Crystal Structure of an Eight-co-ordinate Manganese Complex: Bis-(3,4-di-2-pyridylpyridazine)dinitratomanganese(II)

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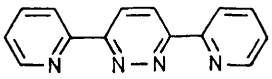
The crystal and molecular structures of the compound [Mn(dppn)$_2$(NO$_3$)$_2$] (dppn = 3,6-di-2-pyridylpyridazine) have been determined by single-crystal *X*-ray diffraction photography, and refined anisotropically by the method of least squares to R 6·6% for 1816 independent observed reflections. The yellow crystals are triclinic, and the unit cell, of dimensions a = 8·88, b = 11·95, c = 14·20 (±0·03) Å, α = 107·0, β = 87·6, γ = 103·0 (±0·3)°, contains two enantiomorphous molecules. All four ligands are bidentate, giving an eight-co-ordinate complex roughly approximating to C_2 symmetry. The dppn molecules are nearly planar, and the two non-co-ordinating N atoms in each ligand are mutually *trans*. The four Mn–N bond lengths are all close to 2·30 Å. The co-ordination of one nitrate ion is symmetrical (Mn–O 2·46 Å), that of the other is unsymmetrical (Mn–O 2·30 and 2·47 Å). This compound and its cadmium analogue are isomorphous. The i.r. spectra in the region of nitrate vibrations are reported.

As part of an attempt to compare the superexchange behaviour of different metal ions in similar binuclear situations, the reactions of various first-row transition-metal ions with 3,6-di-2-pyridylpyridazine (dppn) and related ligands were studied.[1] With Co^{2+}, Ni^{2+}, and Cu^{2+}, 1 : 1 complexes, *e.g.* [M(dppn)(NO$_3$)$_2$]·H$_2$O (M = Co or Ni), were obtained, which appeared from their magnetic and other properties to be binuclear,[2] but with Mn^{2+} and Zn^{2+} only 1 : 2 complexes could be isolated.



dppn

The yellow manganese complex [Mn(dppn)$_2$(NO$_3$)$_2$] was magnetically normal ($\mu_{\text{eff.}}$ 5·96 B.M. at 80 and 300 K) and hence presumably mononuclear, and, as would be expected, its i.r. spectrum showed evidence of nitrate co-ordination. It is evidently analogous to the compound [Mn(bipy)$_2$(NO$_3$)$_2$], for which Addison and Kilner proposed a *cis*-octahedral structure with two unidentate nitrate ligands.[3] The number of i.r. bands suggests, however, the presence of more than one kind of nitrate ion, possibly both uni- and bi-dentate.

In order to ascertain the mode of nitrate bonding and the manganese co-ordination geometry, and if possible to find some reason for the failure of dppn to act as a binucleating ligand towards Mn^{2+} and Zn^{2+}, we have determined the crystal structure of [Mn(dppn)$_2$(NO$_3$)$_2$]. We have also prepared the remaining eight compounds in the series [M(biL)$_2$(NO$_3$)$_2$] (M = Mn, Zn, or Cd; biL = bipy, phen, or dppn) in order to compare their i.r. spectra.

EXPERIMENTAL

Yellow air-stable crystals of [Mn(dppn)$_2$(NO$_3$)$_2$] were prepared by the method previously described for [Ni(dppn)-(NO$_3$)$_2$]·H$_2$O,[2b] *i.e.* mixing hot solutions of dppn and the

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[1] P. W. Ball, Ph.D. Thesis, University of Hull, 1968.

[2] (*a*) J. E. Andrew, P. W. Ball, and A. B. Blake, *Chem. Comm.*, 1969, 143; (*b*) P. W. Ball and A. B. Blake, *J. Chem. Soc.* (*A*), 1969, 1415.

[3] C. C. Addison and M. Kilner, *J. Chem. Soc.* (*A*), 1966, 1249.

metal nitrate hexahydrate in a mixture of methanol and triethyl orthoformate and setting the solution aside overnight. Preliminary Weissenberg and precession photographs revealed a triclinic unit cell. Integrated precession photographs of the levels 0—4*kl*, *h*0—5*l*, and *hhl* to *h*,$\bar{h}$ + 5,*l* were taken with various exposure times, and the intensities were measured by means of a Joyce–Loebl double-beam recording microdensitometer. After application of Lorentz and polarisation corrections, the relative scale factors of the levels were determined from common reflections by the logarithmic least-squares method.[4] Merging the seventeen levels gave 1816 unique reflections, the conventional *R* factor of this process being 0·043. No absorption corrections were applied, since it was estimated that the transmission factor varied by only *ca.* 1% over the range of data collected.

