Crystal and Molecular Structure of Bis(2,2′-Biquinolyl)di-μ-chloro-dimanganese(II), an Intramolecular Antiferromagnet

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The crystal structure of the 2,2′-biquinolyl (biq) complex of manganese(II) chloride, an intramolecular ferromagnet, provides empirical data on the relation between structure and magnetic exchange. The complex is binuclear, with a pair of chlorine atoms bridging the metal atoms in a central Mn_2Cl_2 plane. The bridging Mn–Cl bonds are slightly elongated and three stronger bonds hold the bidentate biq ligands and the remaining chlorine to each metal atom. Crystals are triclinic, space group $P\bar{1}$, with $Z = 1$, in a unit cell of dimensions: $a = 11.275(3)$, $b = 10.115(6)$, $c = 14.681(8)$ Å, $\alpha = 95.71(7)$, $\beta = 133.49(4)$, $\gamma = 118.50(4)°$, $U = 791$ Å^3. The structure was determined from diffractometer data by the heavy-atom method and refined by least-squares to R 2.7% for 1 288 reflections.

A SERIES of complexes of 2,2′-biquinolyl (biq) has been synthesised and investigated.[1-4] The manganese(II) chloride complex of empirical formula $Mn(biq)Cl_2$ exhibits a dramatic rise in magnetic moments at low temperatures, in keeping with the postulate that the complex acts as a discrete binuclear ferromagnet.[4] The ferromagnetic exchange interactions of this and related complexes are being studied in detail with ultra-high-sensitivity magnetic susceptibility measurements.[5] Of especial interest is the relation between the strength and sign of magnetic exchange interactions in transition-metal complexes in general, and the geometry about the metal atom and the bridging ligands.[6-8] The detailed structure of the title complex, particularly in the vicinity of the manganese atoms, is therefore of considerable importance. A more important reason for determining the structure is that the effect of intramolecular ferromagnetic interactions on observed magnetic properties is far less characteristic than that of antiferromagnetic interactions:[9] even with very accurate data, it would be difficult to establish even the dimeric nature of the compound from magnetic data alone.

EXPERIMENTAL

The complex was prepared as a pale yellow precipitate by adding a benzene solution of the ligand (1 mmol) to a methanol solution of manganese(II) chloride (1 mmol). Recrystallisation from nitrobenzene afforded very small pale yellow crystals.

Crystal Data.—$C_{36}H_{24}Cl_4Mn_2N_4$, $M = 764$, Triclinic, $a = 11.275(3)$, $b = 10.115(6)$, $c = 14.681(8)$ Å, $\alpha = 95.71(7)$, $\beta = 133.49(4)$, $\gamma = 118.50(4)°$, $U = 791$ Å^3, ($D_m = 1{\cdot}58$, $Z = 1$, $D_c = 1{\cdot}61$ g cm^{-3}. Space group $P\bar{1}$. Mo-K_α radiation, $\lambda = 0.710\ 7$ Å; μ(Mo-K_α) = 11.3 cm^{-1}.

Preliminary cell dimensions were obtained by use of the Enraf–Nonius program SEARCH to locate 15 independent reflections. Refined cell dimensions and their estimated standard deviations were obtained from a least-squares refinement of the preliminary values *vs.* the observed values of $\pm\theta$ for 28 strong general reflections, centred on the diffractometer for the Mo-$K_{\alpha 1}$ and Mo-$K_{\alpha 2}$ wavelengths.

Diffraction data were collected from a small crystal with poorly developed faces, and having maximum and minimum dimensions 0.07 and 0.05 mm, and volume 0.0002 mm^3. As the crystals were slightly air-sensitive, the crystal used was entirely encased in a film of epoxy resin. The mosaicity of the crystal was examined by means of open-counter ω scans; the width at half-height for strong low-angle reflections averaged 0.10°. Diffraction data were collected on an Enraf–Nonius four-circle computer-controlled diffractometer, by use of graphite-monochromated Mo-K_α radiation. The θ—2θ scan technique was used to record the intensities of all reflections having $0° < 2\theta < 50°$. Background intensities were measured for each reflection during the scan. The intensities of eight standard reflections, monitored at 100 reflection intervals, showed unexpected fluctuations during data collection. Raw intensity data were corrected for Lorentz and polarisation effects, but not for absorption. After averaging the intensities of equivalent reflections, data were reduced to 1 974 independent reflections, of which 1 288, having $F_o^2 > 3\sigma(F_o^2)$, where $\sigma(F_o^2)$ was estimated from counting statistics,[10] were used in the final refinement of the structure parameters.

