Structural Studies in Metal–Purpurate Complexes. Part 7.† Crystal Structures of Diaquanitratopurpurato-cobalt(II) and -zinc(II) Dihydrate

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The crystal structures of the title compounds, $[ML(NO_3)(H_2O)_2]\cdot 2H_2O$ [L = purpurate, M = Co (1) or Zn (2)], have been determined at 295 K by *X*-ray diffraction and refined by least squares to *R* 0.058 (1 117 ' observed ' reflections) and 0.078 (1 995 ' observed ' reflections) respectively. Crystals are monoclinic, space group *A*2/*a* $Z = 8$. For (1), $a = 26.86(4)$, $b = 7.20(1)$, $c = 16.774(6)$ Å, $\beta = 101.65(9)°$; for (2), $a = 26.781(7)$, $b = 7.192(2)$, $c = 16.746(4)$ Å, $\beta = 101.42(2)°$. The isostructural complexes comprise a complex molecule with a tridentate purpurate ligand [M–N, 2.200(7) (1), 2.229(7) (2); M–O, 2.114(7), 2.112(6) (1), 2.104(7), 2.127(7) Å (2)] and an asymmetrically bidentate nitrate group in an approximate central plane [M–O, 2.384(8), 2.254(7) (1); 2.511(8), 2.266(8) Å (2)] with two water molecules axial [$M-OH_2$, 2.146(8), 2.060(9) (1); 2.138(8), 2.014(9) Å (2); O–M–O, 168.8(3) (1); 162.5(3)° (2)]. Very little difference is found in the geometries of the two molecules, the only non-trivial change being in the degree of asymmetry found in the nitrate co-ordination.

ADDITION of murexide {ammonium purpurate, $[NH_4]$-[L] ($L = [C_8H_4N_5O_6]^-$)} to a considerable excess of certain aqueous transition-metal nitrates has led to crystalline derivatives of the type $[ML(NO_3)]\cdot 4H_2O$. With the zinc derivative in particular a considerable yield of yellow crystalline product is easily obtained, although it is difficult to obtain crystals of any reasonable size. It was considered to be of interest to establish the structure of this derivative to investigate (*a*) whether the nitrate was co-ordinated, and, if not (*b*) the influence of the change of metal type and size on the geometry of the $[ML(H_2O)_x]$ species, if formed. Structure determination of $[ZnL(NO_3)]\cdot 4H_2O$ has established the presence of an asymmetrically bidentate nitrate species. Although obtained only in very small quantities, the existence of the cobalt(II) analogue has been established by demonstrating it to be isomorphous with that of the zinc derivative, and since it is relatively rare to find these two metals exhibiting the same co-ordination geometry, it was decided to determine its structure also, and the influence of the change in metal atom on the co-ordination sphere. This paper therefore describes the structure determination of $[CoL(NO_3)]\cdot 4H_2O$ (1) and $[ZnL(NO_3)]\cdot 4H_2O$ (2).

EXPERIMENTAL

Analysis for (2); Found, calc. for $[ZnL(NO_3)]\cdot 4H_2O$: C, 20.8, 20.64; H, 2.7, 2.60; N, 18.1, 18.05; Zn, 14.35, 14.04%. 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.[1]

Crystallographic Data and Procedure.—(1): $C_8H_{12}CoN_6O_{13}$, $M = 459.2$, Monoclinic, space group *A*2/*a* (variant of C_{2h}^6, No. 15), $a = 26.86(4)$, $b = 7.20(1)$, $c = 16.774(6)$ Å, $\beta = 101.65(9)°$, $U = 3\,177(8)$ Å^3, $Z = 8$, $D_c = 1.92$ g cm^{-3}, $F(000) = 1\,864$, crystal size $0.05 \times 0.10 \times 0.06$ mm (prism), $\mu(\text{Mo-}K_\alpha) = 10.8$ cm^{-1} (no absorption correction applied), data range $2\theta < 40°$ yielding 1 505 reflections (1 117 ' observed ') [at the $\sigma(I)$ level], final $R = 0.058$, $R' = 0.043$ ($n = 1$).

