Structural Studies in Metal–Purpurate Complexes. Part 2.† Crystal Structures of Diaquabis(purpurato)-calcium and -cadmium Dihydrate. Stereochemistry of the [M(tridentate ligand)$_2$(unidentate ligand)$_2$] Complexes

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The crystal structures of the title compounds, $[ML_2(H_2O)_2]\cdot 2H_2O$ {$[L]^-$ = purpurate, M = calcium (1) or cadmium (2)}, have been determined at 295 K by *X*-ray diffraction and refined by least squares to *R* 0.055 (3 253 ' observed ' reflections) and 0.052 (3 351 ' observed ' reflections) respectively. Crystals of both are triclinic, space group $P\bar{1}$. For (1), a = 13.727(6), b = 10.300(3), c = 9.223(4) Å, α = 96.45(3), β = 99.39(3), γ = 104.29(3)°, Z = 2; for (2), a = 13.623(5), b = 10.190(5), c = 9.314(2) Å, α = 97.74(3), β = 98.96(3), γ = 104.78(4)°, Z = 2. In both compounds, the metal atom of the complex molecule is eight-co-ordinated by two tridentate purpurate ligands [(1): Ca–N, 2.630(3), 2.560(3); Ca–O, 2.400(3)—2.600(5); (2): Cd–N, 2.467(5), 2.383(5); Cd–O, 2.317(5)—2.630(4) Å], each twisted appreciably with respect to the median plane, and two pseudo-axial water molecules [Ca–O, 2.306(4), 2.428(3); Cd–O, 2.271(6), 2.451(5) Å; O–Ca–O, 169.1(1); O–Cd–O, 167.0(2)°]. The stereochemistry is intermediate between that of a square antiprism and a hexagonal bipyramid as predicted by repulsion calculations.

PREVIOUS work[1,2] has shown that basic calcium–' murexide ' {ammonium purpurate, $[NH_4][L]$ ($L^- = [C_8H_4N_5O_6]^-$)} solutions deposit a complex analysing as $[Ca][L]\cdot H_2O$ as a powder; the existence of 1 : 1 calcium–purpurate species in solution has also been demonstrated.[3] Attempts to prepare calcium–murexide derivatives yielded orange monoclinic crystals when ethanolic calcium nitrate was used and these were subsequently shown by analysis to be $[CaL(NO_3)]\cdot 5H_2O$. A 1 : 1 aqueous solution of calcium–murexide yielded small deep orange-red crystals of a complex (1) shown by analysis to be $[CaL_2]\cdot 4H_2O$ and subsequently structurally confirmed.

When set aside, a filtered cadmium–murexide aqueous solution yields small dark red crystals of a derivative (2) the analysis for which is consistent with its formulation as $[CdL_2]\cdot 4H_2O$; crystallographic examination showed that this derivative was isomorphous with (1). This paper describes the structure determinations of (1) and (2) by *X*-ray crystallography, together with an investigation of the stereochemistry of the [M(tridentate ligand)$_2$(unidentate)$_2$] system using a repulsion model. The structure of $[CaL(NO_3)]\cdot 5H_2O$ is described in Part 8 of the series.[4]

EXPERIMENTAL

Analyses.—(1) Found, calc. for $CaL_2\cdot 4H_2O$: C, 29.6, 29.82; H, 2.3, 2.50; N, 21.5, 21.74; Ca, 6.2, 6.22%.

(2) Found, calc. for $CdL_2\cdot 4H_2O$: C, 26.4, 26.81; H, 2.15, 2.25; N, 18.95, 19.54; Cd, 15.5, 15.68%.

Also: Found, calc. for $CaL(NO_3)\cdot 5H_2O$: C, 20.55, 20.97; H, 2.75, 3.08; N, 18.35, 18.34%.

Studies of the formation constants of Ca–L species and Cd–L species have been reported [3a,5,6] and rate constants for association as well.[5c,7]

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.[8]

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† Part 1 is the preceding paper.

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TABLE 1

Atomic fractional cell co-ordinates [(*x*,*y*,*z*); H, × 10^3; Ca, Cd, × 10^5; others × 10^4) and thermal parameters (U_{ij}, × 10^3 Å^2) with least-squares estimated standard deviations in parentheses. Values for (2) (the cadmium derivative) are given immediately below those for (1) (the calcium derivative)