Solution and Refinement of the Structure.—Full-matrix least-squares refinement was based on F, and the function minimised was $\Sigma w(|F_o| - |F_c|)^2$. Weights w were taken as $[2F_o/\sigma(F_o^2)]^2$. Atomic scattering factors for non-hydrogen atoms were taken from ref. 11, those for hydrogen from ref. 12. The effects of anomalous dispersion ($\Delta f'$, $\Delta f''$) were included in F_c using values from ref. 13.

To minimise computer time, structure solution was carried out on the first 690 reflections collected. The position of the one independent manganese atom was obtained from the $2x$, $2y$, $2z$ peak. A difference-Fourier synthesis showed the positions of the remaining non-hydrogen atoms. By use of isotropic temperature factors refinement of the model converged with R 0.073 and R' 0.074 $\{R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}\}$. With the remaining diffraction data added to the calculation, and one cycle of full-matrix least-squares refinement, R was 0.066 and R' 0.069. Intro-

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TABLE 1

Positional and thermal * parameters ($\times 10^4$), with estimated standard deviations in parentheses

Atom	x/a	y/z	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
M	15 452(9)	635(1)	3 181(7)	3 275(9)	184(1)	1 377(5)	383(1)	3 713(9)	212(1)
Cl(1)	1 725(1)	114(2)	1 350(1)	453(2)	312(2)	194(1)	644(3)	536(1)	391(2)
Cl(1)	−4 656(2)	−4 017(2)	−1 114(1)	416(2)	189(2)	200(1)	400(3)	493(2)	252(3)
N	0 952(4)	1 471(5)	2 937(3)	302(5)	156(6)	143(3)	323(8)	377(4)	201(7)
N′	−2 648(4)	0 759(5)	0 232(3)	098(5)	152(7)	71(3)	153(8)	116(5)	110(8)
C(2)	1 155(5)	2 917(6)	3 243(4)	230(6)	151(8)	119(4)	25(1)	293(5)	174(9)
C(3)	3 185(5)	4 714(6)	4 932(4)	316(7)	154(9)	136(4)	30(1)	359(6)	167(10)
C(4)	4 859(5)	4 935(7)	6 239(4)	233(7)	192(10)	108(4)	26(1)	260(6)	145(10)
C(5)	6 243(6)	3 502(7)	7 262(5)	309(8)	284(11)	145(4)	40(1)	358(7)	254(12)
C(6)	5 885(6)	1 947(7)	6 916(5)	460(8)	369(10)	209(4)	67(1)	547(7)	437(12)
C(7)	3 781(6)	167(7)	5 198(4)	558(7)	319(9)	241(4)	71(1)	671(7)	456(11)
C(8)	2 190(6)	15(7)	3 904(4)	447(7)	262(9)	173(4)	55(1)	502(6)	330(10)
C(9)	2 572(5)	1 630(6)	4 240(4)	274(6)	206(8)	141(4)	37(1)	346(6)	246(10)
C(10)	4 594(5)	3 394(6)	5 950(4)	299(6)	233(9)	129(4)	40(1)	354(6)	249(10)
C(2′)	−815(5)	2 529(6)	1 784(4)	366(6)	198(8)	146(4)	42(1)	416(6)	253(9)
C(3′)	−954(6)	3 837(6)	1 939(4)	409(7)	247(9)	178(4)	53(1)	464(7)	293(11)
C(4′)	−2 943(6)	3 312(7)	0 555(5)	369(7)	213(8)	196(4)	46(1)	462(6)	272(10)
C(5′)	−7 109(6)	0 749(7)	−2 592(5)	356(7)	326(9)	234(4)	58(1)	517(7)	453(11)
C(6′)	−8 938(6)	−1 070(7)	−4 104(5)	294(8)	348(11)	171(5)	50(1)	365(7)	377(12)
C(7′)	−8 699(6)	−2 308(7)	−4 198(5)	344(8)	238(10)	179(5)	40(1)	420(7)	276(12)
C(8′)	−6 649(5)	−1 708(7)	−2 794(4)	231(7)	225(9)	133(4)	35(1)	283(7)	239(11)
C(9′)	−4 664(5)	0 208(6)	−1 163(4)	362(6)	211(8)	163(4)	45(1)	447(6)	291(9)
C(10′)	−4 894(5)	1 461(6)	−1 067(4)	413(6)	281(9)	208(4)	56(1)	540(6)	386(10)

