In memory of S. M. Nelson

Formation of a (4 + 4) Schiff-base Macrocyclic Ligand by a Template Rearrangement. Crystal and Molecular Structures of Two Tetranuclear Manganese(II) Complexes†

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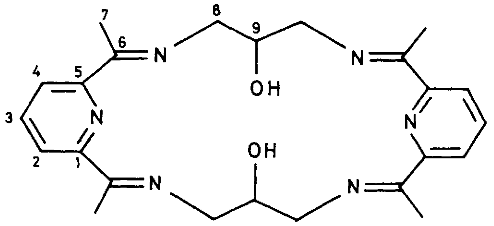
Two tetranuclear manganese(II) complexes (**2**) and (**3**) have been obtained by Schiff-base condensation of 1,3-diamino-2-hydroxypropane and 2,6-diacetylpyridine in the presence of Ba^{2+}, followed by transmetallation using Mn^{2+}. The complexes have been characterised by analytical, spectroscopic, ^{252}Cf plasma desorption mass spectroscopic, and single-crystal *X*-ray diffraction methods. Complex (**2**) contains a 40-membered macrocycle formed by a (4 + 4) Schiff-base condensation of four molecules of 1,3-diamino-2-hydroxypropane with four molecules of 2,6-diacetylpyridine. The macrocycle is wrapped around a cubane-like $Mn_4(alkoxide)_4$ core. Complex (**3**) is dimeric. The asymmetric unit contains two binuclear, 20-membered macrocycles each formed by a (2 + 2) Schiff-base condensation reaction. This complex contains five geometrically distinct thiocyanate groups. Routes for the formation of (**3**) are discussed and the possible significance of the compounds as models for the photosynthetic water-splitting system is noted.

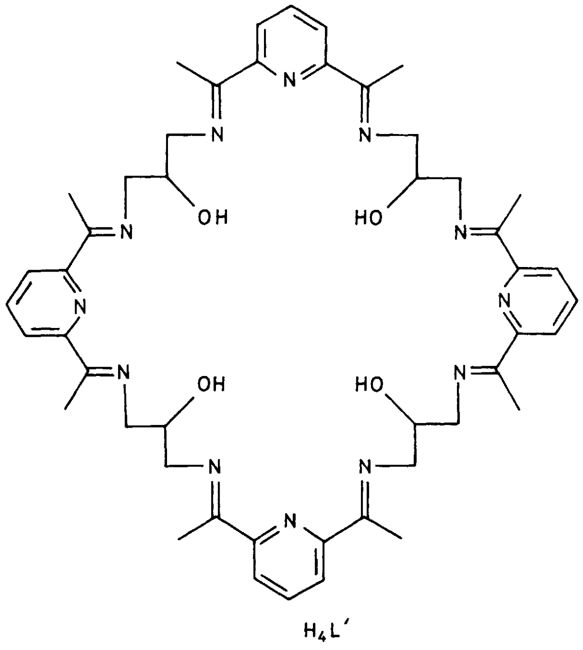
There is much current interest in the nature of the manganese cofactor of photosystem II which is thought to be the active site for the photosynthetic water-splitting reaction.[1,2] For some time it has been accepted that the natural system must involve at least two magnetically coupled manganese centres probably bridged by oxygen donors.[1] The properties of many binuclear synthetic systems have been investigated as models for the photosynthetic site.[3] A tetranuclear cluster has also been proposed to account for the properties of the various intermediates (*S*-states, oxidation levels) in the water-splitting cycle,[4] particularly their complex e.s.r. characteristics.[2,5] As yet, however, few tetranuclear model compounds involving oxidation states II, III, or IV have been characterised.[6] Consequently, low molecular weight model systems involving either bi- or poly-nuclear manganese complexes are potentially of great value in contributing to the understanding of the photosynthetic process.

The (2 + 2) macrocyclic ligand H_2L was chosen for an investigation of the general properties of binuclear manganese systems having endogenous oxygen bridging. It is large enough, and has enough donor atoms, to bind two transition-metal ions and hold them close together. The macrocycle has six imine-type nitrogen donors and two pendant alcohol groups which have the potential to deprotonate and form alkoxide bridges. Bridging is not enforced however, as the ligand has sufficient flexibility for the alcohol groups to twist away from the central cavity. This flexibility means that the ligand can, to some extent, adjust to suit the stereochemical preferences of the co-ordinating metal ions.

The ligand H_2L can be prepared in good yield by a template reaction involving condensation of two molecules of 2,6-diacetylpyridine with two molecules of 1,3-diamino-2-hydroxy-



H_2L



H_4L'

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† *Supplementary data available* (No. SUP 56675, 7 pp.): mass spectra and assignments. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Non-S.I unit employed: 1 a.m.u = 1.6602×10^{-27} kg.