Atom	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ca (1)	76 092(6)	30 768(8)	30 287(10)	26.2(4)	8.1(4)	29.2(5)	1.4(3)	10.5(4)	−1.4(3)
Cd (2)	75 973(4)	31 227(5)	30 491(6)	24.2(2)	13.1(2)	29.0(3)	2.2(2)	10.6(2)	1.5(2)
Purpurate ligand ' a '									
N(0)	8 908(2)	5 497(3)	3 421(4)	20(2)	10(2)	26(2)	3(1)	6(1)	−3(1)
	8 868(4)	5 403(5)	3 375(6)	15(3)	19(3)	19(3)	4(2)	1(2)	0(2)
C(11)	9 702(3)	5 417(4)	2 784(4)	22(2)	12(2)	22(2)	3(2)	7(2)	−1(2)
	9 679)5)	5 314(6)	2 777(7)	24(4)	16(3)	24(4)	10(3)	10(3)	3(3)
C(12)	9 932(3)	4 110(4)	2 823(4)	24(2)	13(2)	24(2)	4(2)	6(2)	−3(2)
	9 919(5)	3 995(7)	2 825(7)	30(4)	22(4)	16(4)	4(3)	10(3)	−2(3)
O(12)	9 454(2)	3 198(3)	3 395(3)	33(2)	13(1)	37(2)	6(1)	18(1)	8(1)
	9 437(4)	3 088(4)	3 348(5)	45(3)	12(2)	40(3)	11(2)	25(3)	9(2)
N(13)	10 751(3)	3 930(3)	2 215(4)	28(2)	12(2)	41(2)	9(1)	18(2)	5(2)
	10 758(4)	3 848(6)	2 256(7)	37(4)	19(3)	39(4)	9(3)	18(3)	5(3)
H(13)	1 084(3)	317(5)	219(5)	38(13)					
	1 082(5)	322(7)	227(8)	41(21)					
C(14)	11 292(3)	4 808(4)	1 454(5)	26(2)	13(2)	36(3)	6(2)	13(2)	0(2)
	11 301(5)	4 735(7)	1 487(8)	25(4)	18(3)	28(4)	6(3)	7(3)	0(3)
O(14)	11 987(2)	4 545(3)	0 882(4)	38(2)	21(2)	54(2)	12(1)	30(2)	7(1)
	12 010(4)	4 490(5)	0 922(6)	38(3)	24(3)	54(4)	9(2)	27(3)	4(2)
N(15)	11 001(3)	5 965(3)	1 328(4)	26(2)	12(2)	35(2)	5(1)	18(2)	6(1)
	10 994(4)	5 886(5)	1 349(6)	29(3)	18(3)	34(4)	6(3)	18(3)	10(3)
Atom	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
H(15)	1 133(3)	649(4)	079(5)	35(12)					
	1 132(4)	648(6)	087(6)	12(15)					
C(16)	10 210(3)	6 332(4)	1 899(5)	20(2)	14(2)	29(2)	4(2)	5(2)	−2(2)
	10 186(5)	6 241(6)	1 908(7)	24(4)	16(3)	21(4)	6(3)	4(3)	1(3)
O(16)	9 946(2)	7 328(3)	1 522(3)	35(2)	16(1)	43(2)	10(1)	17(1)	10(1)
	9 919(4)	7 226(5)	1 535(6)	34(3)	24(3)	44(3)	11(2)	20(3)	15(2)
C(21)	8 576(3)	6 526(4)	3 899(5)	23(2)	7(2)	30(2)	1(2)	7(2)	−5(2)
	8 546(5)	6 466(6)	3 850(7)	21(3)	14(3)	20(4)	3(3)	9(3)	1(3)
C(22)	7 590(3)	6 112(4)	4 366(5)	27(2)	14(2)	30(2)	0(2)	12(2)	−6(2)
	7 526(5)	6 083(7)	4 276(8)	27(4)	17(3)	34(4)	6(3)	10(3)	−4(3)
O(22)	7 116(2)	4 900(3)	4 306(4)	34(2)	12(1)	55(2)	0(1)	25(2)	−2(1)
	7 026(4)	4 868(4)	4 199(6)	32(3)	16(2)	52(4)	1(2)	22(3)	2(2)
N(23)	7 173(3)	7 100(3)	4 860(5)	31(2)	13(2)	66(3)	3(2)	29(2)	−3(2)
	7 146(4)	7 123(6)	4 775(7)	20(3)	21(3)	58(4)	4(3)	22(3)	−1(3)
H(23)	658(3)	687(4)	519(5)	29(12)					
	653(5)	692(6)	478(7)	28(18)					
C(24)	7 628(4)	8 474(4)	5 022(6)	36(3)	11(2)	59(3)	4(2)	21(2)	−6(2)
	7 631(6)	8 506(7)	4 956(9)	42(5)	17(4)	52(5)	10(3)	21(4)	−3(3)
O(24)	7 180(3)	9 298(3)	5 435(5)	50(2)	19(2)	113(3)	12(2)	47(2)	−8(2)
	7 199(4)	9 372(5)	5 318(7)	45(4)	27(3)	92(5)	13(3)	41(3)	2(3)
N(25)	8 582(3)	8 827(3)	4 733(4)	30(2)	7(2)	49(2)	1(1)	18(2)	−5(2)
	8 617(4)	8 839(5)	4 706(7)	25(3)	13(3)	39(4)	−1(2)	9(3)	−6(3)
H(25)	896(4)	963(5)	500(6)	63(17)					
	907(5)	976(7)	509(7)	35(20)					
C(26)	9 137(3)	7 971(4)	4 255(5)	25(2)	11(2)	27(2)	4(2)	9(2)	1(2)
	9 151(5)	7 933(7)	4 235(8)	25(4)	18(3)	27(4)	5(3)	6(3)	1(3)
O(26)	10 047(2)	8 424(3)	4 253(3)	24(2)	12(1)	42(2)	0(1)	11(1)	−2(1)
	10 074(3)	8 360(4)	4 251(5)	23(3)	18(2)	41(3)	6(2)	10(2)	5(2)
Purpurate ligand ' b '									
Atom	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N(0)	6 804(2)	0 626(3)	1 722(4)	23(2)	13(2)	29(2)	4(1)	9(2)	0(1)
	6 849(4)	0 792(5)	1 805(6)	21(3)	14(3)	23(3)	3(2)	8(2)	3(2)
C(11)	7 396(3)	0 077(4)	0 951(3)	22(2)	12(2)	30(2)	5(2)	10(2)	−1(2)
	7 440(5)	0 233(6)	1 014(7)	15(3)	17(3)	29(4)	8(3)	6(3)	6(3)
C(12)	8 124(3)	1 051(4)	0 384(5)	24(2)	15(2)	29(2)	6(2)	9(2)	0(2)
	8 154(5)	1 216(7)	0 390(7)	21(4)	21(3)	25(4)	3(3)	9(3)	−2(3)
O(12)	8 218(2)	2 294(3)	0 635(3)	40(2)	11(1)	37(2)	7(1)	20(1)	0(1)
	8 229(4)	2 459(4)	0 595(5)	37(3)	18(2)	39(3)	7(2)	19(2)	4(2)
N(13)	8 687(3)	0 549(3)	−0 534(4)	30(2)	13(2)	37(2)	8(1)	19(2)	3(2)
	8 703(4)	0 677(5)	−0 523(7)	33(3)	18(3)	36(4)	8(3)	19(3)	6(3)
H(13)	929(3)	125(5)	−093(5)	41(13)					
	926(7)	136(9)	−070(9)	79(29)					
C(14)	8 646(3)	−0 804(4)	−0 864(4)	29(2)	17(2)	40(3)	10(2)	15(2)	5(2)
	8 678(5)	−0 684(7)	−0 829(8)	32(4)	22(4)	37(5)	8(3)	17(4)	9(3)
O(14)	9 132(3)	−1 189(3)	−1 748(4)	54(2)	21(2)	55(2)	19(2)	38(2)	8(2)
	9 137(4)	−1 105(5)	−1 737(6)	62(4)	36(3)	56(4)	27(3)	45(3)	15(3)
N(15)	8 042(3)	−1 668(3)	−0 153(4)	39(2)	13(2)	52(3)	11(2)	28(2)	7(2)
	8 083(5)	−1 543(5)	−0 088(7)	44(4)	15(3)	57(4)	16(3)	32(3)	16(3)
H(15)	814(4)	−246(5)	−019(5)	49(15)					
	819(5)	−235(6)	−015(7)	31(19)					

TABLE 1 (*Continued*)