Atom†	x/a	y/z	z/c	Atom	x/a	y/z	z/c
H(3)	3 346(6)	5 792(6)	5 158(4)	H(3′)	414(6)	5 144(6)	3 087(4)
H(4)	6 334(6)	6 220(7)	7 441(4)	H(4′)	−3 033(6)	4 248(7)	660(5)
H(5)	7 715(6)	4 756(7)	8 465(5)	H(5′)	−7 299(6)	1 610(7)	−2 537(5)
H(6)	7 058(6)	2 044(7)	7 847(5)	H(6′)	−1.0506(6)	−1 574(7)	−5 188(5)
H(7)	3 481(6)	−1 001(7)	4 927(5)	H(7′)	−1.0035(6)	−3 648(7)	−5 303(5)
H(8)	706(6)	−1 261(6)	2 703(4)	H(8′)	−6 495(6)	−2 593(7)	−2 870(4)

* The form of the anisotropic thermal parameter is: $\exp[-(B_{11}{}^*h^*h + B_{22}{}^*k^*k + B_{33}{}^*l^*l + B_{12}{}^*h^*k + B_{13}{}^*h^*l + B_{23}{}^*k^*l)]$.

† For H atoms $B_{iso} = 5.0$ Å^2 (see text).

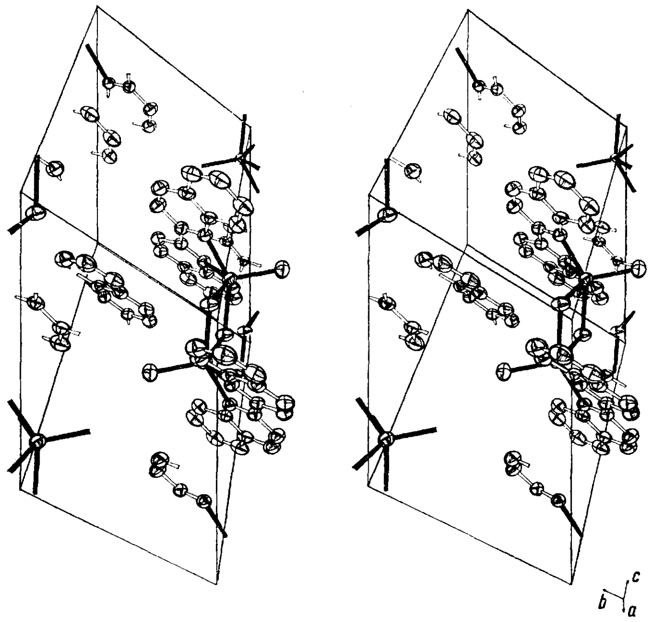

FIGURE 2 Packing in unit cell of [$Mn_2(biq)_2Cl_2$]

duction of anisotropic thermal parameters gave R 0.028, R' 0.029. The positions of these hydrogen atoms were calculated geometrically assuming C–H 1.0 Å, with isotropic temperature factors B 5.0. This model converged with R 0.027, and R' 0.028. A final difference Fourier map was featureless. A structure-factor calculation with all observed and unobserved reflections included (no refinement) gave R 0.045; on this basis, it was decided that careful measurement of reflections rejected automatically during data collection would not significantly improve the result.

RESULTS AND DISCUSSION

Final positional and thermal parameters for the atoms are given in Table 1. Estimated standard deviations in the least significant figures quoted, were derived from the inverse matrix in the course of least-squares refinement calculations. Tables 2 and 3 give bond lengths and angles. Figures 1 and 2 show the dimeric structure and the packing.

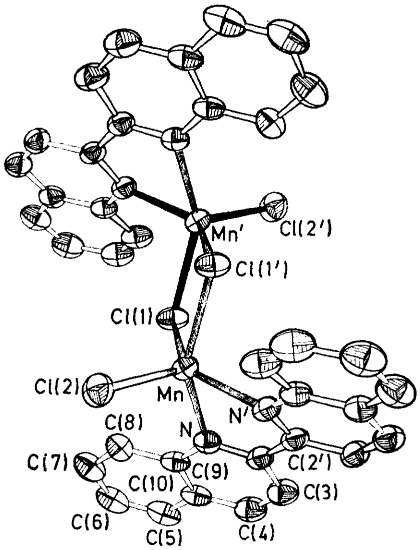

FIGURE 1 Molecular structure

TABLE 2

Bond distances and selected intramolecular distances (Å)

