Structural Studies in Metal–Purpurate Complexes. Part 3.† Crystal Structures of Triaquapurpuratoiron(II) Purpurate Hexahydrate and Tetra-aquapurpuratomanganese(II) Purpurate Hexahydrate. Stereochemistry of the [M(tridentate ligand)(unidentate ligand)$_3$] Complexes

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The crystal structures of the title compounds, $[FeL(H_2O)_3][L]\cdot 6H_2O$ (1) and $[MnL(H_2O)_4][L]\cdot 6H_2O$ (2) (L = purpurate), have been determined at 295 K by *X*-ray diffraction and refined by least squares to *R* 0.046 (3 706 ' observed ' reflections) and 0.076 (2 132 ' observed ' reflections) respectively. Crystals of both complexes are triclinic, space group $P\bar{1}$. For (1), a = 15.146(3), b = 10.182(3), c = 9.934(2) Å, α = 105.50(2), β = 102.99(2), γ = 98.34(2)°, Z = 2; for (2), a = 13.590(10), b = 11.354(8), c = 10.121(7) Å, α = 103.40(3), β = 99.74(3), γ = 98.98(3)°, Z = 2. In both compounds, one of the purpurate species is co-ordinated to the metal as a tridentate ligand [(1): Fe–O, 2.103(3), 2.094(3), Fe–N, 2.205(3); (2): Mn–O, 2.303(7), 2.417(6), Mn–N, 2.422(9) Å], the other existing as an anionic lattice species. The remainder of the metal-atom co-ordination sphere is occupied by co-ordinated water molecules [M–O: (1), 2.066(4)—2.138(3); (2), 2.177(9)—2.247(8) Å], the iron atom being six- and the manganese seven-co-ordinate. The geometry in (1) provides probably the most accurate and unperturbed example available for the unco-ordinated purpurate species. The stereochemistry of the cation in (1) is described in terms of a repulsion model.

SLOW cooling of a filtered aqueous solution of 5 : 1 ferrous sulphate–murexide {ammonium purpurate, $[NH_4][L]$, L = $[C_8H_4N_5O_6]^-$} solution from 80 °C during 24 h yields dichroic red-green crystals (1); a similar procedure using manganese(II) sulphate yields somewhat efflorescent dichroic red-green crystals (2). Both derivatives form as polycrystalline, extensively twinned masses. Both complexes are seriously deficient in water as determined by analysis relative to the structural sample, although analytical figures for the apparently homogeneous bulk samples give excellent agreement for the metal : C : N ratios relative to the composition established crystallographically as $[FeL_2]\cdot 9H_2O$ (1) and $[MnL_2]\cdot 10H_2O$ (2). A red cobalt derivative (3) prepared similarly is isomorphous with (1), but does not show this deficiency. A further red isomorph, (4), was obtained with zinc as a by-product in a preparation of $[ZnL_2]\cdot 4H_2O$;[1] insufficient sample was available for analysis and the complex was identified crystallographically.

EXPERIMENTAL

Analytical Data for (1), (2), *and* (3).—(1) Found, calc. for $FeL_2\cdot 9H_2O$, calc. for $FeL_2\cdot 5H_2O$: C, 28.3, 29.87, 28.32; H, 2.65, 3.49, 2.68; N, 20.45, 18.67, 20.65; Fe, 8.2, 7.44, 8.23.

(2) Found, calc. for $MnL_2\cdot 10H_2O$, calc. for $MnL_2\cdot 2.5H_2O$: C, 30.4, 25.04, 30.39; H, 2.3, 3.68, 2.07; N, 21.85, 18.25, 22.15; Mn, 8.8, 7.16, 8.65%.

(3) Found, calc. for $CoL_2\cdot 9H_2O$: C, 25.8, 25.51; H, 3.4, 3.48; N, 19.0, 18.59; Co, 7.9, 7.82%.

The only previous work carried out on iron(II)– or manganese(II)–purpurate systems is concerned with the formation constants and rates of formation of $[MnL]^+$ in solution; similar studies have been reported for cobalt(II) species.[2]

The definition of the atom numbering scheme within the purpurate anion together with other details common to all structure determinations in this series is given in Part 1. Structure-factor tables have been deposited.‡

Crystallographic Data and Procedure.—Compound (1). $C_{16}H_{26}FeN_{10}O_{21}$, M = 750.4, Triclinic, space group $P\bar{1}$ (C_i^1, No. 2), a = 15.146(3), b = 10.182(3), c = 9.934(2) Å, α = 105.50(2), β = 102.99(2), γ = 98.34(2)°, U = 1 403.9(6) Å^3, D_m = 1.77(1) g cm^{-3}, Z = 2, D_c = 1.77 g cm^{-3}, $F(000)$ = 772, crystal size 0.12 × 0.12 × 0.30 mm (prism), μ(Mo-K_α) = 5.85 cm^{-1} (no absorption correction applied), data range $2\theta < 50°$ yielding 4 970 independent reflections (3 706 ' observed '), final R = 0.046, R' = 0.048 (n = 3).

The structure was solved by the heavy-atom method and refined by 9 × 9 block-diagonal least squares; in the final refinement stages, the parameters of the metal atom and those atoms in its immediate environment were refined as a single block, the atom parameters of each of the purpurate anionic and ligand ring systems being refined similarly. Positional parameters only of all hydrogen atoms were refined, U(isotropic) being constrained at 0.10 Å^2; the thermal motion of the remaining atoms was refined anisotropically.

Compound (2). $C_{16}H_{28}MnN_{10}O_{22}$, M = 767.4, Triclinic, space group $P\bar{1}$ (C_i^1, No. 2), a = 13.590(10), b = 11.354(8), c = 10.121(7) Å, α = 103.40(3), β = 99.74(3), γ = 98.98(3)°, U = 1 466(1) Å^3, D_m = 1.73(1) g cm^{-3}, Z = 2, D_c = 1.74 g cm^{-3}, $F(000)$ = 790, crystal size 0.11 × 0.06 × 0.10 mm (small irregular coated fragment of twin), μ(Mo-K_α) = 5.02 cm^{-1} (no absorption correction applied), data range $2\theta < 45°$ yielding 3 867 independent reflections (2 132 ' observed '), final R = 0.076; R' = 0.059 (n = 3).

The structure was solved by the heavy-atom method; the refinement procedure was as for (1) with the exception that certain of the hydrogen atoms about the lattice water molecules could not be located in difference maps and they are accordingly omitted.

For both (1) and (2), the ligand atom numbering is suffixed ' a ' or ' b ' where necessary to denote which ligand is referred to.

Compound (3) (crystal data only). $C_{16}H_{26}CoN_{10}O_{21}$, Triclinic, a = 15.169(9), b = 10.190(8), c = 9.93(1) Å, α = 104.95(8), β = 103.54(8), γ = 98.08(6)°, U = 1 409(2) Å^3, D_m = 1.77(1) g cm^{-3}, Z = 2, D_c = 1.78 g cm^{-3}.

Compound (4) (crystal data only). $C_{16}H_{26}N_{10}O_{21}Zn$, Tri-

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† Part 2 is the preceding paper.

‡ Supplementary Publication No. SUP 21988 (30 pp., 1 microfiche). For details see Notice to Authors No. 7, in *J.C.S. Dalton*, 1976, Index issue.

[1] A. H. White and A. C. Willis, Part 6, *J.C.S. Dalton*, 1977, 1372.

[2] G. Geier, (*a*) *Helv. Chim. Acta*, 1967, **50**, 1879; (*b*) *ibid.*, 1968, **51**, 94; (*c*) *Ber. Bunsengesellschaft. Phys. Chem.*, 1965, **69**, 617.

clinic, $a = 15.123(4)$, $b = 10.182(7)$, $c = 9.928(8)$ Å, $\alpha = 104.95(6)$, $\beta = 103.41(5)$, $\gamma = 98.62(4)^\circ$, $U = 1\,400(1)$ Å^3, $D_m = 1.80(1)$ g cm^{-3}, $Z = 2$, $D_c = 1.80$ g cm^{-3}.

For compounds (1) and (2), cell co-ordinates and thermal parameters are given in Table 1, bond distances and angles in Table 2, and least-squares planes in Table 3. Figure 1 shows the unit-cell contents for (1) and (2), Figure 2 shows the projections of (1) and (2), and Figure 3 shows the free anion in (1).

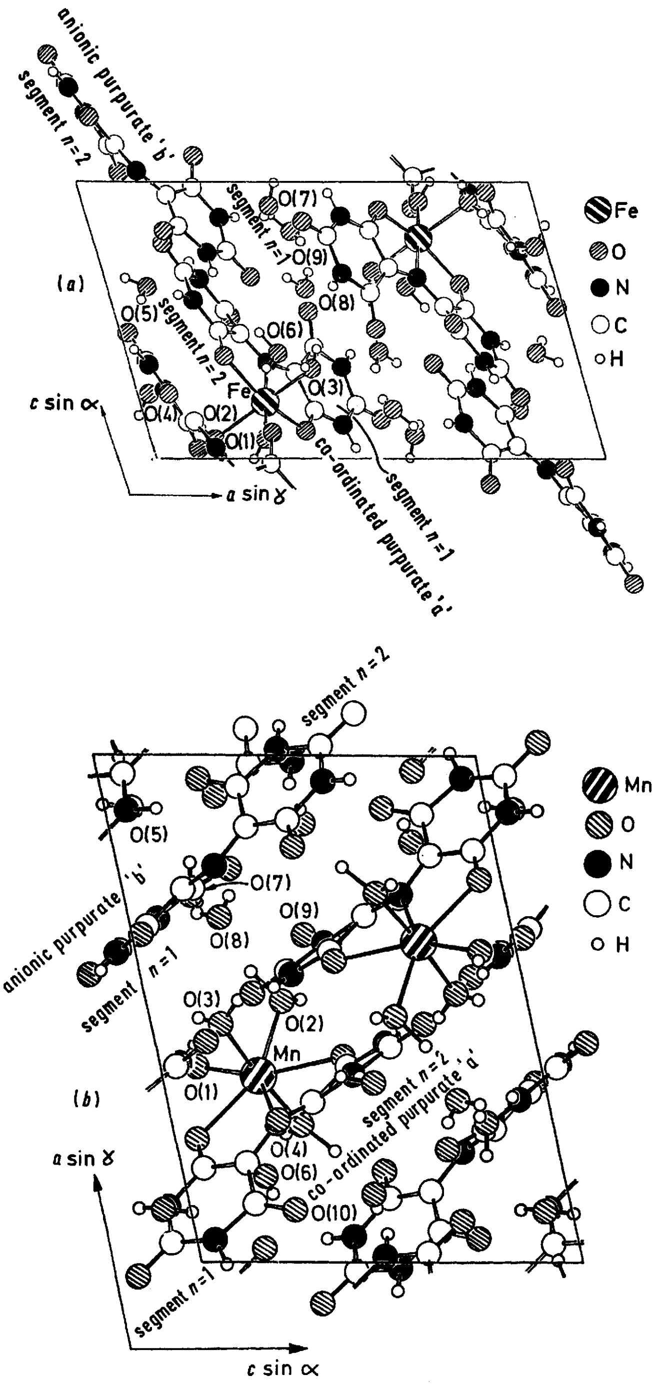

FIGURE 1 Unit-cell contents of (1) (*a*) and (2) (*b*) projected along *b* in each case; labelling of the purpurate segments and water-molecule oxygen atoms is shown