Table 1. Atomic co-ordinates (× 10^4) for $[Mn_4(L')(ClO_4)_4]\cdot 2H_2O$ (**2**) and $[Mn_4(HL)(L)(NCS)_4]NCS$ (**3**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Complex (**2**)							
Mn(1)	5 850(1)	3 837(1)	2 462(1)	C(16)	3 745(2)	768(2)	110(1)
Mn(2)	4 946(1)	2 242(1)	1 663(1)	C(17)	4 050(1)	1 424(2)	520(1)
N(1)	6 509(1)	4 924(2)	1 995(1)	C(18)	3 945(1)	2 462(2)	483(1)
N(2)	6 605(1)	3 127(2)	1 806(1)	C(19)	3 485(2)	2 869(3)	−21(2)
N(3)	5 475(1)	796(2)	1 776(1)	C(20)	4 296(1)	3 967(2)	865(1)
N(4)	4 499(1)	1 153(2)	973(1)	C(21)	4 882(1)	4 342(2)	1 275(1)
N(5)	4 296(1)	2 945(2)	884(1)	C(22)	4 732(1)	5 335(2)	1 502(1)
N(6)	5 743(1)	5 275(2)	2 967(1)	C(23)	6 022(1)	6 003(2)	2 737(1)
C(1)	6 486(1)	5 824(2)	2 188(1)	C(24)	5 927(2)	6 990(2)	2 973(2)
C(2)	6 878(2)	6 509(2)	1 906(1)	O(1)	5 690(1)	2 317(1)	2 518(1)
C(3)	7 296(2)	6 241(2)	1 410(2)	O(2)	5 002(1)	3 750(1)	1 825(1)
C(4)	7 330(2)	5 310(2)	1 225(1)	Cl(1)	2 481(1)	3 966(1)	1 758(1)
C(5)	6 929(1)	4 655(2)	1 537(1)	O(11)	2 122(1)	3 597(2)	1 202(1)
C(6)	6 972(1)	3 614(2)	1 439(1)	O(12)	2 100(1)	3 812(2)	2 335(1)
C(7)	7 462(2)	3 232(3)	967(2)	O(13)	2 598(1)	4 957(2)	1 678(1)
C(8)	6 632(1)	2 108(2)	1 816(1)	O(14)	3 108(1)	3 480(2)	1 811(1)
C(9)	6 249(1)	1 738(2)	2 400(1)	Cl(2)	5 768(1)	2 905(1)	−38(1)
C(10)	6 018(1)	736(2)	2 263(1)	O(21)	5 702(1)	2 463(2)	590(1)
C(11)	5 236(1)	65(2)	1 500(1)	O(22)	5 908(1)	3 889(2)	39(1)
C(12)	5 451(2)	−929(2)	1 622(2)	O(23)	5 159(1)	2 785(2)	−407(1)
C(13)	4 688(1)	256(2)	1 009(2)	O(24)	6 299(1)	2 465(2)	−378(1)
C(14)	4 407(2)	−440(2)	612(2)	O(3)	7 766(2)	347(4)	317(2)
C(15)	3 920(2)	−167(2)	162(2)				
Complex (**3**)							
Mn(1)	1 605(1)	259(2)	1 295(1)	C(27)	618(5)	5 289(17)	−2 428(10)
Mn(2)	1 545(1)	2 628(2)	1 184(1)	C(28)	619(4)	4 250(16)	−2 457(10)
Mn(3)	1 011(1)	3 219(2)	−518(1)	C(29)	704(4)	3 680(13)	−1 922(8)
Mn(4)	825(1)	1 894(2)	476(1)	C(30)	680(4)	2 534(14)	−1 889(8)
O(1)	1 600(2)	1 361(8)	539(4)	N(8)	799(3)	2 165(10)	−1 351(6)
O(2)	1 206(2)	1 405(8)	1 268(4)	C(31)	513(4)	1 959(16)	−2 440(9)
O(3)	1 100(2)	1 606(7)	−202(4)	C(32)	753(4)	1 124(11)	−1 201(7)
O(4)	1 124(2)	3 289(8)	530(4)	C(33)	1 013(4)	765(11)	−631(7)
N(1)	1 952(3)	−714(10)	1 956(6)	N(9)	712(3)	280(10)	87(6)
C(1)	1 900(4)	−1 023(12)	2 491(7)	C(34)	898(4)	−138(12)	−308(7)
C(2)	2 122(4)	−1 586(13)	2 919(8)	C(35)	529(4)	−296(12)	297(7)
C(3)	2 399(4)	−1 796(14)	2 813(8)	C(36)	473(4)	−1 423(13)	212(8)
C(4)	2 466(4)	−1 505(13)	2 274(7)	C(37)	359(4)	252(13)	700(7)
C(5)	2 232(4)	−961(12)	1 838(7)	C(38)	157(4)	−239(14)	998(7)
C(6)	2 254(4)	−620(12)	1 232(7)	C(39)	6(4)	402(14)	1 330(8)
C(7)	2 532(4)	−941(15)	1 031(9)	C(40)	47(4)	1 465(14)	1 355(8)
N(2)	2 036(3)	−58(10)	925(6)	N(10)	410(3)	1 258(10)	732(6)
C(8)	2 005(4)	367(13)	312(7)	C(41)	255(3)	1 863(12)	1 056(7)
C(9)	1 852(3)	1 395(12)	256(7)	C(42)	323(4)	2 969(12)	1 012(7)
C(10)	2 091(4)	2 207(12)	534(8)	N(11)	585(3)	3 175(10)	888(5)
N(3)	1 955(3)	3 069(10)	791(5)	C(43)	85(4)	3 725(15)	1 086(9)
C(11)	2 060(4)	3 970(13)	862(7)	C(44)	674(3)	4 169(12)	738(7)
C(12)	2 330(4)	4 348(14)	620(8)	C(45)	1 028(4)	4 200(12)	748(7)
C(13)	1 946(4)	4 629(13)	1 282(7)	N(12)	969(3)	4 890(10)	−272(5)
C(14)	2 014(4)	5 656(15)	1 417(8)	C(46)	1 086(4)	5 102(12)	389(6)
C(15)	1 917(4)	6 114(15)	1 882(8)	C(47)	889(4)	5 558(13)	−674(8)
C(16)	1 748(4)	5 559(13)	2 211(8)	C(48)	891(5)	6 672(15)	−589(9)
C(17)	1 681(4)	4 556(12)	2 038(7)	N(50)	498(3)	2 738(10)	−408(6)
N(4)	1 768(3)	4 097(10)	1 587(6)	C(51)	246(4)	2 988(13)	−657(7)
C(18)	1 513(3)	3 815(11)	2 361(7)	S(52)	−102(1)	3 326(5)	−999(4)
C(19)	1 498(4)	4 058(15)	3 006(8)	N(60)	1 467(3)	3 409(11)	−676(6)
N(5)	1 409(3)	3 005(9)	2 062(5)	C(61)	1 692(3)	3 477(12)	−822(7)
C(20)	1 271(4)	2 161(12)	2 316(7)	S(62)	2 018(1)	3 538(4)	−1 043(2)
C(21)	1 104(4)	1 404(12)	1 810(7)	N(70)	1 354(3)	−1 172(11)	911(6)
C(22)	1 113(4)	298(12)	2 079(7)	C(71)	1 247(4)	−1 800(15)	1 170(8)
N(6)	1 434(3)	−76(10)	2 128(5)	S(72)	1 091(1)	−2 682(4)	1 514(3)
C(23)	1 592(3)	−677(11)	2 556(7)	N(90)	1 110(4)	−1 388(14)	−1 389(7)
C(24)	1 490(4)	−1 052(13)	3 076(7)	C(91)	868(4)	−1 386(15)	−1 721(8)
N(7)	790(3)	4 143(10)	−1 372(6)	S(92)	524(1)	−1 441(4)	−2 200(3)
C(25)	789(4)	5 157(13)	−1 328(7)	N(80)	1 922(3)	1 627(10)	1 898(5)
C(26)	694(4)	5 796(15)	−1 855(8)	C(81)	2 019(3)	1 532(12)	2 425(7)
H(1)	1 391	1 495	186	S(82)	2 146(1)	1 385(4)	3 175(2)

Table 2. Selected bond lengths (Å) and angles (°) for $[Mn_4(L')(ClO_4)_4]\cdot 2H_2O$ (**2**)*

Mn(1)–N(1)	2.267(2)	Mn(1)–N(2)	2.291(2)
Mn(1)–N(6)	2.309(2)	Mn(1)–O(1)	2.193(2)
Mn(1)–O(2)	2.142(2)	Mn(1)–O(2′)	2.287(2)
Mn(1)–O(14′)	2.610(2)	Mn(2)–N(3)	2.328(2)
Mn(2)–N(4)	2.279(2)	Mn(2)–N(5)	2.286(2)
Mn(2)–O(1)	2.297(2)	Mn(2)–O(2)	2.177(2)
Mn(2)–O(1′)	2.143(2)	Mn(2)–O(21)	2.728(2)