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(16)	7 445(3)	−1 323(4)	0 824(5)	24(2)	13(2)	36(3)	4(2)	9(2)	2(2)
	7 477(5)	−1 188(7)	0 878(8)	21(4)	25(4)	29(4)	4(3)	12(3)	5(3)
O(16)	7 051(2)	−2 157(3)	1 548(4)	41(2)	17(2)	46(2)	7(1)	21(2)	10(1)
	7 076(4)	−2 025(5)	1 584(6)	39(3)	22(3)	47(3)	8(2)	22(3)	16(2)
C(21)	5 894(3)	−0 044(4)	1 926(5)	23(2)	12(2)	27(2)	2(2)	8(2)	−1(2)
	5 935(5)	0 099(6)	1 995(7)	24(4)	19(3)	20(4)	8(3)	8(3)	5(3)
C(22)	5 448(3)	0 731(4)	2 922(5)	24(2)	19(2)	27(2)	3(2)	8(2)	2(2)
	5 472(5)	0 814(7)	3 026(7)	24(4)	21(4)	24(4)	4(3)	6(3)	4(3)
O(22)	5 902(2)	1 895(3)	3 590(3)	29(2)	14(1)	46(2)	0(1)	14(1)	−9(1)
	5 909(4)	1 995(5)	3 747(6)	27(3)	22(3)	42(3)	−2(2)	13(2)	−8(2)
N(23)	4 493(3)	0 086(3)	3 153(4)	23(2)	18(2)	32(2)	1(1)	13(2)	−6(2)
	4 513(4)	0 119(6)	3 214(6)	26(3)	23(3)	33(4)	6(3)	18(3)	−4(3)
H(23)	416(3)	051(4)	367(5)	30(12)					
	419(4)	045(6)	381(6)	15(16)					
C(24)	3 884(3)	−1 156(4)	2 380(5)	22(2)	25(2)	25(2)	1(2)	7(2)	−1(2)
	3 913(6)	−1 160(7)	2 397(8)	28(4)	31(4)	29(4)	10(3)	10(3)	3(3)
O(24)	3 052(2)	−1 668(3)	2 608(4)	30(2)	37(2)	48(2)	−10(2)	21(2)	−10(2)
	3 076(4)	−1 729(5)	2 623(6)	29(3)	44(3)	45(4)	−11(3)	22(3)	−8(3)
N(25)	4 286(3)	−1 739(3)	1 299(4)	24(2)	20(2)	34(2)	−6(2)	10(2)	−10(2)
	4 329(4)	−1 681(5)	1 285(6)	21(3)	23(3)	24(3)	−5(2)	5(3)	−10(3)
H(25)	389(4)	−232(5)	059(5)	51(15)					
	393(5)	−234(7)	062(7)	36(20)					
C(26)	5 227(3)	−1 262(4)	0 937(5)	25(2)	15(2)	29(2)	5(2)	8(2)	1(2)
	5 275(5)	−1 136(7)	0 955(7)	26(4)	24(4)	18(4)	4(3)	9(3)	3(3)
O(26)	5 427(2)	−1 783(3)	−0 193(3)	32(2)	28(2)	34(2)	3(1)	15(1)	−11(1)
	5 476(4)	−1 612(5)	−0 201(5)	31(3)	33(3)	27(3)	3(2)	11(2)	−6(2)
The co-ordinated water molecules.									
O(1)	6 871(2)	4 040(3)	0 974(3)	31(2)	21(2)	36(2)	4(1)	13(1)	1(1)
	6 834(4)	4 017(5)	0 966(5)	26(2)	33(3)	37(3)	7(2)	12(2)	−1(2)
H(1α)	639(4)	447(5)	122(6)	55(16)					
	638(4)	430(5)	118(6)	6(14)					
H(1β)	729(4)	446(6)	051(7)	79(20)					
	741(8)	464(11)	031(12)	121(40)					
O(2)	8 095(2)	2 308(3)	5 215(4)	33(2)	47(2)	45(2)	8(2)	19(2)	21(2)
	8 093(4)	2 548(6)	5 266(6)	33(3)	53(4)	40(3)	10(3)	18(3)	21(3)
H(2α)	776(4)	195(5)	579(5)	51(15)					
	781(7)	216(9)	563(10)	81(30)					
Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
H(2β)	872(4)	212(6)	557(7)	80(20)					
	864(8)	230(11)	528(12)	122(41)					
The lattice water molecules									
O(3)	5 511(3)	5 501(4)	1 449(5)	60(3)	52(3)	104(4)	21(2)	19(3)	22(2)
	5 501(5)	5 572(7)	1 427(8)	75(5)	71(5)	90(6)	34(4)	25(4)	26(4)
H(3) (1)	492(6)	478(8)	138(8)	114(25)					
O(4) *	4 448(14)	3 658(13)	3 469(28)	158(15)	48(8)	341(29)	37(9)	217(19)	48(12)
	4 074(24)	3 532(32)	2 733(35)	91(25)	85(23)	91(25)	−53(18)	82(21)	−52(19)
O(4′) *	5 059(7)	3 634(9)	5 504(15)	117(8)	73(6)	251(14)	33(5)	150(9)	23(7)
	5 063(7)	3 738(9)	5 617(12)	65(6)	60(6)	142(9)	17(5)	77(6)	5(6)

* Populations: O(4), 0.38, 0.23; O(4′), 0.62, 0.77.

Structure-factor amplitudes are deposited as a Supplementary Publication.*

Crystallographic Data and Procedure.—Compound (1). $C_{16}H_{16}CaN_{10}O_{16}$, $M = 644.4$, Triclinic, space group $P\bar{1}$ (C_i^1, No. 2), $a = 13.727(6)$, $b = 10.300(3)$, $c = 9.223(4)$ Å, $\alpha = 96.45(3)$, $\beta = 99.39(3)$, $\gamma = 104.29(3)°$, $U = 1\,230.8(9)$ Å^3, $D_m = 1.76(1)$ g cm^{-3}, $Z = 2$, $D_c = 1.73$ g cm^{-3}, $F(000) = 660$, crystal size $0.10 \times 0.25 \times 0.25$ mm (prism), $\mu(\text{Mo-}K_\alpha) = 2.99$ cm^{-1} (data corrected for absorption), data range $2\theta < 50°$ yielding 4 340 independent reflections (3 253 ' observed '), final $R = 0.055$, $R' = 0.064$ ($n = 5$).

The structure was refined using 9 × 9 block-diagonal least squares, using the solution of (2) to initiate the procedure; in the final refinement stages the parameters of the metal atom and the atoms in its immediate environment were refined as a single block, the atom parameters of each of the purpurate ligand ring segments being refined similarly. Non-hydrogen atom thermal motion was refined anisotropically. One of the lattice water oxygen atoms O(3) was found to be disordered over two sites and the relative populations of these were determined from difference maps and constrained during refinement; in view of the inequivalence of these sites there appeared to be little point in attempting refinement in space group $P1$ and this was not attempted as the remainder of the structure appeared well-behaved. With the exception of certain lattice water hydrogen atoms in the vicinity of the disorder, all hydrogen atoms were located and refined with isotropic thermal parameters. Certain intense low-angle reflections suffered badly from extinction, *viz.* {001}, {010}, {10$\bar{1}$}, {100}, {1$\bar{1}\bar{1}$}, {110}, {2$\bar{1}$0}, {200}, and {21$\bar{1}$}, and were suppressed during refinement.