DISCUSSION

Contrary to our expectations both complexes $[ML_2]\cdot nH_2O$ examined in this study are ionic derivatives of the type $[ML(H_2O)_x][L]\cdot 6H_2O$, the asymmetric unit comprising a complex cation, a free purpurate anion, and lattice water molecules. Surprisingly also, the cations in the two complexes are quite dissimilar. In (1), the cation is $[FeL(H_2O)_3]^+$, the purpurate ion being wrapped around one edge of the co-ordination octahedron in a *mer*-configuration with the water molecules occupying the other sites; the metal–ligand distances are at about the usual values for σ-bonded species co-ordinated to high-spin iron(II). Within the tridentate ligand, the nitrogen N(0a) lies further from the metal than do the oxygens O(12a, 22a) [2.205(3) *cf.* 2.103, 2.094(3) Å]. It is tempting to regard this, together with the fact that C(11a)–N(0a)–C(21a) is greater than the corresponding angle in the free anion [132.1(4), *cf.* 128.1(4)°], as evidence that the central nitrogen N(0a) is more weakly bound than the two oxygens O(12a, 22a); this is supported by

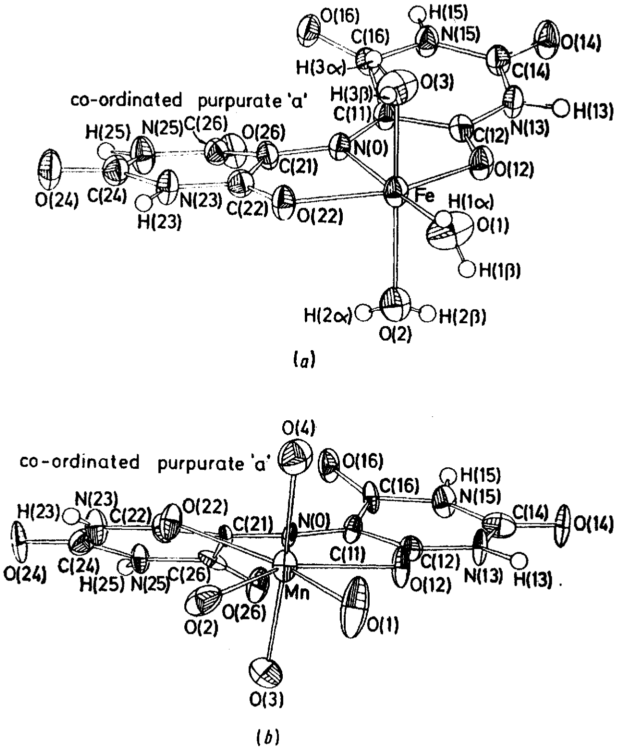

FIGURE 2 Projections of the cationic $[ML(H_2O)_n]^+$ species in (1) (*a*) and (2) (*b*) respectively, showing 50% thermal ellipsoids and atom labelling. Hydrogen atoms have an arbitrary radius of 0.1 Å; those of the water molecules in (2) are omitted

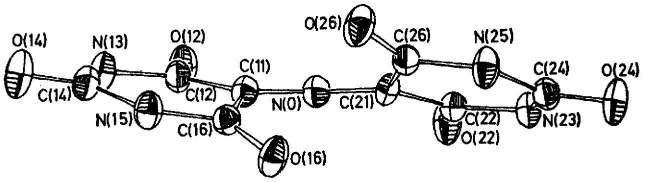

FIGURE 3 The free anion in (1), showing atom labelling and 50% thermal ellipsoids of the non-hydrogen skeleton

TABLE 1

Atomic fractional cell co-ordinates [(x,y,z), H, $\times 10^3$; Fe $\times 10^5$; others $\times 10^4$] and thermal parameters (U_{ij}, $\times 10^3$ Å^2) with least-squares estimated standard deviations in parentheses

(1) (The iron derivative)

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe	27 799(4)	39 373(6)	20 352(6)	32.4(3)	30.3(3)	25.0(3)	14.6(3)	12.8(2)	15.8(2)
The co-ordinated purpurate ligand ' a '									
N(0)	3 064(2)	2 631(3)	3 460(3)	26(2)	25(2)	18(1)	7(1)	9(1)	8(1)
C(11)	2 644(2)	2 821(4)	4 505(4)	24(2)	32(2)	22(2)	12(2)	12(2)	12(2)
C(12)	2 190(3)	4 000(4)	4 608(4)	27(2)	30(2)	25(2)	10(2)	8(2)	11(2)
O(12)	2 151(2)	4 653(3)	3 694(3)	41(2)	34(1)	27(1)	19(1)	19(1)	17(1)
N(13)	1 822(2)	4 407(3)	5 728(3)	42(2)	31(2)	24(2)	17(2)	18(2)	10(1)
H(13)	152(4)	518(5)	591(5)	100(—)					
C(14)	1 794(3)	3 716(4)	6 749(4)	32(2)	39(2)	26(2)	16(2)	11(2)	11(2)
O(14)	1 514(2)	4 171(2)	7 791(3)	54(2)	54(2)	28(1)	27(2)	25(1)	16(1)
N(15)	2 094(2)	2 490(3)	6 496(3)	45(2)	40(2)	33(2)	21(2)	24(2)	23(2)
H(15)	198(4)	197(5)	712(5)	100(—)					
C(16)	2 458(3)	1 902(4)	5 365(4)	24(2)	34(2)	23(2)	11(2)	9(2)	12(2)
O(16)	2 540(2)	0 696(3)	5 116(3)	39(2)	32(2)	37(1)	17(1)	18(1)	19(1)
C(21)	3 631(2)	1 801(4)	3 102(4)	26(2)	23(2)	22(2)	12(2)	11(2)	9(1)
C(22)	3 822(3)	1 809(4)	1 736(4)	25(2)	27(2)	23(2)	6(2)	9(2)	9(2)
O(22)	3 500(2)	2 554(3)	1 013(3)	39(2)	39(2)	25(1)	20(1)	16(1)	21(1)
N(23)	4 362(2)	0 956(3)	1 225(3)	35(2)	33(2)	20(2)	17(2)	15(1)	11(1)
H(23)	450(4)	083(5)	039(5)	100(—)					
C(24)	4 784(3)	0 132(4)	1 944(4)	29(2)	30(2)	25(2)	12(2)	13(2)	13(2)
O(24)	5 241(2)	−0 645(3)	1 423(3)	49(2)	47(2)	31(1)	33(2)	22(1)	19(1)
N(25)	4 695(2)	6 288(3)	3 303(3)	33(2)	38(2)	23(2)	20(2)	13(1)	16(1)
H(25)	497(4)	−020(5)	377(5)	100(—)					
C(26)	4 199(3)	1 162(4)	4 010(4)	24(2)	27(2)	26(2)	9(2)	11(2)	11(2)
O(26)	4 303(2)	1 383(3)	5 314(3)	37(2)	46(2)	20(1)	22(1)	13(1)	15(1)
The purpurate anion ' b '									
N(0)	1 395(2)	9 812(3)	10 406(3)	28(2)	27(2)	26(2)	6(1)	11(1)	10(1)
C(11)	1 901(3)	9 269(4)	9 544(4)	31(2)	23(2)	23(2)	5(2)	11(2)	8(2)
C(12)	1 966(3)	9 913(4)	8 418(4)	26(2)	33(2)	24(2)	8(2)	12(2)	12(2)
O(12)	1 618(2)	10 896(3)	8 237(3)	41(2)	36(2)	35(1)	20(1)	21(1)	21(1)
N(13)	2 436(2)	9 333(3)	7 446(3)	41(2)	33(2)	28(2)	15(2)	19(2)	15(1)
H(13)	244(4)	969(5)	674(5)	100(—)					
C(14)	2 882(3)	8 274(4)	7 508(4)	36(2)	32(2)	26(2)	9(2)	15(2)	8(2)
O(14)	3 246(2)	7 764(3)	6 572(3)	64(2)	49(2)	39(2)	26(2)	34(2)	17(1)
N(15)	2 938(2)	7 860(3)	8 721(3)	37(2)	35(2)	32(2)	18(2)	18(2)	16(1)
H(15)	329(4)	729(5)	873(5)	100(—)					
C(16)	2 517(3)	8 354(4)	9 807(4)	29(2)	27(2)	25(2)	4(2)	10(2)	10(2)
O(16)	2 745(2)	8 058(3)	10 943(3)	49(2)	48(2)	27(1)	20(2)	16(1)	21(1)
C(21)	1 081(3)	9 310(4)	11 346(4)	29(2)	28(2)	18(2)	11(2)	11(2)	8(2)
C(22)	0 719(3)	10 291(4)	12 331(4)	26(2)	29(2)	22(2)	4(2)	9(2)	9(2)
O(22)	0 687(2)	11 491(3)	12 340(3)	56(2)	29(2)	44(2)	17(1)	32(2)	19(1)
N(23)	0 432(2)	9 836(3)	13 382(3)	33(2)	24(2)	29(2)	9(1)	18(2)	11(1)
H(23)	020(4)	1 038(5)	1 393(5)	100(—)					
C(24)	0 403(3)	8 542(4)	13 520(4)	29(2)	27(2)	27(2)	4(2)	13(2)	8(2)
O(24)	0 171(2)	8 245(3)	14 539(3)	60(2)	38(2)	35(2)	20(2)	33(2)	21(1)
N(25)	0 627(2)	7 592(3)	12 481(3)	51(2)	23(2)	36(2)	10(2)	27(2)	12(1)
H(25)	054(4)	670(5)	1 245(5)	100(—)					
C(26)	0 925(3)	7 851(4)	11 325(4)	27(2)	28(2)	24(2)	5(2)	10(2)	7(2)
O(26)	0 988(2)	6 867(3)	10 355(3)	60(2)	28(2)	34(2)	8(1)	25(2)	3(1)
The co-ordinated water molecules [r(Å) is O–H; γ (°) is Fe–O–H and δ (°) H–O–H]									
O(1)	2 558(2)	5 177(3)	0 707(3)	65(2)	41(2)	53(2)	3(2)	−2(2)	32(2)
H(1α)	267(4)	607(6)	095(6)	100(—)	$r = 0.86(5)$; $\gamma = 128(4)$		$\delta = 103(6)$		
H(1β)	217(4)	495(6)	−002(6)	100(—)	$r = 0.77(5)$; $\gamma = 124(5)$				
O(2)	1 432(2)	2 786(3)	0 709(3)	40(2)	32(1)	36(2)	10(1)	14(1)	16(1)
H(2α)	119(4)	227(5)	112(6)	100(—)	$r = 0.84(6)$; $\gamma = 111(3)$		$\delta = 105(6)$		
H(2β)	146(4)	234(5)	009(6)	100(—)	$r = 0.68(5)$; $\gamma = 110(4)$				
O(3)	4 018(2)	5 494(3)	3 238(3)	51(2)	54(2)	47(2)	4(2)	3(2)	17(2)
H(3α)	425(4)	542(5)	395(6)	100(—)	$r = 0.74(6)$; $\gamma = 115(4)$		$\delta = 115(5)$		
H(3β)	389(4)	634(5)	329(6)	100(—)	$r = 0.90(6)$; $\gamma = 103(3)$				
The lattice water molecules									
O(4)	0 250(2)	4 741(3)	2 334(3)	37(2)	37(2)	53(2)	15(1)	14(1)	16(1)
H(4α)	−011(4)	434(5)	156(7)	100(—)	$r = 0.80(5)$	$\delta = 108(5)$			
H(4β)	077(4)	448(5)	233(6)	100(—)	$r = 0.86(6)$				
O(5)	0 884(2)	6 497(3)	6 200(3)	48(2)	45(2)	57(2)	24(2)	24(2)	28(2)
H(5α)	068(4)	702(5)	574(6)	100(—)	$r = 0.84(6)$	$\delta = 107(6)$			
H(5β)	046(4)	620(5)	652(6)	100(—)	$r = 0.83(6)$				
O(6)	3 367(3)	7 870(3)	3 789(3)	103(3)	66(2)	47(2)	34(2)	32(2)	30(2)
H(6α)	308(4)	796(5)	454(6)	100(—)	$r = 0.93(6)$	$\delta = 99(6)$			
H(6β)	302(4)	811(5)	326(6)	100(—)	$r = 0.77(6)$				

