Structural Studies in Metal–Purpurate Complexes. Part 5.† Crystal Structure of Di-μ-aqua-tetrakis(purpurato)distrontium Tridecahydrate

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The crystal structure of the title compound $[Sr_2L_4]\cdot 15H_2O$ (L = purpurate) has been determined at 295 K by *X*-ray diffraction and refined by least squares to *R* 0.082 (2 839 ' observed ' reflections). Crystals are triclinic, space group $P\bar{1}$, a = 17.342(5), b = 15.337(5), c = 10.553(4) Å, α = 86.20(2), β = 91.64(2), γ = 107.71(2)°, Z = 2. Each strontium atom is nine-co-ordinated by a tridentate purpurate species [Sr–N, 2.69(1), 2.75(1); Sr–O, 2.56(1)—2.63(1) Å], with two further contacts to adjacent purpurates [Sr–O, 2.68(1)—3.18(1) Å], two water molecules [Sr–O, 2.61(1)—2.72(1) Å], and two further water molecules which bridge adjacent pairs of nine-co-ordinate strontium atoms [Sr–O, 2.64(1)—2.75(1) Å; Sr–O–Sr, 107.9(4), 107.7(5)°]. Dimeric units are thus formed which are linked polymerically by purpurate species.

ADDITION of a cold aqueous suspension of murexide {ammonium purpurate, $[NH_4][L]$ ($L = [C_8H_4N_5O_6]^-$)} to aqueous strontium nitrate solution yields a magenta solution which deposits small magenta crystals when set aside. Although analysis suggested the stoicheiometry of the complex to be $SrL_2\cdot 5.5H_2O$, subsequent structure determination showed it to be $SrL_2\cdot 7.5H_2O$.

EXPERIMENTAL

Analysis (Found, calc. for $SrL_2\cdot 7.5H_2O$): C, 26.67, 25.45; H, 2.38, 3.07; N, 19.74, 18.55; Sr, 12.02, 11.61%.

Previous studies on the strontium–purpurate system have been concerned with the determination of formation constants for Sr–L in water [1,2] and methanol,[3] together with rate constants for these processes.[4]

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.[5]

Crystallographic Data and Procedure.—$C_{32}H_{46}N_{20}O_{39}Sr_2$, M = 1 510.2, Triclinic, space group $P\bar{1}$ (C_i^1, No. 2), a = 17.342(4), b = 15.337(5), c = 10.553(4) Å, α = 86.20(2), β = 91.64(2), γ = 107.71(2)°, U = 2 668(2) Å^3, D_m = 1.88(1) g cm^{-3}, Z = 2, D_c = 1.88 g cm^{-3}, $F(000)$ = 1 532, crystal size 0.30 × 0.09 × 0.09 mm (prism), μ(Mo-K_α) = 20.6 cm^{-1} (data corrected for absorption), data range $2\theta < 40°$ yielding 5 010 independent reflections (2 839 ' observed '), final R = 0.082, R' = 0.083 (n = 7).

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 two strontium atoms and the atoms of their immediate environment were refined as a single block, the atom parameters of each of the purpurate ligand ring systems being refined similarly. Only the metal-atom thermal parameters could be refined anisotropically in a meaningful manner. Hydrogen atoms were located geometrically about the purpurate ligand and included in the refinement with r_{N-H} held invariant at 1.0 Å.

Observed and calculated structure-factor tables are given in Supplementary Publication No. SUP 21991 (18 pp., 1 microfiche).‡ Fractional cell co-ordinates and thermal parameters are in Table 1, and bond lengths and angles in Table 2.

DISCUSSION

The structure of the present derivative is complex and interesting. The core of the basic structural unit is a pair of crystallographically independent strontium atoms, each nine-co-ordinate and with very similar environments, linked as a dimer by a pair of bridging water molecules O(1) and O(2) [Sr(1) · · · Sr(2) 4.365(3) Å] and this core, together with four associated purpurate groups, makes up the asymmetric unit. The above dimeric cores, however, are linked by the purpurates to adjacent dimers and make up an infinite one-dimensional polymer along *a*.

