Macrocyclic Dimanganese Complexes with 1,1 Bridging Ligands; *X*-Ray Crystallographic Structure Determination of an N-only Bridged Thiocyanato Derivative

Suman Raghunathan,[a] Clarke Stevenson,[a] Jane Nelson,*[b] and Vickie McKee*[c]

[a] *Chemistry Department, Queen's University, Belfast BT9 5AC, U.K.*
[b] *Open University, 40 University Road, Belfast BT7 1SU, U.K.*
[c] *Chemistry Department, University of Canterbury, Christchurch, New Zealand*

X-Ray crystallographic structure determination confirms the inference from i.r. spectra that the μ 1,1 NCS bridge is present in dimanganese(II) complexes of a 22-membered N_6 macrocycle: these complexes show no appreciable magnetic interaction above 93 K, unlike the μ-methoxo-dimanganese(III) complex of the same ligand.

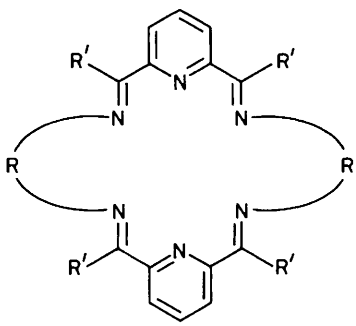
The biological importance of di-, tri-, and tetra-manganese clusters in +2 and higher oxidation states accounts for the current interest in such compounds, particularly where the manganese centres lie within μ-OR bridging distance. Thus, the active site of the thylakoid membrane of photosystem II is known[1] to involve at least two, and possibly four, manganese ions in the oxidation of water to molecular oxygen, and it is believed[2] that the catalase enzyme *Lactobacillus plantarum* contains two manganese ions per protein subunit. Models for the active site of photosystem II require manganese in +3 or +4 oxidation state, an Mn · · · Mn distance of *ca.* 2.7 Å, and O or N donor sites with bridging oxygen. For *Lactobacillus plantarum*, a somewhat longer internuclear distance (*ca.* 3.2 Å)[2] may suffice and oxidation states +2 and +3 are believed to be involved. Many binuclear synthetic complexes have been investigated as models for the photosynthetic site, some of which[3] show photolytic water-splitting activity. Model compounds prepared originally with Mn in the +2 state may be readily oxidised to higher states either by air or permanganate oxidation.[3—5]

We have available a range of binucleating macrocycles (L^1—L^4) with co-ordination site separation in the range 3—6 Å. The reaction of these ligands with Mn^{II} has been explored with the eventual aim of synthesising models for biological dimanganese. Homo- or hetero-binuclear complexes were obtained with L^1—L^3; with L^4, however, only mononuclear manganese(II) complexes resulted.† In order to obtain qualitative information on the separation of the co-ordination sites in the binuclear complexes, thiocyanato derivatives were prepared, because in favourable cases i.r. spectra can easily diagnose[7] the presence of a single-atom >NCS bridge, from the appearance of an intense ν_{as}(NCS) absorption below 2000 cm^{-1}. With L^1 and L^2 the internuclear distance was apparently too short to accommodate the normal symmetric axial–equatorial 3-atom bridge, but too long for the >NCS single-atom bridge. Instead, transmetallation of the $Pb_2L(NCS)_4$ template ($L = L^1$ or L^2) yielded lead–manganese heterobinuclear[9,10] complexes which adopt an asymmetric bridging strategy (both S atoms co-ordinate Pb and both N atoms Mn) in order to achieve a shorter internuclear separation (*ca.* 4.8 Å) than that (*ca.* 5.6 Å) normally required for a symmetric 3-atom bridge.

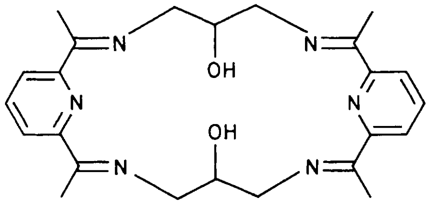
The ligand L^3, subject of the present study, was assembled from diformylpyridine and 1,3-diaminobutane on a Ba^{II} template. Transmetallation with Mn^{2+} in the presence of excess of thiocyanate ion yields a tetrathiocyanato-derivative $Mn_2L^3(NCS)_4$ (**1**) whose i.r. spectrum (Figure 1) conclusively demonstrates the presence, in approximately equal amounts, of both N-terminal and 1,1-NCS bridging thiocyanate. This

---

† Recent work indicates[6] that L^4 can accommodate two manganese ions in higher oxidation levels.



