Structural Studies in Metal–Purpurate Complexes. Part 8.† Crystal Structure of Triaquapurpuratocalcium Nitrate Dihydrate

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The crystal structure of the title compound, $[CaL(H_2O)_3][NO_3]\cdot 2H_2O$ (L = purpurate), has been determined at 295 K by *X*-ray diffraction and refined by least squares to *R* 0.050 (1 545 ' observed ' reflections). Crystals are monoclinic, space group *Pn*, a = 11.282(5), b = 9.111(3), c = 9.045(4) Å, β = 105.70(3)°, Z = 2. Co-ordination about the calcium is approximately eight-co-ordinate dodecahedral. One of the trapezoidal planes comprises the usual tridentate purpurate site [Ca–O, 2.567(4), 2.429(4); Ca–N, 2.600(5) Å] and a further purpurate bridging oxygen [Ca–O, 2.361(5) Å] while the other comprises the three co-ordinated water molecules [Ca–O, 2.372(7), 2.378(5), 2.460(5) Å] and another bridging purpurate oxygen [Ca–O, 2.548(6) Å], an infinite polymer resulting parallel to *bc*. The geometry within the nitrate is very asymmetric [N–O, 1.213(10)—1.282(14) Å, O–N–O, 115.7(8)–122.9(8)°], and is found to correlate closely with the observed hydrogen bonding about the nitrate.

A PREVIOUS paper in this series [1] has described the preparation of calcium–purpurate complexes and the crystal-structure determination of one of them; the present paper reports the crystal-structure determination of a derivative reported in that paper as having the stoicheiometry $[CaL(NO_3)]\cdot 5H_2O$ (L = purpurate, $[C_8H_4N_5O_6]^-$), this stoicheiometry being confirmed in the process.

EXPERIMENTAL

Crystallographic Data and Procedure.—$C_8H_{14}CaN_6O_{14}$, M = 458.3, Monoclinic, space group *Pn* (variant of C_s^2, No. 7), a = 11.282(5), b = 9.111(3), c = 9.045(4) Å, β = 105.70(3)°, U = 895.1(6) Å^3, D_m = 1.70(1) g cm^{-3}, Z = 2, D_c = 1.70 g cm^{-3}, $F(000)$ = 472, crystal size 0.29 × 0.22 × (0.19, 0.42) mm, (trapezoid), μ(Mo-K_α) = 3.77 cm^{-1} (data

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† Part 7 is the preceding paper.

[1] D. L. Kepert, A. H. White, and A. C. Willis, Part 2, *J.C.S. Dalton*, 1977, 1342.

