Crystal and Molecular Structure of Aquadibromo[2-(2-pyridyl)quinolinyl]manganese(II), and the Relation between Structure and Magnetic Properties of Manganese(II) Complexes

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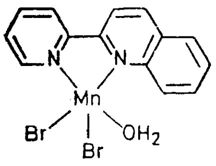
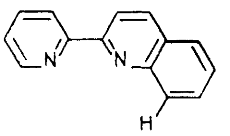
The crystal and molecular structure of the title complex has been determined by heavy-atom techniques. Crystals are monoclinic, $a = 8.172(3)$, $b = 11.868(4)$, $c = 16.456(5)$ Å, $\beta = 98.83(4)°$, space group $P2_1/c$. The structure was refined by least squares to R 8% for 1 577 reflections measured by diffractometer. The complex consists of well-isolated units of five-co-ordinated Mn^{II} molecules, permitting no significant magnetic exchange interaction between neighbouring paramagnetic centres. Comparison with a related structure $[Mn_2(biq)_2Cl_4]$ (biq = 2,2′-biquinolyl) indicates that the presence of the co-ordinated water molecule (Mn–O 2.27 Å) prevents dimerisation of the complex *via* bromide bridges. The MnN_2X_2 (X = Br or Cl) chromophore in this type of complex seeks out an extra ligand to become distorted trigonal bipyramidal five-co-ordinate.

THE title complex, $[Mn(pq)Br_2(H_2O)]$ (1) [pq = 2-(2-pyridyl)quinoline (3)] has been prepared and investigated

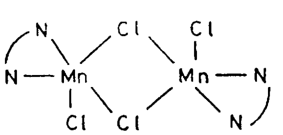


(1)



(3)

as part of a systematic study of 1 : 1 complexes of ligands related to 2,2′-bipyridyl with manganese(II) and transition metals. One complex (2) of this series, $[Mn_2(biq)_2Cl_4]$ (biq = 2,2′-biquinolyl), avoids the four-co-ordinated metal environment which might have been expected from the empirical formula, by forming halogen bridges between pairs of neighbouring metals.[1] This bridging produces pairwise ferromagnetic interactions



(2)

between the neighbouring manganese (high-spin d^5) centres.[2] Slight modifications of the ligands in this molecule are of interest in order to discover if significant structural changes can be induced. The co-ordination number of the metal in $[Mn(pq)Br_2(H_2O)]$ was not known *a priori* because co-ordination of the water molecule could not be unambiguously established from the i.r. spectra.

EXPERIMENTAL

Preparation of the Crystal.—The ligand (3) was prepared as previously described.[3] To a solution of (3) (1 mmol) in acetone was added manganese(II) chloride tetrahydrate (1 mmol) in methanol. The yellow precipitate which formed immediately was recrystallised from nitrobenzene. One of the resulting small yellow crystals was selected for *X*-ray study.

Cell parameters for the crystal were determined and refined from 28 independent reflections, and intensity data collected on an Enraf-Nonius CAD 4 diffractometer as described previously.[1,4] The 2 974 intensities, obtained by use of Mo-K_α radiation, in the range $0° < 2\theta < 50°$ were measured and corrected for Lorentz and polarisation effects and absorption. A spherical absorption correction was used, assuming a diameter of 0.105 mm (max. 0.11, min. 0.10 mm). Final refinement of structure parameters was based on the 1 577 intensities having $F_o^2 > \sigma(F_o^2)$, where $\sigma(F_o^2)$ was estimated from counting statistics as detailed in ref. 5.

Crystal Data.—$C_{14}H_9Br_2MnN_2O$, $M = 436$, $a = 8.172(3)$, $b = 11.868(4)$, $c = 16.456(5)$ Å, $\beta = 98.83(4)°$, $U = 1\,537$ Å^3, $D_m = 1.87$, $Z = 4$, $D_c = 1.88$ g cm^{-3}, $F(000) = 840$. Space group $P2_1/c$. Mo-K_α radiation, $\lambda = 0.7107$ Å; μ(Mo-K_α) = 64.0 cm^{-1}.

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[1] E. Sinn, *J.C.S. Dalton*, 1976, **162**.