The small crystal size and consequent weak data led to considerable difficulty in crystal orientation and cell determination. The very limited quantity of sample available precluded a density determination. 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 atoms in the immediate environment of the metal atoms were refined as a single block, the atom parameters of each of the purpurate ligand rings being refined similarly. Non-hydrogen-atom thermal motion was refined anisotropically. Hydrogen atoms were refined positionally [with two exceptions (see Table 1) which were included in the refinement with positions (estimated from a difference map) held invariant] and with invariant isotropic thermal parameters, $U = 0.10$ Å^2.

(2): $C_8H_{12}ZnN_6O_{13}$, $M = 465.6$, Monoclinic, space group *A*2/*a* (variant of C_{2h}^6, No. 15), $a = 26.781(7)$, $b = 7.192(2)$,

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† Part 6 is the preceding paper.

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

TABLE 1

Atomic fractional cell co-ordinates [(x, y, z); H × 10^3; Co, Zn × 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 zinc derivative) are given immediately below those for (1) (the cobalt derivative)

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co (1)	09 058(5)	04 148(20)	16 976(7)	24(1)	39(1)	18(1)	1(1)	4(1)	1(1)
Zn (2)	09 027(4)	03 007(16)	16 965(6)	12(1)	25(1)	12(0)	4(1)	2(1)	2(1)
The purpurate ligand									
N(0)	1 596(2)	−0 489(11)	2 552(4)	25(5)	28(5)	26(4)	1(5)	6(4)	−7(5)
	1 598(3)	−0 612(11)	2 575(4)	24(4)	32(5)	16(4)	−2(4)	−4(3)	−9(3)
C(11)	1 993(3)	−0 709(14)	2 200(5)	14(6)	35(7)	24(6)	11(5)	−7(5)	7(5)
	1 986(3)	−0 883(14)	2 200(6)	16(5)	37(6)	32(5)	−2(4)	7(4)	−6(5)
C(12)	1 851(3)	− 0722(14)	1 321(5)	21(6)	33(7)	23(6)	4(6)	1(5)	5(6)
	1 851(3)	−0 847(13)	1 321(6)	22(5)	22(5)	31(5)	0(4)	7(4)	4(4)
O(12)	1 413(2)	−0 388(9)	0 947(3)	29(4)	51(5)	26(4)	12(4)	3(3)	−3(4)
	1 409(2)	−0 487(10)	0 943(4)	23(3)	57(5)	30(4)	14(3)	6(3)	−4(4)
N(13)	2 218(3)	−1 204(11)	0 890(4)	26(6)	32(6)	16(4)	4(4)	7(4)	−4(4)
	2 220(3)	−1 302(11)	0 895(5)	28(4)	32(5)	22(4)	6(4)	6(4)	−1(4)
H(13)	212(4)	−146(16)	032(6)	100(—)					
	208(5)	−122(20)	029(8)	100(—)					
C(14)	2 724(4)	−1 386(14)	1 235(6)	30(8)	25(7)	22(7)	−1(6)	−3(6)	4(6)
	2 730(4)	−1 524(13)	1 247(6)	36(6)	23(5)	27(5)	11(4)	15(5)	5(4)
O(14)	3 039(2)	−1 739(10)	0 822(4)	26(4)	51(5)	24(4)	3(4)	12(3)	2(4)
	3 043(2)	−1 863(10)	0 814(4)	21(4)	54(5)	25(4)	4(3)	8(3)	0(3)
N(15)	2 856(3)	−1 121(11)	2 055(5)	29(6)	41(6)	25(5)	10(4)	3(4)	−7(4)
	2 863(3)	−1 281(12)	2 063(5)	21(4)	32(5)	29(5)	2(4)	2(4)	−1(4)
H(15)	312(4)	−144(15)	229(6)	100(—)					
	322(5)	−130(20)	227(8)	100(—)					
C(16)	2 527(3)	−0 676(13)	2 569(6)	22(6)	11(6)	30(6)	13(5)	2(6)	1(5)
	2 533(3)	−0 759(12)	2 585(6)	16(4)	22(5)	29(5)	11(4)	4(4)	−3(4)
O(16)	2 705(2)	−0 057(10)	3 251(4)	43(4)	49(6)	26(4)	2(4)	1(3)	−16(4)