TABLE 1

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

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ca	2 500(—)	1 194(1)	2 500(—)	28.5(6)	10.1(5)	10.7(5)	−0.3(5)	2.6(4)	−1.2(5)
The purpurate ligand									
N(0)	2 830(5)	−0 820(5)	4 610(6)	25(3)	16(3)	17(3)	1(2)	6(2)	−2(2)
C(11)	2 929(6)	−0 346(7)	6 026(7)	27(3)	16(3)	19(3)	1(3)	6(3)	3(2)
C(12)	3 245(6)	1 201(7)	6 302(8)	22(3)	19(3)	21(3)	3(3)	1(3)	0(3)
O(12)	3 339(4)	2 067(4)	5 286(5)	46(3)	11(2)	12(2)	−3(2)	8(2)	3(2)
N(13)	3 488(6)	1 676(6)	7 785(7)	49(4)	13(2)	14(3)	−5(3)	10(2)	−6(2)
H(13)	361(11)	239(13)	787(15)	80(—)					
C(14)	3 278(6)	0 878(7)	8 976(7)	27(3)	25(3)	17(3)	2(3)	6(3)	−2(3)
O(14)	3 471(5)	1 397(5)	10 271(5)	51(3)	28(3)	14(2)	−6(2)	10(2)	−6(2)
N(15)	2 786(6)	−0 491(6)	8 618(6)	46(4)	15(3)	15(3)	−3(3)	10(2)	3(2)
H(15)	265(12)	−110(11)	890(15)	80(—)					
C(16)	2 517(7)	−1 144(7)	7 172(7)	34(4)	25(3)	13(3)	0(3)	8(3)	3(3)
O(16)	1 919(6)	−2 290(6)	6 957(6)	75(4)	32(3)	24(3)	−29(3)	22(3)	−7(3)
C(21)	2 781(6)	−2 202(7)	4 140(6)	26(3)	19(3)	9(3)	−2(3)	1(2)	−4(3)
C(22)	2 413(6)	−2 365(7)	2 476(8)	16(3)	24(3)	17(3)	3(3)	4(2)	3(3)
O(22)	2 251(5)	−1 320(5)	1 570(5)	53(3)	10(2)	16(2)	3(2)	7(2)	5(2)
N(23)	2 265(6)	−3 781(5)	1 917(6)	46(4)	10(3)	11(2)	−2(2)	4(2)	−7(2)
H(23)	218(11)	−394(12)	069(13)	80(—)					
C(24)	2 527(7)	−5 003(6)	2 787(7)	32(3)	10(3)	13(3)	−1(3)	6(3)	1(2)
O(24)	2 375(6)	−6 233(5)	2 190(5)	62(4)	19(2)	20(3)	−2(2)	0(3)	−3(2)
N(25)	3 035(6)	−4 824(6)	4 330(7)	51(4)	7(3)	23(3)	−1(3)	7(3)	4(2)
H(25)	305(11)	−552(13)	477(13)	80(—)					
C(26)	3 245(6)	−3 485(6)	5 073(7)	36(4)	7(3)	17(3)	−2(3)	3(3)	8(2)
O(26)	3 888(5)	−3 448(5)	6 403(5)	66(4)	15(2)	12(2)	−1(2)	−4(2)	6(2)
The water molecules [r(Å) is O–H; γ(°) is M–O–H, and δ(°) is H–O–H]									
Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	0 804(6)	1 184(6)	0 265(6)	43(3)	34(3)	26(3)	−1(3)	−3(2)	3(2)
H(1α)	090(13)	171(14)	−018(16)	80(—)	$r = 0.65(1)$; $\gamma = 67(3)$				
H(1β)	Not located								
O(2)	4 764(5)	1 200(6)	3 320(6)	38(3)	50(3)	14(2)	−1(3)	4(2)	1(2)
H(2α)	508(11)	168(13)	254(13)	80(—)	$r = 1.0(1)$; $\gamma = 110(6)$			$\delta = 81(10)$	
H(2β)	522(11)	208(13)	397(14)	80(—)	$r = 1.0(1)$; $\gamma = 119(7)$				
O(3)	0 680(6)	1 379(7)	3 323(7)	40(7)	63(4)	18(3)	13(3)	6(2)	9(3)
H(3α)	022(11)	177(13)	254(14)	80(—)	$r = 0.8(1)$; $\gamma = 99(10)$			$\delta = 135(14)$	
H(3β)	063(12)	125(13)	413(15)	80(—)	$r = 0.8(1)$; $\gamma = 126(10)$				
O(4)	0 978(6)	6 033(6)	8 843(6)	62(4)	36(3)	29(3)	−7(3)	15(3)	4(2)
H(4α)	129(12)	623(13)	827(14)	80(—)	$r = 0.7(1)$				
H(4β)	Not located								
O(5)	−0 179(8)	5 743(7)	3 455(8)	96(6)	38(3)	46(4)	10(4)	0(4)	5(3)
H(5α)	−001(11)	512(13)	454(13)	80(—)	$r = 1.1(1)$	$\delta = 66(8)$			
H(5β)	−110(11)	547(13)	385(12)	80(—)	$r = 1.2(1)$				
The nitrate ion									
N	0 377(7)	2 766(8)	6 744(7)	69(5)	44(4)	25(3)	16(4)	13(3)	11(3)
O(a)	0 437(7)	1 466(7)	6 483(7)	76(5)	45(4)	51(4)	−1(3)	14(3)	−10(3)
O(b)	0 177(6)	3 245(6)	7 946(6)	79(4)	37(3)	31(3)	3(3)	21(3)	−3(3)
O(c)	0 702(15)	3 725(11)	5 892(11)	277(16)	96(8)	70(6)	62(8)	95(8)	46(5)

corrected for absorption), data range $2\theta < 50°$ yielding 1 580 reflections (1 545 ' observed '), final $R = 0.051$, $R' = 0.051$ ($n = 1$).

The structure was solved by the heavy-atom method and refined using 9×9 block-diagonal least squares; 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 systems being refined similarly. Non-hydrogen-atom thermal motion was refined anisotropically. Hydrogen atom positional parameters were all refined, U(isotropic) being constrained at 0.08 Å^2.