[2] R. J. Butcher and E. Sinn, unpublished work.

[3] A. P. Smirnoff, *Helv. Chim. Acta*, 1921, **4**, 802.

[4] R. J. Butcher and E. Sinn, *J.C.S. Dalton*, 1975, 2517.

[5] P. W. R. Corfield, D. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, 1967, **6**, 197.

Elucidation and Refinement of the Structure.—The heavy atoms were located by standard methods from a three-dimensional Patterson function, in which the vectors associated with Mn, Br(1), and Br(2) appeared collinear: Br(1)–Br(2) at 0.5, 0, 0 (4.1 Å); Br(1)–Br(1) and Br(2)–Br(2) at 0, 0.38, 0.07 ($2x$, $2y$, $2z$, 4.6 Å), 0. 0.10, 0.5 (0, $2y - 0.5$, 0.5, 8.1 Å), and 0, 0.5, 0.58 ($2x$, 0.5, $0.5 + 2z$, 8.9 Å); Mn–Br(1) and Mn–Br(2) at 0.25, 0.05, 0.07 (2.4 Å). The remaining atoms were located from Fourier difference maps. Anisotropic temperature factors were introduced for all non-hydrogen atoms, which were introduced as fixed atoms in the trigonal positions of the unsubstituted phenyl ring carbons, with isotropic temperature factors of 5.0 and assuming C–H 1.00 Å.

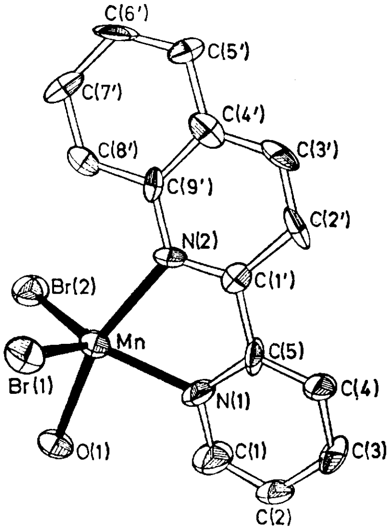

FIGURE 1

TABLE 1

Positional parameters, with estimated standard deviations in parentheses

	X	Y	Z
Br(1)	−0.005 2(3)	0.202 3(2)	0.035 7(1)
Br(2)	0.516 0(3)	0.188 3(2)	0.045 8(1)
Mn	0.272 8(4)	0.151 4(2)	0.118 5(2)
O(1)	0.270(2)	−0.032(1)	0.069 5(7)
N(1)	0.237(2)	0.078(1)	0.237 8(8)
N(2)	0.275(2)	0.303(1)	0.206 2(8)
C(1)	0.229(3)	−0.037(2)	0.255(1)
C(2)	0.177(3)	−0.079(1)	0.324(1)
C(3)	0.141(3)	0.002(2)	0.384(1)
C(4)	0.153(3)	0.116(1)	0.367(1)
C(5)	0.206(2)	0.152(2)	0.298(1)
C(1′)	0.223(3)	0.280(2)	0.277(1)
C(2′)	0.205(3)	0.367(2)	0.340(1)
C(3′)	0.226(3)	0.478(2)	0.321(1)
C(4′)	0.280(3)	0.509(2)	0.246(1)
C(5′)	0.295(3)	0.630(2)	0.223(1)
C(6′)	0.348(3)	0.653(1)	0.150(1)
C(7′)	0.364(3)	0.566(2)	0.091(1)
C(8′)	0.337(3)	0.451(2)	0.111(1)
C(9′)	0.295(3)	0.419(2)	0.188(1)
H(1)	0.262(3)	−0.092(2)	0.216(1)
H(2)	0.164(3)	−0.161(1)	0.333(1)
H(3)	0.107(3)	−0.024(2)	0.436(1)
H(4)	0.124(3)	0.174(1)	0.407(1)
H(2′)	0.179(3)	0.345(2)	0.393(1)
H(3′)	0.202(3)	0.538(2)	0.359(1)
H(5′)	0.274(3)	0.691(2)	0.258(1)
H(6′)	0.371(3)	0.733(1)	0.135(1)
H(7′)	0.398(3)	0.584(2)	0.038(1)
H(8′)	0.345(3)	0.391(2)	0.070(1)