Compound (2). $C_{16}H_{16}CdN_{10}O_{16}$, $M = 716.8$, Triclinic, space group $P\bar{1}$ (C_i^1, No. 2), $a = 13.623(5)$, $b = 10.190(5)$, $c = 9.314(2)$ Å, $\alpha = 97.74(3)$, $\beta = 98.96(3)$, $\gamma = 104.78(4)°$, $U = 1\,214.2(8)$ Å^3, $D_m = 1.96(1)$ g cm^{-3}, $Z = 2$, $D_c = 1.96$ g cm^{-3}, $F(000) = 716$, crystal size $0.08 \times 0.15 \times 0.17$ mm (prism), $\mu(\text{Mo-}K_\alpha) = 8.96$ cm^{-1} (data corrected for absorption), data range $2\theta < 50°$ yielding 4 312 independent

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* Supplementary Publication No. SUP 21989 (29 pp., 1 microfiche). For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1976, Index issue.

TABLE 2

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

(*a*) The purpurate geometry; as in the previous paper in this series, the geometries of the two halves of the barbiturate rings are tabulated in parallel columns. The two components within each entry are for the two barbiturate segments *n* = 1 or 2 respectively of the purpurate species. Values for compound (2) (the cadmium derivative) are given below the corresponding values for compound (1) (the calcium derivative)

Ligand	‘ a ’	‘ b ’
Segment *n*	1 2	1 2
N(0)–C(*n*1)	1.335(6), 1.313(6)	1.345(6), 1.324(5)
	1.329(9), 1.317(9)	1.350(9), 1.317(8)
C(*n*1)–C(*n*2)	1.459(6), 1.465(6)	1.440(6), 1.454(7)
	1.467(10), 1.476(10)	1.457(9), 1.444(10)
C(*n*2)–O(*n*2)	1.229(5), 1.248(5)	1.246(5), 1.243(4)
	1.198(8), 1.238(8)	1.231(8), 1.243(7)
C(*n*2)–N(*n*3)	1.379(6), 1.356(6)	1.375(6), 1.378(6)
	1.366(10), 1.352(10)	1.366(10), 1.368(9)
N(*n*3)–H(*n*3)	0.81(5), 0.90(4)	1.09(5), 0.86(5)
	0.67(8), 0.81(6)	0.94(8), 0.85(6)
N(*n*3)–C(*n*4)	1.358(6), 1.379(5)	1.378(6), 1.385(5)
	1.369(9), 1.370(9)	1.368(10), 1.393(10)
C(*n*4)–O(*n*4)	1.233(6), 1.277(6)	1.227(6), 1.197(5)
	1.232(9), 1.219(9)	1.222(9), 1.205(9)
C(11)–N(0)–C(21)	132.6(3)	124.5(3)
	132.0(5)	123.8(5)
C(*n*2)–C(*n*1)–C(*n*6)	118.6(4), 117.5(4)	119.3(4), 119.0(4)
	119.4(6), 117.6(6)	119.9(6), 118.7(6)
N(0)–C(*n*1)–C(*n*2)	112.2(3), 113.3(3)	114.0(4), 114.2(3)
	113.1(6), 114.1(5)	114.5(6), 116.1(5)
C(*n*1)–C(*n*2)–O(*n*2)	123.6(4), 122.9(4)	122.6(4), 123.2(4)
	123.7(7), 122.5(7)	122.8(7), 123.3(6)
O(*n*2)–C(*n*2)–N(*n*3)	119.5(4), 119.1(4)	120.2(4), 120.3(4)
	120.2(7), 120.1(7)	120.7(6), 119.9(7)
C(*n*1)–C(*n*2)–N(*n*3)	116.9(4), 118.0(3)	117.1(4), 116.5(3)
	116.1(6), 117.3(5)	116.4(6), 116.8(5)
C(*n*2)–N(*n*3)–H(*n*3)	115(3), 119(3)	120(3), 121(3)
	111(6), 116(5)	112(6), 123(3)
H(*n*3)–N(*n*3)–C(*n*4)	119(3), 116(3)	115(3), 112(2)
	122(7), 116(5)	120(6), 111(3)
C(*n*2)–N(*n*3)–C(*n*4)	125.4(4), 124.9(4)	124.5(4), 125.1(4)
	125.7(6), 126.0(7)	125.5(6), 125.3(6)
N(*n*3)–C(*n*4)–O(*n*4)	121.5(4), 120.5(4)	121.0(4), 122.7(4)
	122.1(7), 121.4(7)	121.8(7), 122.3(7)
N(*n*3)–C(*n*4)–N(*n*5)	116.0(4), 115.9(4)	116.2(4), 115.1(4)
	116.0(7), 115.8(7)	115.8(7), 114.7(6)
M–N(0)–C(*n*1)	109.4(2), 116.4(3)	115.7(2), 119.6(3)
	111.3(4), 115.3(4)	116.4(4), 119.7(4)
M–O(*n*2)–C(*n*2)	112.2(3), 121.9(3)	114.1(3), 119.0(3)
	110.0(3), 118.9(5)	108.9(5), 113.6(5)

	‘ a ’	‘ b ’
	1 2	1 2
C(*n*1)–C(*n*6)	1.441(6), 1.469(5)	1.452(6), 1.465(5)
	1.440(10), 1.476(8)	1.452(10), 1.467(8)
C(*n*6)–O(*n*6)	1.237(5), 1.221(5)	1.222(6), 1.221(6)
	1.225(10), 1.218(8)	1.218(9), 1.221(9)
C(*n*6)–N(*n*5)	1.394(6), 1.381(6)	1.386(7), 1.373(6)
	1.394(10), 1.381(10)	1.385(11), 1.366(9)
N(*n*5)–H(*n*5)	0.87(5), 0.84(5)	0.85(5), 0.85(4)
	0.87(6), 0.96(6)	0.87(7), 0.86(6)
N(*n*5)–C(*n*4)	1.358(6), 1.348(6)	1.361(6), 1.368(6)
	1.357(9), 1.364(9)	1.369(9), 1.365(10)
O(16) · · · O(26)	2.609(5)	2.663(5)
	2.589(7)	2.687(7)
N(0)–C(*n*1)–C(*n*6)	128.2(4), 128.2(4)	126.2(4), 124.2(4)
	126.5(7), 127.4(6)	125.3(6), 122.9(6)
C(*n*1)–C(*n*6)–O(*n*6)	125.2(4), 124.8(4)	125.3(4), 124.8(4)
	125.9(7), 124.8(7)	125.7(7), 125.0(6)
O(*n*6)–C(*n*6)–N(*n*5)	118.9(4), 119.8(4)	119.8(4), 120.4(3)
	118.5(7), 119.7(5)	119.8(7), 119.7(5)
C(*n*1)–C(*n*6)–N(*n*5)	115.7(4), 115.1(4)	114.9(4), 114.6(4)
	115.4(6), 115.4(6)	114.4(6), 115.0(6)
C(*n*6)–N(*n*5)–H(*n*5)	118(3), 111(5)	118(4), 110(4)
	115(4), 112(4)	119(5), 113(5)
H(*n*5)–N(*n*5)–C(*n*4)	115(3), 121(4)	115(4), 120(4)
	119(4), 120(4)	114(5), 118(5)
C(*n*6)–N(*n*5)–C(*n*4)	126.5(4), 127.4(3)	126.4(4), 127.7(3)
	126.4(6), 126.8(5)	126.9(6) 127.6(5)
N(*n*5)–C(*n*4)–O(*n*4)	122.5(4), 123.6(4)	122.8(4) 122.1(4)
	121.8(7), 122.8(6)	122.4(7) 123.0(6)