TABLE 1 (*Continued*)

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(7)	4 109(3)	5 995(3)	9 150(4)	110(4)	81(3)	83(3)	60(3)	8(3)	23(2)
H(7α)	436(4)	620(6)	998(6)	100(—)	$r = 0.78(5)$	$\delta = 114(6)$			
H(7β)	395(4)	520(6)	877(6)	100(—)	$r = 0.77(5)$				
O(8)	4 384(3)	5 820(4)	6 144(4)	84(3)	109(3)	61(2)	48(3)	22(2)	19(2)
H(8α)	456(4)	534(5)	674(5)	100(—)	$r = 0.88(6)$	$\delta = 105(6)$			
H(8β)	406(4)	632(6)	654(6)	100(—)	$r = 0.85(6)$				
O(9)	4 426(5)	3 294(5)	8 217(6)	278(8)	102(4)	113(4)	109(5)	−29(5)	−8(3)
H(9α)	407(4)	331(5)	881(6)	100(—)	$r = 0.88(6)$	$\delta = 141(6)$			
H(9β)	459(4)	368(5)	786(6)	100(—)	$r = 0.65(6)$				
(2) (The manganese derivative)									
Mn	3 677(1)	0 260(2)	2 529(2)	29(1)	20(1)	24(1)	8(1)	−1(1)	4(1)
The co-ordinated purpurate ligand ' a '									
N(0)	2 737(6)	1 915(7)	2 743(8)	23(6)	23(5)	7(5)	−1(4)	−3(4)	0(5)
C(11)	1 956(7)	1 820(9)	1 742(10)	22(7)	22(7)	13(6)	10(5)	−3(5)	5(5)
C(12)	1 853(7)	0 722(10)	0 579(10)	16(7)	34(7)	21(7)	5(6)	−1(5)	13(6)
O(12)	2 427(5)	−0 029(6)	0 573(7)	32(5)	27(5)	23(5)	16(4)	−16(4)	−1(4)
N(13)	1 092(7)	0 566(7)	−0 564(8)	33(6)	12(5)	15(5)	5(4)	−8(4)	−12(4)
H(13)	106(8)	−023(10)	−134(11)	80(—)					
C(14)	0 379(9)	1 314(10)	−0 669(12)	32(8)	20(7)	39(8)	3(6)	12(7)	13(6)
O(14)	−0 284(6)	1 097(7)	−1 726(7)	39(5)	36(5)	16(5)	11(4)	−15(4)	−5(4)
N(15)	0 440(6)	2 249(8)	0 470(9)	24(6)	26(6)	25(6)	11(5)	3(4)	−11(5)
H(15)	−005(8)	272(10)	064(11)	80(—)					
C(16)	1 155(8)	2 524(9)	1 733(11)	24(7)	9(7)	20(7)	−2(5)	−8(5)	−5(5)
O(16)	1 035(5)	3 282(6)	2 745(7)	29(5)	28(5)	23(5)	3(4)	−2(4)	−10(4)
C(21)	3 159(7)	2 926(9)	3 807(9)	12(6)	20(6)	11(6)	−3(5)	−3(5)	3(5)
C(22)	3 870(8)	2 670(9)	4 909(10)	24(7)	21(7)	25(7)	3(6)	−2(5)	7(5)
O(22)	4 060(1)	1 623(6)	4 853(7)	40(5)	18(4)	20(4)	9(4)	−6(4)	4(4)
N(23)	4 327(6)	3 639(8)	6 041(9)	33(6)	14(5)	28(6)	4(5)	−8(5)	0(4)
H(23)	458(8)	337(10)	656(11)	80(—)					
C(24)	4 264(8)	4 851(10)	6 139(11)	27(8)	33(8)	19(7)	8(6)	7(6)	3(6)
O(24)	4 705(5)	5 685(6)	7 163(7)	30(5)	26(5)	28(5)	3(4)	−16(4)	−12(4)
N(25)	3 704(6)	5 084(7)	5 009(8)	24(6)	12(5)	18(5)	0(4)	−3(4)	−2(4)
H(25)	367(8)	599(10)	517(11)	80(—)					
C(26)	3 162(7)	4 209(9)	3 793(11)	11(7)	14(6)	33(7)	0(5)	9(5)	4(5)
O(26)	2 809(5)	4 558(7)	2 795(7)	34(5)	38(5)	18(4)	15(4)	−7(4)	9(4)
The purpurate anion ' b '									
N(0)	7 812(6)	7 650(8)	2 552(8)	13(5)	41(6)	18(5)	5(5)	−8(4)	1(5)
C(11)	7 353(8)	6 584(10)	1 591(10)	21(7)	35(8)	18(6)	10(6)	−1(5)	12(6)
C(12)	6 613(7)	6 711(9)	0 455(11)	14(6)	18(6)	29(7)	−1(6)	9(5)	4(5)
O(12)	6 445(6)	7 703(6)	0 237(7)	52(6)	19(5)	25(5)	0(4)	−14(4)	4(4)
N(13)	6 080(6)	5 612(7)	−0 502(8)	25(6)	21(6)	15(5)	0(4)	−13(4)	1(5)
H(13)	573(8)	577(10)	−100(11)	80(—)					
C(14)	6 134(9)	4 442(11)	−0 410(11)	43(9)	29(8)	23(7)	23(7)	7(6)	11(6)
O(14)	5 648(6)	3 519(7)	−1 327(8)	43(6)	27(5)	31(5)	6(4)	−16(4)	−8(4)
N(15)	6 768(7)	4 387(8)	0 761(9)	36(6)	29(6)	27(6)	10(5)	−1(5)	11(5)
H(15)	672(8)	375(10)	093(11)	80(—)					
C(16)	7 368(9)	5 390(10)	1 856(11)	41(8)	25(7)	13(7)	6(6)	−1(6)	−8(6)
O(16)	7 762(6)	5 191(7)	2 924(7)	40(5)	39(5)	19(5)	4(4)	−12(4)	9(4)
C(21)	8 595(8)	7 802(9)	3 593(10)	21(7)	10(6)	24(7)	6(5)	1(5)	3(5)
C(22)	8 730(8)	8 919(10)	4 715(11)	27(7)	30(7)	29(7)	12(6)	5(6)	12(6)
O(22)	8 199(5)	9 714(6)	4 703(7)	32(5)	27(5)	26(6)	7(4)	−5(4)	−1(4)
N(23)	9 492(7)	9 086(8)	5 866(8)	29(6)	27(6)	22(6)	6(5)	−10(5)	5(4)
H(23)	953(8)	978(10)	658(11)	80(—)					
C(24)	10 181(8)	8 326(10)	5 990(11)	30(8)	25(7)	19(7)	2(6)	−8(6)	4(6)
O(24)	10 816(5)	8 527(6)	7 057(7)	29(5)	26(5)	21(5)	4(4)	−8(4)	−4(4)
N(25)	10 118(6)	7 374(8)	4 837(8)	25(6)	27(6)	14(5)	12(5)	−11(4)	−4(5)
H(25)	1 056(8)	678(10)	502(11)	80(—)					
C(26)	9 385(8)	7 073(9)	3 582(11)	18(7)	20(7)	19(7)	−5(6)	−3(5)	9(6)
O(26)	9 527(6)	6 321(7)	2 607(7)	34(5)	41(5)	24(5)	12(4)	8(4)	−6(4)
The co-ordinated water molecules [r (Å) is O–H; γ (°) is Mn–O–H and δ (°) H–O–H]									
O(1)	3 852(7)	−1 326(7)	0 964(8)	97(8)	42(6)	39(6)	39(5)	−24(5)	−11(5)
H(1α) *	403(8)	−186(10)	107(11)	80(—)	$r = 0.7(1)$; $\gamma = 129(8)$				
O(2)	5 148(6)	−0 124(7)	3 560(7)	43(6)	63(6)	32(5)	26(5)	13(4)	29(5)
H(2α)	572(8)	004(10)	292(11)	80(—)	$r = 1.1(1)$; $\gamma = 108(6)$	$\delta = 125(11)$			
H(2β)	518(8)	−050(10)	406(11)	80(—)	$r = 0.7(1)$; $\gamma = 125(11)$				
O(3)	4 692(6)	1 561(7)	1 829(8)	38(6)	37(5)	42(5)	−6(4)	9(4)	8(4)
H(3α)	482(8)	133(10)	128(11)	80(—)	$r = 0.6(1)$; $\gamma = 115(10)$	$\delta = 115(12)$			
H(3β)	516(8)	214(10)	241(11)	80(—)	$r = 0.9(1)$; $\gamma = 122(10)$				
O(4)	2 712(6)	−0 950(7)	3 388(8)	53(6)	34(5)	39(5)	7(5)	12(5)	3(4)
H(4α)	254(8)	−157(10)	293(11)	80(—)	$r = 0.7(1)$; $\gamma = 112(10)$	$\delta = 120(10)$			
H(4β)	220(8)	−055(10)	411(11)	80(—)	$r = 1.2(1)$; $\gamma = 120(6)$				

TABLE 1 (*Continued*)

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
The lattice water molecules									
O(5)	8 965(5)	3 710(8)	0 710(8)	52(6)	81(7)	43(6)	37(5)	−1(5)	8(5)
H(5α) *	902(8)	389(9)	−003(11)	80(—)	r = 0.8(1)				
O(6)	1 695(7)	6 470(8)	2 161(9)	74(7)	50(6)	52(6)	16(5)	16(5)	15(5)
H(6α) *	134(8)	623(10)	225(11)	80(—)	r = 0.5(1)				
O(7)	7 231(6)	2 214(7)	1 756(8)	53(6)	33(5)	65(6)	16(5)	−7(5)	9(5)
H(7α)	711(8)	167(10)	189(11)	80(—)	r = 0.7(1)	δ = 108(12)			
H(7β)	788(8)	241(10)	192(11)	80(—)	r = 0.9(1)				
O(8α)	6 794(6)	−0 096(7)	2 390(8)	43(5)	41(5)	37(5)	20(4)	3(4)	7(4)
H(8α)	686(8)	−066(16)	185(11)	80(—)	r = 0.8(1)	δ = 82(11)			
H(8β)	722(8)	−021(10)	276(11)	80(—)	r = 0.7(1)				
O(9)	6 454(7)	2 459(8)	4 496(10)	79(8)	35(6)	99(8)	16(5)	−6(6)	−3(6)
H(9α) *	633(8)	259(10)	532(11)	80(—)	r = 0.9(1)				
O(10)	1 344(7)	5 617(8)	4 890(8)	78(7)	67(7)	42(6)	41(6)	10(5)	21(5)
H(10α) *	106(8)	532(10)	491(11)	80(—)	r = 0.5(1)				

* H(1β, 5β, 6β, 9β, 10β) not located.

the observation that of the three water ligands, that opposite N(0a) [O(1)] has a shorter contact to the metal than the other two [2.066(4), *cf.* 2.131, 2.138(3) Å]. However, the difference of *ca.* 0.1 Å in metal–oxygen and –nitrogen distances is a usual one, persisting throughout the present series except for the extreme class B metals, and it is likely that the above variation in the C(11)–N(0)–C(21) angle is simply a consequence of distortion due to co-ordination. It is of interest that the O(2)–Fe–O(3) axis is non-linear (166.5°); this and the general stereochemical consequences of the present co-ordination type are examined in detail below.