L^1 : R = $(CH_2)_5$ R′ = Me
L^2 : R = $(CH_2)_6$ R′ = Me
L^3 : R = $(CH_2)_4$ R′ = H
L^4 : R = $(CH_2)_3$ R′ = H



L_5

compound did not afford crystals of sufficient size for diffraction measurements; however, existence of a 1,1-NCS bridge is confirmed by *X*-ray crystallographic structure determination of the mono-methoxo derivative $Mn_2L^3(NCS)_3OMe$ (**2**), obtained by recystallisation of (**1**) from (9:1) DMF/MeOH at −20 °C (DMF = dimethyl formamide).‡ The i.r. spectrum of (**2**), Figure 1, also shows $\nu_{as}(NCS)$ absorption at unusually low frequency (2005 cm^{-1}), albeit some 30 cm^{-1} higher than in the tetrathiocyanato derivative (**1**). A blue shift of this magnitude[11] is commonly observed in $\nu_{as}(NCS)$ where the >NCS bridge is coupled with μ-OR-bridging.

The molecule (Figure 2) is centrosymmetric and contains two crystallographically equivalent manganese atoms. These are six-co-ordinate and have irregular geometry, being bonded to three nitrogen donors from the macrocycle, one terminal N-bonded thiocyanate, one N-bridging thiocyanate and one bridging methoxide group. The bridging thiocyanate and methoxide are disordered, each with 50% occupancy of the two equivalent sites.

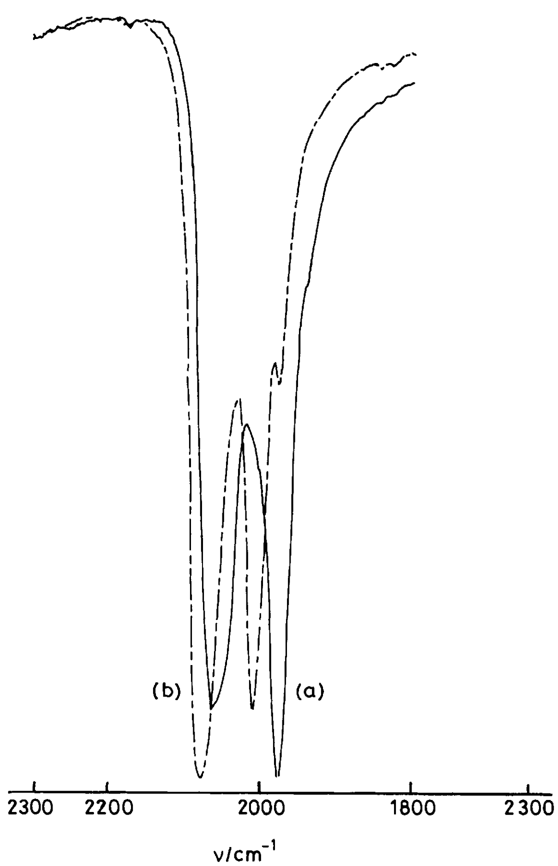


Figure 1. I.r. absorption spectra (KBr disc) of (a) (**1**) and (b) (**2**) in the $\nu_{as}(NCS)$ region.

The macrocyclic ligand is folded allowing the metal ions to be linked by single atom bridges [Mn–Mn′ 3.418(6) Å]. Since the bridging thiocyanate is disordered the precision of bond lengths and angles pertaining to it is reduced. Nevertheless, it is apparent that the Mn–N(21) distance is significantly longer than the Mn′–N(21) bond. Possibly this could be ascribed to an unfavourable interaction of S(21) with the adjacent pyridine ring [S(21) is 3.6 Å out of the plane of the ring].