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† Part 4 is the preceding paper.

‡ For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1976, Index issue.

[1] G. Geier, *Helv. Chim. Acta*, 1967, **50**, 1879.

[2] H. Feschotte-Ostertag, *Compt. rend.*, 1960, **250**, 1061.

[3] R. Winkler, *Structure and Bonding*, 1972, **10**, 1.

[4] G. Geier, *Helv. Chim. Acta*, 1968, **51**, 94.

[5] R. L. Martin, A. H. White, and A. C. Willis, Part 1, *J.C.S. Dalton*, 1977, 1336.

About each strontium, the two bridging water molecules together with a further pair [Sr(1), O(3,4); Sr(2), O(5,6)] occupy a cluster of four adjacent sites in each co-ordination sphere (Sr–O 2.61—2.76 Å; O–Sr–O 68—139°), and a further three co-ordination sites are occupied by a conventionally co-ordinated tridentate purpurate with no inter-strontium bridging affiliations [Sr–N(0b,d) 2.69, 2.75(1); Sr–O(*n*2b,d) 2.56—2.63(1) Å]. As expected, the Sr–N(0b,d) distances are *ca.* 0.1 Å longer than the Sr–O. The remaining two co-ordination sites about each strontium are filled by the remaining two ligands in a bridging capacity: in the case of Sr(1)

TABLE 1

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

The strontium parameters

	x	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sr(1)	3 353(1)	6 408(1)	5 072(2)	46(2)	24(1)	10(1)	−7(1)	10(1)	−2(1)
Sr(2)	1 606(1)	3 722(1)	4 557(2)	34(1)	15(1)	12(1)	1(1)	4(1)	−3(1)