TABLE 1

Atomic fractional co-ordinates and vibrational parameters (Å²),* with estimated standard deviations in parentheses

Atom	10^4x	10^4y	10^4z	10^3U_{11}	10^3U_{22}	10^3U_{33}	10^3U_{12}	10^3U_{23}	10^3U_{31}
Mn	2515(3)	3451(3)	2330(2)	29(1)	33(1)	40(1)	5(2)	19(2)	−3(2)
C(1)	18(26)	933(17)	1499(16)	61(13)	32(10)	64(12)	8(19)	28(18)	7(22)
C(2)	−1436(27)	125(18)	1168(15)	69(14)	47(12)	54(12)	−9(22)	35(19)	−25(22)
C(3)	−2760(26)	582(19)	1447(16)	57(13)	51(12)	57(12)	−4(22)	21(20)	−26(22)
C(4)	−2583(24)	1770(19)	2063(16)	42(11)	46(11)	63(13)	−8(20)	14(20)	−24(20)
C(5)	−1115(22)	2485(15)	2338(13)	42(11)	32(9)	41(10)	−3(17)	32(15)	−2(17)
C(6)	−856(20)	3728(17)	3023(13)	31(9)	54(10)	44(10)	26(17)	33(17)	−13(17)
C(7)	−2050(23)	4256(18)	3447(16)	40(10)	47(11)	59(12)	35(18)	5(19)	2(20)
C(8)	−1679(23)	5376(18)	4092(16)	41(11)	42(10)	72(13)	19(18)	23(19)	−24(20)
C(9)	−95(23)	5960(17)	4217(14)	45(11)	41(11)	43(10)	−4(19)	15(18)	−2(19)
C(10)	425(25)	7212(17)	4887(14)	61(12)	40(10)	39(10)	17(19)	13(17)	−11(19)
C(11)	1935(24)	7725(19)	5158(15)	47(12)	59(12)	52(11)	−6(21)	31(19)	−24(20)
C(12)	2407(31)	8917(23)	5742(18)	87(18)	73(15)	65(14)	−8(28)	30(24)	−51(26)
C(13)	1235(32)	9558(20)	6028(18)	100(19)	48(12)	71(15)	23(25)	15(23)	−16(28)
C(14)	−326(32)	8952(21)	5721(18)	98(19)	50(13)	67(15)	4(27)	18(23)	2(29)
N(1)	191(17)	2092(13)	2056(11)	35(8)	40(8)	50(9)	29(13)	12(14)	1(15)
N(2)	637(17)	4327(13)	3186(11)	40(8)	35(8)	43(8)	11(14)	7(14)	−10(15)
N(3)	1020(18)	5455(14)	3798(12)	43(9)	45(9)	51(9)	20(15)	10(16)	3(16)
N(4)	−712(21)	7809(15)	5151(14)	59(11)	43(9)	72(11)	20(17)	15(17)	24(19)
C(1′)	4836(25)	6079(19)	3243(16)	45(12)	44(12)	66(13)	−30(21)	10(21)	−24(22)
C(2′)	5903(28)	7138(21)	3213(18)	64(14)	57(13)	77(15)	−9(24)	24(23)	−48(24)
C(3′)	5971(30)	7532(20)	2377(18)	83(16)	58(13)	82(15)	22(24)	54(22)	−11(27)
C(4′)	4960(28)	6848(19)	1568(19)	62(14)	43(12)	92(17)	7(22)	19(24)	−6(27)
C(5′)	3938(23)	5770(17)	1650(14)	42(11)	47(11)	52(11)	17(19)	27(18)	26(19)
C(6′)	2833(21)	5027(16)	831(14)	38(10)	38(9)	53(11)	24(16)	33(16)	20(18)
C(7′)	2705(26)	5317(18)	−44(15)	64(13)	47(11)	46(11)	8(20)	25(18)	−22(21)
C(8′)	1641(26)	4544(19)	−748(15)	58(13)	54(12)	53(11)	−15(22)	42(19)	16(21)
C(9′)	727(23)	3511(18)	−517(14)	48(11)	60(12)	42(11)	28(19)	23(18)	−5(19)
C(10′)	−516(23)	2619(16)	−1212(13)	53(11)	42(10)	39(10)	20(18)	32(16)	−1(18)
C(11′)	−1545(24)	1745(18)	−913(16)	47(12)	47(11)	66(12)	2(20)	46(19)	12(21)
C(12′)	−2640(25)	899(20)	−1591(16)	56(12)	75(13)	52(12)	44(20)	30(20)	−13(21)
C(13′)	−2657(27)	1021(20)	−2525(17)	73(14)	53(12)	60(13)	26(23)	−1(22)	−39(23)
C(14′)	−1630(38)	1923(25)	−2768(19)	133(25)	79(16)	66(15)	−79(35)	59(25)	−48(32)
N(1′)	3909(17)	5396(13)	2458(11)	40(9)	41(8)	50(9)	28(14)	12(14)	7(15)
N(2′)	1951(19)	4035(14)	997(11)	46(9)	47(9)	46(9)	13(15)	19(15)	−4(16)
N(3′)	876(18)	3288(14)	326(11)	46(10)	49(9)	41(9)	−5(16)	24(14)	−1(16)
N(4′)	−583(27)	2721(18)	−2105(13)	102(16)	84(13)	57(10)	−54(25)	69(18)	−45(21)
O(1)	5001(18)	3306(12)	1537(11)	81(10)	43(8)	69(10)	18(15)	−4(15)	−10(17)
O(2)	3094(18)	1882(15)	893(13)	57(10)	96(11)	97(11)	9(17)	81(17)	8(18)
O(3)	5305(19)	1878(14)	253(12)	92(11)	77(10)	70(10)	65(17)	5(17)	78(17)
N(5)	4495(19)	2359(15)	881(12)	53(10)	57(9)	47(9)	23(16)	33(15)	31(17)
O(1′)	3291(22)	1936(16)	2950(13)	92(12)	78(11)	72(10)	0(20)	8(18)	−9(19)
O(2′)	3742(19)	3718(13)	3803(12)	78(10)	54(8)	84(10)	13(16)	38(15)	36(18)
O(3′)	4500(19)	2423(17)	4341(12)	80(10)	165(12)	95(10)	85(17)	148(15)	−38(16)
N(5′)	3880(18)	2673(14)	3734(12)	38(9)	50(9)	55(10)	18(15)	23(15)	2(16)