N(1)–Mn(1)–N(2)	69.4(1)	N(1)–Mn(1)–N(6)	69.3(1)
N(2)–Mn(1)–N(6)	136.6(1)	N(1)–Mn(1)–O(1)	141.7(1)
N(2)–Mn(1)–O(1)	72.3(1)	N(6)–Mn(1)–O(1)	146.8(1)
N(1)–Mn(1)–O(2)	104.4(1)	N(2)–Mn(1)–O(2)	98.5(1)
N(6)–Mn(1)–O(2)	104.3(1)	O(1)–Mn(1)–O(2)	81.9(1)
N(1)–Mn(1)–O(2′)	139.8(1)	N(2)–Mn(1)–O(2′)	150.7(1)
N(6)–Mn(1)–O(2′)	71.4(1)	O(1)–Mn(1)–O(2′)	78.4(1)
O(2)–Mn(1)–O(2′)	77.7(1)	N(1)–Mn(1)–O(14′)	84.4(1)
N(2)–Mn(1)–O(14′)	73.3(1)	N(6)–Mn(1)–O(14′)	89.8(1)
O(1)–Mn(1)–O(14′)	84.0(1)	O(2)–Mn(1)–O(14′)	165.3(1)
O(2′)–Mn(1)–O(14′)	103.3(1)	N(3)–Mn(2)–N(4)	68.7(1)
N(3)–Mn(2)–N(5)	135.6(1)	N(4)–Mn(2)–N(5)	69.1(1)
N(3)–Mn(2)–O(1)	70.9(1)	N(4)–Mn(2)–O(1)	139.2(1)
N(5)–Mn(2)–O(1)	151.3(1)	N(3)–Mn(2)–O(2)	146.6(1)
N(4)–Mn(2)–O(2)	141.8(1)	N(5)–Mn(2)–O(2)	72.7(1)
O(1)–Mn(2)–O(2)	78.8(1)	N(3)–Mn(2)–O(1′)	104.3(1)
N(4)–Mn(2)–O(1′)	106.7(1)	N(5)–Mn(2)–O(1′)	100.6(1)
O(1)–Mn(2)–O(1′)	77.8(1)	O(2)–Mn(2)–O(1′)	82.0(1)
Mn(1)–O(1)–Mn(2)	95.7(1)	Mn(2)–O(1)–Mn(2′)	102.0(1)
Mn(1)–O(1)–Mn(2′)	100.5(1)	Mn(1)–O(2)–Mn(2)	100.9(1)
Mn(1)–O(2)–Mn(1′)	101.9(1)	Mn(2)–O(2)–Mn(1′)	96.6(1)

* Atoms marked ′ are related by a two-fold rotation axis to those given in Table 1. They have co-ordinates $1-x, y, \frac{1}{2}-z$.

propane in the presence of Ba^{2+}.[7] The resulting complex, $[Ba(H_2L)(H_2O)_2][ClO_4]_2$ (**1**), undergoes facile transmetallation reactions in which the barium ion can be replaced by two transition-metal ions; this reaction is generally accompanied by deprotonation of one or both of the alcohol groups. We have previously reported the structure and properties of a binuclear, singly-bridged copper(II) complex of the monodeprotonated ligand HL^-.[7,8] A number of binuclear complexes of iron(III) with L^{2-} have also been prepared; these contain seven-co-ordinate iron bridged by both alkoxide groups.[9] In this paper we report the preparation and structures of two tetranuclear manganese(II) complexes derived from H_2L. One of these is a dimer, $[Mn_4(HL)(L)(NCS)_4]NCS$ (**3**) while the second is a complex of the larger macrocycle H_4L', with stoicheiometry $[Mn_4(L')(ClO_4)_4]\cdot 2H_2O$ (**2**). The structure of the latter complex has been communicated previously,[10] the ligand has the same connectivity as H_2L but the ring has been expanded to twice the size. The mechanism by which the (4 + 4) macrocycle H_4L' is formed, and the potential of the complexes as models for the photosynthetic system are discussed.

Results and Discussion

Synthesis of the Complexes.—The (2 + 2) macrocycle H_2L was synthesised as the barium(II) complex $[Ba(H_2L)(H_2O)_2][ClO_4]_2$ (**1**) in *ca.* 75% yield *via* a Ba^{2+} ion template reaction from 2,6-diacetylpyridine and 1,3-diamino-2-hydroxypropane. The identity of this complex was established from i.r., ^{13}C n.m.r., and mass spectral data; an *X*-ray structural determination has also been carried out.[11] When methanol or ethanol solutions of (**1**) were treated with an excess of $Mn(ClO_4)_2\cdot 6H_2O$, the single Ba^{2+} ion of the precursor could be replaced by manganese(II) ions yielding the perchlorate complex. Addition of excess NaNCS to the refluxing solution gave the corresponding thiocyanate complex. The macrocyclic products all showed a band at *ca.* 1 620 cm^{-1} in their i.r. spectra attributed to the imine bonds. The disappearance of the carbonyl signal at *ca.* 1 700 cm^{-1} was taken as an indication of the formation of a closed macrocyclic ring rather than an open chain system.

Table 3. Selected bond lengths (Å) and angles (°) for $[Mn_4(HL)(L)(NCS)_4]NCS$ (**3**)

Mn(1)–O(1)	2.244(11)	Mn(1)–O(2)	2.314(10)
Mn(1)–N(1)	2.241(12)	Mn(1)–N(2)	2.323(15)
Mn(1)–N(6)	2.264(14)	Mn(1)–N(70)	2.242(14)
Mn(1)–N(80)	2.461(12)	Mn(2)–O(1)	2.277(11)
Mn(2)–O(2)	2.247(10)	Mn(2)–O(4)	2.229(9)
Mn(2)–N(3)	2.304(14)	Mn(2)–N(4)	2.251(13)
Mn(2)–N(5)	2.288(13)	Mn(2)–N(80)	2.388(12)
Mn(3)–O(3)	2.242(10)	Mn(3)–O(4)	2.300(10)
Mn(3)–N(7)	2.277(13)	Mn(3)–N(8)	2.333(13)
Mn(3)–N(12)	2.289(13)	Mn(3)–N(50)	2.441(14)
Mn(3)–N(60)	2.163(15)	Mn(4)–O(2)	2.211(8)
Mn(4)–O(3)	2.238(11)	Mn(4)–O(4)	2.251(10)
Mn(4)–N(9)	2.304(13)	Mn(4)–N(10)	2.237(14)
Mn(4)–N(11)	2.322(14)	Mn(4)–N(50)	2.410(12)