Observed and calculated structure factors are deposited as Supplementary Publication No. SUP 21994 (6 pp., 1 microfiche).* Atom fractional cell co-ordinates are in Table 1.

DISCUSSION

The structure determination confirms the stoicheiometry as being $[CaL(NO_3)]\cdot 5H_2O$, the asymmetric unit comprising this formula unit: the structure, however, is not simply represented by this description, being polymeric and complex. This complexity arises as a result of interspecies interactions originating in the bridging of neighbouring calcium atoms by polydentate purpurate ligands; the latter, while co-ordinating to the calcium in the usual tridentate manner through O(12, 22) and N(0) also co-ordinate to adjacent calcium atoms by way of O(14, 24) so that a wrinkled two-dimensional polymer parallel to the *bc* plane is formed, the purpurate occupying five of the eight co-ordination sites about each calcium atom. The remaining three co-ordination sites about the calcium are occupied by the water-molecule oxygen atoms O(1, 2, and 3); the remaining two water molecules and the nitrate ion occupy lattice sites so that the formulation of the complex is $[\{CaL(H_2O)_3\}_n][NO_3]_n$.

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* For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1976, Index issue (items less than 10 pp. are supplied as full-size copies).

TABLE 2

Interatomic distances (Å) and angles (°) with least-squares estimated standard deviations in parentheses. Intramolecular geometries of the water molecules are inaccurate and are not given

(*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. Entries within each column are for the two rings *n* = 1 and 2

N(0)–C(*n*1)	1.327(8), 1.326(8)		
C(*n*1)–C(*n*2)	1.459(9), 1.456(9)	C(*n*1)–C(*n*6)	1.443(10), 1.453(8)
C(*n*2)–O(*n*2)	1.238(8), 1.238(8)	C(*n*6)–O(*n*6)	1.230(9), 1.226(7)
C(*n*2)–N(*n*3)	1.364(9), 1.379(8)	C(*n*6)–N(*n*5)	1.394(8), 1.382(8)
N(*n*3)–H(*n*3)	0.7(1), 1.1(1)	N(*n*5)–H(*n*5)	0.7(1), 0.7(1)
N(*n*3)–C(*n*4)	1.372(10), 1.349(8)	N(*n*5)–C(*n*4)	1.369(9), 1.368(8)
C(*n*4)–O(*n*4)	1.227(8), 1.235(7)	O(16) · · · O(26)	2.627(9)
C(11)–N(0)–C(21)	127.1(6)		
N(0)–C(*n*1)–C(*n*2)	115.6(6), 113.8(5)	N(0)–C(*n*1)–C(*n*6)	124.8(6), 126.9(5)
C(*n*1)–C(*n*2)–O(*n*2)	123.6(6), 123.7(6)	C(*n*1)–C(*n*6)–O(*n*6)	125.7(6), 124.9(5)
O(*n*2)–C(*n*2)–N(*n*3)	119.6(6), 119.7(6)	O(*n*6)–C(*n*6)–N(*n*5)	118.8(7), 118.6(5)
C(*n*1)–C(*n*2)–N(*n*3)	116.7(6), 116.5(5)	C(*n*1)–C(*n*6)–N(*n*5)	115.4(6), 116.1(5)
C(*n*2)–N(*n*3)–H(*n*3)	114(12), 117(6)	C(*n*6)–N(*n*5)–H(*n*5)	90(11), 121(9)
H(*n*3)–N(*n*3)–C(*n*4)	120(12), 115(6)	H(*n*5)–N(*n*5)–C(*n*4)	144(11), 113(8)
C(*n*2)–N(*n*3)–C(*n*4)	124.9(6), 124.9(5)	C(*n*6)–N(*n*5)–C(*n*4)	125.6(6), 124.8(5)
N(*n*3)–C(*n*4)–O(*n*4)	121.5(6), 120.7(5)	N(*n*5)–C(*n*4)–O(*n*4)	122.2(7), 121.6(5)
N(*n*3)–C(*n*4)–N(*n*5)	116.3(6), 117.5(5)		
C(*n*2)–C(*n*1)–C(*n*6)	118.3(6), 118.4(5)		
Ca–N(0)–C(*n*1)	115.9(4), 116.7(4)		
Ca–O(*n*2)–C(*n*2)	116.7(4), 120.9(4)		
Ca–O(*n*4)–C(*n*4)	136.4(5), 148.4(4)		