In (2), the cation is the seven-co-ordinate $[MnL(H_2O)_4]^+$ species. This expansion of co-ordination number on passing from iron(II) to manganese(II) is probably a consequence of the larger radius of manganese(II), together with the compact nature of the tridentate ligand, O(12a)–M–O(22a) being reduced from 151.1(3)° in (1) to only 134.1(3)° in (22). (Only two other seven-co-ordinate species appear to be structurally verified [3,4] for Mn and in both there is the common circumstance of the presence of a compact multidentate ligand.) Probably as a consequence of the relative crowding of the tridentate site we find the manganese–tridentate-ligand distances to be appreciably longer than those to the more sparsely distributed water ligands; the overall stereochemistry is not a bad representation of a pentagonal bipyramid in this case and, unlike the iron(II) derivative, there appears to be no systematic difference in the bond lengths from the metal to the axial or equatorial water molecules.

The purpurate anion in the iron(II) complex is a more accurate and apparently unperturbed example than the anions found in the ammonium and potassium salts previously studied,[5] in which the anion is effectively 'co-ordinated' by the purpurate as in a normal metal complex. Significant differences are found between the geometries of the present unco-ordinated species and the co-ordinated species accurately described in the iron(II) and calcium derivatives [6] and a number of monotonic trends delineated by italicizing those entries where this is observed in the compilation in Table 4; these are summarized in Figure 4(a), where a + sign indicates an increase in a bond length or angle and a — sign a decrease on passing from free anion to the ion in the calcium and iron(II) complexes, *i.e.* as the strength of the metal–ligand interaction increases. The variations observed in the angular geometry are easily accounted for simply as a result of chelation by the N–C–C–O fragments; the variations in bond lengths, surprisingly, are confined to the segment of the barbiturate ring running from O(*n*2) through to O(*n*4). The uninegative purpurate species may be represented by a combination of neutral and negatively charged barbiturate rings in terms of the types of resonance forms given in Figure 5. Clearly, if the contribution of forms (b) and/or (d) increases at the expense of (a), (c), and/or (e), the overall effect is a transfer of negative charge from O(*n*4) to O(*n*2) with the result of effectively neutralizing the charge on the co-ordinated metal ion. By contrast, in a series of dipicolinate complexes studied [free acid, calcium salt, iron(III) complex], although the variations in angles are much as expected, the variations in bond length appear to be confined entirely to the co-ordinating C–O bond (Table 4).

It is also of interest to compare the present geometries with those found in the most similar and accurately determined barbiturate system, namely violuric acid (HV) in its free and co-ordinated forms.[7] (Unfortunately, no geometry of comparable accuracy is available for violurate as a free anion or complexed with an alkaline or alkaline earth metal.) Here again the expected angular changes are found as the violurate species is chelated to the iron(II), the complex formed being $[FeV_3]^-$ (*fac*-isomer).[8] However, the nature of the variation observed in bond lengths is quite different to that of the purpurate system, occurring primarily within the N–C–C–O chelate ring [Figure 4(b)]. Likewise, if we compare the geometries of co-ordinated purpurate and violurate species, it is evident that the most sig-

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TABLE 2

Interatomic distances (Å) and angles (°) with least-squares estimated standard deviations in parentheses

(1) (The Fe derivative)

(*a*) The purpurate geometry; as in previous papers in this series, the geometries of the two halves of the barbiturate ring are tabulated in parallel columns

Purpurate	' a ' (co-ord.)		' b ' (free)	
Segment *n*	1	2	1	2
N(0)–C(*n*1)	1.322(5)	1.329(5)	1.339(5)	1.321(5)
C(*n*1)–C(*n*2)	1.461(6)	1.452(6)	1.456(6)	1.461(5)
C(*n*2)–O(*n*2)	1.258(5)	1.254(5)	1.234(5)	1.229(5)
C(*n*2)–N(*n*3)	1.348(5)	1.375(5)	1.384(5)	1.378(6)
N(*n*3)–H(*n*3)	0.96(6)	0.89(6)	0.88(6)	0.84(5)
N(*n*3)–C(*n*4)	1.387(6)	1.377(5)	1.361(6)	1.357(5)
C(*n*4)–O(*n*4)	1.211(5)	1.215(5)	1.223(5)	1.238(5)
C(11)–N(0)–C(21)	132.1(4)		128.3(4)	
N(0)–C(*n*1)–C(*n*2)	112.6(4)	112.4(3)	114.3(3)	114.4(3)
C(*n*1)–C(*n*2)–O(*n*2)	121.5(4)	122.8(4)	125.7(4)	125.8(4)
O(*n*2)–C(*n*2)–N(*n*3)	119.6(4)	119.4(4)	117.8(4)	117.9(4)
C(*n*1)–C(*n*2)–N(*n*3)	118.9(4)	117.9(4)	116.4(4)	116.2(3)
C(*n*2)–N(*n*3)–H(*n*3)	126(4)	126(4)	116(4)	117(4)
H(*n*3)–N(*n*3)–C(*n*4)	111(4)	109(4)	119(4)	117(4)
C(*n*2)–N(*n*3)–C(*n*4)	123.8(4)	124.8(3)	125.6(4)	125.9(3)
N(*n*3)–C(*n*4)–O(*n*4)	121.5(4)	122.4(4)	122.2(4)	121.3(4)
N(*n*3)–C(*n*4)–N(*n*5)	115.9(4)	115.9(4)	115.9(4)	116.8(4)
C(*n*2)–C(*n*1)–C(*n*6)	117.8(4)	118.0(4)	117.9(4)	118.4(4)
Fe–N(0)–C(*n*1)	114.4(3)	113.5(3)		
Fe–O(*n*1)–C(*n*1)	115.6(2)	114.6(2)		

	' a ' (co-ord.)		' b ' (free)	
	1	2	1	2
C(*n*1)–C(*n*6)	1.465(6)	1.452(6)	1.443(6)	1.465(6)
C(*n*6)–O(*n*6)	1.218(5)	1.223(5)	1.234(5)	1.223(5)
C(*n*6)–N(*n*5)	1.391(5)	1.397(5)	1.390(5)	1.398(6)
N(*n*5)–H(*n*5)	0.95(6)	0.85(6)	0.84(6)	0.89(5)
N(*n*5)–C(*n*4)	1.370(6)	1.356(5)	1.369(6)	1.354(5)
O(16) · · · O(26)	2.608(4)		2.622(4)	
N(0)–C(*n*1)–C(*n*6)	128.8(4)	128.2(3)	126.4(4)	126.4(3)
C(*n*1)–C(*n*6)–O(*n*6)	126.0(4)	125.6(4)	125.4(4)	125.3(4)
O(*n*6)–C(*n*6)–N(*n*5)	120.0(4)	119.4(4)	118.0(4)	119.0(4)
C(*n*1)–C(*n*6)–N(*n*5)	113.8(3)	114.8(3)	116.4(4)	115.6(3)
C(*n*6)–N(*n*5)–H(*n*5)	118(3)	117(4)	125(4)	114(4)
H(*n*5)–N(*n*5)–C(*n*4)	114(3)	116(4)	110(4)	121(4)
C(*n*6)–N(*n*5)–C(*n*4)	127.2(4)	126.4(4)	125.2(4)	125.6(3)
N(*n*5)–C(*n*4)–O(*n*4)	122.6(4)	121.7(4)	121.8(4)	121.9(4)

(*b*) The metal environment

Fe–O(1)	2.066(4)	Fe–N(0)	2.205(3)
Fe–O(2)	2.131(2)	Fe–O(12)	2.103(3)
Fe–O(3)	2.138(3)	Fe–O(22)	2.094(3)
O(1)–Fe–O(2)	82.3(1)	O(2)–Fe–O(22)	95.5(1)
O(1)–Fe–O(3)	85.7(1)	O(3)–Fe–N(0)	92.9(1)
O(1)–Fe–N(0)	178.2(1)	O(3)–Fe–O(12)	90.2(1)
O(1)–Fe–O(12)	105.7(1)	O(3)–Fe–O(22)	93.2(1)
O(1)–Fe–O(22)	103.2(1)	N(0)–Fe–O(12)	75.3(1)
O(2)–Fe–O(3)	166.5(1)	N(0)–Fe–O(22)	75.8(1)
O(2)–Fe–N(0)	99.2(1)	O(12)–Fe–O(22)	151.1(1)
O(2)–Fe–O(12)	87.2(1)		

(*c*) Interspecies hydrogen-bonding interactions (O · · · H <2.5 Å); the angle subtended at the hydrogen is given in parentheses

(*i*) The ligand hydrogen atoms

H(13a) · · · O(5)	1.77(6) [174(4)]	H(15a) · · · O(12b^{I})	1.86(6) [174(5)]
H(23a) · · · O(24a^{II})	1.89(6) [177(5)]	H(25a) · · · O(26^{III})	2.01(6) [174(6)]
H(13b) · · · O(16a^{IV})	2.15(6) [176(4)]	H(15b) · · · O(7)	2.00(6) [169(5)]
H(25b) · · · O(4^{V})	1.95(5) [175(5)]		

(*ii*) The water hydrogen atoms

H(1α) · · · O(16b^{VI})	2.01(6) [164(5)]	H(1β) · · · O(14a^{VI})	2.06(5) [161(6)]
H(2α) · · · O(22b^{VII})	1.85(6) [168(5)]	H(2β) · · · O(12b^{VII})	2.11(5) [176(7)]
H(3α) · · · O(8)	2.07(6) [149(6)]	H(3β) · · · O(6)	1.85(6) [159(6)]
H(4α) · · · O(26b^{VIII})	2.00(4) [174(6)]	H(4β) · · · O(12a)	2.18(5) [143(4)]
H(5α) · · · O(24b^{VI})	2.06(6) [178(4)]	H(5β) · · · O(4^{VIII})	2.05(6) [162(6)]
H(6α) · · · O(14b)	2.04(6) [142(5)]	H(6β) · · · O(16b^{I})	2.23(6) [136(6)]
H(7α) · · · O(9^{IX})	2.15(5) [153(6)]	H(7β) · · · O(9)	2.15(6) [144(5)]
H(8α) · · · O(3^{X})	2.43(6) [119(5)]	H(8β) · · · O(14b)	2.04(6) [152(6)]

I	$(x, y - 1, z)$	VI	$(x, y, z - 1)$
II	$(1 - x, \bar{y}, \bar{z})$	VII	$(x, y - 1, z - 1)$
III	$(1 - \bar{x}, \bar{y}, 1 - z)$	VIII	$(\bar{x}, 1 - y, 1 - z)$
IV	$(x, 1 + y, z)$	IX	$(1 - x, 1 - y, 2 - z)$
V	$(x, y, z + 1)$	X	$(1 - x, 1 - y, 1 - z)$

(2) (The Mn derivative)