O(1)–Mn(1)–O(2)	73.0(4)	O(1)–Mn(1)–N(1)	138.3(4)
O(2)–Mn(1)–N(1)	140.6(4)	O(1)–Mn(1)–N(2)	71.3(4)
O(2)–Mn(1)–N(2)	143.6(4)	N(1)–Mn(1)–N(2)	70.0(5)
O(1)–Mn(1)–N(6)	146.0(4)	O(2)–Mn(1)–N(6)	73.9(4)
N(1)–Mn(1)–N(6)	69.7(5)	N(2)–Mn(1)–N(6)	139.6(4)
O(1)–Mn(1)–N(70)	110.1(4)	O(2)–Mn(1)–N(70)	104.0(4)
N(1)–Mn(1)–N(70)	87.7(5)	N(2)–Mn(1)–N(70)	94.5(5)
N(6)–Mn(1)–N(70)	85.3(5)	O(1)–Mn(1)–N(80)	80.8(4)
O(2)–Mn(1)–N(80)	81.7(4)	N(1)–Mn(1)–N(80)	81.9(4)
N(2)–Mn(1)–N(80)	86.0(4)	N(6)–Mn(1)–N(80)	87.0(4)
N(70)–Mn(1)–N(80)	168.7(4)	O(1)–Mn(2)–O(2)	73.7(4)
O(1)–Mn(2)–O(4)	94.1(3)	O(2)–Mn(2)–O(4)	82.9(3)
O(1)–Mn(2)–N(3)	72.8(4)	O(2)–Mn(2)–N(3)	146.0(4)
O(4)–Mn(2)–N(3)	104.5(4)	O(1)–Mn(2)–N(4)	141.3(5)
O(2)–Mn(2)–N(4)	144.3(5)	O(4)–Mn(2)–N(4)	97.7(4)
N(3)–Mn(2)–N(4)	68.6(5)	O(1)–Mn(2)–N(5)	145.0(4)
O(2)–Mn(2)–N(5)	75.0(4)	O(4)–Mn(2)–N(5)	97.2(4)
N(3)–Mn(2)–N(5)	134.8(4)	N(4)–Mn(2)–N(5)	69.5(5)
O(1)–Mn(2)–N(80)	81.8(4)	O(2)–Mn(2)–N(80)	84.8(4)
O(4)–Mn(2)–N(80)	167.6(4)	N(3)–Mn(2)–N(80)	85.5(4)
N(4)–Mn(2)–N(80)	92.7(4)	N(5)–Mn(2)–N(80)	80.2(4)
O(3)–Mn(3)–O(4)	74.7(4)	O(3)–Mn(3)–N(7)	141.0(4)
O(4)–Mn(3)–N(7)	141.7(4)	O(3)–Mn(3)–N(8)	72.2(4)
O(4)–Mn(3)–N(8)	142.4(4)	N(7)–Mn(3)–N(8)	68.8(5)
O(3)–Mn(3)–N(12)	148.3(4)	O(4)–Mn(3)–N(12)	73.6(4)
N(7)–Mn(3)–N(12)	69.5(5)	N(8)–Mn(3)–N(12)	136.8(4)
O(3)–Mn(3)–N(50)	79.0(4)	O(4)–Mn(3)–N(50)	81.6(4)
N(7)–Mn(3)–N(50)	91.4(4)	N(8)–Mn(3)–N(50)	75.2(5)
N(12)–Mn(3)–N(50)	94.9(5)	O(3)–Mn(3)–N(60)	94.1(5)
O(4)–Mn(3)–N(60)	102.4(4)	N(7)–Mn(3)–N(60)	90.3(5)
N(8)–Mn(3)–N(60)	97.2(5)	N(12)–Mn(3)–N(60)	94.0(5)
N(50)–Mn(3)–N(60)	170.9(5)	O(2)–Mn(4)–O(3)	94.1(3)
O(2)–Mn(4)–O(4)	83.2(3)	O(3)–Mn(4)–O(4)	75.7(4)
O(2)–Mn(4)–N(9)	94.8(4)	O(3)–Mn(4)–N(9)	71.5(4)
O(4)–Mn(4)–N(9)	146.9(5)	O(2)–Mn(4)–N(10)	100.5(4)
O(3)–Mn(4)–N(10)	139.0(4)	O(4)–Mn(4)–N(10)	143.7(5)
N(9)–Mn(4)–N(10)	69.3(5)	O(2)–Mn(4)–N(11)	102.5(4)
O(3)–Mn(4)–N(11)	142.6(4)	O(4)–Mn(4)–N(11)	73.3(4)
N(9)–Mn(4)–N(11)	138.5(5)	N(10)–Mn(4)–N(11)	70.6(5)
O(2)–Mn(4)–N(50)	166.2(4)	O(3)–Mn(4)–N(50)	79.8(4)
O(4)–Mn(4)–N(50)	83.3(4)	N(9)–Mn(4)–N(50)	94.9(4)
N(10)–Mn(4)–N(50)	92.1(4)	N(11)–Mn(4)–N(50)	76.3(4)
Mn(1)–O(1)–Mn(2)	87.8(4)	Mn(3)–O(3)–Mn(4)	88.8(4)
Mn(1)–O(2)–Mn(4)	128.6(4)	Mn(2)–O(4)–Mn(4)	95.4(4)
Mn(1)–O(2)–Mn(2)	86.8(3)	Mn(2)–O(4)–Mn(3)	125.8(5)
Mn(2)–O(2)–Mn(4)	96.1(4)	Mn(3)–O(4)–Mn(4)	87.1(3)

Description of the Structures.—Crystals of $[Mn_4(L')(ClO_4)_4]\cdot 2H_2O$ (**2**) and $[Mn_4(HL)(L)(NCS)_4]NCS$ (**3**) were obtained

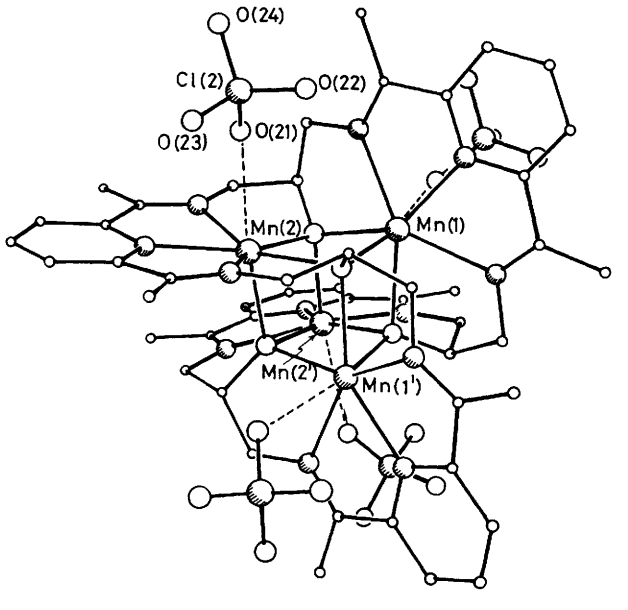


Figure 1. The structure of complex (**2**). Dotted lines represent the long Mn–$OClO_3$ bonds

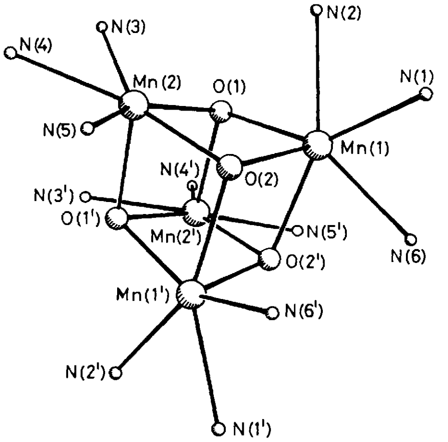


Figure 2. The cubane core of complex (**2**) in the same orientation as Figure 1

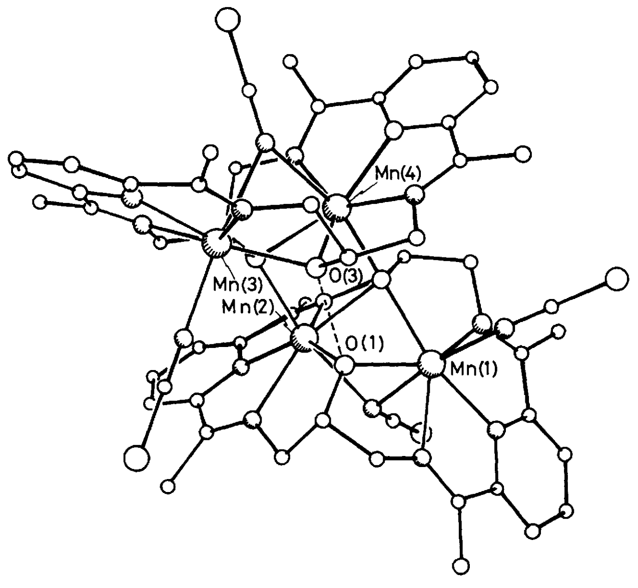


Figure 3. The structure of complex (**3**); the ionic thiocyanate has been omitted. The dotted line represents the hydrogen bond