	2 707(2)	−0 222(11)	3 264(4)	32(4)	56(5)	31(4)	0(4)	−5(3)	−16(4)
C(21)	1 544(3)	−0 553(14)	3 321(5)	26(6)	27(7)	18(5)	12(6)	6(4)	−10(5)
	1 543(3)	−0 666(12)	3 337(5)	14(4)	18(5)	29(5)	0(4)	2(4)	−3(4)
C(22)	1 052(3)	0 094(13)	3 424(5)	39(6)	24(7)	19(6)	−2(5)	11(5)	−8(5)
	1 044(3)	0 025(12)	3 441(5)	39(5)	14(5)	19(4)	−7(4)	8(4)	2(4)
O(22)	0 702(2)	0 506(10)	2 849(3)	18(4)	49(5)	22(3)	9(4)	−2(3)	9(4)
	0 703(2)	0 479(10)	2 862(4)	28(4)	52(5)	22(3)	4(3)	4(3)	2(3)
N(23)	0 982(3)	0 280(13)	4 206(5)	29(5)	46(7)	18(5)	13(5)	7(4)	−2(5)
	0 978(3)	0 236(12)	4 227(4)	27(4)	35(4)	21(4)	3(4)	8(3)	2(4)
H(23)	073(4)	073(19)	430(7)	100(—)					
	067(5)	097(20)	432(8)	100(—)					
C(24)	1 335(4)	−0 198(15)	4 901(5)	30(7)	42(8)	15(6)	1(6)	−4(5)	0(6)
	1 323(4)	−0 261(15)	4 921(5)	30(5)	39(6)	20(5)	−1(5)	4(4)	1(5)
O(24)	1 229(2)	0 059(10)	5 568(3)	56(5)	48(5)	10(4)	1(4)	9(3)	0(4)
	1 227(3)	0 000(11)	5 585(4)	52(4)	51(5)	21(3)	12(4)	5(3)	3(4)
N(25)	1 772(3)	−0 971(11)	4 775(5)	22(6)	34(5)	21(5)	8(5)	−1(4)	4(4)
	1 764(3)	−1 085(12)	4 792(5)	27(4)	34(5)	22(4)	1(4)	3(3)	6(4)
H(25)	201(4)	−157(18)	521(7)	100(—)					
	203(5)	−170(19)	531(8)	100(—)					
C(26)	1 897(4)	−1 384(15)	4 016(5)	26(7)	22(7)	21(6)	−4(6)	4(5)	−8(5)
	1 881(4)	−1 488(14)	4 037(6)	34(6)	26(6)	26(5)	8(5)	1(4)	8(4)
O(26)	2 249(3)	−2 403(10)	3 983(4)	43(5)	45(5)	33(4)	21(4)	5(4)	0(4)
	2 233(3)	−2 541(10)	4 001(4)	38(4)	44(5)	30(4)	20(4)	2(3)	1(3)
The co-ordinated nitrate ion									
N(1)	0 141(3)	2 123(12)	0 635(5)	49(7)	29(6)	27(6)	1(5)	−5(5)	−5(5)
	0 130(3)	2 133(12)	0 635(5)	29(5)	32(5)	40(5)	−3(4)	−3(4)	−1(4)
O(a)	0 114(3)	2 020(11)	1 374(4)	54(6)	76(7)	34(5)	−13(5)	3(4)	−14(5)
	0 084(3)	2 103(13)	1 354(4)	66(6)	74(7)	31(4)	−14(5)	5(4)	0(4)
O(b)	−0 181(3)	2 977(12)	0 154(4)	64(6)	78(7)	32(5)	40(5)	−10(4)	−4(5)
	−0 178(3)	2 970(12)	0 122(4)	60(6)	60(6)	39(5)	31(5)	−17(4)	−3(4)
O(c)	0 511(2)	1 284(10)	0 438(4)	35(5)	53(5)	63(5)	19(4)	10(4)	−5(4)
	0 493(3)	1 257(11)	0 447(5)	36(5)	48(5)	67(6)	5(4)	22(4)	−5(4)
The co-ordinated water molecules [r (Å) is O–H; γ (°) is M–O–H and δ (°) H–O–H]									
O(1)	1 171(2)	3 212(9)	1 933(3)	35(4)	40(5)	27(4)	−3(4)	12(3)	11(4)
	1 159(3)	3 102(11)	1 932(4)	28(4)	50(5)	20(4)	−1(4)	7(3)	3(3)
H(1α)	125(4)	396(16)	143(6)	100(—)	r = 1.1(1); γ = 117(6); δ = 116(10)				
	120(5)	374(20)	144(8)	100(—)	r = 1.0(1); γ = 112(8); δ = 114(13)				
H(1β)	096(4)	359(16)	212(6)	100(—)	r = 0.8(1); γ = 99(9)				
	090(5)	343(22)	211(9)	100(—)	r = 0.8(2); γ = 94(10)				
O(2)	0 515(3)	−2 056(11)	1 483(4)	89(6)	66(6)	23(4)	−17(5)	5(4)	−7(4)
	0 457(4)	−1 977(13)	1 497(4)	74(6)	47(6)	27(4)	−15(5)	4(4)	−3(4)
H(2α)	033(4)	−227(16)	099(6)	100(—)	r = 0.9(1); γ = 119(7); δ = 116(12)				
	042(6)	−230(23)	109(8)	100(—)	r = 0.7(1); γ = 113(13); δ = 115(16)				
H(2β)	040(4)	−196(17)	175(6)	100(—)	r = 0.6(1); γ = 95(11)				
	046(5)	−297(21)	192(8)	100(—)	r = 1.0(1); γ = 123(8)				