It is clear from the position of the sulphur atom S(21) that the bridging group does not lie in the Mn, N(21), Mn′, O(21)′ plane. The sulphur atom lies a perpendicular distance of 0.88 Å from this plane, and the N(21)–S(21) vector is inclined at *ca.* 18° to it. The terminal thiocyanate group is approximately linear and lies in the plane of Mn, N(21), Mn′, and O(21)′. There are no indications of any intermolecular interactions.

The magnetic moments of both (**1**) and (**2**) over the temperature range 273—93 K are normal, close to 6.1 μ_B/Mn^{2+} ion, with no indication of magnetic interaction even at 93 K. The internuclear separation of 3.42 Å compares with 3.13 Å observed in a dimeric $Mn_4L_2{}^5(NCS)_4$ cluster of the related ligand[12] L^5, where the pair of macrocyclic units is bridged by μ_3-OR and which also incorporates two 1,1 NCS bridges in addition to an endogenous Mn–O–Mn link. This complex likewise fails to exhibit any significant magnetic interaction between manganese centres, as indeed is the case with the biological system[1].

Air oxidation of (**1**) or (**2**) in MeOH/MeCN (3:1) over a

---

‡ *Crystal data:* $C_{26}H_{29}Mn_2N_9OS_3$, brown crystal, monoclinic, space group $P2_1/a$, a = 9.186(4), b = 16.221(4), c = 10.976(3) Å, β = 107.83(3)°, U = 1557.0(9) Å^3, Z = 2, $F(000)$ = 708, μ = 10.07 cm^{-1}, crystal dimensions 0.60 × 0.16 × 0.16 mm^3. Data collected at 160 K on a Nicolet R3m four-circle diffractometer using graphite-monochromated Mo-K_α radiation. Using 2° ω scans at 2.93° min^{-1}, 2030 unique reflections were collected in the range $4 < 2\theta < 45°$ and 1151 with $I > 3\sigma(I)$ were used in the refinement. The structure was solved using Patterson methods and the least-squares refinement converged with R = 0.0452, R_w = 0.0448. Hydrogen atoms were inserted at calculated positions using a riding model with thermal parameters equal to 1.2U of their carrier atoms. All non-hydrogen atoms were refined anisotropically. The function minimised was $\Sigma w(|F_o| - |F_c|)^2$ where $w = [\sigma^2(F_o) + 0.00016\,F_o{}^2]^{-1}$. All programs used in data collection and structure solution are contained in the SHELXTL package.[13] Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