* The temperature factor is given by $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^*\cos\gamma^* + 2U_{23}klb^*c^*\cos\alpha^* + 2U_{31}lhc^*a^*\cos\beta^*)]$.

Crystal Data.—$C_{28}H_{20}MnN_{10}O_6$, $M = 647{\cdot}5$, Triclinic, $a = 8{\cdot}88$, $b = 11{\cdot}95$, $c = 14{\cdot}20$ ($\pm0{\cdot}03$) Å, $\alpha = 107{\cdot}0$, $\beta = 87{\cdot}6$, $\gamma = 103{\cdot}0$ ($\pm0{\cdot}3$)°, $U = 1404 \pm 11$ Å³, $D_m = 1{\cdot}53 \pm 0{\cdot}02$, $Z = 2$, $D_c = 1{\cdot}53$, $F(000) = 662$. Mo-K_α radiation, $\lambda = 0{\cdot}7107$ Å; μ(Mo-K_α) = 5·6 cm⁻¹.

Several statistical tests for the presence of a centre of symmetry were applied to the intensities, but the results were ambiguous, and the centrosymmetric space group $P\bar{1}$ was therefore assumed for convenience. The subsequent successful refinement indicates that any deviation from centric symmetry of the unit cell must be very small.

Structure Determination and Refinement.—The position of the Mn atom was determined from a three-dimensional sharpened Patterson map, and two cycles of phase calculation and Fourier synthesis (assuming an overall temperature factor of 3·0 Å²) then revealed all the remaining atom positions (other than hydrogen), with *R* 0·30.

Atomic parameters were refined by the method of least squares, first assuming individual isotropic temperature factors for all non-hydrogen atoms, then with anisotropic temperature factors, convergence being reached at *R* 0·0675. After rescaling the data so that $\Sigma|F_c|$ and $\Sigma|F_o|$ were equal for each level, refinement was continued, and reached final

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[4] A. B. Blake and R. C. Elder, *X*-Ray Crystallographic Intensity Treatment Program (MIXCIT) for the IBM 709/7090, SHARE Distribution No. 3352, IBM Corporation, New York, 1965; A. D. Rae, *Acta Cryst.*, 1965, **19**, 683.

convergence at R 0·0658. The maximum co-ordinate shift in the last cycle was 0·2σ, the average shift being much smaller. The quantity minimised was $\Sigma w\Delta^2$, where $\Delta = |F_o| - |F_c|$ and $w = \{1 + [(F^* - F_o)/G^*]^2\}^{-1}$, the values $F^* = 16$, $G^* = 30$ being chosen so that $w\Delta^2$ showed no systematic dependence on $|F_o|$.

A final three-dimensional difference-Fourier synthesis was essentially flat. No attempt was made to locate hydrogen atoms.

Atomic scattering factors were taken from ref. 5. No corrections were made for anomalous dispersion. Computation was done on the Hull University I.C.L. 1905E computer, using programs of ref. 6.