TABLE 1 (*Continued*)

The lattice water molecules

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(3)	0 444(3)	5 168(11)	2 533(4)	60(5)	33(5)	37(4)	−5(4)	14(4)	15(4)
	0 453(3)	5 165(11)	2 516(4)	44(5)	43(5)	41(4)	−4(4)	10(4)	0(4)
H(3α)	053(4)	516(20)	305(7)	100(—)	r = 0.9(1); δ = 117(—)				
	064(4)	525(21)	310(9)	100(—)	r = 1.0(1); δ = 106(13)				
H(3β) *	058(—)	606(—)	227(—)	100(—)	r = 0.9(—)				
	018(4)	454(21)	252(7)	100(—)	r = 0.9(1)				
O(4)	1 008(3)	5 584(14)	4 050(4)	75(6)	71(7)	37(5)	−7(5)	−5(5)	0(6)
	1 003(3)	5 564(14)	4 064(5)	51(6)	78(7)	49(5)	−8(5)	9(4)	6(5)
H(4α) *	107(—)	443(—)	425(—)	100(—)	r = 0.9(—); δ = 90(—)				
	121(6)	466(22)	416(9)	100(—)	r = 0.9(1); δ = 104(14)				
H(4β)	100(5)	592(21)	446(7)	100(—)	r = 0.7(1)				
	082(5)	555(21)	455(8)	100(—)	r = 1.0(1)				

* Estimated in (1) from difference map.

$c = 16.746(4)$ Å, $\beta = 101.42(2)°$, $U = 3\ 162(2)$ Å^3, $D_m = 1.98(2)$ g cm^{-3}, $Z = 8$, $D_c = 1.96$ g cm^{-3}, $F(000) = 1\ 888$, crystal size $0.06 \times 0.20 \times 0.11$ mm (prism), μ(Mo-K_α) = 15.5 cm^{-1} (no absorption correction applied), data range $2\theta < 50°$ yielding 2 799 reflections [1 995 'observed' (at the $3\sigma(I)$ level)], final $R = 0.078$, $R' = 0.080$ ($n = 2$).

