal Structure Analysis*, Delft Instruments, X-ray Diffraction B.V., 1990). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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