(*b*) Calcium geometry

Ca–O(1)	2.378(5)	Ca–O(12)	2.567(4)
Ca–O(2)	2.460(5)	Ca–O(22)	2.429(4)
Ca–O(3)	2.372(7)	Ca–O(14$^{\mathrm{I}}$)	2.548(6)
Ca–N(0)	2.600(5)	Ca–O(24$^{\mathrm{II}}$)	2.361(5)
O(1)–Ca–O(2)	141.9(2)	O(3)–Ca–O(12)	77.9(2)
O(1)–Ca–O(3)	72.6(2)	O(3)–Ca–O(22)	98.4(2)
O(1)–Ca–N(0)	122.9(2)	O(3)–Ca–O(14$^{\mathrm{I}}$)	146.8(2)
O(1)–Ca–O(12)	146.5(2)	O(3)–Ca–O(24$^{\mathrm{II}}$)	86.4(2)
O(1)–Ca–O(22)	73.2(2)	N(0)–Ca–O(12)	63.7(1)
O(1)–Ca–O(14$^{\mathrm{I}}$)	75.4(2)	N(0)–Ca–O(22)	64.5(2)
O(1)–Ca–O(24$^{\mathrm{II}}$)	83.9(2)	N(0)–Ca–O(14$^{\mathrm{I}}$)	128.7(2)
O(2)–Ca–O(3)	145.3(2)	N(0)–Ca–O(24$^{\mathrm{II}}$)	141.2(2)
O(2)–Ca–N(0)	81.4(2)	O(12)–Ca–O(22)	127.5(1)
O(2)–Ca–O(12)	68.1(2)	O(12)–Ca–O(14$^{\mathrm{I}}$)	129.1(2)
O(2)–Ca–O(22)	96.9(2)	O(12)–Ca–O(24$^{\mathrm{II}}$)	78.6(1)
O(2)–Ca–O(14$^{\mathrm{I}}$)	66.7(2)	O(22)–Ca–O(14$^{\mathrm{I}}$)	80.1(2)
O(2)–Ca–O(24$^{\mathrm{II}}$)	93.3(2)	O(22)–Ca–O(24$^{\mathrm{II}}$)	153.8(1)
O(3)–Ca–N(0)	77.5(2)	O(14$^{\mathrm{I}}$)–Ca–O(24$^{\mathrm{II}}$)	81.9(2)

(*c*) The nitrate geometry

N–O(a)	1.213(10)	O(a)–N–O(b)	122.9(8)
N–O(b)	1.247(10)	O(a)–N–O(c)	120.6(9)
N–O(c)	1.282(14)	O(b)–N–O(c)	115.7(8)

(*d*) 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(13) · · · O(5$^{\mathrm{III}}$)	2.2(1) [154(13)]	H(23) · · · O(4$^{\mathrm{IV}}$)	1.8(1) [140(10)]
		H(25) · · · O(12$^{\mathrm{V}}$)	2.3(1) [157(13)]

(*ii*) The water hydrogen atoms

H(1α) · · · O(b$^{\mathrm{I}}$)	2.2(1) [149(15)]	H(2α) · · · O(14$^{\mathrm{I}}$)	2.4(1) [103(8)]
H(2α) · · · O(16$^{\mathrm{VI}}$)	2.3(1) [143(8)]	H(2α) · · · O(4$^{\mathrm{VII}}$)	2.5(1) [102(8)]
H(2β) · · · O(4$^{\mathrm{VII}}$)	1.9(1) [144(10)]	H(3α) · · · O(26$^{\mathrm{VIII}}$)	2.2(1) [151(12)]
H(3β) · · · O(a)	2.2(1) [166(13)]	H(5α) · · · O(c)	1.8(1) [155(11)]
H(4α) · · · O(16$^{\mathrm{II}}$)	2.0(1) [153(13)]		

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

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

$2n\mathrm{H_2O}$. (This contrasts with the cobalt and zinc derivatives $[\mathrm{ML(NO_3)(H_2O)_2}]\cdot\mathrm{2H_2O}$ described in the previous paper in which the complex species is seven-co-ordinate.[2])

The bonding distances and angles about the calcium are irregular but generally similar to those observed in the previously described complex $[\mathrm{CaL_2(H_2O)_2}]$ species.[1] In addition to the already described purpurate bridging in the structure, the structure contains the usual strong hydrogen-bonding interactions from the purpurate and the water molecules (Table 2).