The structure was solved and refined as described for (1) above, the positional parameters of all hydrogen atoms being refined in the present case.

Observed and calculated structure factors are deposited in Supplementary Publication No. SUP 21993 (15 pp., 1 microfiche).* Atomic fractional cell co-ordinates are in Table 1, bond distances and angles in Table 2.

DISCUSSION

Because of the isostructural nature of (1) and (2), initial discussion will be carried out in general terms; reference should be made throughout to the accompanying Tables. The lattice comprises discrete [ML(NO$_3$)(H$_2$O)$_2$] complex molecules; one of these, together with two further unco-ordinated lattice solvent molecules, comprises the asymmetric unit (Figure 1). The metal atom is seven-co-ordinated by a tridentate purpurate and a bidentate nitrate group disposed approximately equatorially with the two water molecules axial; as in a number of the other structures in the series, the disposition of the barbiturate ring segments appears to influence, or be influenced by, the crystal packing, the ring planes lying approximately parallel to the ac plane (Figure 2). The co-ordination of the purpurate ion to the metal is of the usual type with short M–O(12, 22) distances and a central M–N(0) distance some 0.1 Å longer; the distances and angles are quite similar to that observed for the [FeL(H$_2$O)$_3$]$^+$ species.[2] The purpurate ion adopts the distorted conformation previously described: the O(16) $\cdots$ O(26) distances are significantly shorter than any others observed in the series, the deviations of O(16, 26) from the barbiturate ring plane are among the highest observed, and the angles between the plane normals the lowest. The metal atom deviates appreciably from the barbiturate planes (Table 3); the equatorial co-ordination 'plane' about the metal is quite irregular and the angle enclosed by the molecular axis defined by the co-ordinated water molecules deviates considerably from 180°. The metal–water bond lengths are significantly different from each other.

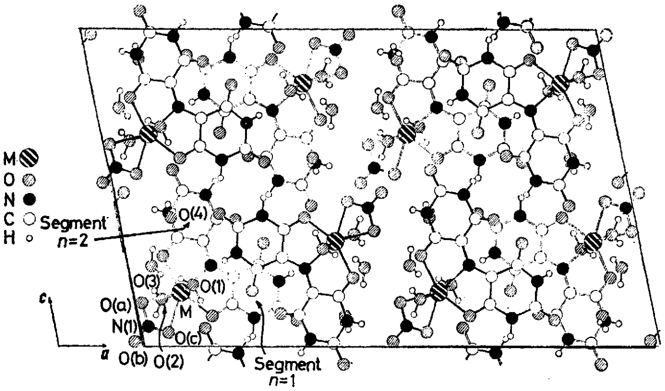

FIGURE 1 Unit-cell contents projected down b, showing labelling of the water-molecule oxygen atoms, the nitrate group, and the purpurate segments

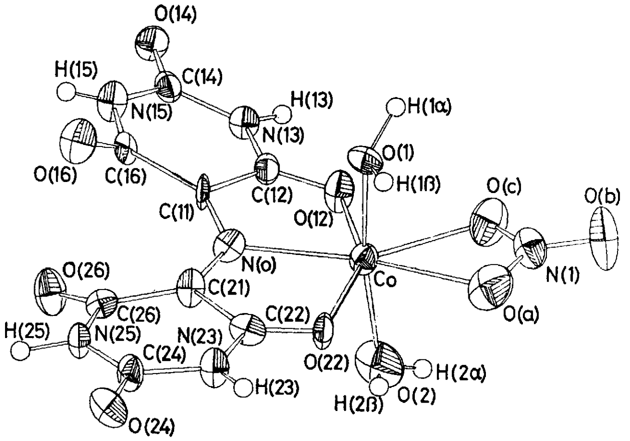

FIGURE 2 Diagram of the complex molecule (1), showing 50% thermal ellipsoids and atom labelling. Hydrogen atoms are given an arbitrary radius of 0.10 Å

About the metal atom, only small differences have been observed between the two derivatives in respect of the purpurate co-ordination, its internal geometry, and the

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

[2] M. C. Favas, D. L. Kepert, A. H. White, and A. C. Willis, Part 3, *J.C.S. Dalton*, 1977, 1350.