RESULTS AND DISCUSSION

Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21259 (5 pp., 1 microfiche).* Table 1 gives the final fractional co-ordinates and vibrational parameters of the atoms, with their estimated standard deviations. Figure 1 shows a general view of the molecule, with the atomic numbering scheme, and Table 2 gives the bond lengths and angles. Table 3 lists the equations of weighted least-squares planes passing through certain groups of atoms, the distances of various atoms from these planes, and the angles between the planes. Table 4 gives some distances between non-bonded atoms.

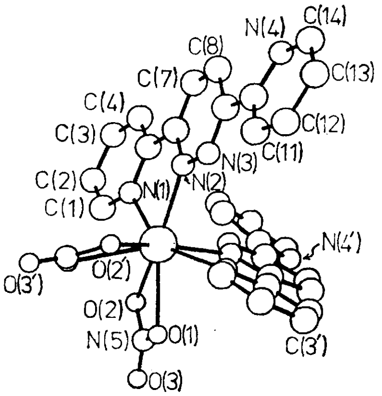

FIGURE 1 The molecule viewed from the [111] direction

TABLE 2

Bond lengths (Å) and angles (°)

(a) MnN_4O_4 Co-ordination sphere

Mn–N(1)	2·289(13)	Mn–N(1′)	2·333(10)
Mn–N(2)	2·286(14)	Mn–N(2′)	2·308(14)
Mn–O(1)	2·454(16)	Mn–O(1′)	2·465(11)
Mn–O(2)	2·460(15)	Mn–O(2′)	2·304(16)

N(1)–Mn–N(2)	70·3(4)	N(1′)–Mn–N(2′)	69·7(5)
N(1)–Mn–N(2′)	88·6(5)	N(1′)–Mn–N(2)	86·4(4)
N(1)–Mn–N(1′)	148·5(4)	N(2)–Mn–N(2′)	89·1(5)
N(1)–Mn–O(1)	129·9(4)	N(1′)–Mn–O(1′)	127·5(5)
N(1)–Mn–O(1′)	82·7(5)	N(1′)–Mn–O(1)	72·2(4)
N(1)–Mn–O(2)	78·9(5)	N(1′)–Mn–O(2′)	84·8(4)
N(1)–Mn–O(2′)	114·7(5)	N(1′)–Mn–O(2)	115·3(5)
N(2)–Mn–O(1)	158·5(3)	N(2′)–Mn–O(1′)	148·3(5)
N(2)–Mn–O(1′)	116·0(5)	N(2′)–Mn–O(1)	84·7(5)
N(2)–Mn–O(2)	146·1(5)	N(2′)–Mn–O(2′)	154·4(4)
N(2)–Mn–O(2′)	89·1(5)	N(2′)–Mn–O(2)	75·9(4)
O(1)–Mn–O(2)	51·3(5)	O(1′)–Mn–O(2′)	51·5(4)
O(1)–Mn–O(2′)	87·7(5)	O(1′)–Mn–O(2)	72·5(5)
O(1)–Mn–O(1′)	77·9(5)	O(2)–Mn–O(2)′	117·2(5)

TABLE 2 (*Continued*)

(b) MnN_6 Pseudo-octahedron

N(5)–Mn–N(1)	104·6(5)	N(5′)–Mn–N(1′)	106·3(4)
N(5)–Mn–N(1′)	93·5(4)	N(5′)–Mn–N(1)	99·8(4)
N(5)–Mn–N(2)	167·1(5)	N(5′)–Mn–N(2′)	166·3(5)
N(5)–Mn–N(2′)	78·8(4)	N(5′)–Mn–N(2)	103·9(5)
N(5)–Mn–N(5′)	88·5(4)		