The purpurate ligands

	ligand 'a'				ligand 'b'			
Atom	*x*	*y*	*z*	*U*	*x*	*y*	*z*	*U*
N(0)	1 139(9)	7 239(10)	7 169(13)	27(4)	3 767(9)	7 397(10)	7 138(13)	27(4)
C(11)	0 659(11)	6 916(12)	8 205(15)	21(5)	3 326(11)	7 069(12)	8 219(15)	20(5)
C(12)	−0 062(11)	6 169(12)	7 977(16)	25(5)	2 653(11)	6 283(12)	8 062(15)	22(5)
O(12)	−0 378(7)	5 955(8)	6 926(10)	24(3)	2 435(7)	5 888(8)	7 031(10)	28(3)
N(13)	−0 510(9)	5 709(10)	9 032(12)	23(4)	2 188(9)	5 892(9)	9 095(12)	20(4)
H(13)	−101(—)	519(—)	890(—)	80(—)	167(—)	540(—)	897(—)	80(—)
C(14)	−0 272(11)	5 961(12)	10 265(16)	26(5)	2 423(11)	6 172(12)	10 303(15)	20(5)
O(14)	−0 731(8)	5 528(8)	11 161(11)	35(4)	1 937(7)	5 759(8)	11 217(10)	28(3)
N(15)	0 438(9)	6 584(9)	10 470(12)	21(4)	3 082(8)	6 843(9)	10 445(12)	19(4)
H(15)	061(—)	671(—)	1 137(—)	80(—)	323(—)	704(—)	1 132(—)	80(—)
C(16)	0 964(11)	7 072(14)	9 507(16)	24(5)	3 594(11)	7 299(11)	9 484(15)	16(5)
O(16)	1 612(7)	7 591(8)	9 822(11)	29(3)	4 278(7)	7 819(8)	9 750(10)	29(3)
C(21)	1 708(11)	8 042(11)	7 092(15)	16(5)	4 314(10)	8 197(11)	6 930(14)	9(4)
C(22)	2 283(11)	8 200(12)	6 043(16)	23(5)	4 804(11)	8 311(12)	5 828(16)	23(5)
O(22)	2 347(7)	7 561(8)	5 408(10)	28(3)	4 709(7)	7 684(8)	5 066(10)	25(3)
N(23)	2 812(8)	9 034(9)	5 840(11)	14(4)	5 407(9)	9 106(10)	5 623(13)	25(4)
H(23)	322(—)	912(—)	516(—)	80(—)	580(—)	914(—)	494(—)	80(—)
C(24)	2 847(12)	9 771(13)	6 481(17)	29(5)	5 502(12)	9 863(13)	6 292(17)	29(5)
O(24)	3 344(8)	10 568(8)	6 242(11)	32(4)	6 044(8)	10 581(8)	6 053(11)	31(3)
N(25)	2 280(9)	9 664(10)	7 415(13)	31(4)	4 951(9)	9 792(10)	7 202(15)	27(4)
H(25)	229(—)	1 022(—)	788(—)	80(—)	499(—)	1 036(—)	764(—)	80(—)
C(26)	1 702(12)	8 854(13)	7 755(16)	28(5)	4 344(11)	9 032(12)	7 581(15)	24(5)
O(26)	1 164(8)	8 864(8)	8 510(11)	30(3)	3 836(7)	9 078(8)	8 328(11)	30(3)
	ligand 'c'				ligand 'd'			
N(0)	3 670(9)	2 691(9)	3 198(12)	20(4)	1 354(8)	2 704(9)	2 456(12)	14(4)
C(11)	4 145(11)	3 004(12)	2 174(16)	23(5)	1 809(10)	3 098(11)	1 413(14)	10(4)
C(12)	4 871(12)	3 690(13)	2 341(17)	30(5)	2 460(11)	3 892(12)	1 657(16)	22(5)
O(12)	5 182(8)	4 001(9)	3 375(11)	40(4)	2 677(7)	4 190(8)	2 722(10)	23(3)
N(13)	5 339(9)	4 091(10)	1 263(13)	24(4)	2 955(9)	4 296(10)	0 629(13)	25(4)
H(13)	587(—)	457(—)	140(—)	80(—)	347(—)	479(—)	079(—)	80(—)
C(14)	5 113(12)	3 859(12)	0 050(16)	27(5)	2 764(10)	4 050(11)	−0 595(15)	13(4)
O(14)	5 554(8)	4 255(8)	−0 861(11)	31(3)	3 219(8)	4 476(8)	−1 501(11)	36(4)
N(15)	4 396(9)	3 237(10)	−0 126(13)	25(4)	2 070(9)	3 402(9)	−0 808(12)	22(4)
H(15)	423(—)	310(—)	−102(—)	80(—)	193(—)	327(—)	−171(—)	80(—)
C(16)	3 865(11)	2 765(12)	0 858(16)	25(5)	1 538(12)	2 906(13)	0 121(16)	28(5))
O(16)	3 203(8)	2 299(8)	0 583(11)	31(3)	0 881(8)	2 426(8)	−0 199(11)	34(4)
C(21)	3 071(11)	1 914(12)	3 267(16)	22(5)	0 828(11)	1 890(12)	2 562(15)	19(5)
C(22)	2 475(11)	1 836(12)	4 288(15)	17(5)	0 319(11)	1 680(12)	3 687(16)	26(5)
O(22)	2 437(7)	2 506(8)	4 865(10)	28(3)	0 390(7)	2 258(8)	4 487(11)	30(3)
N(23)	1 908(9)	0 981(10)	4 522(13)	28(4)	−0 200(9)	0 806(10)	3 910(13)	26(4)
H(23)	149(—)	093(—)	519(—)	80(—)	−054(—)	068(—)	469(—)	80(—)
C(24)	1 879(11)	0 222(12)	3 921(16)	26(5)	−0 275(12)	0 092(12)	3 119(17)	31(5)
O(24)	1 356(7)	−0 520(8)	4 186(11)	32(3)	−0 799(8)	−0 647(8)	3 377(11)	31(3)
N(25)	2 456(9)	0 259(10)	3 035(13)	23(4)	0 240(9)	0 262(9)	2 162(12)	21(4)
H(25)	245(—)	−031(—)	263(—)	80(—)	022(—)	−026( )	163(—)	80(—)
C(26)	3 047(12)	1 062(13)	2 704(17)	36(6)	0 810(11)	1 092(12)	1 839(15)	20(5)
O(26)	3 588(7)	1 016(8)	1 976(11)	29(3)	1 317(8)	1 108(9)	1 014(12)	41(4)