(*b*) The metal environment geometry; the two components with each entry are for compounds (1) and (2) respectively

M–O(1)	2.428(3), 2.451(5)	M–O(2)	2.306(4), 2.271(6)
M–N(0a)	2.630(3), 2.467(5)	M–N(0b)	2.560(3), 2.383(5)
M–O(12a)	2.469(3), 2.488(5)	M–O(12b)	2.600(4), 2.630(5)
M–O(22a)	2.400(3), 2.317(5)	M–O(22b)	2.524(3), 2.521(5)
O(1)–M–O(2)	169.1(1), 167.0(2)	N(a)–M–O(12a)	62.6(1), 65.0(2)
O(1)–M–N(a)	78.5(1), 79.7(2)	N(a)–M–O(12b)	92.0(1), 87.1(2)
O(1)–M–N(b)	93.7(1), 92.2(2)	N(a)–M–O(22a)	63.9(1), 68.2(2)
O(1)–M–O(12a)	118.3(1), 119.6(2)	N(a)–M–O(22b)	141.0(1), 140.7(2)
O(1)–M–O(12b)	70.6(1), 66.8(2)	N(b)–M–O(12a)	101.3(1), 96.8(2)
O(1)–M–O(22a)	78.1(1), 77.0(2)	N(b)–M–O(12b)	62.2(1), 64.7(2)
O(1)–M–O(22b)	94.7(1), 96.1(2)	N(b)–M–O(22a)	139.2(1), 136.9(2)
O(2)–M–N(a)	102.2(1), 99.4(2)	N(b)–M–O(22b)	63.7(1), 67.0(2)
O(2)–M–N(b)	90.1(1), 94.4(2)	O(12a)–M–O(12b)	65.4(1), 64.1(2)
O(2)–M–O(12a)	70.8(1), 70.7(2)	O(12a)–M–O(22a)	117.9(1), 125.0(1)
O(2)–M–O(12b)	120.1(1), 126.2(2)	O(12a)–M–O(22b)	145.3(1), 141.9(2)
O(2)–M–O(22a)	92.4(1), 90.5(2)	O(12b)–M–O(22a)	143.8(1), 139.3(2)
O(2)–M–O(22b)	77.8(1), 76.3(2)	O(12b)–M–O(22b)	122.3(1), 127.5(1)
N(a)–M–N(b)	154.0(1), 151.4(2)	O(22a)–M–O(22b)	77.1(1), 72.8(2)

(*c*) The co-ordinated water-molecule geometry; values given are the O–H(α,β) distances and the angles H(α)–O–H(β), M–O–H(α), M–O–H(β). Values for compound (2) are given below the corresponding values for compound (1)

Molecule 1	0.93(6), 0.84(6), 116(6), 112(2), 115(4)
	0.79(6), 1.18(11), 120(7), 109(4), 117(5)
Molecule 2	0.82(5), 0.94(6), 99(5), 132(4), 128(4)
	0.64(9), 0.85(13), 107(12), 129(8), 110(8)

{For non-co-ordinated molecule 3, the only experimentally determined geometry is *r*[O–H(α)] = 0.94(6) in (1). Molecule 4, being disordered, is poorly defined}

TABLE 2 (*Continued*)

(*d*) Interspecies hydrogen-bonding interactions (O ··· H, <2.5 Å); the angle subtended at the hydrogen is given in parentheses. Values for compound (2) are given below the corresponding values for compound (1)

(*i*) Ligand hydrogen-bonding interactions

H(13a) ··· O(14b^{I})	2.05(5) [169(4)]	H(15a) ··· O(12b^{II})	1.98(5) [168(4)]
	2.16(7) [166(7)]		1.93(6) [166(5)]
H(23a) ··· O(4^{III})	2.04(5) [162(4)]	H(23a) ··· O(4^{III})	2.15(4) [143(4)]
			2.06(6) [171(6)]
H(25a) ··· O(26a^{IV})	2.10(5) [176(5)]	H(13b) ··· O(16a^{II})	1.78(4) [165(4)]
	1.93(6) [176(6)]		1.93(9) [163(8)]
H(15b) ··· O(14a^{I})	2.13(5) [162(4)]	H(23b) ··· O(24a^{III})	2.18(5) [154(3)]
	2.13(6) [159(5)]		2.21(6) [155(4)]
H(25b) ··· O(1^{V})	2.08(4) [167(5)]		
	2.03(6) [172(7)]		

(*ii*) Water-molecule hydrogen-bonding interactions

H(1α) ··· O(3)	1.81(6) [169(5)]	H(1β) ··· O(14a^{II})	1.97(6) [168(6)]
	1.99(6) [160(5)]		1.71(11) [167(9)]
H(2α) ··· O(24b^{VI})	2.00(5) [162(5)]	H(2β) ··· O(26a^{VII})	1.90(7) [165(5)]
	2.20(10) [156(10)]		2.03(12) [168(11)]
H(3) ··· O(4)	2.45(8) [125(5)]		

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

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

reflections (3 351 ' observed '), final $R = 0.052$, $R' = 0.053$ ($n = 2$). Reflections suppressed because of extinction: {100}, {11$\bar{1}$}, {2$\bar{1}$0}, and {20$\bar{1}$}. Refinement as for (1); solution by the heavy-atom method.

For both (1) and (2), the ligand atom numbering is suffixed ' a ' or ' b ' where necessary to denote which ligand is referred to. Fractional cell co-ordinates and thermal parameters are in Table 1.

