A Manganese(II) Penta-co-ordinated Complex with Monodentate Urea Ligands; *X*-Ray Crystal Structure of Dibromotris-(*NN*′-dimethylurea)manganese(II)

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Summary *X*-Ray structure analysis shows that the high-spin complex dibromotris(*NN*′-dimethylurea-*O*)manganese(II) has a trigonal bipyramidal geometry with the bromine atoms in equatorial positions and with two types of bonding for the neutral ligands, one of them being very unusual.

STRUCTURAL information on penta-co-ordinated manganese(II) complexes is very sparse. We report here the first example, to our knowledge, of a high-spin molecular complex where manganese(II) is co-ordinated by five monodentate ligands.

The reaction of *NN*′-dimethylurea (dmu) with manganese bromide in dry ethanol and precipitation with ether yields white plates of formula $Mn(dmu)_3Br_2$.[1]

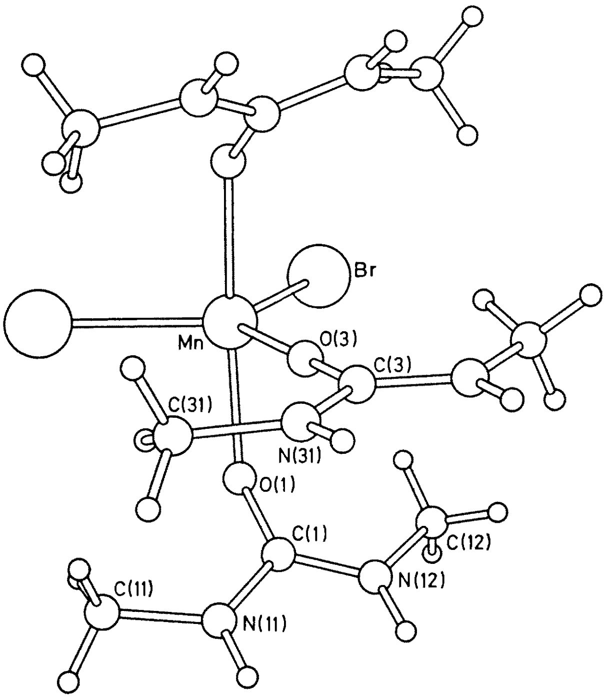

FIGURE. Structure of Mn(dmu)$_3$Br$_2$. Selected bond distances and angles: Mn–Br, 2·563(2); Mn–O(1), 2·175(8); Mn–O(3), 2·035(12); O(1)–C(1), 1·271(16); C(1)–N(11), 1·336(20); C(1)–N(12), 1·328(18); O(3)–C(3), 1·249(21); C(3)–N(31), 1·331(15) Å; ∠Br–Mn–Br′, 114·00; O(3)–Mn–Br, 123·00(20); O(1)–Mn–O′(1), 174·16; Mn–O(3)–C(3), 180·00; Mn–O(1)–C(1), 129·50°.

Crystal data: $C_9H_{24}Br_2MnN_6O_3$, M = 479·09, monoclinic, space group $C2/c$, a = 13·211(3), b = 8·670(3), c = 16·593(4) Å, β = 106·23(3)°, Z = 4, D_c = 1·739 g cm^{-3}, D_m = 1·74(1) g cm^{-3}, μ(Mo-K_α radiation) = 53·7 cm^{-1}. The structure was solved by conventional heavy atom methods. Anisotropic least-squares refinement (except for the hydrogen atoms) converged at R = 0·054 for 856 reflections measured on an automated diffractometer, with $I \geqslant 3\sigma(I)$ (total number of observed reflections: 1616).†

The molecular structure is shown in the Figure. The geometry of the co-ordination polyhedra is very close to trigonal bipyramidal. Selected bond distances and angles are given. The molecule lies on a C_2 axis through Mn, O(3), and C(3). The bromine atoms are in equatorial positions and the dmu ligands are oxygen-bonded, but two types of co-ordination occur. The axial dmu ligands are normally co-ordinated: the oxygen atom shares one lone pair with the metal ion giving an Mn–O(1)–C(1) angle of 129·5°. The equatorial dmu ligand is unusually linearly bonded, however, with an angle Mn–O(3)–C(3) of 180°. This is highly unusual for a carbonyl oxygen atom and it probably implies a delocalization of the electrons: the Mn–O(3) distance is significantly shorter than the Mn–O(1) distance. Packing considerations or intermolecular hydrogen bonds are not responsible for this difference in co-ordination.

With the very similar ligand *NN′*-diethylurea (deu) this type of co-ordination does not occur: the compound with the same stoichiometry has, in fact, a mixed octahedral–tetrahedral structure: Mn(deu)$_6$.MnBr$_4$.[1]

We thank Dr. Cl. Pascard (Gif-sur-Yvette) for the data collection on an automated diffractometer.

(*Received*, 1*st May* 1980; *Com.* 454.)

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† The atomic co-ordinates 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.

[1] J. P. Barbier and R. Hugel, *J. Inorg. Nucl. Chem.*, 1973, **35**, 781, 3026.

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