(*a*) The purpurate geometry, tabulated as above

N(0)–C(*n*1)	1.31(1)	1.35(1)	1.35(1)	1.32(1)
C(*n*1)–C(*n*2)	1.47(1)	1.46(1)	1.45(1)	1.46(1)
C(*n*2)–O(*n*2)	1.24(1)	1.25(1)	1.24(1)	1.24(1)
C(*n*2)–N(*n*3)	1.37(1)	1.37(1)	1.39(1)	1.38(1)
N(*n*3)–H(*n*3)	1.0(1)	0.7(1)	0.7(1)	0.9(1)
N(*n*3)–C(*n*4)	1.39(2)	1.37(1)	1.37(2)	1.38(1)
C(*n*4)–O(*n*4)	1.22(1)	1.22(1)	1.23(1)	1.21(1)
C(11)–N(0)–C(21)	125.9(9)		126.4(10)	
N(0)–C(*n*1)–C(*n*2)	111.6(9)	112.9(9)	114.9(10)	114.6(10)
C(*n*1)–C(*n*2)–O(*n*2)	123.7(9)	122.9(7)	125.6(8)	124.3(9)

C(*n*1)–C(*n*6)	1.45(2)	1.46(1)	1.44(2)	1.46(1)
C(*n*6)–O(*n*6)	1.23(1)	1.22(1)	1.21(1)	1.21(1)
C(*n*6)–N(*n*5)	1.41(1)	1.39(1)	1.42(1)	1.41(1)
N(*n*5)–H(*n*5)	0.9(1)	1.0(1)	0.8(1)	1.0(1)
N(*n*5)–C(*n*4)	1.36(1)	1.37(1)	1.36(1)	1.37(1)
O(16) · · · O(26)	2.60(1)		2.64(1)	
N(0)–C(*n*1)–C(*n*6)	128.9(9)	126.4(9)	122.4(10)	125.2(9)
C(*n*1)–C(*n*6)–O(*n*6)	125.1(9)	125.8(8)	126.9(9)	127.9(9)

TABLE 2 (*Continued*)

Purpurate	'a' (co-ord.)		'b' (free)	
Segment *n*	1	2	1	2
O(*n*2)–C(*n*2)–N(*n*3)	119.7(8)	120.2(9)	118.7(9)	118.5(10)
C(*n*1)–C(*n*2)–N(*n*3)	116.6(9)	117.0(9)	115.6(9)	117.2(10)
C(*n*2)–N(*n*3)–H(*n*3)	112(6)	107(7)	107(8)	115(7)
H(*n*3)–N(*n*3)–C(*n*4)	122(6)	128(7)	126(8)	121(7)
C(*n*2)–N(*n*3)–C(*n*4)	125.3(8)	124.7(10)	126.8(9)	124.9(8)
N(*n*3)–C(*n*4)–O(*n*4)	120.9(9)	122.1(11)	122.0(10)	120.5(9)
N(*n*3)–C(*n*4)–N(*n*5)	116.4(9)	116.5(8)	114.5(8)	116.2(9)
C(*n*2)–C(*n*1)–C(*n*6)	118.9(8)	118.9(7)	120.5(10)	119.4(8)
Mn–N(0)–C(*n*1)	118.0(6)	115.4(6)		
Mn–O(*n*1)–C(*n*1)	118.2(5)	114.2(6)		
O(*n*6)–C(*n*6)–N(*n*5)	118.9(9)	119.2(9)	119.1(9)	117.2(8)
C(*n*1)–C(*n*6)–N(*n*5)	115.9(8)	114.8(9)	113.8(9)	114.8(8)
C(*n*6)–N(*n*5)–H(*n*5)	106(6)	121(6)	115(7)	120(5)
H(*n*5)–N(*n*5)–C(*n*4)	127(6)	112(6)	117(7)	113(6)
C(*n*6)–N(*n*5)–C(*n*4)	125.8(9)	126.4(9)	127.6(10)	126.0(9)
N(*n*5)–C(*n*4)–O(*n*4)	122.7(10)	121.3(11)	123.5(11)	123.2(11)

(*b*) The metal environment

Mn–O(1)	2.178(8)
Mn–O(2)	2.247(8)
Mn–O(3)	2.182(8)
Mn–O(4)	2.177(9)
O(1)–Mn–O(2)	78.8(3)
O(1)–Mn–O(3)	92.8(3)
O(1)–Mn–O(4)	90.7(3)
O(1)–Mn–N(0)	139.8(3)
O(1)–Mn–O(12)	72.2(3)
O(1)–Mn–O(22)	153.3(3)
O(2)–Mn–O(3)	83.3(3)
O(2)–Mn–O(4)	94.9(3)
O(2)–Mn–N(0)	138.9(2)
O(2)–Mn–O(12)	150.0(3)
O(2)–Mn–O(22)	75.6(3)
Mn–N(0)	2.422(9)
Mn–O(12)	2.303(7)
Mn–O(22)	2.417(6)
O(3)–Mn–O(4)	175.7(3)
O(3)–Mn–N(0)	81.5(3)
O(3)–Mn–O(12)	90.9(3)
O(3)–Mn–O(22)	91.7(3)
O(4)–Mn–N(0)	97.4(3)
O(4)–Mn–O(12)	92.6(3)
O(4)–Mn–O(22)	84.0(3)
N(0)–Mn–O(12)	68.2(2)
N(0)–Mn–O(22)	66.9(2)
O(12)–Mn–O(22)	134.1(3)

(*c*) Interspecies hydrogen-bonding interactions (O···O <2.5 Å); the angle subtended at the hydrogen is given in parentheses

(*i*) The ligand hydrogen atoms

H(13a)···O($24b^{I}$)	1.8(1) [167(10)]
H(23a)···O($14b^{III}$)	2.3(1) [153(10)]
H(13b)···O($24a^{V}$)	2.1(1) [162(10)]
H(23a)···O(14^{VI})	1.9(1) [171(11)]
H(15a)···O(5^{II})	1.9(1) [170(11)]
H(25a)···O(9^{IV})	1.8(1) [177(10)]
H(15b)···O(7)	2.3(1) [158(10)]
H(25b)···O(10^{VII})	1.8(1) [165(10)]

(*ii*) The water hydrogen atoms

H(1α)···O($14b^{VIII}$)	2.1(1) [172(11)]
H(2β)···O(22^{IX})	2.1(1) [152(12)]
H(3β)···O(9)	2.4(1) [140(10)]
H(4α)···O(6^{X})	2.2(1) [158(13)]
H(5α)···O(6^{XI})	2.1(1) [144(9)]
H(7β)···O($24b^{XII}$)	2.4(1) [131(10)]
H(8β)···O(22^{X})	2.2(1) [153(12)]
H(2α)···O(8)	1.6(1) [154(10)]
H(2β)···O(2^{IX})	2.5(1) [124(10)]
H(3β)···O($24a^{IV}$)	2.4(1) [128(10)]
H(4β)···O($22b^{IV}$)	1.6(1) [163(8)]
H(7α)···O(8)	2.2(1) [176(11)]
H(8α)···O($12b^{X}$)	2.1(1) [157(10)]

Transformations of the asymmetric unit (x, y, z) are denoted by the following superscripts:

I ($x - 1, y - 1, z - 1$)
II ($x - 1, y, z$)
III ($x, y, 1 + z$)
IV ($1 - x, 1 - y, 1 - z$)
V ($x, y, z - 1$)
VI ($1 + x, 1 + y, 1 + z$)
VII ($1 + x, y, z$)
VIII ($1 - x, \bar{y}, \bar{z}$)
IX ($1 - x, \bar{y}, 1 - z$)
X ($x, y - 1, z$)
XI ($1 - x, 1 - y, y, \bar{z}$)
XII ($2 - x, 1 - y, 1 - z$)

nificant bond-length variations observed occur in the N(0)–C(*n*1) and C(*n*1)–C(*n*2) bonds [Figure 4(c)], the net effect being primarily an increase in the contribution of resonance form (d) at the expense of form (a), presumably a result of the necessity to involve the oxime oxygen in some multiple bonding. A number of interacting factors and points may account for, depend on, or be relevant to this observation: (i) iron(II) in the violurate complex $[FeV_3]^-$ has a low-spin ground state whereas in the present complex a magnetic-moment determination has shown $[FeL(H_2O)_3]^+$ to be high-spin, an observation in agreement with the relative metal–ligand distances (Table 4). (ii) Because of (i), it is likely that metal–ligand bonding in the violurate complex may involve a much greater π component, capable of interacting with the π system of the N–C–C–O chelate ring much more effectively than in the purpurate where the bonding is likely to be basically σ in nature. (iii) Metal–ligand π interactions in the purpurate will be hindered to a considerable extent by the strain likely to be necessary in distorting the tridentate ligand to interact with the metal atom at the much shorter distances needed to produce the low-spin (strong-field) ground state. (iv) It is apparent in the violurate complex that the Fe–N bond distance is much shorter than that for Fe–O, the reverse situation with that found for the co-ordinated purpurate. Production of the low-spin state in $[FeV_3]^-$ may be consequent upon both the greater number of nitrogen atoms available for co-ordination and the fact that, because of the proximity of the attached oxygen, the bonding properties of the violurate nitrogen will differ greatly from the purpurate nitrogen N(0), which will probably be much less negative. As well as the intra-purpurate variations in bond lengths and angles discussed both above and previously, a number of other geometrical parameters of the purpurate are found to vary widely throughout the series of compounds studied; the most important of these are given in Table 5. Attempts to find systematic variations among these have met with mixed success; the most

TABLE 3

(a) Least-squares planes, calculated through the C(n1, n2, n4, n6),N(n3, n5) skeleton of each barbiturate segment of the ligand (n = 1,2) in the form $pX + qY + rZ = s$, where the right-handed orthogonal (Å) frame is defined with X parallel to a, Z in the ac plane. Atom deviations and the estimated standard deviation of the defining atoms are in Å. The angle between the normals to the two barbiturate planes of each ligand is θ°

	Co-ordinated species ' a '				free anion ' b '			
Compound	(1)		(2)		(1)		(2)	
Segment (n)	1	2	1	2	1	2	1	2
10^4p	7 143	6 128	5 795	8 782	6 127	7 986	8 586	5 876
10^4q	5 268	7 718	6 019	0 960	7 153	2 629	−0 277	5 800
10^4r	4 608	1 700	−5 494	−4 685	3 361	5 415	−5 120	−5 642
s	4.757	4.623	1.638	1.757	8.190	4.795	7.265	9.952
σ	0.07	0.06	0.05	0.05	0.07	0.06	0.05	0.05
χ^2	962	651	100	128	458	251	77	96
C(n1)	0.11	0.10	0.07	0.08	0.11	0.08	0.07	0.08
C(n2)	−0.06	−0.05	−0.04	−0.06	−0.06	−0.05	−0.04	−0.05
N(n3)	−0.03	−0.03	−0.01	0.01	−0.03	−0.02	−0.01	−0.01
C(n4)	0.06	0.05	0.03	0.03	0.06	0.05	0.03	0.04
N(n5)	0.00	0.00	0.00	−0.02	−0.01	−0.01	0.00	−0.01
C(n6)	−0.08	−0.08	−0.05	−0.04	−0.07	−0.06	−0.05	−0.05
N(0)	0.22	0.12	0.10	0.02	0.15	0.12	−0.06	0.12
O(n2)	−0.19	−0.17	−0.12	−0.23	−0.18	−0.13	−0.13	−0.19
O(n4)	0.17	0.10	0.04	0.07	0.15	0.13	0.09	0.11
O(n6)	−0.37	−0.34	−0.27	−0.27	−0.35	−0.28	−0.29	−0.29
M	−0.17	−0.35	−0.19	−1.09				
θ	22.7		34.5		30.8		39.0	

(b) Least-squares ' planes ' in the same form defined by M, N(0a), O(12,22a) and the opposed water molecule(s)