(c) Dipyridylpyridazine ligands

	dppn	dppn′
N(1)–C(1)	1·36(2)	1·35(3)
C(1)–C(2)	1·43(3)	1·41(2)
C(2)–C(3)	1·40(3)	1·39(3)
C(3)–C(4)	1·41(2)	1·42(4)
C(4)–C(5)	1·39(3)	1·43(2)
C(5)–N(1)	1·35(2)	1·35(2)
C(5)–C(6)	1·49(2)	1·49(3)
C(6)–C(7)	1·38(2)	1·40(3)
C(7)–C(8)	1·36(2)	1·38(3)
C(8)–C(9)	1·42(3)	1·43(2)
C(9)–N(3)	1·31(2)	1·32(2)
N(2)–N(3)	1·35(2)	1·35(2)
N(2)–C(6)	1·35(2)	1·34(2)
C(9)–C(10)	1·50(2)	1·51(3)
C(10)–C(11)	1·36(3)	1·38(2)
C(11)–C(12)	1·40(3)	1·40(3)
C(12)–C(13)	1·41(3)	1·38(3)
C(13)–C(14)	1·43(4)	1·36(3)
C(14)–N(4)	1·34(2)	1·35(3)
N(4)–C(10)	1·34(2)	1·31(2)
C(5)–N(1)–C(1)	116·9(15)	119·3(13)
N(1)–C(1)–C(2)	124·7(17)	121·5(18)
C(1)–C(2)–C(3)	116·6(14)	120·1(21)
C(2)–C(3)–C(4)	118·6(18)	118·7(17)
C(3)–C(4)–C(5)	120·1(17)	117·7(18)
C(4)–C(5)–N(1)	123·0(12)	122·6(18)
C(4)–C(5)–C(6)	122·5(15)	120·1(16)
N(1)–C(5)–C(6)	114·5(16)	117·3(13)
C(5)–C(6)–N(2)	115·4(14)	114·2(14)
C(5)–C(6)–C(7)	123·0(15)	123·7(13)
N(2)–C(6)–C(7)	121·6(13)	122·1(17)
C(6)–C(7)–C(8)	118·0(17)	117·9(14)
C(7)–C(8)–C(9)	117·3(16)	117·0(17)
C(8)–C(9)–N(3)	123·7(14)	122·8(17)
C(9)–N(3)–N(2)	118·1(15)	119·5(13)
N(3)–N(2)–C(6)	121·0(13)	120·7(14)
C(8)–C(9)–C(10)	121·3(16)	122·1(16)
N(3)–C(9)–C(10)	114·9(16)	115·1(13)
C(9)–C(10)–N(4)	114·3(17)	117·2(15)
C(9)–C(10)–C(11)	122·9(15)	121·1(16)
N(4)–C(10)–C(11)	122·7(14)	121·7(18)
C(10)–C(11)–C(12)	122·0(17)	119·5(18)
C(11)–C(12)–C(13)	116·2(22)	117·0(16)
C(12)–C(13)–C(14)	118·5(17)	120·6(21)
C(13)–C(14)–N(4)	122·8(19)	121·3(22)
C(14)–N(4)–C(10)	117·7(19)	119·8(18)

(d) Nitrate ligands

	NO_3	NO_3'
N(5)–O(1)	1·24(2)	1·25(2)
N(5)–O(2)	1·25(2)	1·26(1)
N(5)–O(3)	1·22(1)	1·18(2)
O(1)–N(5)–O(2)	117·4(16)	112·0(14)
O(2)–N(5)–O(3)	119·7(15)	123·8(16)
O(3)–N(5)–O(1)	122·9(16)	124·2(11)

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1974, Index issue.

[5] 'International Tables for *X*-Ray Crystallography,' vol. 3, Kynoch Press, Birmingham, 1962.

[6] Structure-factor, Fourier-synthesis, and anisotropic (block-diagonal) least-squares programs by Dr. C. H. Morgan, Centre for Computer Studies, University of Hull; data-reduction, statistical-analysis, and molecular-geometry programs by A. B. Blake and L. R. Fraser; molecule-drawing program PAMOLE by A. J. Cole and P. G. Adamson, *Acta Cryst.*, 1969, **A25**, 535.

The compound consists of molecules in which the manganese atom is in eightfold co-ordination, with two bidentate nitrate groups and two bidentate dppn ligands, each of the latter having one pyridine and one pyridazine nitrogen atom not involved in co-ordination. The molecules possess no symmetry, the extent to which they deviate from C_2 symmetry being evident from Figure 2, which is a view along a line approximately bisecting the N(1)–Mn–N(1′) and N(2)–Mn–N(2′) angles. Two enantiomorphous molecules occupy the unit cell in the arrangement shown in Figure 3.

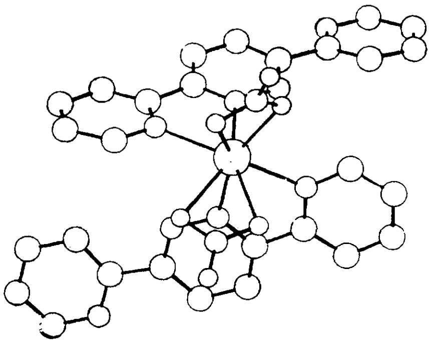

FIGURE 2 View of the molecule along a line approximately bisecting the two chelating N–Mn–N angles, illustrating the deviation from two-fold symmetry

TABLE 3

Planes of best (least-squares) fit to selected groups of atoms

(*a*) Atoms defining the planes [a]

Plane	Group	Atoms [b]
(*A*)	Ligand pyridyl	C(1)—(5), N(1)
(*B*)	Pyridazine	C(6)—(9), N(2), N(3)
(*C*)	Free pyridyl	C(10)—(14), N(4)
(*D*)	Nitrate	N(5), O(1)—(3)
(*E*)	MnN_2	Mn, N(1), N(2)
(*F*)	MnO_2	Mn, O(1), O(2)