Full-matrix least-squares refinement was based on F (not F^2), and the function minimised was $\Sigma w(|F_o| - |F_c|)^2$, where weights w were taken as $[2F_o/\sigma(F_o)]^2$. Atomic scattering factors for non-hydrogen atoms were taken from ref. 6 and for hydrogen from ref. 7. The effects of anomalous dispersion were included in F_c with values for $\Delta f'$ and $\Delta f''$ from ref. 8. The computing system and programmes used are described elsewhere.[9] After convergence, hydrogen atoms were inserted at their calculated positions. The model converged with R 8.0 and R' 7.9% $\{R' = [\Sigma w|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}\}$. A final Fourier difference map was featureless. Final observed and calculated structure factors are listed in Supplementary Publication No. SUP 21669 (12 pp., 1 microfiche).* Results are shown in Tables 1—3, and a diagram of the molecule, showing the atom numbering system, in Figure 1.

TABLE 2

Bond lengths (Å)

Mn–N(1)	2.198(12)	C(4)–C(5)	1.36(2)
Mn–N(2)	2.272(11)	C(5)–C(1′)	1.52(2)
Mn–O(1)	2.265(9)	C(1′)–C(2′)	1.47(2)
Mn–Br(1)	2.533(3)	C(2′)–C(3′)	1.34(2)
Mn–Br(2)	2.508(3)	C(3′)–C(4′)	1.41(2)
N(1)–C(1)	1.37(2)	C(4′)–C(5′)	1.46(2)
N(1)–C(5)	1.36(2)	C(4′)–C(9′)	1.43(2)
N(2)–C(1′)	1.33(2)	C(5′)–C(6′)	1.37(2)
N(2)–C(9′)	1.39(2)	C(6′)–C(7′)	1.42(2)
C(1)–C(2)	1.36(2)	C(7′)–C(8′)	1.40(2)
C(2)–C(3)	1.42(2)	C(8′)–C(9′)	1.41(2)
C(3)–C(4)	1.36(2)		

TABLE 3

Bond angles (°)

N(1)–Mn–N(2)	73.6(4)	C(1)–C(2)–C(3)	117.5(14)
N(1)–Mn–O(1)	88.0(4)	C(2)–C(3)–C(4)	118.7(14)
N(2)–Mn–O(1)	161.5(4)	C(3)–C(4)–C(5)	120.8(15)
Br(1)–Mn–Br(2)	114.5(1)	N(1)–C(5)–C(4)	122.5(14)
Br(1)–Mn–O(1)	93.9(2)	N(1)–C(5)–C(1′)	114.7(13)
Br(1)–Mn–N(1)	109.7(3)	C(4)–C(5)–C(1′)	122.6(14)
Br(1)–Mn–N(2)	94.6(3)	N(2)–C(1′)–C(5)	116.3(13)
Br(2)–Mn–O(1)	87.3(2)	N(2)–C(1′)–C(2′)	123.8(14)
Br(2)–Mn–N(1)	135.7(3)	C(5)–C(1′)–C(2′)	119.3(13)
Br(2)–Mn–N(2)	104.0(3)	C(1′)–C(2′)–C(3′)	117.6(14)
Mn–N(1)–C(1)	125.6(11)	C(2′)–C(3′)–C(4′)	121.3(14)
Mn–N(1)–C(5)	118.1(9)	C(3′)–C(4′)–C(5′)	121.4(15)
C(1)–N(1)–C(5)	116.1(13)	C(3′)–C(4′)–C(9′)	117.5(15)
Mn–N(2)–C(1′)	115.3(15)	C(5′)–C(4′)–C(9′)	120.4(16)
Mn–N(2)–C(9′)	127.0(10)	C(4′)–C(5′)–C(6′)	117.9(15)
C(1′)–N(2)–C(9′)	116.6(13)	C(5′)–C(6′)–C(7′)	122.7(15)
N(1)–C(1)–C(2)	124.0(15)	C(6′)–C(7′)–C(8′)	118.5(15)
		C(7′)–C(8′)–C(9′)	121.9(14)
		N(2)–C(9′)–C(4′)	122.6(15)
		N(2)–C(9′)–C(8′)	119.5(14)
		C(4′)–C(9′)–C(8′)	117.8(15)

RESULTS AND DISCUSSION

The structure consists of distorted trigonal bipyramidal molecules which are well isolated, but in which

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* See Notice to Authors No. 7 in *J.C.S Dalton*, 1975, Index issue.