	10^4p	10^4q	10^4r	s	σ	χ^2
(1)	6 737	6 477	3 559	4.837	0.03	163

[Deviations: Fe, 0.00; N(0a), 0.03; O(12a), −0.03; O(22a), −0.03; O(1), 0.02]

(2)	5 949	6 102	−5 232	1.643	0.18	2 824

[Deviations: Mn, −0.06; N(0a), 0.22; O(12a), −0.06; O(22a), −0.24; O(1), −0.07; O(2), 0.21]

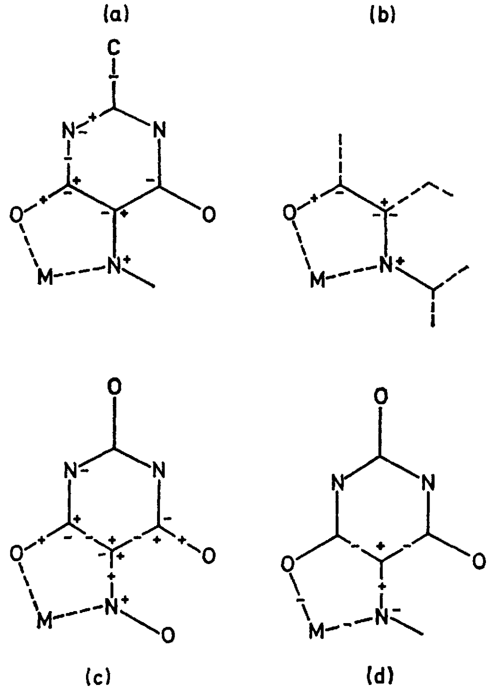

FIGURE 4 Diagram showing the significant changes in comparative geometry between related N–C–C–O species; + denotes an increase in bond length or angle, − a decrease, on passing from left to right in the following series: (a) free anion purpurate ⟶ co-ordinated purpurate in calcium salt ⟶ co-ordinated purpurate in (1). (b) dipicolinic acid ⟶ co-ordinated dipicolinate in calcium salt ⟶ co-ordinated dipicolinate in iron(II) derivative. (c) violuric acid ⟶ violurate in tris(violurato)ferrate(II). (d) co-ordinated purpurate in (1) ⟶ co-ordinated violurate in tris(violurato)-ferrate(II)

convincing correlation found is that depicted in Figure 6 which shows that a fairly convincing straight line may be drawn to relate metal–oxygen O(n2) distance with increasing non-coplanarity of the two barbiturate segments, provided those purpurate species with bridging interactions are ignored. Other less clear-cut correlations may be drawn with the angle subtended at the purpurate central nitrogen by the purpurate segments and the O(16) · · · O(26) distance; these latter parameters however appear to be much less sensitive to co-ordination variation. Variations in torsion angles about the N(0)–C(n1) bonds, although wide, appear to be rather random and may reflect packing forces within the lattice rather strongly. It is notable that the torsion angles τ_1 and τ_2 are generally *not* complementary to τ_3 and τ_4; this appears to be a result of distortion within the barbiturate segments caused by the O(16) · · · O(26) interaction.

As in the remaining structures in the series, crystal packing forces appear to be dominated by hydrogen-bonding interactions; these are tabulated in Table 2. Perhaps the most interesting consequence of these is observed in (2), where the bonding of the purpurate ligand oxygens O(n2) about the manganese is significantly asymmetric; in this case we find that the manganese also deviates considerably from the plane of that purpurate ring.

The stereochemistry of [M(tridentate ligand)(unidentate ligand)$_3$]$^{n+}$ was calculated by minimization of the total repulsion energy assuming a completely flexible tridentate ligand, as described previously.[9] The axes

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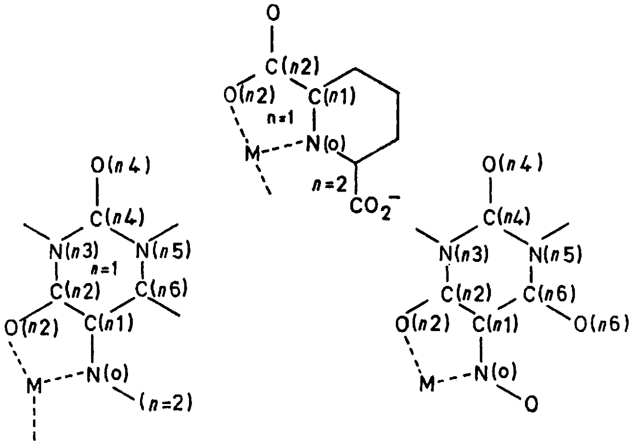
[9] D. L. Kepert, *J.C.S. Dalton*, 1974, 612.

are defined by reference to Figure 7. One axis through the metal atom M is normal to the three donor atoms ABC of the tridentate ligand such that $\phi_A = \phi_B = \phi_C$. The second axis is such that $\theta_B = 180°$. The other co-ordinates of the tridentate ligand are calculated from the normalized bite b of each chelate ring: $\theta_A = -\theta_C =$ angle ABC $= 180 - 2\ \mathrm{asin}(b/2)°$. No symmetry elements were assumed in the calculations. The stereochemistry is therefore completely defined by b, ϕ_A, and the angular co-ordinates of the three unidentate ligands, D, E, F.

TABLE 4

This table gives comparative geometries of the free purpurate anion, L$^-$, and the co-ordinated anions in the calcium salt $[\mathrm{CaL_2(H_2O)_2}]\cdot 2\mathrm{H_2O}$, $[\mathrm{L_{Ca}}]^-$, and the present iron(II) salt, $[\mathrm{L_{Fe}}]^-$. The geometries of the common structural elements are also given for dipicolinic acid, H$_2$dipic (for that half of the molecule in which the carboxyl CO group is *cis* to the nitrogen), and the co-ordinated dipicolinate anion in the calcium $[\mathrm{dipic_{Ca}}]^{2-}$ and the iron(III) $[\mathrm{dipic_{Fe}}]^{2-}$ complexes, as well as for violuric acid, HV, and the co-ordinated violurate anion in the iron(II) complex $[\mathrm{V_{Fe}}]^-$. The numbering scheme used for the purpurate species has been superimposed on the dipicolinate and violurate groups. Values given are the mean geometries where more than one independent ligand segment occurs in the complex cited. Where significant monotonic changes are observed for a given geometrical parameter within the sequence of three compounds in the purpurate and dipicolinate entries, attention has been drawn to these by italicization.

For each compound cited $\sigma(r)$ (Å) is the average estimated standard deviation for an individual X–Y distance and $\sigma(\theta)$ (°) the same for an X–Y–Z angle, where X, Y, Z may be any of C, N, or O



	purpurate L$^-$			dipicolinate dipic^{2-}			violurate V$^-$	
	$[\mathrm{L}]^-$ [a]	$[\mathrm{L_{Ca}}]^-$ [b]	$[\mathrm{L_{Fe}}]^-$ [c]	H$_2$dipic [d]	$[\mathrm{dipic_{Ca}}]^{2-}$ [e]	$[\mathrm{dipic_{Fe}}]^{2-}$ [f]	HV [g]	$[\mathrm{V_{Fe}}]^-$ [h]
N(0)–C(*n*1)	1.33_0	1.32_9	1.32_5	1.33_6	1.33_2	1.33_5	1.27_3	1.36_0
C(*n*1)–C(*n*2)	1.45_8	1.45_5	1.45_7	1.51_1	1.50_4	1.50_9	1.46_7	1.41_5
C(*n*1)–C(*n*6)	1.45_4	1.45_7	1.45_8	1.38_8	1.38_7	1.38_4	1.50_4	1.40_0
C(*n*2)–O(*n*2)	*1.23_1*	*1.24_2*	*1.25_6*	*1.18_1*	*1.25_5*	*1.27_3*	1.21_1	1.25_5
C(*n*6)–O(*n*6)	1.22_8	1.22_5	1.22_0				1.17_5	1.22_5
C(*n*2)–N(*n*3)	*1.38_1*	*1.37_2*	*1.35_3*				1.37_1	1.36_5
C(*n*6)–N(*n*5)	1.39_4	1.38_4	1.39_4				1.37_1	1.37_8
N(*n*3)–C(*n*4)	*1.35_9*	*1.37_5*	*1.38_2*				1.37_8	1.38_1
N(*n*5)–C(*n*4)	1.36_1	1.35_9	1.36_3				1.36_1	1.36_6
C(*n*4)–O(*n*4)	*1.23_0*	*1.22_1*	*1.21_3*				1.22_3	1.21_3
C(11)–N(0)–[C(21),O]	*128.3*	*128.6*	*132.1*	*116.8*	*119.6*	*122.7*	117.9	120.4
C(*n*2)–C(*n*1)–N(0)	*114.4*	*113.4*	*112.5*	*115.3*	*114.8*	*111.3*	115.1	111.7
C(*n*6)–C(*n*1)–N(0)	*126.4*	*126.7*	*128.5*	*123.3*	*122.1*	*120.6*	125.7	127.2
C(*n*2)–C(*n*1)–C(*n*6)	118.1	118.6	117.9	*121.4*	*123.0*	*128.1*	119.2	121.0
O(*n*2)–C(*n*2)–C(*n*1)	*125.7*	*123.0*	*122.1*	*124.8*	*116.7*	*114.9*	124.1	121.3
O(*n*6)–C(*n*6)–C(*n*1)	125.3	125.0	125.8				124.5	126.6
N(*n*3)–C(*n*2)–C(*n*1)	*116.3*	*117.1*	*118.4*				116.4	118.2
N(*n*5)–C(*n*6)–C(*n*1)	*116.0*	*115.1*	*114.3*				114.4	113.7
O(*n*2)–C(*n*2)–N(*n*3)	117.8	119.8	119.5				119.5	120.4
O(*n*6)–C(*n*6)–N(*n*5)	118.5	119.7	120.2				121.1	119.5
C(*n*2)–N(*n*3)–C(*n*4)	*125.7*	*125.0*	*124.3*				125.9	123.8
C(*n*6)–N(*n*5)–C(*n*4)	125.4	127.0	126.8				128.0	127.4
N(*n*3)–C(*n*4)–O(*n*4)	121.8	121.4	122.0				119.8	121.1
N(*n*5)–C(*n*4)–O(*n*4)	121.8	122.8	122.2				124.0	123.7
N(*n*3)–C(*n*4)–N(*n*5)	116.4	115.8	115.9				116.1	115.3
M–N(0)		2.59_5	2.20_5		2.49_1	2.07_0		1.87_7
M–O(*n*2)		2.49_8	2.09_9		2.46_5	2.06_6		1.98_3
$\sigma(r)$	0.006	0.006	0.006	0.006	0.01	0.006	0.008	0.01
$\sigma(\theta)$	0.4	0.4	0.4	0.4	0.9	0.5	0.6	1.0

[a] Ref. 5. [b] Ref. 6. [c] This work. [d] F. Takusagawa, K. Hirotsu, and A. Shimada, *Bull. Chem. Soc. Japan*, 1973, **46**, 2020. [e] G. Strahs and R. E. Dickerson, *Acta Cryst.*, 1968, **B24**, 571. [f] J. A. Thich, C. C. Ou, D. Powers, B. Vasiliou, D. Mastropaolo, J. A. Potenza, and H. J. Schugar, *J. Amer. Chem. Soc.*, 1976, **98**, 1425. [g] Ref. 7. [h] Ref. 8.