The bridging water molecules

O(1)	1 993(7)	5 571(8)	3 888(10)	23(3)
O(2)	2 986(7)	4 592(8)	5 763(11)	30(3)

The co-ordinated water molecules

O(3)	4 057(9)	5 670(9)	3 476(12)	48(4)
O(4)	3 400(8)	7 489(8)	3 001(11)	32(4)
O(5)	0 819(8)	4 429(9)	6 072(11)	39(4)
O(6)	1 306(8)	2 751(9)	6 834(11)	36(4)

The lattice water molecules

O(7)	0 463(10)	7 460(10)	2 842(14)	64(5)
O(8)	6 139(8)	7 524(9)	2 529(12)	45(4)
O(9)	4 958(8)	8 431(9)	2 068(11)	38(4)
O(10)	2 460(9)	8 575(10)	1 940(13)	60(5)
O(11)	7 784(9)	8 740(10)	1 386(13)	57(4)
O(12)	3 778(13)	9 564(14)	0 677(19)	118(7)
O(13)	9 151(8)	3 824(9)	5 083(11)	41(4)
O(14)	9 482(8)	1 144(9)	9 106(12)	42(4)
O(15)	5 874(8)	6 221(9)	4 584(12)	46(4)

one of the co-ordination positions is filled by O(22a) at 2.88(1) Å, from the other ligand segment; O(12a) occupies a co-ordination site about Sr(2) in an adjacent *dimer at* 2.75(1) Å. The other co-ordination position about Sr(2) is filled by O(22c) at 2.68(1) Å; the similar oxygen from the other ligand segment, O(12c), fills a co-ordination site about Sr(1) from an adjacent dimer at 3.18(1) Å. These strontium–oxygen ' bonds ' from the bridging purpurates are generally rather longer than those from the tridentate ligands and it will be seen from

TABLE 2

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

(*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. Each entry comprises four components across the page, corresponding to purpurates ' a ', ' b ', ' c ', and ' d ', respectively, the value for barbiturate ring $n = 2$ lying below that for ring 1 in each case where appropriate