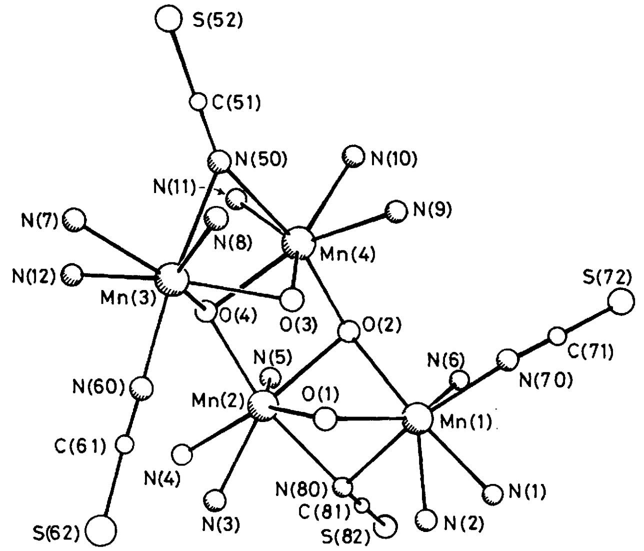


Figure 4. The manganese co-ordination spheres of structure (**3**) in the same orientation as Figure 3

from acetonitrile solution and their *X*-ray crystal structures have been determined. Atomic co-ordinates are listed in Table 1 and selected bond lengths and angles are given in Tables 2 and 3. The structure of (**2**) contains the (4 + 4) ligand co-ordinated to four manganese centres and utilising all 16 potential donor atoms (Figure 1). The alcohol groups have been deprotonated and each one bridges three manganese centres, forming a central cubane-type structure with stoicheiometry $Mn_4(alkoxide)_4$ (Figure 2). Alternatively, this structure may be viewed as two interpenetrating tetrahedra [Mn_4 and $(alkoxide)_4$] but the Mn–Mn separations [3.33(1)—3.45(1) Å] suggest that there are no metal–metal bonds. The macrocycle is able to wrap itself around this cluster by virtue of the flexible propane links which permit a 90° twist of the ligand between successive rigid pyridine–di-imine units.

Each manganese(II) is seven-co-ordinate, bonded to three alkoxide oxygen donors, three nitrogen atoms from a pyridine-di-imine unit, and one perchlorate oxygen. The geometry about each metal centre is approximately pentagonal bipyramidal, although the Mn–$OClO_3$ distances are rather long [2.610(2) and 2.728(2) Å] so that the anions may be better described as semi-co-ordinated, occupying the otherwise vacant site above each manganese. There are also two unco-ordinated water molecules for each macrocyclic unit in the lattice. A crystallographic two-fold axis passes through the centres of the cubane faces defined by Mn(1), O(2), Mn(1'), O(2') and Mn(2), O(1), Mn(2'), O(1'). There is also an approximate, non-crystallographic S_4 axis coincident with the C_2. Within the cubane core, angles about manganese are all acute (78—82°), while those about oxygen are obtuse (96—102°); this would be expected in view of their respective co-ordination geometries. A few manganese(I) cubane structures with formulae $[Mn_4(CO)_{12}X_4]$ (X = F, OH, or OR, where R = alkyl)[12,13] have been reported previously but to our knowledge, complex (**2**) is the first example in either the Mn^{II} oxidation state or in the absence of carbonyl ligands.

The thiocyanate complex (**3**) has a dimeric structure with two (2 + 2) macrocyclic units linked together as shown in Figure 3;

the co-ordination sphere is shown in Figure 4. The two halves of the structure are crystallographically independent and show considerable geometrical differences. As for (**2**), each manganese(II) ion is seven-co-ordinate and has approximate pentagonal-bipyramidal geometry. In every case the donors in the pentagonal plane are the three nitrogen atoms of a pyridine–di-imine unit and two alkoxide donors, all from the same macrocycle. Each manganese has the nitrogen atom of an *N*-bridged thiocyanate group as one axial ligand; Mn(1) and Mn(2) are both bonded to N(80), while Mn(3) and Mn(4) are bridged by N(50). The co-ordination spheres about Mn(1) and Mn(3) are completed by the nitrogen donors of terminally bonded thiocyanates [N(70) and N(60) respectively]. For Mn(2) and Mn(4) the seventh donor is an alkoxide oxygen atom from the adjacent macrocycle and it is these two interactions [Mn(2)–O(4) and Mn(4)–O(2)] which hold the dimer together. Consequently, the alkoxides O(1) and O(3) are doubly bridging but O(2) and O(4) are triply bridging. The atoms O(1) and O(3) are linked *via* a hydrogen bond; this was indicated by the O(1)–O(3) distance of 2.42(1) Å and is required for the stoicheiometry; the hydrogen atom was located from difference Fourier maps.

The macrocycles themselves are non-planar, each is folded to accommodate the bridging thiocyanate groups by reducing the metal–metal distances to 3.135(5) Å for both Mn(1)–Mn(2) and Mn(3)–Mn(4). The extent of the folding is indicated by the angles between the least-squares planes of the donors in the pentagonal plane for each pair of manganese atoms. The angle