Two stereochemistries corresponding to potential

TABLE 5

This table gives the torsion angles about the central purpurate C(*n*1)–N(0) bonds for all species studied in this series, the signs being adjusted throughout to conform with those of the co-ordinated purpurate species in the present iron(II) derivative:

τ_1 C(12)–C(11)–N(0)–C(21) τ_2 C(22)–C(21)–N(0)–C(11)
τ_3 C(16)–C(11)–N(0)–C(21) τ_4 C(26)–C(21)–N(0)–C(11)

Also given are other intraligand parameters which vary throughout the series and which might be expected to reflect ligand distortion due to co-ordination; the previously studied lithium salt is also included. Distances are in Å and angles in degrees; θ° is the angle between the normals to the two barbiturate ligand ' planes ' defined by C(*n*1, *n*2, *n*4, *n*6), N(*n*3, *n*5). An asterisk,*, signifies a bridging ligand

Compound	Ligand	τ_1	τ_2	τ_3	τ_4	θ	⟨M–O(*n*2)⟩	M–N(0)	C(11)–N(0)–C(21)	O(16) · · · O(26)
$KL\cdot3H_2O$ [a]		162.7		−30.2		49.2	2.81	2.99	126.3	2.60
$NH_4L\cdot H_2O$ [a]		165.3		−28.5		41.0			125.8	2.65
$[CaL_2(H_2O)_2]\cdot2H_2O$ [b]	a	173.0	163.9	−18.7	−27.1	31.2	2.43	2.63	132.6	2.61
	b	174.1	156.8	−24.4	−31.5	39.0	2.56	2.56	124.5	2.66
$[CdL_2(H_2O)_2]\cdot2H_2O$ [b]	a	172.9	162.4	−18.4	−28.9	33.3	2.40	2.47	132.0	2.59
	b	172.4	154.0	−25.1	−32.1	41.4	2.58	2.38	123.8	2.69
$[FeL(H_2O)_3]L\cdot6H_2O$ [c]	a	171.7	172.0	−19.1	−21.8	22.7	2.10	2.21	132.1	2.61
	b	167.4	167.9	−26.1	−22.9	30.8			128.3	2.62
$[MnL(H_2O)_4]L\cdot6H_2O$ [c]	a	165.7	167.6	−23.4	−28.0	34.5	2.36	2.42	125.9	2.60
	b	171.2	161.0	−25.6	−29.4	39.0			126.4	2.64
$PbL_2\cdot4H_2O$ [d]	a	168.1	167.6	−23.0	−29.2	31.7	2.67	2.83	124	2.62
	b*	171.7	166.9	−23.8	−27.8	34.1	2.56	2.75	129	2.58
$PbL_2\cdot H_2O$ [d]	a	172.8	154.0	−21.9	−27.3	35.6	2.72	2.66	126	2.61
	b*	163.9	171.2	−31.6	−21.1	32.2	2.61	2.67	125	2.62
$2SrL_2\cdot15H_2O$ [e]	a*	163.2	166.9	−36.8	−28.9	47.8	2.82		124	2.62
	b	165.6	168.0	−31.5	−25.3	39.7	2.57	2.69	128	2.65
	c*	163.2	161.6	−26.8	−35.5	48.9	2.93		124	2.61
	d	166.2	169.7	−30.7	−25.0	38.3	2.60	2.75	127	2.61
$[CuL_2]\cdot5H_2O$ [f]		163.9		−30.7		47.7	2.42	1.93	127.1	2.69
$[ZnL_2]\cdot4H_2O$ [f]	a	173.2		−26.2		28.2	2.19	2.07	127	2.55
	b	173.6		−20.2		18.7	2.10	2.14	137	2.50
$[CoL(NO_3)(H_2O)]\cdot2H_2O$ [g]		173.3	169.9	−15.9	−17.7	19.3	2.11	2.20	132.8	2.54
$[ZnL(NO_3)(H_2O)]\cdot2H_2O$ [g]		173.4	171.3	−21.2	−16.2	20.1	2.12	2.23	134.7	2.56
$CaL(NO_3)\cdot5H_2O$ [h]	*	166.5	167.7	−26.5	−23.6	31.8	2.50	2.60	127.1	2.63
$LiL\cdot2H_2O$ [i]	*	173.5	168.2	−21.0	−22.4	27.4	2.07	2.13	134.0	2.61

[a] Ref. 5. [b] Ref. 6. [c] This work. [d] Part 4, following paper. [e] Part 5, *J.C.S. Dalton*, 1977, 1368. [f] Ref. 1. [g] Part 7, *J.C.S. Dalton*, 1977, 1377. [h] Part 8, *J.C.S. Dalton*, 1977, 1381. [i] H. B. Bürgi, S. Djurić, M. Dobler, and J. D. Dunitz, *Helv. Chim. Acta*, 1972, **55**, 1771.

energy minima were located. The first contains a mirror plane through MABCE, so that the stereochemistry is completely defined by ϕ_D, θ_D, and θ_E, which are shown as a function of *b* in Figure 8, the other parameters being $\phi_A = \phi_E = 90$, $\phi_F = 180 - \phi_D$, $\theta_F = \theta_D$°. At low values of *b*, the tridentate ligand ABC is projected over the DEF triangle, and normal to the DF edge. For values of *b* above about 1.0 (1.08 for $n = 1$, 1.02 for $n = 6$, 1.04 for $n = 12$), $\theta_D = \theta_E = 0°$ and there is a second mirror plane through MBDEF. At

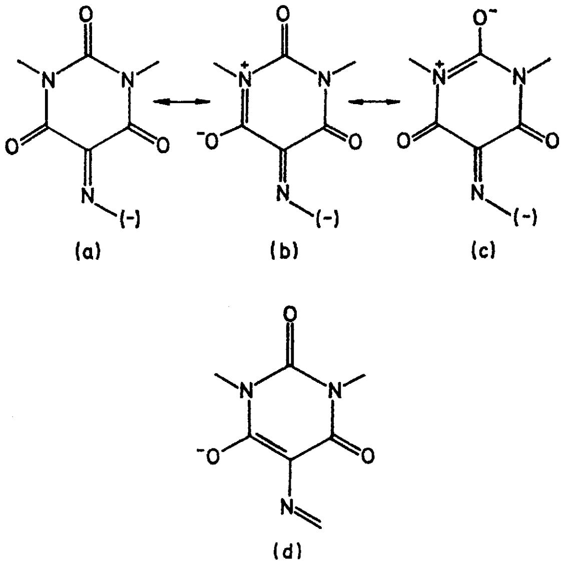


FIGURE 5 Diagram showing those resonance forms which are the most likely contributors to purpurate and violurate structures

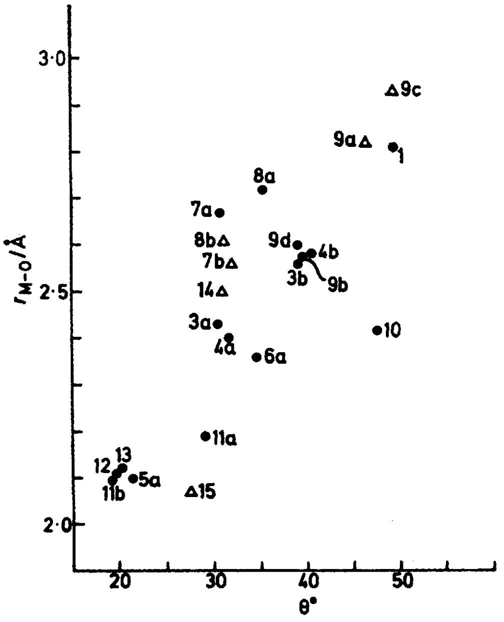


FIGURE 6 Plot of angle between the two barbiturate ' planes ' of the purpurate ligand, θ°, *versus* average M–O(*n*2) distance, for all tridentate purpurate ligands described in this series. Triangular points are given for those ligands in which additional bridging co-ordination is found

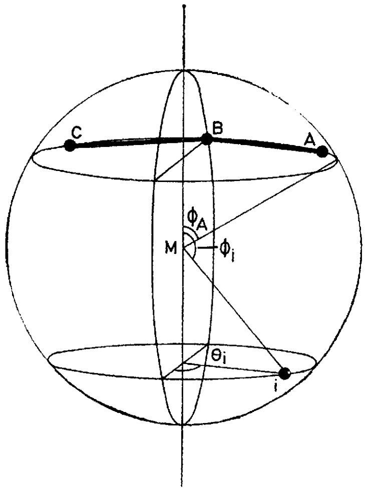


FIGURE 7 General stereochemistry for [M(tridentate)(unidentate)$_3$]$^{n\pm}$

$b = 2^{\frac{1}{2}}$, $\theta_A = 90°$ with the formation of the regular *mer*-octahedral structure.

The second stereochemistry contains a mirror plane through MBF, so that the stereochemistry is completely defined by ϕ_A, ϕ_D, θ_D, and θ_F, which are shown as a function of b in Figure 9, the other parameters being $\phi_E = \phi_D$, $\theta_E = -\theta_D$, and $\theta_F = 0°$. At low values of b, the tridentate ligand is again projected over the DEF triangle, but is now parallel to DE. At $b = 2^{\frac{1}{2}}$, $\phi_D = \phi_F = 180 - \text{asin}(2/3)^{\frac{1}{2}} = 125.3$, $\theta_A = 60$, and $\theta_D = 120°$, with the formation of the regular *fac*-octahedral structure.

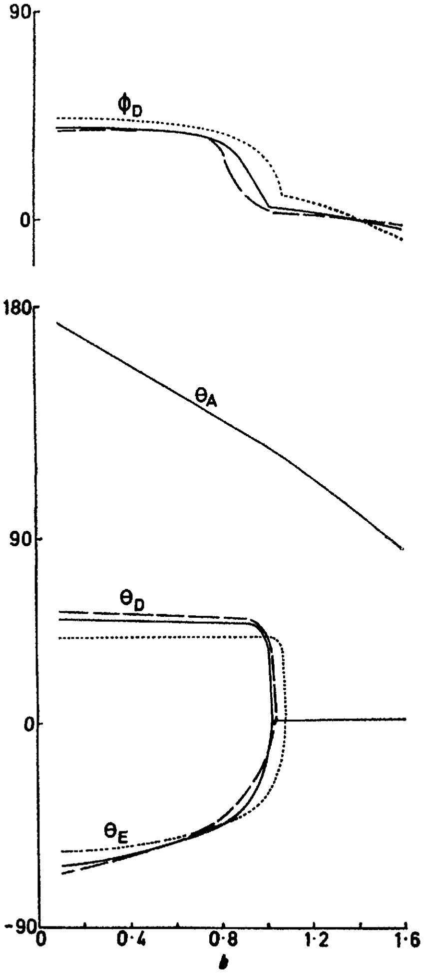


FIGURE 8 Angular parameters (°) for *mer*-[M(tridentate)(unidentate)$_3$] as a function of normalized bite, b; (· · · ·), $n = 1$; (——), $n = 6$; (— — —), $n = 12$

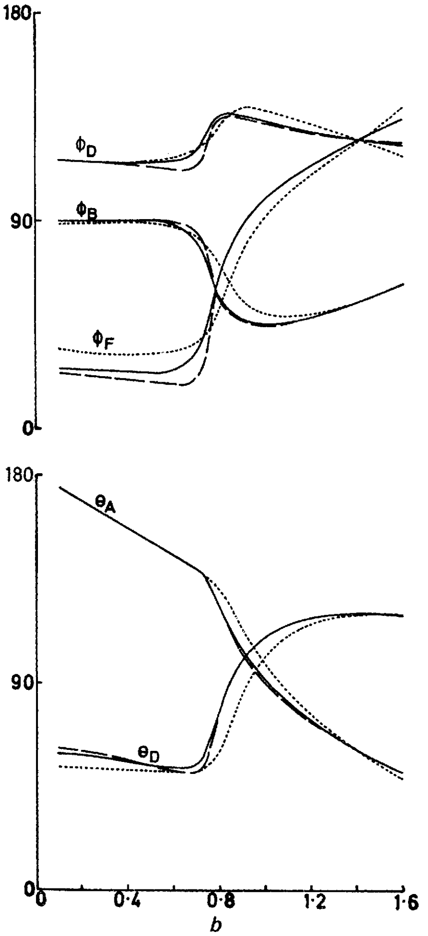


FIGURE 9 Angular parameters (°) for *fac*-[M(tridentate)(unidentate)$_3$] as a function of normalized bite, b; (· · · ·), $n = 1$; (——), $n = 6$; (— — —), $n = 12$