The nitrate ion, although not co-ordinated, has an interesting geometry which may be closely related to its lattice environment; as in the previous nitrate structures

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[2] A. H. White and A. C. Willis, Part 7, preceding paper.

in the series, the N–O(i) distances correlate closely with the O(j)–N–O(k) angles, the longest distance being opposed to the smallest angle. In the 'isolated' lattice nitrate, the variation in N–O(i) shows an unusually wide range varying between 1.213(10) and 1.282(14) Å, while the enclosed angles range between 115.7(8) and 122.9(8)°. Examination of the hydrogen bonding about the nitrate shows that all nitrate oxygens are associated with hydrogen bonds, the shortest of which is associated with the largest N–O(i) distance. The thermal motion of O(c) is excessively high in comparison with the remainder of the structure and may be indicative of disorder.

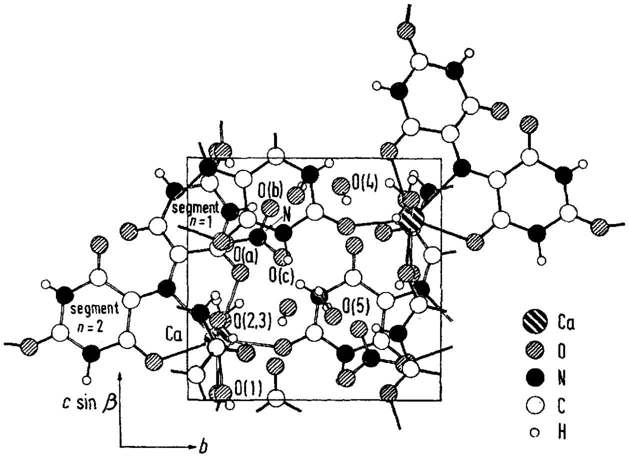

FIGURE 1 Unit-cell contents projected down a; purpurate ligands lying at x *ca.* 0.25 are shown with open bonds, those at x *ca.* 0.75 with solid bonds

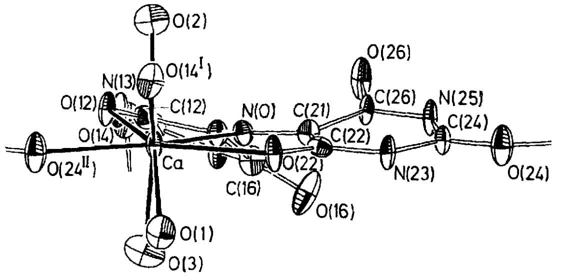

FIGURE 2 Projection of the calcium environment showing the distribution of the ligating atoms into the two approximately normal planes of the dodecahedral arrangement. 50% thermal ellipsoids are shown; hydrogen atoms are omitted for clarity

TABLE 3

(*a*) Least-squares planes, calculated through the C(n1, n2, n4, n6),N(n3, n5) skeleton of each barbiturate segment of the purpurate 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 (Å) are given in square parentheses, values for segment 1 preceding those for segment 2. The estimated standard deviations of the defining atoms are in Å The angle between the normals to the two barbiturate planes of each ligand is θ°

Segment n	1	2
10^4p	9 016	9 927
10^4q	−3 566	−0 512
10^4r	2 449	−1 093
s	2.941	1.700
σ	0.07	0.06
χ^2	233	159
θ	31.8	

[C(11) 0.11, 0.09; C(12) −0.08, −0.05; N(13) 0.00, −0.01; C(14) 0.04, −0.05; N(15) −0.01, −0.01; C(16) −0.06, −0.06; N(0) 0.17, 0.13; O(12) −0.26, −0.23; O(14) 0.06, 0.07; O(16) −0.30, −0.33; Ca −0.80, −0.31]

(*b*) Least-squares 'planes' in the same form defined by (*i*) Ca, N(0), O(12,22), O(24^{II}), and (*ii*) Ca, O(1,2,3), O(14^{I})

	10^4p	10^4q	10^4r	s	σ	χ^2
(*i*)	9 981	−0 291	−0 528	2.028	0.12	607

[Deviations: Ca, 0.03; N(0), −0.16; O(12), 0.14; O(22), 0.09; O(24^{II}), −0.09]

	10^4p	10^4q	10^4r	s	σ	χ^2
(*ii*)	0 057	10 000	0 063	1.180	0.10	371

[Deviations: Ca, −0.07; O(1) ,−0.10; O(2), −0.04; O(3), 0.09; O(14^{I}), 0.11]

[6/1550 *Received, 9th August,* 1976]