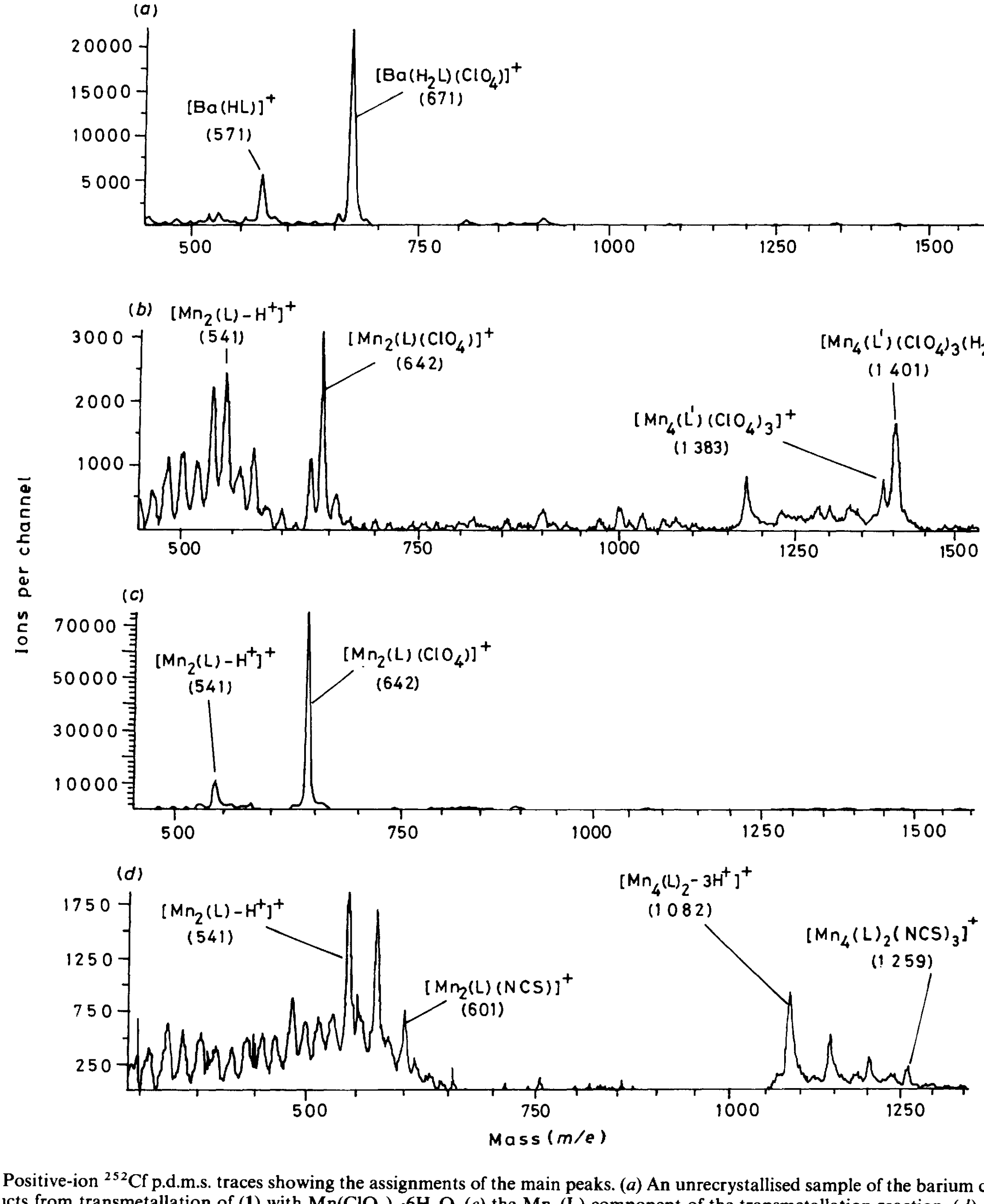


Figure 5. Positive-ion ^{252}Cf p.d.m.s. traces showing the assignments of the main peaks. (*a*) An unrecrystallised sample of the barium complex (**1**), (*b*) the products from transmetallation of (**1**) with $Mn(ClO_4)_2{\cdot}6H_2O$, (*c*) the $Mn_2(L)$ component of the transmetallation reaction, (*d*) a recrystallised sample of complex (**3**)

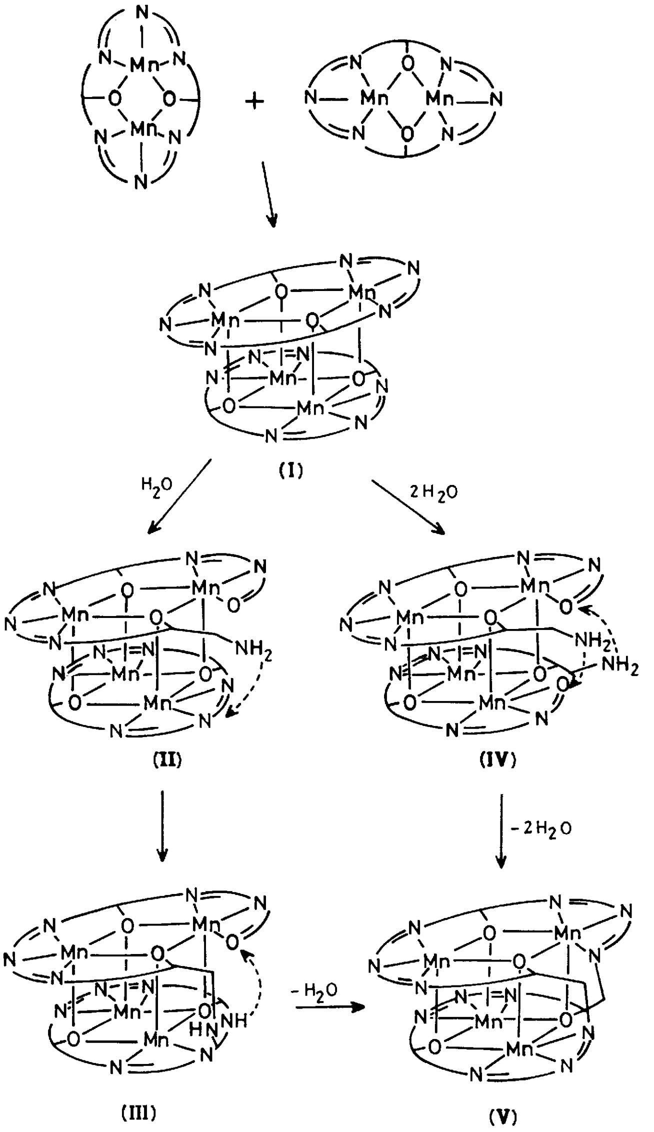
between the mean planes of Mn(1), N(1), N(2), N(6), O(1), O(2), and Mn(2), N(3), N(4), N(5), O(1), O(2) is 104.6° and that between Mn(3), N(7), N(8), N(12), O(3), O(4), and Mn(4), N(9), N(10), N(11), O(3), O(4), is 108.6°.

An unusual feature of the structure is the presence of four distinctly different bonding geometries for thiocyanate, in addition to the unco-ordinated counter ion. One of the two terminal thiocyanate groups is bonded in approximately linear fashion [Mn(3)–N(60)–C(61) 173(1)°], whereas the other is distinctly bent [Mn(1)–N(70)–C(71) 128(1)°]. A similar effect is observed for the two bridging thiocyanates; N(80)–C(81)–S(82) is inclined at 33(1)° to the Mn(1), Mn(2), N(80) plane but N(50)–C(51)–S(52) makes an angle of only 7(1)° with the Mn(3), Mn(4), N(50) plane. In addition, the Mn–N–C angles show wide variation; 139(1) and 119(1)° for Mn(1)- and Mn(2)–N(80)–C(81) respectively compared with 133(1) and 145(1)° for Mn(3)- and Mn(4)–N(50)–C(51). There are no striking inter- or intra-molecular interactions to account for these differences; the environments of the two terminal thiocyanates and of the two bridging groups, while not identical, show no major differences. The individual geometries can be ascribed to a number of weak interactions and to crystal-packing effects. For example, S(72) is *ca.* 3.8 Å from six macrocyclic ring atoms, 3 Å from the same asymmetric unit [N(6), C(23), C(36)], and 3 Å from an adjacent unit [C(15), C(16), and C(46)]. Any straightening of the N(70)–C(71)–S(72) angle is prevented by this network of interactions. There are six previous structurally characterised examples of *N*-bridging thiocyanate ligands.[14–18] In most cases the bridging NCS is associated with an i.r. band in the region below 2 000 cm^{-1}. The i.r. spectrum (in Nujol) of (3) shows four peaks due to the C–N stretch of the thiocyanates at *ca.* 2 085, 2 065, 2 045, and 2 025 cm^{-1} and the envelope is broadened on the low-energy side, but there is no distinct signal below 2 000 cm^{-1}.

Formation of the (4 + 4) *Macrocycle* H_4L'.—On first isolating the (4 + 4) macrocycle H_4L' it was not clear at which stage in the template and transmetallation reactions the larger ring had been formed. The first possibility is that it formed as a minor product in the barium template reaction and crystallised out preferentially in the subsequent manganese transmetallation step. A plausible driving force for this reaction is the expected preference of Ba^{2+} for alcohol donors rather than the softer imine nitrogens. The presence of a mixture of H_2L and H_4L' ligands in the barium product would not necessarily be detected by the normal methods of characterisation as the differences between a mononuclear H_2L complex and the binuclear H_4L' equivalent might not be very obvious. Microanalytical results would be identical, i.r. and n.m.r. spectra would be very similar, and recrystallisation would tend to remove the minor component. The major difference between the two complexes would be their masses, so the obvious way of detecting any H_4L' component is mass spectroscopy. The technique of californium-252 plasma desorption mass spectroscopy[19] (^{252}Cf p.d.m.s.) was chosen since it enables spectra to be obtained without excessive fragmentation of the complexes.