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 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

Compound	(1)	(2)
Segment	1 2	1 2
N(0)–C(*n*1)	1.327(11), 1.326(11)	1.331(12), 1.312(12)
C(*n*1)–C(*n*2)	1.447(12), 1.446(13)	1.442(13), 1.468(13)
C(*n*2)–O(*n*2)	1.240(10), 1.239(9)	1.253(10), 1.236(10)
C(*n*2)–N(*n*3)	1.379(13), 1.367(12)	1.367(13), 1.369(12)
N(*n*3)–H(*n*3)	1.0(1), 0.8(1)	1.0(1), 1.0(1)
N(*n*3)–C(*n*4)	1.373(13), 1.390(11)	1.383(12), 1.379(11)
C(*n*4)–O(*n*4)	1.224(13), 1.224(12)	1.235(12), 1.204(12)
C(11)–N(0)–C(21)	132.8(7)	134.7(7)
N(0)–C(*n*1)–C(*n*2)	112.6(7), 112.6(7)	114.7(7), 112.7(7)
C(*n*1)–C(*n*2)–O(*n*2)	122.8(8), 123.5(8)	122.6(9), 123.0(8)
O(*n*1)–C(*n*2)–N(*n*3)	119.3(8), 119.6(8)	119.5(8), 120.5(8)
C(*n*1)–C(*n*2)–N(*n*3)	117.9(7), 116.9(7)	117.8(7), 116.4(7)
C(*n*2)–N(*n*3)–H(*n*3)	120(6), 121(8)	110(8), 118(7)
H(*n*3)–N(*n*3)–C(*n*4)	116(6), 114(8)	125(8), 115(7)
C(*n*2)–N(*n*3)–C(*n*4)	123.7(7), 125.2(8)	124.0(8), 126.0(8)
N(*n*3)–C(*n*4)–O(*n*4)	121.3(8), 118.9(9)	120.0(8), 120.5(9)
N(*n*3)–C(*n*4)–N(*n*5)	116.6(9), 116.0(8)	117.0(9), 115.5(8)
C(*n*2)–C(*n*1)–C(*n*6)	118.1(8), 119.6(8)	118.0(8), 118.5(8)
M–N(0)–C(*n*1)	113.1(5), 113.8(6)	111.0(5), 114.2(6)
M–O(12)–C(12)	114.3(6), 114.2(6)	114.1(6), 114.9(6)

	(1)	(2)
	1 2	1 2
C(*n*1)–C(*n*6)	1.445(12), 1.473(12)	1.480(12), 1.455(12)
C(*n*6)–O(*n*6)	1.231(11), 1.207(13)	1.203(11), 1.218(12)
C(*n*6)–N(*n*5)	1.391(12), 1.412(13)	1.411(13), 1.391(13)
N(*n*5)–H(*n*5)	0.8(1), 1.0(1)	1.0(1), 1.1(1)
N(*n*5)–C(*n*4)	1.362(12), 1.352(14)	1.353(11), 1.376(13)
O(16) · · · O(26)	2.542(10)	2.557(10)
N(0)–C(*n*1)–C(*n*6)	128.7(8), 127.4(8)	125.6(8), 128.4(8)
C(*n*1)–C(*n*6)–O(*n*6)	124.6(9), 126.5(9)	126.6(9), 125.2(9)
O(*n*6)–C(*n*6)–N(*n*5)	119.0(8), 120.1(8)	119.8(8), 119.2(8)
C(*n*1)–C(*n*6)–N(*n*5)	115.6(8), 113.3(8)	113.6(8), 115.5(8)
C(*n*6)–N(*n*5)–H(*n*5)	112(8), 111(8)	119(8), 114(8)
H(*n*5)–N(*n*5)–C(*n*4)	121(8), 121(8)	114(8), 119(8)
C(*n*6)–N(*n*5)–C(*n*4)	126.1(8), 126.8(7)	126.0(8), 125.9(7)
N(*n*5)–C(*n*4)–O(*n*4)	122.1(9), 125.1(8)	122.9(8), 124.0(8)