N(0)–C(11)	1.37(2), 1.37(2), 1.35(2), 1.37(2)
N(0)–C(21)	1.32(2), 1.31(2), 1.32(2), 1.30(2)
C(11)–C(12)	1.44(2), 1.41(2), 1.39(2), 1.42(2)
C(21)–C(22)	1.47(2), 1.43(2), 1.49(3), 1.46(2)
C(12)–O(12)	1.24(2), 1.27(2), 1.26(2), 1.25(2)
(C22)–O(22)	1.26(2), 1.26(2), 1.25(2), 1.24(2)
C(12)–N(13)	1.40(2), 1.37(2), 1.41(2), 1.39(2)
C(22)–N(23)	1.34(2), 1.35(2), 1.39(2), 1.38(2)
N(13)–C(14)	1.40(2), 1.38(2), 1.37(2), 1.38(2)
N(23)–C(24)	1.34(2), 1.36(2), 1.35(2), 1.39(2)
C(14)–O(14)	1.27(2), 1.30(2), 1.25(2), 1.27(2)
C(24)–O(24)	1.28(2), 1.23(2), 1.24(2), 1.24(2)
C(11)–N(0)–C(21)	124(1), 128(1), 124(1), 127(1)
N(0)–C(11)–C(12)	115(1), 114(1), 118(2), 114(1)
N(0)–C(21)–C(22)	117(2), 117(1), 115(2), 117(2)
C(11)–C(12)–O(12)	126(1), 126(1), 127(2), 126(1)
C(21)–C(22)–O(22)	122(1), 122(1), 123(1), 121(1)
O(12)–C(12)–N(13)	116(1), 115(1), 114(1), 118(1)
O(22)–C(22)–N(23)	119(2), 119(1), 120(1), 120(2)
C(11)–C(12)–N(13)	118(1), 119(1), 119(2), 116(1)
C(21)–C(22)–N(23)	119(2), 119(2), 117(2), 119(2)
C(12)–N(13)–C(14)	121(1), 121(1), 124(1), 123(1)
C(22)–N(23)–C(24)	126(2), 124(2), 125(2), 124(1)
N(13)–C(14)–O(14)	117(1), 116(1), 120(1), 120(1)
N(23)–C(24)–O(24)	124(2), 122(2), 121(2), 118(2)
N(13)–C(14)–N(15)	120(1), 119(1), 118(1), 118(1)
N(23)–C(24)–N(25)	117(1), 116(1), 120(1), 116(1)
C(12)–C(11)–C(16)	120(1), 118(1), 118(1), 120(1)
C(22)–C(21)–C(26)	116(1), 116(1), 116(1), 115(1)
Sr–O(12)–C(12)	137(1), 119(1), 128(1), 118(1)
Sr–O(22)–C(22)	143(1), 118(1), 135(1), 123(1)
Sr–N(0)–C(11)	118(1) 116(1)
Sr–N(0)–C(21)	114(1) 117(1)

C(11)–C(16)	1.47(2), 1.43(2), 1.49(2), 1.45(2)
C(21)–C(26)	1.47(3), 1.48(3), 1.46(3), 1.48(3)
C(16)–O(16)	1.22(2), 1.25(2), 1.19(2), 1.21(2)
C(26)–O(26)	1.25(2), 1.23(2), 1.25(3), 1.25(2)
C(16)–N(15)	1.40(2), 1.37(2), 1.41(2), 1.38(2)
C(26)–N(25)	1.37(2), 1.35(2), 1.37(2), 1.38(2)
N(15)–C(14)	1.33(2), 1.30(2), 1.33(2), 1.33(2)
N(25)–C(24)	1.38(2), 1.35(2), 1.38(2), 1.33(2)
0(16) · · · O(26)	2.62(2), 2.65(2), 2.61(2), 2.61(2)
N(0)–C(11)–C(16)	122(1), 125(1), 123(1), 123(1)
N(0)–C(21)–C(26)	124(1), 124(2), 127(2), 127(2)
C(11)–C(16)–O(16)	126(1), 124(1), 125(2), 126(2)
C(21)–C(26)–O(26)	124(1), 124(1), 122(2), 124(1)
O(16)–C(16)–N(15)	118(1), 119(1), 119(2), 119(2)
O(26)–C(26)–N(25)	119(2), 121(1), 117(2), 118(2)
C(11)–C(16)–N(15)	116(1), 116(1), 116(1), 115(1)
C(21)–C(26)–N(25)	117(2), 115(2), 121(2), 118(2)
C(16)–N(15)–C(14)	124(1), 125(1), 125(1), 125(1)
C(26)–N(25)–C(24)	125(2), 127(2), 122(2), 126(2)
N(15)–C(14)–O(14)	123(1), 124(1), 122(2), 122(1)
N(25)–C(24)–O(24)	118(2), 122(2), 119(2), 125(2)