[6] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 511.

[7] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[8] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

[9] D. P. Freyberg, G. M. Mockler, and E. Sinn, *J.C.S. Dalton*, 1976, 447.

very weak intermolecular hydrogen bonding interaction (indicated in Figure 2) may exist between the water hydrogens and bromine atoms of neighbouring molecules [O(1) · · · Br(1) 3.23(1), O(1) · · · Br(2) 3.31(1) Å]. O(1) and N(2) form the apices of the trigonal bipyramid, with O(1)–Mn–N(2) bent away from linearity such that the electronic interaction of the electronegative O(1) with Br(1) and Br(2) is minimised. The three planes formed from the two apices and one of the other three ligands form angles of 115, 102, and 143° with each other, compared to the 120° expected for an undistorted trigonal bipyramid (Table 4). A further measure of the distortion is given by the distance of the metal atom from each of the planes. The resulting distortion of the pq ligand (3) is indicated by the non-coplanarity of 4.5° of the pyridyl and quinolyl rings. Two other trigonal bipyramidal arrangements are sterically possible: that with two bromines apical, and that with one and N(2) apical. These are presumably ruled out because they require a closer approach of O(1) to both or to one of the bromines, than is found in the structure actually adopted.

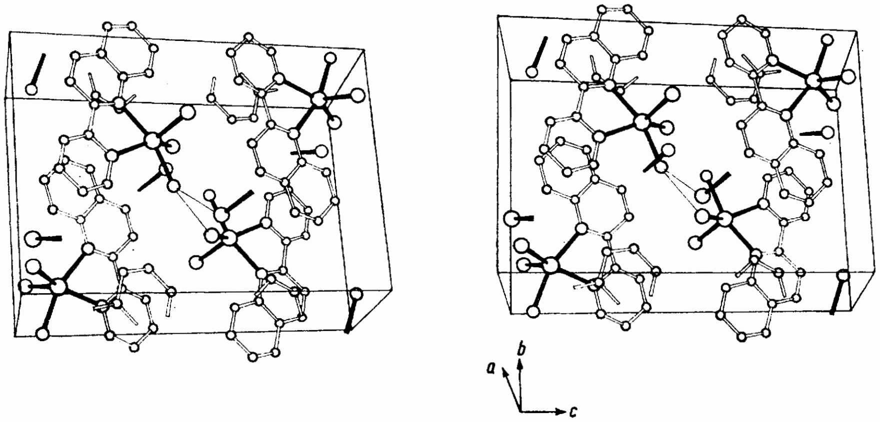

FIGURE 2

The smallness of the crystal limited the intensity and accuracy of the X-ray intensity data, resulting in the relatively high estimated standard deviations in bond lengths and angles, compared for example to those for (2). The high proportion of the molecule's total electron-density possessed by the $MnBr_2$ fragment causes these three atoms to dominate the X-ray scattering, thereby imposing further limitations on the accuracy of atomic positions, especially in the pq ligand. However, there are some significant features. The water molecule is as firmly bound as are the other ligands (Mn–O 2.27 Å). The metal–bromide distances differ by 0.025 Å, in contrast with the situation in (2) where mean bridging Mn–Cl distances are 0.2 Å longer than the non-bridging Mn–Cl bonds. The Mn–N distances are also significantly dissimilar. The quinolyl nitrogen is at a greater distance than that of the pyridyl ring, from steric distortions due to the quinoline hydrogen nearest the nitrogen. This steric effect has been studied indirectly in various ligands derived from 2,2'-bipyridyl and 2,2',2''-terpyridyl, where the repulsion produced five-co-ordinate gold(III) complexes and where metal–ligand bond-lengthening made the difference between high- and low-spin iron(II).[10] The direct effect of this quinoline hydrogen, as measured in [Mn(pq)Br_2(H_2O)],