These two structures are now compared with structur-

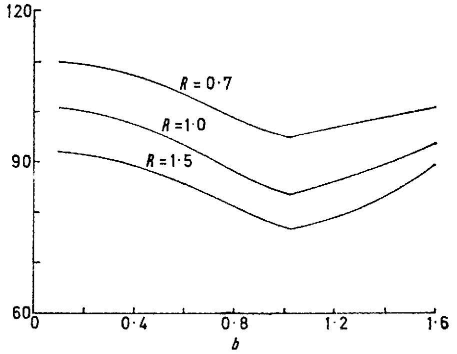


FIGURE 10 Bond angle DME (°) for *mer*-[M(tridentate)(unidentate)$_3$] as a function of normalized bite, b, and bond-length ratio, R ($n = 6$)

TABLE 6

Structural parameters for compounds *mer*-[M(tridentate)(unidentate)$_3$] [a]

	b	θ_A	ϕ_D	DME	ME/MD	Ref.
[Rh{HN(CH$_2$CH$_2$NEt$_2$)$_2$}(N$_3$)$_3$]·0.81EtOH	1.34	96.2	−4.0	94.0	1.00	*c*
[Ga(terpy)Cl$_3$]	1.25	102.8	−2.3	92.3	0.94	*d*
[FeL(H$_2$O)$_3$]L·6H$_2$O	1.23	104.4	6.1	83.9	0.97	*e*
[Ti{MeN(CH$_2$·C$_5$H$_3$NMe)$_2$}Cl$_3$]	1.21	105.4	−0.5	90.5	0.96	*f*

[a] terpy = 2, 2′: 6′, 2″-terpyridine, L = purpurate. [c] R. F. Ziolo, R. M. Shelby, R. H. Stanford, and H. B. Gray, *Cryst. Struct. Comm.*, 1974, **3**, 469. [d] G. Beran, K. Dymock, H. A. Patel, A. J. Carty, and P. M. Boorman, *Inorg. Chem.*, 1972, **11**, 896. [e] This work. [f] R. K. Collins, M. G. B. Drew, and J. Rodgers, *J.C.S. Dalton*, 1972, 899.

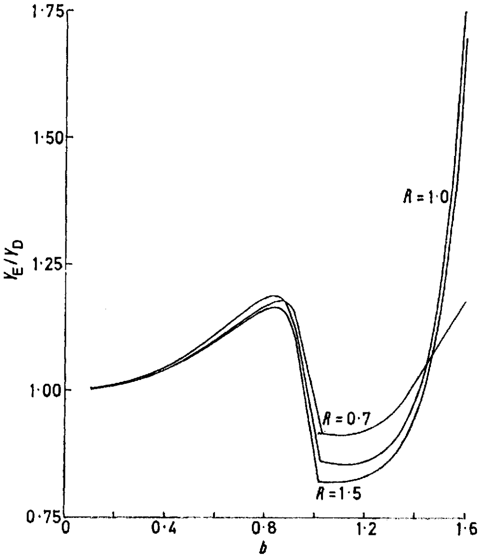


FIGURE 11 Ratio of the individual atom-repulsion coefficients for the unidentate ligands in *mer*-[M(tridentate)(unidentate)$_3$] as a function of normalized bite, b, and bond-length ratio, R ($n = 6$)

ally characterized molecules, restricted to those containing a symmetric tridentate ligand and three equivalent unidentate ligands. There still remain three different types of metal–ligand bond, and close agreement between experimental and calculated bond angles would not be expected. The following discussion is therefore restricted to the bond angles between the three metal–unidentate ligand bonds, and their relative bond length.

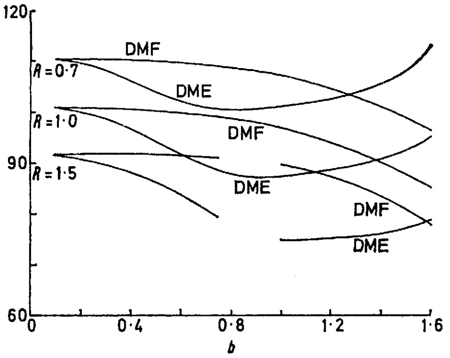


FIGURE 12 Bond angles DME and DMF (°) for *fac*-[M(tridentate)(unidentate)$_3$] as a function of normalized bite, b, and bond-length ratio, R ($n = 6$)

mer-Isomer.—The average structural parameters using complete C_{2v} symmetry are shown in Table 6. The observed range of normalized bite, b = 1.21—1.34, is typical for five-membered chelate rings. Over this range, the predicted value of ϕ_D is *ca.* 3° (Figure 8), *i.e.* DME = EMF = *ca.* 87°. Table 6 shows that for the three compounds containing uncharged tridentate ligands, ϕ_D is *ca.* −2 and DME = EMF = *ca.* 92°, due to greater repulsion associated with these metal–unidentate ligand bonds. Conversely in (1), which contains

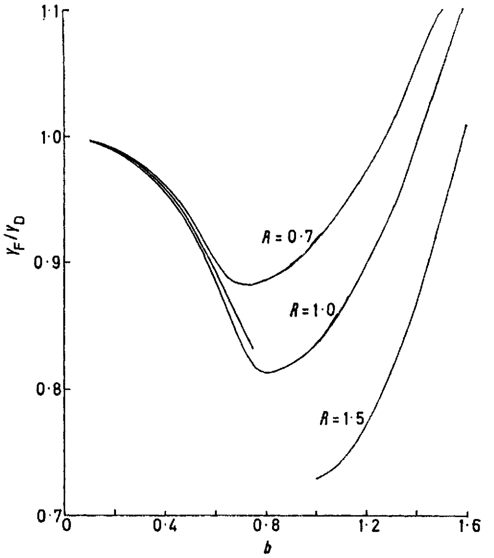


FIGURE 13 Ratio of the individual atom-repulsion coefficients for the unidentate ligands in *fac*-[M(tridentate)(unidentate)$_3$] as a function of normalized bite, b, and bond-length ratio, R ($n = 6$)

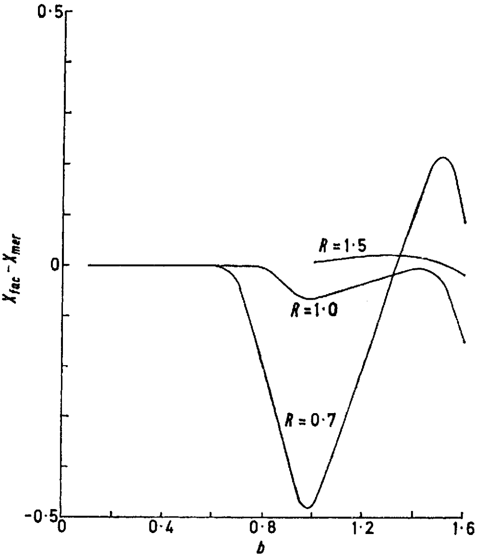


FIGURE 14 Difference in stability between *mer*- and *fac*-[M(tridentate)(unidentate)$_3$] as a function of normalized bite, b, and bond-length ratio, R, ($n = 6$). At $b = 2\frac{1}{2}$, $R = 1.0$, $X_{mer} = X_{fac} = 1.297$

the anionic tridentate purpurate ligand and uncharged water molecules, $\phi_D = 6$ and DME = EMF = 84°. This feature can be satisfactorily incorporated into the repulsion energy calculations by including the bond-length ratio $R = (M\text{–}U)/(M\text{–}T)$, where U = D, E, F, and T = A, B, C (Figure 10; similar curves are obtained for $n = 1$ and 12).

The second prediction from these calculations is that over this range of b the repulsion energy (Y_E) associated with the unidentate ligand E is less than that associated with the unidentate ligands D and F (Y_D) (Figure 11; similar curves are obtained for $n = 1$ and 12). This is in agreement with the shorter M–E bonds compared with the M–D and M–F bonds experimentally observed (Table 6).

fac-*Isomer*.—The averaged structural parameters are shown in Table 7. In all cases angle DMF is greater than angle DME, which is in accordance with the predictions for this range of b (Figure 12; similar curves are obtained for $n = 1$ and 12). Also as predicted, this difference is the greatest for the zinc complex containing a charged tridentate ligand and an uncharged unidentate ligand, and least for the molybdenum complex containing an uncharged tridentate ligand and doubly charged O^{2-} unidentate ligands. Similarly the average angle between the unidentate ligands is greater for this last complex. However, the predicted lower repulsion energy associated with the M–F bond (Figure 13; similar curves are obtained for $n = 1$ and 12) is not reflected in the relative bond lengths (Table 7).

TABLE 7

Structural parameters for compounds *fac*-[M(tridentate)(unidentate)$_3$] [a]

	b	θ_A	ϕ_A	ϕ_D	θ_D	ϕ_F	DME	DMF	MF/MD	Ref.
[Cr(dien)Cl$_3$]	1.33	64	52	124	119	118	92.2	95.5	1.01	*c*
[Zn{S(CH$_2$CO$_2$)$_2$}(H$_2$O)$_3$]·H$_2$O	1.28	70	51	126	123	116	85.1	98.1	1.00	*d*
[Cr(dien)(CO)$_3$]	1.26	66	49	131	120	126	81.7	85.9	1.00	*e*
[Mo(dien)(CO)$_3$]	1.21	70	47	131	120	124	82.4	86.7	1.01	*f*
[Mo(dien)O$_3$]	1.19	65	45	114	120	110	105.3	106.8	1.00	*g*

[a] dien = diethylenetriamine. [c] A. D. Fowlie, D. A. House, W. T. Robinson, and S. S. Rumball, *J. Chem. Soc.* (*A*), 1970, 803. [d] M. G. B. Drew, D. A. Rice, and C. W. Timewell, *J.C.S. Dalton*, 1975, 144. [e] F. A. Cotton and D. C. Richardson, *Inorg. Chem*, 1966, **5**, 1851. [f] F. A. Cotton and R. M. Wing, *Inorg. Chem.*, 1965, **4**, 314. [g] F. A. Cotton and R. C. Elder, *Inorg. Chem.*, 1964, **3**, 397.

Relative Stability of mer- *and* fac-*Isomers*.—For flexible tridentate ligands, and for $R \leqslant 1$ and $b < 1.3$, it is predicted that the *fac*-isomer will be more stable than the *mer*-isomer (Figure 14; similar curves are obtained for $n = 1$ and 12).

An additional important consideration is the design of the tridentate ligand, and how this limits the available range for the tridentate angle ABC. With the above choice of axes, this angle ABC is equal to θ_A (Figures 8 and 9). Flexible ligands such as dien can clearly be *mer* or *fac*. On the other hand complexes of ligands such as terpyridyl or purpurate can only be *mer*, and ligands such as $[S(CH_2COO)_2]^{2-}$ can only be *fac*.[9]

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