(*b*) The strontium environments

Sr(1)		Sr(2)	
Sr–O(22a)	2.88(1)	Sr–O(22c)	2.68(1)
Sr–O(12b)	2.58(1)	Sr–O(12d)	2.63(1)
Sr–N(0b)	2.69(1)	Sr–N(0d)	2.75(1)
Sr–O(22b)	2.56(1)	Sr–O(22d)	2.57(1)
Sr–O(1)	2.64(1)	Sr–O(1)	2.75(1)
Sr–O(2)	2.71(1)	Sr–O(2)	2.69(1)
Sr–O(3)	2.61(2)	Sr–O(5)	2.62(1)
Sr–O(4)	2.64(1)	Sr–O(6)	2.72(1)
Sr–O(12c^{I})	3.18(1)	Sr–O(12a^{II})	2.75(1)
O(22a)–Sr–O(12b)	67.2(4)	O(22c)–Sr–O(12d)	75.5(4)
O(22a)–Sr–N(0b)	67.1(4)	O(22c)–Sr–N(0d)	71.4(4)
O(22a)–Sr–O(22b)	96.6(4)	O(22c)–Sr–O(22d)	82.5(4)
O(22a)–Sr–O(1)	76.5(4)	O(22c)–Sr–O(1)	135.2(4)
O(22a)–Sr–O(2)	126.3(4)	O(22c)–Sr–O(2)	74.4(4)
O(22a)–Sr–O(3)	147.0(4)	O(22c)–Sr–O(5)	134.8(4)
O(22a)–Sr–O(4)	70.6(4)	O(22c)–Sr–O(6)	67.9(4)
O(22a)–Sr–O(12c^{I})	134.5(3)	O(22c)–Sr–O(12d)	139.8(3)
O(12b)–Sr–N(0b)	62.4(4)	O(12d)–Sr–N(0d)	60.8(3)
O(12b)–Sr–O(22b)	123.8(4)	O(12d)–Sr–O(22d)	120.9(4)
O(12b)–Sr–O(1)	81.7(3)	O(12d)–Sr–O(1)	69.2(4)
O(12b)–Sr–O(2)	65.6(4)	O(12d)–Sr–O(2)	76.8(3)
O(12b)–Sr–O(3)	137.8(4)	O(12d)–Sr–O(5)	141.5(4)
O(12b)–Sr–O(4)	136.1(4)	O(12d)–Sr–O(6)	141.3(4)
O(12b)–Sr–O(12c^{I})	90.6(4)	O(12d)–Sr–O(12d)	94.4(4)
N(0b)–Sr–O(22b)	61.8(4)	N(0d)–Sr–O(22d)	60.3(4)
N(0b)–Sr–O(1)	136.2(4)	N(0d)–Sr–O(1)	111.5(4)
N(0b)–Sr–O(2)	109.9(4)	N(0d)–Sr–O(2)	130.6(4)
N(0b)–Sr–O(3)	137.7(5)	N(0d)–Sr–O(5)	140.4(4)
N(0b)–Sr–O(4)	110.9(4)	N(0d)–Sr–O(6)	115.8(4)
N(0b)–Sr–O(12c^{I})	67.4(5)	N(0d)–Sr–O(12a^{II})	69.7(4)

TABLE 2 (*Continued*)

Sr(1)		Sr(2)	
O(22b)–Sr–O(1)	149.2(3)	O(22d)–Sr–O(1)	139.6(4)
O(22b)–Sr–O(2)	130.7(4)	O(22d)–Sr–O(2)	146.3(4)
O(22b)–Sr–O(3)	84.5(4)	O(22d)–Sr–O(5)	90.5(4)
O(22b)–Sr–O(4)	72.1(4)	O(22d)–Sr–O(6)	66.9(4)
O(22b)–Sr–O(12c$^{\mathrm{I}}$)	62.4(4)	O(22d)–Sr–O(12a$^{\mathrm{II}}$)	69.4(4)
O(1)–Sr–O(2)	72.8(4)	O(1)–Sr–O(2)	71.5(4)
O(1)–Sr–O(3)	85.8(4)	O(1)–Sr–O(5)	72.4(4)
O(1)–Sr–O(4)	77.3(3)	O(1)–Sr–O(6)	132.4(4)
O(1)–Sr–O(12c$^{\mathrm{I}}$)	141.5(4)	O(1)–Sr–O(12a$^{\mathrm{II}}$)	70.9(3)
O(2)–Sr–O(3)	72.2(4)	O(2)–Sr–O(5)	88.7(4)
O(2)–Sr–O(4)	139.2(4)	O(2)–Sr–O(6)	81.7(3)
O(2)–Sr–O(12c$^{\mathrm{I}}$)	69.7(3)	O(2)–Sr–O(12a$^{\mathrm{II}}$)	142.0(4)
O(3)–Sr–O(4)	78.5(4)	O(5)–Sr–O(6)	68.4(4)
O(3)–Sr–O(12c$^{\mathrm{I}}$)	74.9(4)	O(5)–Sr–O(12a$^{\mathrm{II}}$)	75.3(4)
O(4)–Sr–O(12c$^{\mathrm{I}}$)	128.7(4)	O(6)–Sr–O(12a$^{\mathrm{II}}$)	121.6(4)
Sr(1) ··· Sr(2)	4.365(3)		
Sr(1)–O(1)–Sr(2)	107.9(4)	Sr(1)–O(2)–Sr(2)	107.7(5)