TABLE 4

Coefficients of least-squares planes for the equation $AX + BY + CZ = D$, with, in square brackets, distances (Å) of relevant atoms from the planes

	A	B	C	D
Plane (I): Br(1), Br(2), N(1)	−0.0200	−0.9198	−0.3920	−2.3772
[N(2), −2.1984, Mn −0.0276, O(1) 2.2303]				
Plane (II): N(1), N(2), O(1)	−0.9547	0.0872	−0.2846	−2.2946
[Mn 0.0565, Br(1) 2.4604, Br(2) −1.6424]				
Plane (III): Br(1), N(2), O(1)	0.6687	0.4096	−0.6206	0.5089
[Mn 0.3027, Br(2) 2.6624, N(1) −1.6457]				
Plane (IV): Br(2), N(2), O(1)	−0.5864	0.3676	−0.7218	−2.1422
[Mn 0.2631, Br(1) 2.6610, N(1) −1.0979]				
Plane (V): pq ligand	−0.9089	−0.0572	−0.4131	−2.7613
[N(1) 0.0035, N(2) 0.0092, C(1) −0.0901, C(2) −0.0382, C(3) 0.0174, C(4) 0.0782, C(5) 0.0175, C(1') 0.0646, C(2') −0.0249, C(3') −0.0166, C(4') −0.0690, C(5') 0.009, C(6') −0.0559, C(7') 0.0261, C(8') 0.0611, C(9') 0.0161, Mn 0.3112]				
Plane (VI): Pyridyl ring	−0.8968	0.0175	−0.4421	−2.9183
[N(1) 0.0285, C(1) −0.0218, C(2) 0.0099, C(3) −0.0050, C(4) 0.0127, C(5) −0.0244, Mn 0.3662]				
Plane (VII): Quinolyl ring	−0.9145	0.0788	−0.3868	−2.5970
[N(2) −0.0346, C(1') 0.0371, C(2') −0.0124, C(3') 0.0173, C(4') −0.0505, C(5') 0.0424, C(6') −0.0314, C(7') 0.0118, C(8') 0.0249, C(9') −0.0046, Mn 0.2052]				

Interplanar angles (°): (I)–(II) 87.1, (I)–(III) 98.4, (I)–(IV) 92,5 (I)–(V) 82.7, (II)–(III) 115.2, (III)–(IV) 101.9, (II)–(IV) 142.9, (VI)–(VII) 4.5

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[10] C. M. Harris, H. R. H. Patil, and E. Sinn, *Inorg. Chem.*, 1967, **6**, 1102; 1969, **8**, 101; C. M. Harris, S. Kokot, H. R. H. Patil, E. Sinn, and H. Wong, *Austral. J. Chem.*, 1972, **25**, 1631; W. T. Robinson and E. Sinn, *J.C.S. Dalton*, 1975, 726.

is to cause a Mn–N bond-length difference of 0.07 Å. The bond distances in pq show the expected differences between the co-ordinated pyridine and quinoline fragments.

Comparison between (2) [$Mn_2(biq)_2Cl_4$], which attains five-co-ordinate metal atoms by halogen bridging, and [$Mn(pq)Br_2(H_2O)$], which achieves five-co-ordination by the addition of the H_2O ligand, suggests that the reason (2) is binuclear and [$Mn(pq)Br_2(H_2O)$] is not is the presence of the water molecule. Dehydration should therefore produce a halogen-bridged binuclear complex from such compounds as [$Mn(pq)Br_2(H_2O)$], together with magnetic-exchange interactions, as observed in the binuclear complex (2). This tendency to form five-co-ordinated complexes is in contrast with complexes of the same ligands with cobalt(II) and cadmium(II) for which [$Co(biq)Cl_2$], [$Co(pq)Cl_2$], and [$Cd(biq)Br_2$] contain only four-co-ordinated metal atoms, in distorted tetrahedral ligand environments.[11]

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[11] R. J. Butcher, H. R. H. Patil, and E. Sinn, unpublished work.