(*b*) Equations of planes [c] in the form

$$lX + mY + nZ = p$$

	10^3l	10^3m	10^3n	10^3p
(*A*)	−49	−570	820	−1382
(*B*)	33	−639	769	−962
(*C*)	−151	−546	824	−1880
(*D*)	192	−785	589	−232
(*E*)	166	−597	785	−1246
(*F*)	178	−776	605	−227
(*A′*)	−705	602	375	−1740
(*B′*)	−695	592	408	−1793
(*C′*)	−654	701	287	−2426
(*D′*)	884	122	−452	−670
(*E′*)	−761	416	499	−1087
(*F′*)	899	101	−427	−802

(*c*) Distances (Å) [d] of the Mn atom from the planes

(*A*) −0·40, (*A′*) −0·43, (*B*) −0·16, (*B′*) −0·39, (*C*) −1·04, (*C′*) −1·03, (*D*) −0·05, (*D′*) 0·08

(*d*) Angles between planes (°)

	dppn	dppn′
(*A*)–(*B*)	6·8	2·1
(*B*)–(*C*)	12·2	9·6
(*A*)–(*C*)	6·0	8·1

(*E*)–(*E′*) 89, (*E*)–(*F*) 15, (*E*)–(*F′*) 104, (*F*)–(*F′*) 100, (*E′*)–(*F′*) 149, (*E′*)–(*F*) 99

[a] Atoms defining the planes were given weights proportional to their atomic numbers. [b] In planes (*A*)–(*D*), the deviation of each component atom from its plane is less than the root-mean-square standard deviation (*ca.* 0·03 Å) of its co-ordinates. [c] Orthogonal co-ordinates X, Y, Z are related to the fractional co-ordinates of Table 1 as follows: $X = ax \sin\gamma - cz \sin\alpha \cos\beta^*$, $Y = by + ax \cos\gamma + cz \cos\alpha$, $Z = cz \sin\alpha^* \sin\beta$. l, m, n Are the direction cosines of the plane normal, and p is in Å. [d] The root-mean-square standard deviation of the Mn co-ordinates is 0·004 Å.

TABLE 4

Selected distances (Å) between non-bonded atoms

(*a*) Intramolecular

N(1) ··· N(2)	2·63	O(1) ··· O(2)	2·13
N(1′) ··· N(2′)	2·65	O(1′) ··· O(2′)	2·08
N(1) ··· N(2′)	3·21	O(1) ··· O(2′)	3·30
N(1′) ··· N(2)	3·16	O(1′) ··· O(2)	2·91
N(2) ··· N(2′)	3·22	O(1) ··· O(1′)	3·09
N(1) ··· O(1′)	3·15	N(1) ··· O(2)	3·02
N(1′) ··· O(1)	2·82	N(1′) ··· O(2′)	3·13
N(2) ··· O(2′)	3·22	N(2′) ··· O(1)	3·21
N(2′) ··· O(2)	2·93	N(3′) ··· O(2)	3·13
C(1) ··· O(2)	2·91	C(1′) ··· O(2′)	3·09
C(5′) ··· O(1)	3·25		

(*b*) Intermolecular [a,b]

$C(11') \cdots C(1^{I})$	3·62	$C(11) \cdots C(5^{III})$	3·67
$C(12') \cdots C(1^{I})$	3·57	$C(11) \cdots C(6^{III})$	3·50
$C(14') \cdots C(10^{II})$	3·51	$C(12) \cdots C(4^{III})$	3·47
$C(14') \cdots C(11^{II})$	3·57	$C(12) \cdots C(5^{III})$	3·62
$C(7') \cdots C(9'^{II})$	3·60	$C(9) \cdots C(9^{III})$	3·66
$C(7') \cdots C(10'^{II})$	3·51	$C(8') \cdots C(9'^{II})$	3·53
$C(4) \cdots N(5^{IV})$	3·45	$C(4') \cdots C(13'^{II})$	3·55
$C(3) \cdots O(3^{IV})$	3·35	$C(14) \cdots N(5'^{III})$	3·50
$C(4) \cdots O(3^{IV})$	3·29	$C(2) \cdots O(2^{I})$	3·34
$C(4) \cdots O(1^{IV})$	3·35	$C(4') \cdots O(3^{V})$	3·40
$C(14) \cdots O(1'^{III})$	3·33	$C(7') \cdots O(1^{V})$	3·39
$C(11) \cdots O(3'^{VI})$	3·33	$C(11') \cdots O(3^{IV})$	3·20
$C(1') \cdots O(3'^{VI})$	3·38	$C(12') \cdots O(3^{IV})$	3·21
$C(2') \cdots O(3'^{VI})$	3·37	$C(12') \cdots O(1'^{I})$	3·31
$N(4) \cdots N(5'^{III})$	3·19	$C(13') \cdots O(1'^{I})$	3·33