Mn–Mn	3.887(1)	Cl(1)–Cl(1′)	3.273(1)
Mn–Cl(1)	2.543(1)	Mn–Cl(1′)	2.539(1)
Mn–Cl(2)	2.322(1)		
Mn–N	2.235(2)	Mn–N′	2.246(2)
N–C(2)	1.342(5)	N′–C(2′)	1.357(5)
N–C(9)	1.367(6)	N′–C(9′)	1.351(6)
C(2)–C(3)	1.418(7)	C(2′)–C(3′)	1.420(6)
C(2)–C(2′)	1.458(5)		
C(3)–C(4)	1.349(5)	C(3′)–C(4′)	1.348(5)
C(4)–C(10)	1.396(5)	C(4′)–C(10′)	1.410(5)
C(5)–C(6)	1.359(6)	C(5′)–C(6′)	1.353(5)
C(5)–C(10)	1.419(5)	C(5′)–C(10′)	1.426(6)
C(6)–C(7)	1.419(5)	C(6′)–C(7′)	1.413(5)
C(7)–C(8)	1.356(6)	C(7′)–C(8′)	1.347(6)
C(8)–C(9)	1.405(6)	C(8′)–C(9′)	1.435(5)
C(9)–C(10)	1.425(6)	C(9′)–C(10′)	1.422(5)

As is evident from the packing diagram (Figure 2) and from the nearest intermolecular contact distances, the crystal structure consists of well-separated neutral binuclear complex molecules. The bulky biq ligands are especially effective in holding the Mn_2Cl_4 unit in isolation, and no significant intermolecular interactions are likely to exist in comparison to the magnitude of the intramolecular interactions. The intermolecular interactions which do occur should result mainly from electron spin density delocalised onto biq ligands of neighbouring molecules, similar to that observed in an iron(III) dithiocarbamate,[5] where the metal atoms are well-separated, but the ligands are within van der Waals contact distances.

The other significant features of the molecule are best described in terms of the least-squares planes fitted to various groups of atoms (Table 4). The two quinolyl fragments of the biquinolyl ligand are at 13.3° to each other, and at 8.8 and 5.6°, to the biq plane. The angles of the phenyl and the pyridyl rings of the same quinolyl fragment are 1.0 and 2.2° for the two quinolyls. The angle between the adjacent pyridyl rings is 11.3° and that between the extreme phenyl rings is 14.8°. This distortion corresponds to a marked curving of the biq ligand, essentially into a banana shape, with curvature in the quinolyl rings as well as the central single bond. On the other hand, there is no significant twist of the planes of the aromatic rings around the single bond, probably owing to the metal chelation. The Mn,Cl(1),Mn′,Cl(1′) bridging plane forms angles of 80.0 and 79.3° with the biq ligand and with the Cl(2),Mn,Mn′,Cl(2′) plane. When the biq rings are distorted by intramolecular repulsion of the chlorine atoms, the Mn–Cl co-ordination is distorted in turn, so that the biq distortion gives a crude measure of how much the co-ordination geometry has been affected, and therefore how much it might respond to alteration of the ligands.

TABLE 3

Bond angles (°)

Mn–Cl(1)–Mn′	99.8(1)	Cl(1)–Mn–Cl(1′)	80.2(1)
Cl(1)–Mn–Cl(2)	103.7(1)	Cl(1′)–Mn–Cl(2)	117.0(1)
Cl(1)–Mn–N	93.5(1)	Cl(1′)–Mn–N	130.4(2)
Cl(1)–Mn–N′	147.0(1)	Cl(1′)–Mn–N′	85.4(1)
Cl(2)–Mn–N	112.4(1)	Cl(2)–Mn–N′	109.3(1)
N–Mn–N′	73.7(2)		
Mn–N–C(2)	112.7(3)	Mn–N′–C(2′)	112.6(2)
Mn–N–C(9)	125.6(2)	Mn–N′–C(9′)	127.0(2)
C(2)–N–C(9)	120.5(3)	C(2′)–N′–C(9′)	119.5(5)
N–C(2)–C(2′)	117.4(3)	N′–C(2′)–C(2)	116.7(3)
N–C(2)–C(3)	120.3(4)	N′–C(2′)–C(3′)	120.4(4)
C(3)–C(2)–C(2′)	122.3(4)	C(3′)–C(2′)–C(2)	122.8(3)
C(2)–C(3)–C(4)	120.0(3)	C(2′)–C(3′)–C(4′)	120.6(4)
C(3)–C(4)–C(10)	120.7(4)	C(3′)–C(4′)–C(10′)	120.0(3)
C(6)–C(5)–C(10)	121.5(3)	C(6′)–C(5′)–C(10′)	120.6(3)
C(5)–C(6)–C(7)	118.7(4)	C(5′)–C(6′)–C(7′)	120.6(4)
C(6)–C(7)–C(8)	121.8(4)	C(6′)–C(7′)–C(8′)	121.2(5)
C(7)–C(8)–C(9)	120.2(3)	C(7′)–C(8′)–C(9′)	120.2(3)
C(8)–C(9)–C(10)	119.2(4)	C(8′)–C(9′)–C(10′)	118.7(3)
N–C(9)–C(8)	120.3(3)	N′–C(9′)–C(8′)	119.2(4)
N–C(9)–C(10)	120.4(4)	N′–C(9′)–C(10′)	122.1(4)
C(4)–C(10)–C(5)	123.7(3)	C(4′)–C(10′)–C(5′)	123.7(4)
C(4)–C(10)–C(9)	117.8(4)	C(4′)–C(10′)–C(9′)	117.4(3)
C(5)–C(10)–C(9)	118.4(5)	C(5′)–C(10′)–C(9′)	118.8(4)

