Structure of a Manganese(II) Complex of a New *N,O*-Bidentate 1,5-Benzodiazepine Derivative Synthesised via Metal Ion Promoted Oxidation of a Methyl Group

ZOLTÁN SZEVERÉNYI, VILMOS FÜLÖP, ALAJOS KÁLMÁN and LÁSZLÓ I. SIMÁNDI*

Central Research Institute for Chemistry, Hungarian Academy of Sciences, H-1525 Budapest, P.O. Box 17, Hungary

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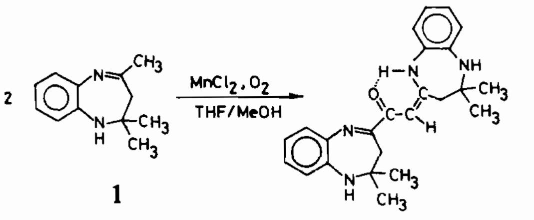
Metal ion catalysed oxidations under mild conditions continue to attract attention because of their relevance to biological oxygenations and considerable potential in synthetic organic chemistry [1]. Of particular interest is the oxidative cleavage of aliphatic and aromatic C–H bonds. As part of our programme to search for oxidative transformations which use dioxygen and metal complexes we have found [2] that manganese(II) chloride promotes the conversion of 1H-2,3-dihydro-2,2,4-trimethyl-1,5-benzodiazepine (**1**) to the new compound **L** according to eqn. (1). The observed inhibition of reaction (1) by compound **L** has drawn our attention to the possible involvement of the manganese complexes of **L** in this effect. Complexation of manganese(II) may eliminate its ability to promote oxidative reactions of **1**. In a search for these complexes we have found that if 50 mmol of **1** in 100 ml THF in the presence of 25 mmol $MnCl_2 \cdot 4H_2O$ in 20 ml MeOH are stirred for 24 h at room temperature (RT) in contact with air, a purple complex of the composition $MnCl_2L_2 \cdot 2H_2O$ precipitates.



1

L

(1)

The structure of $MnCl_2L_2 \cdot 2H_2O$ has been determined by X-ray diffraction. Single crystals have been grown by diffusion of diethyl ether into a MeOH solution of the complex.

Crystal data

Enraf-Nonius CAD-4 diffractometer using graphite monochromated Cu Kα radiation ($\lambda = 1.54184$ Å). Scintillation counter, ω–2θ scan in the range $3° < 2\theta < 150°$. $T = 296$ K, empirical absorption correc-

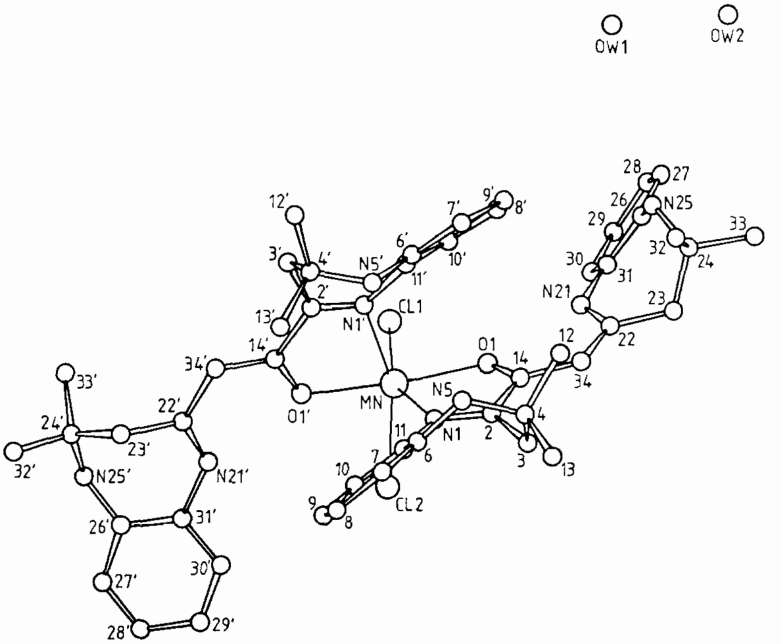


Fig. 1. Molecular structure of $MnCl_2L_2 \cdot 2H_2O$. Selected bond lengths (Å): Mn–Cl(1) = 2.480(1); Mn–Cl(2) = 2.470(2); Mn–O(1) = 2.144(3); Mn–O(1)' = 2.145(3); Mn–N(1) = 2.399(3); Mn–N(1)' = 2.337(3); O(1)–C(14) = 1.276(4); O(1)'–C(14)' = 1.272(5); C(22)–C(34) = 1.397(6); C(22)'–C(34)' = 1.405(6). Intramolecular NH...O hydrogen bonds: N(21)–H(21)...O(1) D...A 2.632(3) Å, D...A 1.84(1) Å, ∢DH...A 138(1)°; N(21)'–H(21)'––O(1) D...A 2.583(3) Å, D...A 1.81(1) Å, ∢DH...A 137(1)°.