DISCUSSION

The unit cells of (1) and (2) are isostructural (Figure 1); the asymmetric unit comprises a complex molecule $[ML_2]\cdot 2H_2O$ (in which the metal atom is eight-co-ordinated by two tridentate L ligands in an approximate equatorial plane, and a pair of axial water molecules) with a pair of lattice water molecules; one of the lattice water molecules [O(2)] lies near to the centre of symmetry at $(\frac{1}{2},\frac{1}{2},0)$ and is only some 2.760(6) (1), 2.740(9) Å (2) from its inversion image. The other water is disordered over two sites 2.72(2) (1), 2.77(3) Å (2) apart. Both waters occupy a tunnel running through the centre of the lattice and the cell parallel to c. As in other structures in this series, there is considerable hydrogen bonding in the lattice and this is summarized in Table 2. The formation of isostructural complexes of this type between two such dissimilar metals is rather surprising, although their ionic radii are almost identical. The structure is unlike that of calcium dipicolinate $[\{Ca(dipic)(H_2O)_3\}_2]$ which is stoicheiometrically quite different as a consequence of the dinegative anion, and is dimeric, one of the ligand carboxylate oxygens bridging the calciums; the latter have essentially a [Ca(tridentate)(unidentate)$_5$] co-ordination type and are reasonably approximated by the dodecahedral stereochemistry.[9] In (1) and (2), the metal-atom stereochemistry (Figure 2) is neither of the usual eight-co-ordinate forms (square antiprism or dodecahedron) but some other type; this is presumably a result of the incorporation of two tridentate ligands into the metal atom co-ordination sphere and a generalized electron-repulsion treatment for the general case of the [M(tridentate)$_2$(unidentate)$_2$] system is given below.

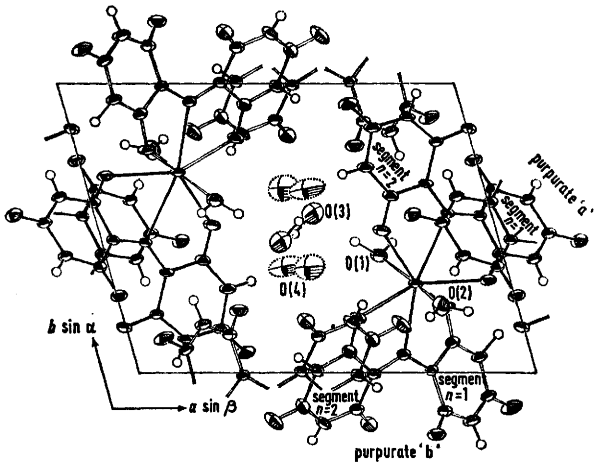

FIGURE 1 Unit-cell contents projected down c, showing 50% thermal ellipsoids of the calcium derivative (1). Bonds of ligand (a) have been shown as solid for clarity. The water molecule shown in broken outline is disordered. Hydrogen-atom radii have been arbitrarily set at 0.1 Å. Labelling of the ligand segments and water-molecule oxygen atoms is shown

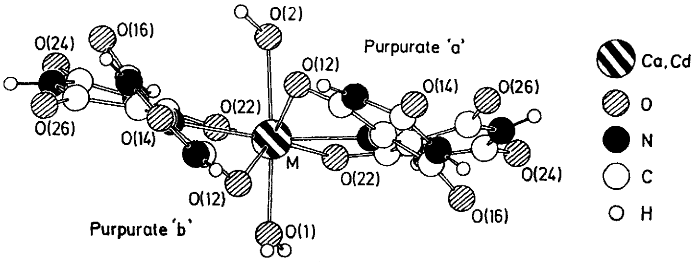

FIGURE 2 View of the molecule $ML_2\cdot 2H_2O$, projected normal to the H_2O–M–OH_2 and N(0)–M–N(0) axes. Labelling of the oxygen atoms is shown, that of the remainder being omitted for clarity

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[9] G. Strahs and R. E. Dickerson, *Acta Cryst.*, 1968, **B24**, 571.

General aspects of the ligand geometry have been discussed in the preceding paper.[8] Within both (1) and (2), we find that the geometries of the two ligands differ significantly and non-trivially in respect of their co-ordination about the metal, one of the ligands (' a ') lying closer to the metal than the other (' b '). This is achieved by contraction of the M–O(12,22) distances in the former relative to the latter, although M–N(0) lengthens slightly. Although the M–O(n2) distances cover a wide range in both (1) and (2), we find that their means are similar [$\langle$M–O(n2)$\rangle$, 2.50 (1), 2.49 Å (2)]; this is not true however of the mean M–N(0) distances where that of (2) is clearly shorter than that of (1) [$\langle$M–N(0)$\rangle$, 2.60 (1), 2.43 Å (2)], presumably a consequence of the class B metal character of cadmium.

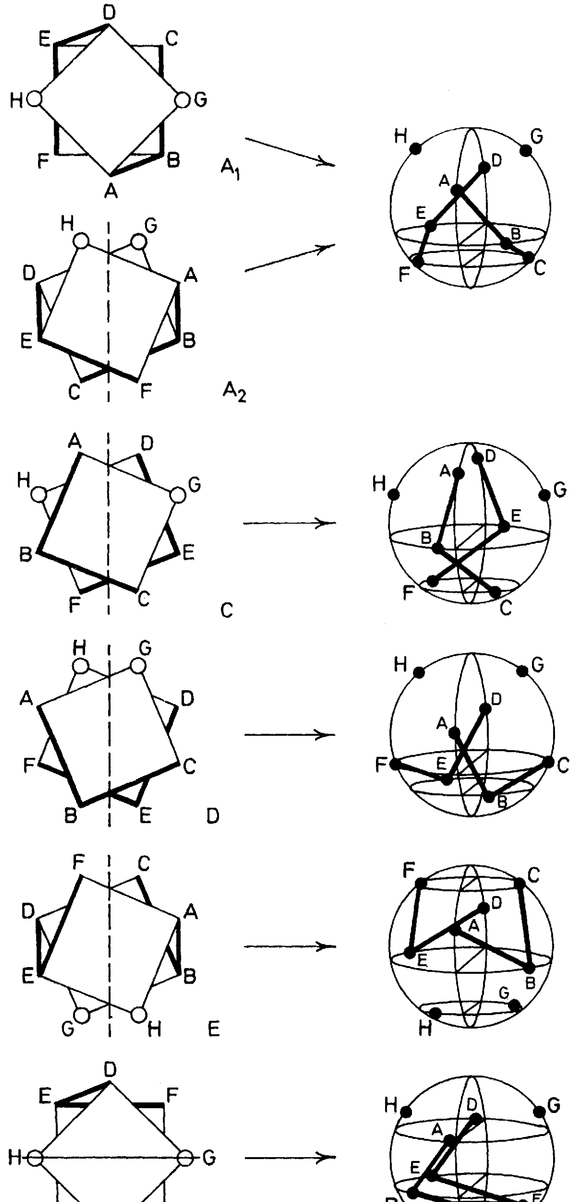

FIGURE 3 Stereochemistries for [M(tridentate)$_2$(unidentate)$_2$]