(*c*) Ligand–hydrogen-bonded interactions (O ··· H $<$2.5 Å); the angle subtended at the hydrogen is given in parentheses

H(13a) ··· O(14b$^{\mathrm{III}}$)	1.8(176)	H(15a) ··· O(7$^{\mathrm{IV}}$)	2.1(142)
H(23a) ··· O(24b$^{\mathrm{V}}$)	1.8(172)	H(25a) ··· O(11$^{\mathrm{V}}$)	1.9(173)
H(13b) ··· O(14a$^{\mathrm{III}}$)	1.8(177)	H(15b) ··· O(4$^{\mathrm{IV}}$)	1.9(173)
H(23b) ··· O(24a$^{\mathrm{V}}$)	1.9(169)	H(25b) ··· O(9$^{\mathrm{V}}$)	1.9(161)
H(13c) ··· O(14d$^{\mathrm{VI}}$)	1.8(173)	H(15c) ··· O(8$^{\mathrm{VI}}$)	1.9(164)
H(23c) ··· O(24d$^{\mathrm{VII}}$)	1.9(168)	H(25c) ··· O(10$^{\mathrm{VIII}}$)	1.9(176)
H(13d) ··· O(14c$^{\mathrm{VI}}$)	1.9(172)	H(15d) ··· O(6$^{\mathrm{IV}}$)	1.9(160)
H(23d) ··· O(24c$^{\mathrm{VII}}$)	1.8(164)	H(25d) ··· O(14$^{\mathrm{V}}$)	1.8(160)

Transformations of the asymmetric unit (x, y, z) are represented by the following Roman superscripts

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

the Figure and Table 3 that the strontium lies much further from the ligand plane than is the case with the tridentate ligand. Whereas the displacement of the ligand planes with respect to each other is as expected for the tridentate ligands, a considerably greater twisting effect about the central nitrogen is found for the bridging ligands (Table 3). Hydrogen bonding in the lattice is widespread and summarized in Table 2 for the ligands only. Ligand geometries about the rings are generally as expected within the rather large error limits. An interesting arrangement of ligand segments is found, all segments with $n = 1$ lying approximately parallel, and also approximately parallel to c, while segments with $n = 2$ form an independent approximately parallel set (Table 3).