Figure 5 shows the ^{252}Cf p.d.m.s. traces of the complexes. The spectrum of the unrecrystallised barium complex [Figure 5(*a*)] is quite simple and the major peaks can readily be assigned. There is no indication of any signal at twice the mass of the assigned peaks to suggest a $Ba_2(H_4L')$ species and the absence of an extensive fragmentation pattern makes it unlikely that a (4 + 4) complex was present but disintegrated in the instrument. The minor peaks at 807 and 907 a.m.u. are likely to be addition complexes of the assigned species with $BaClO_4$.

The spectrum of the Mn^{II} transmetallation product [Figure 5(*b*)] shows signals in two well defined regions. Those centred at *ca.* 1 400 a.m.u. are due to the $Mn_4(L')$ complex (2) while signals in the region *ca.* 540 a.m.u. correspond to various $Mn_2(L)$ fragments. Most of the peaks in the lower mass region appear to be due to fragmentation of (2); by comparison with spectrum (*c*) only the signals at 642 and 541 a.m.u. arise from the presence of a $Mn_2(L)$ complex in the transmetallation mixture (see Experimental section).



Scheme.

The spectrum of the thiocyanate complex [Figure 5(*d*)] shows extensive fragmentation, consistent with a dimer held together by metal–ligand bonds. The peak ratios indicate that the signals around 1 200 a.m.u. correspond to the parent ion. It is significant that, in spite of the expected facile cleavage of the dimer, the spectrum of (3) gives clear indication of the presence of the parent ion. This supports the conclusion that the barium complex contains no (4 + 4) component and hence that the (4 + 4) macrocycle in (2) must be formed during the transmetallation reaction with manganese and not in the initial template process.

Comparison of the structures of (2) and (3) (Figures 1 and 3) suggests a possible route for the formation of the (4 + 4) macrocyclic product H_4L' (Scheme). In (3) the two bimetallic macrocyclic units are held together by axial co-ordination of an alkoxide from one macrocycle to a manganese centre in the second unit. In this complex only two such 'intermolecular' bonds are formed because the strongly co-ordinated thiocyanate ligands occupy the equivalent axial site on the second manganese centre in each (2 + 2) macrocycle. If the terminal thiocyanate groups were not present, four Mn–alkoxide bonds could be formed between two binuclear macrocyclic units in a cofacial orientation (**I**). The resulting system has the cubane-like core found in (**2**) but still retains two discrete (2 + 2) ligands. Structure (**I**) might be expected to show reasonable stability since it is held together by four metal–ligand bonds.

The next step is hydrolysis of an imine bond from one macrocycle to form (**II**). The terminal amine group is then free to rotate (about the saturated C–C bond) and can add at an imine group on the second macrocycle by nucleophilic attack at the carbon atom, (**III**). One of the C–N single bonds then breaks, either reforming (**II**), or leaving a new 'intermolecular' imine link and releasing another free amine which undergoes a Schiff-base condensation with the free carbonyl to form the product (**V**). Similar attack by nucleophilic amine groups on co-ordinated imino ligands has been implicated in the mechanism of transamination reactions in related systems.[20]

An alternative route involves the hydrolysis of two imine groups, one in each macrocycle, (**IV**). Each free amine then attacks the carbonyl of the adjacent ligand to give the product (**V**). This seems a less likely process since it involves simultaneous hydrolysis of two imine groups in the correct spatial orientation.

The resulting complex (**V**) has the structure and conformation observed for the (4 + 4) complex (**2**). In effect, the (4 + 4) macrocycle is formed by a template reaction where the templating moiety is the Mn_4(alkoxide)$_4$ cluster. The cubane core itself forms as a result of the requirement of Mn^{II} for a good donor in the axial position. This pseudo-cubane core then holds the ligands in an orientation favouring the formation of the (4 + 4) macrocycle, normally the role of a single metal ion in a template reaction. Imine bonds are frequently observed to be susceptible to hydrolysis when not co-ordinated to a metal ion but are generally thought to be relatively stable once co-ordinated. Indeed, this is the reasoning behind the use of the transmetallation reaction to prepare complexes which are inaccessible by other methods; where, for example the metal ion is an ineffective template and the free ligand is unstable.[20] The observed rearrangement of the (2 + 2) macrocycle during the transmetallation reaction with manganese shows that the macrocycle structures in general, and the imine bonds in particular, are quite labile. Formation of a macrocyclic product, however, depends on the presence of a templating moiety since in the absence of any metal ion the only products isolated are poorly characterised viscous oils, probably of oligomeric or polymeric composition.

The fact that bi- and tetra-nuclear products can be isolated from labile transmetallation mixtures implies that these are the most stable products (at least in the kinetic sense). If this is the case, it follows that the same products should be accessible by direct template synthesis. Accordingly we have attempted to prepare the complexes using manganese(II) as template. Reaction of 2,6-diacetylpyridine with 1,3-diamino-2-hydroxypropane in the presence of Mn^{2+} yielded a product with mass spectrum, i.r. spectrum, and analysis identical to those obtained from the transmetallation reaction. Addition of NCS^- to the template mixture also resulted in the formation of (**3**). However, the yield of a second, insoluble, carbonyl-containing component was increased with respect to the transmetallation route. The probable explanation of this effect is that the thiocyanate ions, by co-ordinating to some of the metal sites, reduce the number of sites available for amine or carbonyl co-ordination. Hence the efficiency of the templating ion is reduced and the insoluble product precipitates before ring closure can occur. A similar carbonyl-containing complex can be isolated if the reaction is carried out using strontium as template.[21]

Similar direct preparations have been attempted with other transition metals. Iron(II) has proved an effective template for the formation of bimetallic complexes of L^{2-9} but copper(II) and iron(III) have not been successful in our hands. This may be a function of the size of the metal ions since the two effective ions, manganese(II) and iron(II), have rather similar radii.

Bioinorganic Model Studies.—Both (**2**) and (**3**) are of interest as models for the photosynthetic water-splitting system. Recent work in this area suggests that the protein complex may contain four manganese centres in a mixed valence Mn^{III}–Mn^{IV} cluster.[2] Accordingly we are attempting to purify bulk samples of (**2**) and (**3**) and to investigate the electrochemical, e.s.r., and magnetic properties of these complexes and their derivatives. Preliminary magnetic susceptibility data suggest that the manganese centres in these complexes interact with each other only weakly,[9] this is in accord with the properties of the biological system.[2]

Experimental

Preparation of Complexes.—$[Ba(H_2L)(H_2O)_2][ClO_4]_2$. 2,6-Diacetylpyridine (0.025 mol) and barium perchlorate (0.015 mol) were dissolved in methanol (200 cm^3) and heated to reflux. 1,3-Diamino-2-hydroxypropane (0.025 mol) in methanol (20 cm^3) was added and the refluxing continued for 2.5 h. The white product crystallised on cooling and was filtered off; a second crop was obtained by evaporation of the filtrate under reduced pressure. Yield: 75% (Found: C, 35.7; H, 4.2; N, 10.3. Calc. for $C_{24}H_{34}BaCl_2N_6O_{12}$: C, 35.7; H, 4.2; N, 10.4%). ^{13}C N.m.r. in $(CD_3)_2SO$: δ 165.62 (C^1), 123.91 (C^2), 139.69 (C^3), 154.98 (C^6), 16.01 (C^7), 57.42 (C^8), and 68.60 p.p.m. (C^9).