If the bridging chlorines were replaced by a single atom lying between them, the manganese co-ordination geometry could be described as a distorted tetrahedron, the most common geometry of transition-metal dihalide complexes with biq.[4] The bridging Mn–Cl bonds are slightly elongated (2.54 Å) and three stronger Mn–N (2.24 Å) and Mn–Cl (2.32 Å) bonds hold the biq ligands and the remaining chlorine to each metal atom. The Mn · · · Mn distance (3.9 Å) is quite large for a ligand-bridged dimer and would seem to rule out any strong direct metal–metal interactions. However, the bridging Mn—Cl bonds are sufficiently strong to permit significant superexchange interaction *via* the ligand bridges. The metal orbitals most involved in the superexchange will be those which have maximum overlap with the halogen *p* orbitals.[6] For a pure tetrahedral Mn this would be the t_2 more than the *e* orbitals, but the lower symmetry elements in the present complex will diminish the difference between the two types of orbitals, and the exchange pathway cannot be predicted. In any case, this overlap is critically affected by the manganese geometry, which determines the spatial orientation of the *d* orbitals; similarly the orbital pathway for the superexchange is strongly affected by the Mn–Cl–Mn angles. Thus, changes in these factors, brought about by modifications in the ligands, must affect the magnetic interaction, throwing light on the exchange mechanism. For example, in the simpler case of certain chlorine-bridged copper(II) dimers, the balance between ferro- and antiferro-magnetic exchange is reached at *ca.* 94°.[14] Although the structure of $[Mn_2(biq)_2Cl_4]$ is unique among manganese(II) complexes reported to date, there is already good evidence for the existence of a series of analogous manganese(II) dimers with suitably modified ligands.[4]

TABLE 4

Coefficients of least-squares planes: $AX + BY + CZ = D$

	Atoms in plane	*A*	*B*	*C*	*D*
(I):	N′, C(2′)—(10′)	0.7263	0.6819	−0.0866	−2.2897
(II):	N′, C(2′)—(4′), C(9′), C(10′)	0.7297	0.6805	−0.0665	−2.2961
(III):	C(5′)—(10′)	0.7233	0.6827	−0.1033	−2.2365
(IV):	Mn, N, N′, C(2), C(2′)	−0.6742	−0.7278	−0.1255	1.8628
(V):	N, N′, C(2)—(10), C(2′)—(10′)	0.8221	0.5670	−0.0522	−2.9382
(VI):	N, C(2)—(10)	−0.8493	−0.5268	−0.0328	2.5993
(VII):	N, C(2)—(4), C(9) C(10)	−0.8338	−0.5508	−0.0382	2.5390
(VIII):	C(5)—(10)	−0.8602	−0.5092	−0.0285	2.5930
(IX):	Mn, Cl(1), Mn′, Cl(1′)	0.1802	−0.6380	−0.7486	0
(XI):	Mn, Cl(2), N	−0.8527	0.3881	−0.3498	1.1008
(XII):	Mn, Cl(2), N′	0.3249	0.4158	−0.8494	−1.1149
(XIII):	Mn, N, N′	−0.5588	−0.7970	−0.2293	1.5547
(XIV):	Mn, Cl(2), Mn′, Cl(2′)	−0.3482	0.5228	−0.7781	0

Final observed and calculated structure factors and intermolecular contact distances are listed in Supplementary Publication No. SUP 21525 (9 pp., 1 microfiche).*

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* For details of Supplementary Publications, see Notice to Authors No. 7 in *J.C.S. Dalton*, 1975, Index issue.

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