[a] Distances not included are C ··· C >3·7, C ··· N >3·5, C ··· O >3·4, N ··· N >3·7, and N ··· O >3·3 Å. [b] Roman numeral superscripts denote equivalent positions relative to x, y, z:

I	$-x, -y, -z$	IV	$x - 1, y, z$
II	$-x, 1 - y, -z$	V	$1 - x, 1 - y, -z$
III	$-x, 1 - y, 1 - z$	IV	$1 - x, 1 - y, 1 - z$

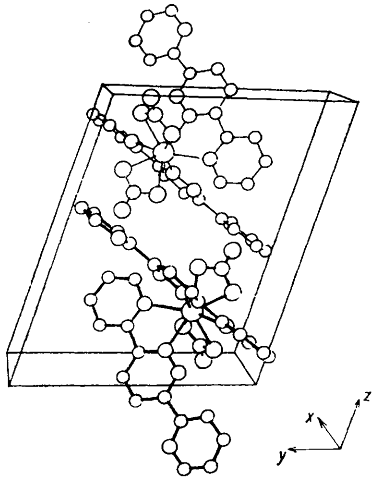

FIGURE 3 Arrangement of molecules in the unit cell

The co-ordination sphere is filled fairly uniformly by the eight ligand atoms, the distances between adjacent atoms belonging to different ligands lying in the ranges 2·9—3·3 for O ··· O {*cf.* 3·1—3·3 in $[Mn(NO_3)_4]^{2-}$, ref. 7},

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[7] J. Drummond and J. S. Wood, *J. Chem. Soc.* (*A*), 1970, 226.

2·8—3·2 for O · · · N, and 3·1—3·2 Å for N · · · N contacts. Not surprisingly, however, the geometrical arrangement is not particularly close to either of the common regular eightfold co-ordination polyhedra (D_{4d} square antiprism and D_{2d} dodecahedron), though it can be viewed as a distorted form of either. Alternatively, it is possible to regard each nitrate ligand as occupying only a single co-ordination site,[8] the resulting pseudo-octahedron being distorted in consequence of the 70° angles subtended at Mn by the dppn groups, but not much more so than would be expected in a *cis*-octahedral bis-chelate {*e.g.* $[Ga(bipy)_2Cl_2]^+$, ref. 9}.

The four Mn–N and one of the Mn–O bond lengths are close to 2·30 Å, the other three Mn–O bonds being *ca.* 2·46 Å long. All these bonds are rather longer than those commonly observed in six-co-ordinate manganese(II) complexes (*ca.* 2·1—2·2 Å),[10] though bonds of similar length have also been found in the seven-co-ordinate ion $[Mn(edta)H_2O]^{2-}$ [Mn–O *ca.* 2·24, Mn–N, *ca.* 2·38 Å (ref. 11)] and eight-co-ordinate $[Mn(NO_3)_4]^{2-}$ [Mn–O 2·28—2·40 Å (ref. 7)]. This expansion of the co-ordination sphere is less common with ions such as Ni^{2+} for which ligand-field effects tend to favour an octahedral arrangement, but presumably a spherical ion like Mn^{2+} can achieve as much stability with seven or eight ligand atoms at somewhat greater distances as with six at the ' normal ' distance.

The two dppn ligands show no significant differences in internal geometry, and the six-membered rings are all planar, with bond lengths and angles as expected. In each ligand the pyridine and pyridazine rings involved in chelation are approximately coplanar, the dihedral angles of 2 and 7° being within the range commonly encountered in complexes of 2,2′-bipyridyl.[12] The non-co-ordinating pyridine rings also make rather small angles (10 and 12°) with their respective pyridazine rings; the approximate overall planarity is doubtless favoured by molecular packing requirements. The two non-co-ordinating nitrogen atoms in each dppn molecule are mutually *trans* (as are the nitrogen atoms in 2,2′-bipyridyl itself[13]), presumably to minimise steric interactions between hydrogen atoms.

The nitrate ligands are planar. One is symmetrically bidentate (Mn–O 2·46 Å), and its geometry does not differ significantly from that of free nitrate (N–O 1·25 Å).[14] The other co-ordinates unsymmetrically [Mn–O 2·47(1) and 2·30(2) Å, N–O–Mn 94(1) and 102(1)°], and its terminal N–O bond is shorter and the chelating O–N–O angle smaller than in the free ion by amounts which are probably significant. The difference in the co-ordination geometry of the two nitrate ligands, together with the low overall symmetry of the complex, is doubtless responsible for the complexity of the i.r. absorption attributed to nitrate vibrations (see later).