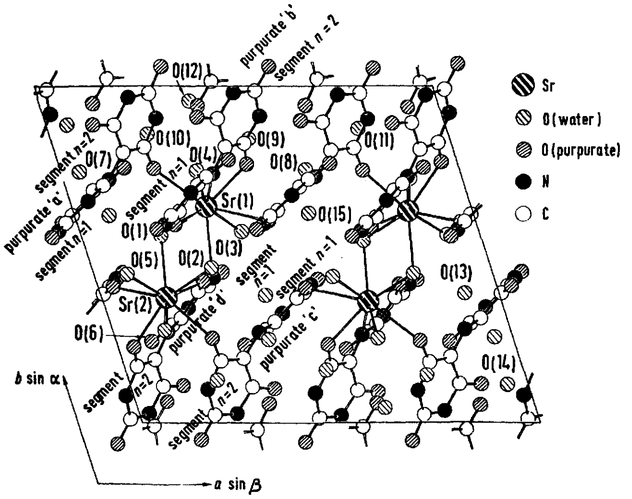
TABLE 3

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°

Segment (na,b)	1a	1b	2a	2b	3a	3b	4a	4b
10^4p	−7 288	7 260	7 608	7 296	−7 048	6 856	7 537	7 914
10^4q	6 846	−2 230	−6 461	−2 724	7 087	−2 139	−6 551	−2 424
10^4r	0 157	6 505	0 602	6 272	−0 318	6 959	0 520	5 612
s	8.677	1.942	−4.345	4.214	−0.985	4.928	−1.722	1.376
σ	0.05	0.03	0.04	0.06	0.02	0.02	0.06	0.04
χ^2	40.0	10.9	34.9	52.3	4.7	9.6	72.7	27.2
C(n1)	0.07	0.04	0.07	0.08	0.02	0.04	0.10	0.06
C(n2)	−0.03	−0.03	−0.05	0.07	−0.02	−0.02	−0.08	−0.02
N(n3)	−0.03	0.00	0.01	0.01	−0.01	0.00	0.01	−0.03
C(n4)	0.05	0.02	0.01	0.04	0.02	0.02	0.04	0.04
N(n5)	0.00	−0.01	0.00	−0.03	0.01	−0.01	−0.03	0.00
C(n6)	−0.05	−0.02	−0.05	−0.03	−0.01	−0.02	−0.04	−0.04
N(0)	−0.14	−0.14	−0.05	0.07	−0.11	−0.18	0.05	−0.06
O(12)	0.05	0.00	−0.23	−0.26	−0.05	−0.01	−0.14	−0.19
O(14)	0.08	0.00	0.08	0.09	0.01	0.03	0.05	0.12
O(16)	−0.17	−0.20	−0.28	−0.22	−0.19	−0.17	−0.30	−0.26
Sr	1.97	1.76	−0.70	−1.10	−2.32	1.90	−0.88	−0.91
θ	47.8		39.7		48.9		38.3	

The present structure forms an interesting contrast to that of strontium dipicolinate tetrahydrate, Sr(dipic)·4H_2O.[6] In the latter, the structure comprises an infinite polymeric chain of nine-co-ordinated strontium atoms; these are linked by bridging carboxylate oxygen atoms of the dipicolinate ligands, so that dipicolinate oxygen and nitrogen atoms occupy five of

[6] K. J. Palmer, R. Y. Wong, and J. C. Lewis, *Acta Cryst.*, 1972, **B28**, 223.



Unit-cell contents projected down *c*, showing the formation of dimeric species, the adjacent strontiums being bridged by water molecules. Numbering of the purpurate segments and water oxygens is shown. Hydrogen atoms are omitted for the sake of clarity

the co-ordination positions about the strontium. The remaining four co-ordination positions are occupied by the water molecules, *none* of which are bridging. The difference between the two structures appears to be a consequence of the greater negative charge residing on the carboxylate oxygen atoms of the dipicolinate ligand in contrast to the carbonyl oxygen atoms of the purpurate ligand: the strontium–carboxylate-oxygen distances in the dipicolinate are slightly shorter than the mean strontium–carbonyl-oxygen distances of the present structure (2.592, 2.643, *cf.* 2.73 Å) in spite of the generally non-bridging role of the latter, while the mean strontium–water-oxygen distance in the purpurate derivative is slightly shorter than the strontium–water-oxygen distance in the dipicolinate (2.67_5, *cf.* 2.697, 2.729 Å) in spite of the non-bridging role of the water molecules in the latter and the location of their associated hydrogen atoms. In the dipicolinate derivative all the dipicolinate ligands are parallel to each other.

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