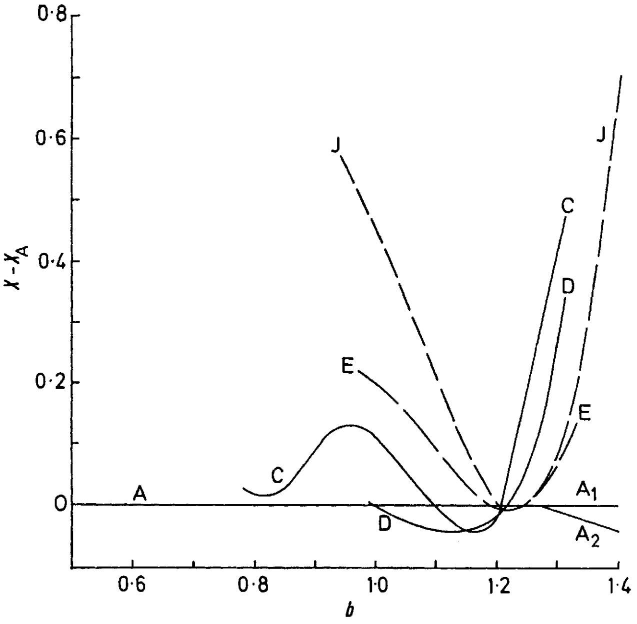

FIGURE 4 Repulsion-energy coefficients of isomers of [M(tridentate)$_2$(unidentate)$_2$] relative to that of isomer A and A$_1$; $n = 6$. $X_A = 2.430$ at $b = 0.6$, 5.052 at $b = 1.4$

Stereochemistry of [*M*(*tridentate ligand*)$_2$(*unidentate ligand*)$_2$] *Complexes*.—The normal procedure[10] for the calculation of the stereochemistry of complexes, by the minimization of the total repulsion energy, must be modified for complexes containing tridentate ligands.[11] The tridentate ligand, incorporating the donor atoms ABC,

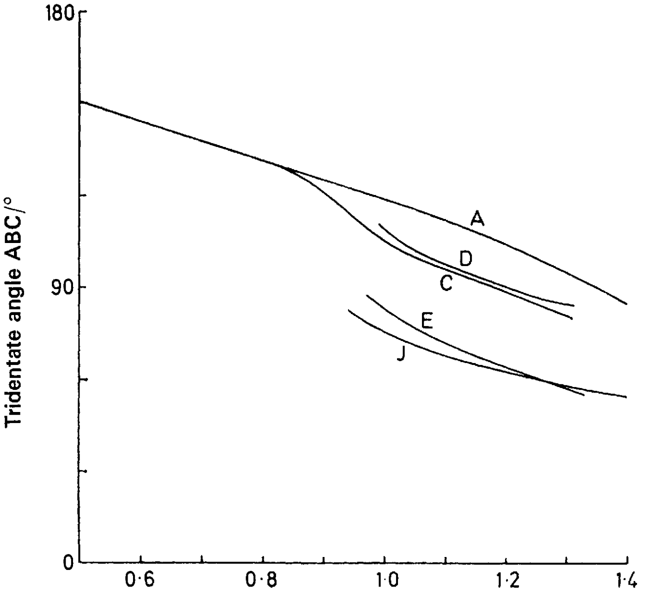

FIGURE 5 Tridentate angle ABC (°) as a function of normalised bite b for isomers of [M(tridentate)$_2$(unidentate)$_2$], $n = 6$

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[10] D. L.Kepert, *J.C..S Dalton*, 1975, 963, and refs. therein.

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

can either be considered to be freely flexible and hinged about the donor atom B with repulsions between donor atoms A and C included in the calculations, or can be considered to be completely rigid with constant repulsion between A and C, as well as between A and B, and B and C. The calculations will generate the same stereochemistry using either limiting assumption if the value of the tridentate angle ABC obtained for the flexible tridentate case is the same as that used in the rigid tridentate case. For structurally complicated molecules, as in the present case, it is most convenient to calculate the stereochemistry assuming a flexible geometry, as this will generate a sufficiently large range of tridentate ligand geometries. These results can then be modified by varying the tridentate angle assuming a rigid ligand.

TABLE 3

Least-squares planes, calculated through the C(*n*1,*n*2,*n*4,*n*6),N(*n*3,*n*5) 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°

Compound	(1)				(2)			
Segment (*n*a,b)	1a	1b	2a	2b	1a	1b	2a	2b
10^4p	4 334	2 859	6 097	4 093	4 167	2 631	6 214	4 399
10^4q	4 435	−0 448	1 504	−4 870	4 738	−0 454	1 887	−4 948
10^4r	7 846	9 572	7 783	7 716	7 758	9 637	7 604	7 495
s	8.615	4.909	6.852	4.483	8.373	4.553	6.958	4.640
σ	0.04	0.05	0.06	0.06	0.04	0.05	0.04	0.06
χ^2	224	407	626	915	140	203	200	399
C(*n*1)	0.06	0.07	0.09	0.09	0.06	0.07	0.07	0.09
C(*n*2)	−0.05	−0.04	−0.05	−0.07	−0.05	−0.03	−0.04	−0.06
N(*n*3)	0.01	−0.02	−0.02	0.00	0.02	−0.02	−0.01	−0.01
C(*n*4)	0.02	0.04	0.04	0.04	0.01	0.04	0.04	0.05
N(*n*5)	−0.01	0.00	0.00	−0.01	−0.01	0.00	−0.01	−0.02
C(*n*6)	−0.03	−0.05	−0.06	−0.05	−0.03	−0.05	−0.04	−0.05
N(0)	0.01	0.06	0.18	0.00	0.01	0.05	0.15	0.02
O(*n*2)	−0.14	−0.13	−0.12	−0.21	−0.18	−0.14	−0.09	−0.21
O(*n*4)	0.01	0.10	0.13	0.08	−0.01	0.14	0.15	0.10
O(*n*6)	−0.24	−0.29	−0.29	−0.30	−0.21	−0.28	−0.23	−0.31
M	−1.50	0.24	−0.98	−0.44	−1.41	0.14	−0.97	−0.45
θ	31.2		39.0		33.3		41.4	