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*Author to whom correspondence should be addressed.

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tion. $C_{48}H_{56}Cl_2MnN_8O_2 \cdot 2H_2O$, $M = 938.91$, monoclinic, space group $P2_1/n$, $a = 14.583(2)$, $b = 24.053(2)$, $c = 14.825(3)$ Å, $\beta = 109.42(1)°$, $Z = 4$, $D_c = 1.27$ g cm^{-3}, μ(Cu Kα) = 36.1 cm^{-1}, crystal dimensions 0.08 × 0.14 × 0.45 mm, 4100 unique reflections, $R(R_w) = 0.043$ (0.047) for 3059 reflections with $F^2 > 3.0\sigma(F^2)$ (568 variables, H atoms were included in calculated positions with isotropic temperature factors, $Bi_H = Bi_X + 1$ Å^2 where X = C or N; no hydrogen positions could be generated to the water molecules); all other atoms were refined anisotropically. Maximum peak height in final $\Delta\rho$ map was 0.38(7) e Å^{-3}.

Calculations were performed by the Enraf-Nonius program system [3] run on a PDP-11/34 minicomputer. The molecular structure is shown in Fig. 1. This also provides confirmation of the structure of free **L**, originally deduced from NMR data.

The complex has no crystallographically imposed symmetry, but – apart from the outer wings of the dibenzodiazepine ligands **L** – does approach C_2 symmetry with a twofold axis passing through Mn and the midpoints of the O(1)...O(1)′, N(1)...N(1)′, etc., vectors. In each ligand two benzodiazepine moieties are linked together by a =CH–CO– bridge. However, while in ligand L_A (with primed atoms) there are two rather similar benzodiazepine conformers which differ slightly in the pucker of the hetero ring, in ligand L_B (with non-primed atoms) two enantiomers are fused together. This difference in the ligands accounts for the lack of twofold rotational symmetry between the outer wings of L_A and L_B ligands. Apart from the difference in the pucker of the 1,3-diplanar seven-membered hetero rings, they are quasi-mirror related.

L is a novel type of O,N-donor chelating ligand. The donor atoms are in a C=O and C=N group, resulting in relatively weak metal–ligand interaction, thus longer bond distances. The six donor atoms form a distorted octahedron around the Mn(II) ion (Fig. 2). Mn is situated below the almost perfect plane of O(1), O(1)′, N(1), Cl(1) atoms at a distance of 0.246(1) Å. The N(1)′...Cl(2) vector is almost perpendicular to that plane (88.5(1)°), thus the two chloride ions occupy the *cis* positions.

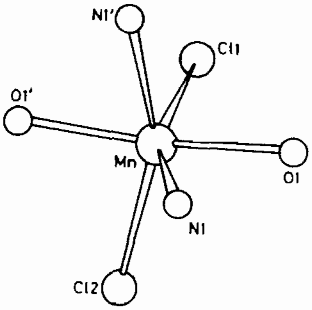

Fig. 2. Perspective drawing of the coordination sphere of Mn(II) by optimised Cartesian coordinate. Selected bond angles (°): Cl(1)–Mn–Cl(2) = 102.7(1); Cl(1)–Mn–O(1) = 87.5(1); Cl(1)–Mn–N(1) = 155.6(2); Cl(1)–Mn–O(1)′ = 102.5(1); Cl(1)–Mn–N(1)′ = 92.7(2); Cl(2)–Mn–O(1) = 105.1(1); Cl(2)–Mn–N(1) = 92.3(1); Cl(2)–Mn–O(1)′ = 86.8(1); Cl(2)–Mn–N(1)′ = 154.6(2); O(1)–Mn–N(1) = 69.8(2); O(1)–Mn–O(1)′ = 162.5(2); O(1)–Mn–N(1)′ = 95.5(2); N(1)–Mn–N(1)′ = 80.9(2).

Supplementary Material

The atomic coordinates and vibrational parameters for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

References

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