$[Mn_4(L')(ClO_4)_4]\cdot 2H_2O$. (*a*) *By transmetallation.* $[Ba(H_2L)(H_2O)_2][ClO_4]_2$ (2 mmol) was suspended in refluxing methanol (100 cm^3) and a solution of $Mn(ClO_4)_2\cdot 6H_2O$ (4.2 mmol) in methanol (20 cm^3) was added. Refluxing was continued overnight and a yellow product separated on cooling. This was collected and a further crop obtained by evaporation of the filtrate under reduced pressure. Yield: 35%. The reaction can also be carried out in ethanol.

(*b*) *By template.* 2,6-Diacetylpyridine (6 mmol) and manganese(II) perchlorate (6 mmol) were dissolved in methanol (100 cm^3) and heated to reflux. 1,3-Diamino-2-hydroxypropane (6 mmol) dissolved in cold methanol (40 cm^3) was added slowly to the refluxing mixture, and refluxing continued overnight. The solution was cooled, reduced in volume by evaporation under reduced pressure, and the yellow product collected. Yield: 30%. The products obtained from both routes were indistinguishable; they were recrystallised from acetonitrile by vapour diffusion of diethyl ether (Found: C, 37.8, H, 3.8; N, 11.2. Calc. for $C_{48}H_{60}Cl_4Mn_4N_{12}O_{22}$: C, 37.9; H, 4.0; N, 11.1%).

^{252}Cf p.d.m.s. data indicated that this product contained both (**2**) and an equivalent complex of the (2 + 2) ligand. Both compounds can be dissolved in acetonitrile but the solubility of the (2 + 2) complex appears to be lower than that of (**2**). Hence, by repeated washing with acetonitrile a sample of the (2 + 2) complex was collected and its mass spectrum recorded [Figure 5(*c*)]. This complex has not been further characterised as attempts at recrystallisation always yielded (**2**) as the only crystals large enough for *X*-ray analysis along with yellow powders, presumed to contain the (2 + 2) portion.

$[Mn_4(HL)(L)(NCS)_4]NCS\cdot 2H_2O$. $[Ba(H_2L)(H_2O)_2][ClO_4]_2$ (1.2 mmol) was suspended in refluxing methanol (100 cm^3). $Mn(ClO_4)_2\cdot 6H_2O$ (2.5 mmol) in methanol (30 cm^3) was added, quickly followed by NaNCS (10 mmol) in methanol (50 cm^3). Refluxing was continued overnight and the yellow product collected by filtration of the cooled solution. The product was recrystallised from acetonitrile–ethanol (5:1) containing NaNCS. A small amount of yellow material insoluble in acetonitrile can be separated before recrystallisaton but reforms in the dissolved sample and is difficult to remove completely (Found: C, 44.8; H, 4.2; N, 16.3. Calc. $C_{53}H_{61}Mn_4N_{17}O_6S_5$: C, 45.0; H, 4.3; N, 16.8%).

Crystallography.—Crystal data for $[Mn_4(L')(ClO_4)_4]\cdot 2H_2O.C_{48}H_{60}Cl_4Mn_4N_{12}O_{22}$, orange, crystal dimensions 0.75 × 0.25 × 0.25 mm, monoclinic, $a = 20.209(10)$, $b = 14.241(3)$, $c = 20.596(9)$ Å, $\beta = 91.07(4)°$, $U = 5\,924(4)$ Å^3, space group $C2/c$, $Z = 4$, $F(000) = 5926.4$. Using 1.8° θ—2θ scans with variable scan rates (4—29° min^{-1}), 6 806 unique reflections were collected in the range $3 < 2\theta < 55°$. 5 547 Reflections, for which $I > 3\sigma(I)$ were used for the structural analysis.

Crystal data for $[Mn_4(HL)(L)(NCS)_4]NCS$. $C_{53}H_{57}Mn_4N_{17}O_4S_5$, yellow, crystal dimensions 0.35 × 0.19 × 0.15 mm, monoclinic, $a = 44.193(10)$, $b = 13.082(4)$, $c = 22.621(4)$ Å, $\beta = 105.73(2)°$, $U = 12\,588(5)$ Å^3, space group $C2/c$, $Z = 8$, $F(000) = 5\,646.63$. 2° ω-scans with variable scan rates (3—29° min^{-1}) were used to collect 8 144 unique reflections in the range $3 > 2\theta > 45°$ and of these 3 435 having $I > 3\sigma(I)$ were used in the subsequent calculations.

Data for both crystals were collected at −140 °C on a Nicolet *R*3*m* four-circle diffractometer using graphite-monochromated Mo-K_α radiation. The cell parameters were determined by least-squares refinement of 25 accurately centred reflections ($2\theta > 23°$). Crystal stability was monitored by recording three check reflections every 100 reflections, no significant variations were observed. The data sets were corrected for Lorentz–polarisation effects and empirical absorption corrections were applied based on ψ-scan data.

Both structures were solved by direct methods using the program SOLV [22] and refined by blocked-cascade least-squares techniques. The refinement of (**2**) converged with $R = 0.043$ and $R' = 0.062$. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were inserted at calculated positions using a riding model with thermal parameters equal to 1.2 U of their carrier atoms. For (**3**) the refinement converged with $R = 0.074$ and $R' = 0.094$. The manganese, oxygen, and sulphur atoms were refined anisotropically, the remaining non-hydrogen atoms were refined isotropically and, as for (**2**) all the hydrogen atoms except the hydroxy hydrogen H(1) were inserted at calculated positions. H(1) was located from a difference map, inserted at that position and not further refined. The function minimised in the refinement was $\Sigma w(|F_o| - |F_c|)^2$ where $w = [\sigma^2(F_o) + gF_o^2]^{-1}$ and $g = 0.0075$ and 0.0013 for (**2**) and (**3**) respectively. The final difference maps showed no significant features. All programs used for data collection and structure solution are contained in the SHELXTL (version 4.0) package.[22]

^{252}Cf *P.D.M.S.*—Samples were dissolved in a suitable solvent (CH_3CN or CH_3OH–H_2O) and applied to the aluminised surface of a thin (10 micron) mylar film. The solvent was evaporated and the sample placed in the ^{252}Cf p.d.m.s. instrument and raised to a potential of 10 kV. A ^{257}Cf source (15 μC) was placed behind the sample foil and an acceleration grid (at ground potential) positioned 2—3 mm in front of the sample. ^{252}Cf fission particles passed through the foil and ionised the sample on the front surface. The ions were accelerated by the 10 kV potential and travelled 42 cm to a detector. When a fission event occurred a clock was started in the instrument and the times of flight for the sample ions were determined from their arrival at the stop detector. Times were integrated for a period of 6–18 h and the spectra were calibrated from the time of flight of the inherent sodium and hydrogen ions.

Infrared Spectra.—These were recorded as KBr discs or Nujol mulls on a Pye Unicam SP3-300 infrared spectrophotometer.

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