We have also prepared similarly the compounds $[M(dppn)_2(NO_3)_2]$ (M = Zn or Cd). *X*-Ray powder photographs indicate that the Mn and Cd compounds are isomorphous, but the Zn compound has a different crystal structure. Possibly this is because the smaller size of Zn^{2+} does not allow both nitrate ligands to be bidentate.

On the question of why, under similar conditions, Ni, Co, and Cu nitrates gave binuclear complexes with dppn whereas Mn and Zn nitrates failed to do so, we can only suggest that perhaps this is one of those marginal cases where ligand-field effects make the critical difference: when dppn and nitrate share the co-ordination sphere of a spherical cation, the *cis*-arrangement with irregular seven- or eight-co-ordination is preferred, but the ***trans***-binuclear structure becomes slightly more stable when the shape of the cation electron cloud favours octahedral geometry.

I.r. Spectra and Nitrate Co-ordination.—The nitrate ion (symmetry D_{3h}) has four normal modes of vibration, ν_1—ν_4, of which ν_3 and ν_4 are doubly degenerate. On co-ordination the symmetry decreases to C_{2v} or C_s and six non-degenerate vibrations become allowed in i.r. absorption: ν_1 and ν_2 of NO_3^- at *ca.* 1000 and 800 cm^{-1}, the two components of ν_3 in the ranges 1250—1350 and 1450—

TABLE 5

Infrared absorption spectra in the regions 1500—1250, 1050—1000, and 850—800 cm^{-1}

	$M(dppn)_2(NO_3)_2$	
dppn	Mn	Cd
1475m	1480m,sh	1480m
1463mw	1475m,sh	1475m,sh
1455mw,sh	1460s,br *	1460s *
1441m	1453s *	1450s *
1427m	1435s	1432s
1414s	1419s	1419s
1376w	1379m	1377m
1347w	1355w	1352w
	1325s,br *	
	1310s,sh *	1316s,br *
1296w	1296ms *	1297m,sh *
		1290m,sh
		1284m
	1270w	1270sh
1048m	1056mw	1052mw
1043w,sh	1044w	1041w
1038w	1039w	1037mw
	1032mw	1033mw
	1026mw,sh *	1029m *
	1008m *	1007m *
837vw		842vw
	823mw *	821m *
	818m *	817m *
812w	813w	810w
799w	804vw	801w

w = Weak, m = medium, s = strong, br = broad, sh = shoulder, v = very.

* Bands assigned to nitrate vibrations. All spectra were recorded on a Perkin-Elmer 457 instrument, by use of Nujol mulls.

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1550 cm^{-1}, and those of ν_4, with a smaller splitting, in the range 700—750 cm^{-1}.[15,16]

The i.r. spectra of dppn and the Mn and Cd complexes in the regions of interest are given in Table 5. The presence of dppn vibrations makes assignment of the nitrate bands difficult, but there appear to be at least three bands in the ν_3, and two each in the ν_1 and ν_2 regions. (We were unable to find any bands which could definitely be assigned to ν_4 of NO_3^-.) The number of bands observed can be explained as a result of the presence of two distinctly different kinds of co-ordinated nitrate. A similar situation occurs in [Ni(dien)(NO_3)$_2$], where three co-ordination sites are available to NO_3^- ions, and two sets of nitrate bands are observed.[16] The pattern of ν_2 and ν_3 bands in this compound (ν_3 1480 and 1300, and ν_2 808 assigned to bidentate NO_3^-; ν_3 1440 and 1315, and ν_2 816 cm^{-1} assigned to unidentate NO_3^-) in fact resembles that in the dppn complexes, suggesting that the asymmetry of the co-ordination of one nitrate ion in the latter is sufficient to have a fairly marked effect on the force constants involved.

We have also prepared in a similar manner the six compounds [M(biL)$_2$(NO_3)$_2$] (M = Mn, Zn, or Cd; biL = 2,2′-bipyridyl or 1,10-phenanthroline) and examined their *X*-ray powder diffraction patterns and i.r. spectra.[17] In both cases the Mn and Cd i.r. spectra resemble each other more than the Zn spectrum, but no isomorphisms are observed. As with the dppn complexes, there is evidence for more than one set of nitrate i.r. bands, and we surmise that at least one nitrate ion is bidentate in these compounds also.

We thank Mrs. J. Lockyer for preparative assistance, and the University of Hull and the S.R.C. for studentships. All computing was carried out at the Centre for Computer Studies, University of Hull.

[4/1912 *Received*, 18*th September*, 1974]

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