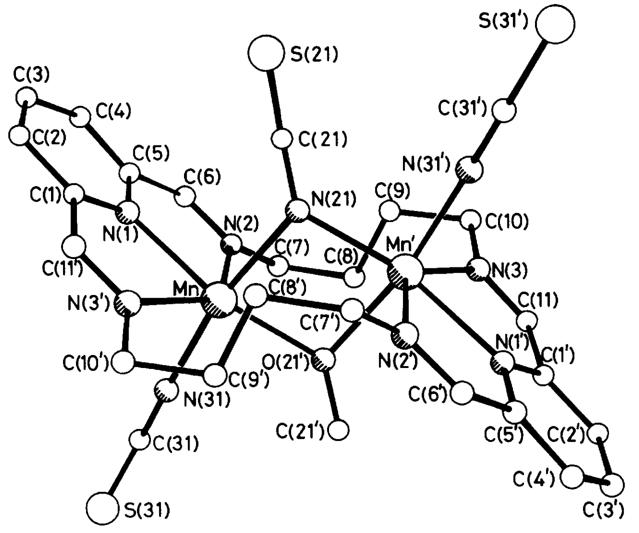


Figure 2. Thermal ellipsoid plot of $Mn_2L^3(NCS)_3OMe$ (**2**). The bridging thiocyanate and methoxy groups are disordered, each with 50% occupancy of both sites. Selected interatomic distances (Å) and angles (°): Mn–Mn′ 3.418(6), Mn–N(1) 2.228(6), Mn–N(2) 2.357(6), Mn–N(21) 2.230(5), Mn–N(31) 2.133(6), Mn-N(3′) 2.398(6), Mn–O(21′) 2.121(6), Mn–N(21)–Mn′ 103.5(3), N(21)–Mn–N(31) 169.9(3), N(21)–Mn–O(21′) 76.5(3), N(1)–Mn–N(2) 70.9(2), N(1)–Mn–N(21) 88.3(2), N(1)–Mn–N(31) 101.8(2), N(1)–Mn–N(3′) 66.9(2), N(1)–Mn–O(21′) 164.6(3), N(2)–Mn–N(21) 91.6(2), N(2)–Mn–N(31) 90.7(2), N(2)–Mn–N(3′) 140.5(2), N(2)–Mn–O(21′) 110.7(2), N(21)–Mn–N(3′) 91.9(2), N(31)–Mn–N(3′) 92.5(2), N(31)–Mn–O(21′) 93.5(2), N(3′)–Mn–O(21′) 108.4(2).

period of days at room temperature yields, as expected, intensely coloured dark brown Mn^{III} containing products and transmetallation of $BaL^3(ClO_4)_2$ with $Mn(OAc)_3$ in the presence of excess of thiocyanate yields a very dark brown crystalline product analysing as $[Mn_2(OMe)_4L^3][Mn(NCS)_4]$ (**3**). Preliminary magnetic susceptibility measurements for (**3**) suggest a methoxy-mediated ferromagnetic interaction between the Mn^{III} centres. Electrochemical investigations of these dimanganese complexes are planned and should be of interest, in particular the one-electron oxidation of (**3**), in view of the similarity[13] of properties of a recently isolated Mn^{III}/Mn^{IV} dimer to those of photosystem II.

Received, 15th June 1988; Com. 8/02393J

References

1 G. C. Dismukes, *Photochem. Photobiol.*, 1986, **43**, 99, and references therein.
2 Y. Kono and I. J. Fridorivich, *J. Biol. Chem.*, 1983, **258**, 6015; W. G. Beyer and I. J. Fridorivich, *Biochemistry*, 1985, **24**, 6460.
3 F. M. Ashmawy, C. A. McAuliffe, R. V. Parish, and J. Tames, *J. Chem. Soc., Dalton Trans.*, 1985, 1391; C. A. McAuliffe, R. V. Parish, F. M. Ashmawy, R. M. Issa, and S. A. Amer, *J. Chem. Soc., Dalton Trans.*, 1987, 2009, and references therein.
4 J. B. Vincent, H. R. Chang, K. Folting, J. C. Huffman, G. Christou, and D. N. Hendrickson, *J. Am. Chem. Soc.*, 1987, **109**, 5703.
5 J. E. Sheats, R. S. Czernuszewicz, G. C. Dismukes, A. L. Rheingold, V. Petroulias, J. Stubbe, W. A. Armstrong, R. H. Beer, and S. J. Lippard, *J. Am. Chem. Soc.*, 1987, **109**, 1435.
6 V. McKee and S. Brooker, unpublished observations.
7 G. A. van Albada, R. A. G. de Graaff, J. G. Haasnoot, and J. Reedijk, *Inorg. Chem.*, 1984, **23**, 1404, and references therein.
8 B. Murphy, J. Nelson, S. M. Nelson, M. G. B. Drew, and P. Yates, *J. Chem. Soc., Dalton Trans.*, 1987, 123, and references therein.
9 M. G. B. Drew, P. C. Yates, B. Murphy, J. Nelson, and S. M. Nelson, *J. Chem. Soc., Dalton Trans.*, 1988, 1001.
10 J. Nelson, unpublished observations.
11 D. McDowell, S. Raghunathan, C. Stevenson, and J. Nelson to be published.
12 S. Brooker, V. McKee, W. B. Shepard, and L. K. Pannell, *J. Chem. Soc., Dalton Trans.*, 1987, 2555.
13 K. Weighardt, U. Bosek, L. Zsolnai, G. Huttner, G. Blondin, J. J. Girard, and F. Babonneau, *J. Chem. Soc. Chem., Commun.*, 1987, 651.
14 G. M. Sheldrick, 'SHELXTL User Manual', revision 4.1, Nicolet XRD Corporation, Madison, Wisconsin, 1984.