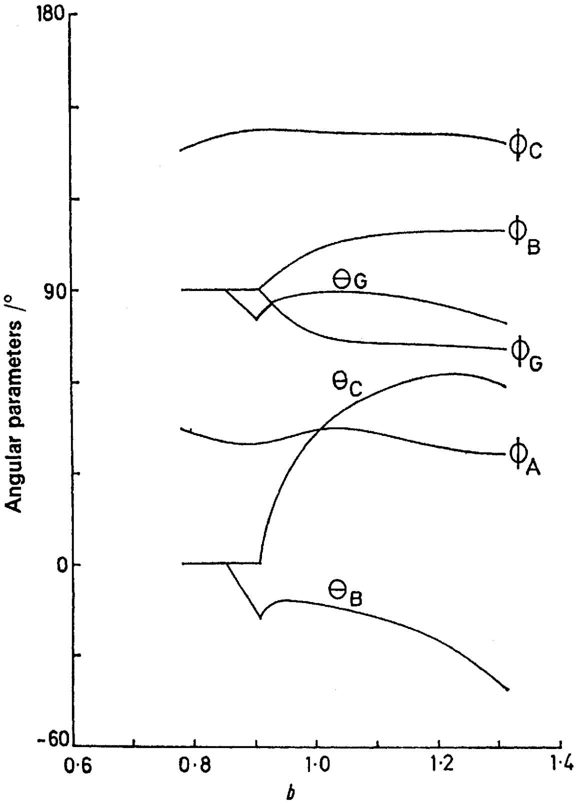

FIGURE 6 Angular parameters (°) as a function of normalised bite *b* for stereochemistry C of [M(tridentate)$_2$(unidentate)$_2$], $n = 6$

The stereochemistry of [M(tridentate ligand)$_2$(unidentate ligand)$_2$] is defined by nine angular co-ordinates. Two angular co-ordinates define the position of each unidentate ligand. Of the six angular co-ordinates required to define the positions of the three donor atoms of each tridentate ligand, two can be calculated from the other four plus the normalized bite of each chelate ring, *b*. Three co-ordinates can be fixed when defining the co-ordinate axes.

The repulsion-energy coefficients *X*, which are a direct measure of the stability of the particular stereochemistry, were calculated as before.[10] The minima on the potential-energy surfaces were located to the nearest 0.1° in each of the angular co-ordinates. The previous custom of using values of 1, 6, and 12 for *n* in the repulsive energy expression was continued.

At normalized bites of 1.20—1.25, eleven separate isomers could be located as potential-energy minima. These are most readily envisaged as the eleven possible ways of arranging two tridentate and two unidentate ligands along the edges of (distorted) square antiprisms.

On reducing the normalized bite to 1.0—1.1, as in the present complexes, only five of these isomers remain as potential energy minima. These five stereochemistries are shown in Figure 3, both for $b = 1.20$—1.25 (depicted as square antiprisms), and for *b ca.* 1.05 (as in the purpurate complexes). Stereochemistries A$_1$, A$_2$, C, D, and E contain a two-fold axis, while J contains a mirror plane. The relative energies as a function of *b*, and their range of existence as discrete minima, are shown in Figure 4.

For stereochemistries A_1 and A_2 and $b = 1.20$—1.25, each tridentate ligand is spread across two polyhedral faces, with angle ABC *ca.* 102°. These two potential-energy minima coalesce below $b = 1.08$ ($n = 6$) to form sterochemistry A. As b is further decreased a distorted tetrahedron is eventually formed with each coalesced tridentate ligand occupying one apical site. At $b = 1.20$—1.25, each tridentate ligand occupies a square face in stereochemistries C and D with angle ABC *ca.* 90°. Stereochemistries E and J are two of the six ways the tridentate ligands can be arranged on triangular faces of the square antiprism with angle ABC *ca.* 60°.

The increase in tridentate angle ABC with decreasing normalized bite for these stereochemistries is shown in Figure 5.

The tridentate angle in the unco-ordinated purpurate ion is about 115°,[8,12] and is slightly reduced to 100—110° in a range of complexes containing co-ordinated purpurate.[12] Stereochemistries E and J are clearly not compatible with these ligand requirements.

The remaining three stereochemistries can be conveniently classified as follows: Stereochemistry A: a *cis*-arrangement of unidentate ligands and an approximately *trans*-arrangement of hinging B atoms. Stereochemistry C: an approximately *trans*-arrangement of unidentate ligands and an approximately *trans*-arrangement of hinging B atoms. Stereochemistry D: a *cis*-arrangement of unidentate ligands and a *cis*-arrangement of hinging B atoms.

The calcium and cadmium purpurate complexes are clearly of stereochemistry C. The dimeric lead complex is also of this stereochemistry, whereas the infinite polymeric lead complex has the D *cis*-arrangement of unidentate ligands.[13]

The angular parameters for stereochemistry C are shown in Figure 6. The co-ordinate axes are defined with reference to Figure 3. ϕ_i is the angle between the M–i bond and the two-fold axis bisecting the unidentate ligands G and H. θ_i is the angle between the vertical plane incorporating the M–i bond and the vertical plane incorporating the M–A bond. At $b = 1.19$ ($n = 6$) the stereochemistry is a regular square antiprism. As the normalized bite is decreased, the square antiprism progressively distorts until at $b = 0.91$ the angular parameters are $\phi_B = \phi_G = 90$, $\phi_C = 180 - \phi_A$, and $\theta_C = 0°$, corresponding to a puckered hexagonal bipyramid with the puckered plane formed by the two tridentate ligands. At $b = 0.85$—0.78, a planar hexagonal bipyramid is formed with $\theta_B = 0$ and $\theta_G = 90°$. This stereochemistry ceases to exist as a discrete minimum below $b = 0.78$.

A detailed comparison between the angular parameters of (1) and (2) and the calculated parameters for stereochemistry C is made in Table 4. The biggest departure from prediction is the large values observed for θ_B and θ_G, arising from the tridentate angle of *ca.* 110 being significantly greater than the *ca.* 100° predicted from these calculations assuming a completely flexible tridentate ligand. A much better agreement between prediction and experiment is obtained if it is now assumed that each tridentate ligand is rigid, with larger tridentate angles (Table 4). Closer agreement would not be expected because of the considerable differences in the metal–ligand bond lengths.

TABLE 4

Angular parameters (°) of (1) and (2), and stereochemistry C

	b	ABC	ϕ_A	ϕ_B	θ_B	ϕ_C	θ_C	ϕ_G	θ_G
(1)	1.05	112	39	102	5	147	62	85	103
(2)	1.09	109	36	103	10	148	73	84	104
Flexible tridentate									
$n = 1$	1.05	101	43	105	−14	141	51	74	88
$n = 6$	1.05	99	45	105	−15	141	49	74	89
$n = 12$	1.05	98	46	107	−17	141	51	72	89
Rigid tridentate									
$n = 6$	1.05	100	43	105	−16	141	50	74	88
$n = 6$	1.05	105	43	106	−6	143	60	73	92
$n = 6$	1.05	110	43	106	7	144	74	72	94

In summary, the stereochemistry of (1) and (2) is not that normally expected for eight-co-ordinate complexes, namely the square antiprism or the dodecahedron. However the stereochemistry is very well described as being intermediate between the square antiprism and a hexagonal bipyramid, due to the relatively small normalized bite of each chelate ring, with smaller distortions arising from the rigidity of the ligand structure.

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[13] A. H. White and A. C. Willis, Part 4, *J.C.S. Dalton*, 1977, 1362.