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

M–O(12)	2.114(7), 2.104(7)	M–O(2)	2.060(9), 2.014(9)
M–O(22)	2.112(6), 2.127(7)	M–O(a)	2.384(8), 2.511(8)
M–N(0)	2.200(7), 2.229(7)	M–O(c)	2.254(7), 2.266(8)
M–O(1)	2.146(8), 2.138(8)		
O(12)–M–O(22)	150.5(2), 151.2(2)	N(0)–M–O(1)	87.3(3), 87.8(3)
O(12)–M–N(0)	75.4(3), 76.3(3)	N(0)–M–O(2)	101.0(3), 105.0(3)
O(12)–M–O(1)	97.8(3), 98.2(3)	N(0)–M–O(a)	152.5(3), 151.5(3)
O(12)–M–O(2)	91.5(3), 96.4(3)	N(0)–M–O(c)	150.3(3), 152.3(3)
O(12)–M–O(a)	130.5(2), 129.7(2)	O(1)–M–O(2)	168.8(3), 162.5(3)
O(12)–M–O(c)	75.8(2), 77.3(3)	O(1)–M–O(a)	80.5(3), 77.8(3)
O(22)–M–N(0)	75.7(2), 75.1(3)	O(1)–M–O(c)	89.3(2), 87.9(3)
O(22)–M–O(1)	86.6(3), 84.5(3)	O(2)–M–O(a)	88.8(3), 85.5(3)
O(22)–M–O(2)	88.3(3), 87.3(3)	O(2)–M–O(c)	87.1(3), 86.1(3)
O(22)–M–O(a)	79.0(2), 79.1(2)	O(a)–M–O(c)	54.7(3), 52.6(3)
O(22)–M–O(c)	133.5(2), 131.6(3)		

(*c*) The nitrate geometry; the two components within each entry are for compounds (1) and (2), respectively

N–O(a)	1.259(12), 1.233(12)	N–O(b)	1.221(11), 1.225(11)
N–O(c)	1.262(12), 1.249(12)		
N–O(a)–M	91.6(6), 88.9(6)	N–O(c)–M	97.7(5), 100.3(6)
O(a)–N–O(b)	120.5(9), 120.6(9)	O(b)–N–O(c)	123.8(9), 121.3(9)
O(a)–N–O(c)	115.7(8), 118.0(8)		

(*d*) Interspecies hydrogen-bonding interactions of the ligand hydrogen atoms (O · · · H, <2.5 Å); the angle subtended at the hydrogen is given in parentheses

	(1)	(2)
H(13) · · · $O(14^{I})$	1.9(1) [175(10)]	1.9(1) [159(12)]
H(15) · · · $O(1^{II})$	2.1(1) [168(11)]	2.0(1) [155(12)]
H(23) · · · $O(b^{III})$	2.1(1) [165(11)]	1.9(1) [160(11)]
H(25) · · · $O(26^{IV})$	2.2(1) [160(11)]	2.2(1) [155(11)]
H(1α) · · · $O(24^{V})$	1.6(1) [166(8)]	1.7(1) [174(13)]
H(1β) · · · O(3)	2.0(1) [166(12)]	1.9(2) [156(15)]
H(2α) · · · $O(b^{VI})$	1.9(1) [159(10)]	2.1(1) [170(17)]
H(2β) · · · $O(3^{VII})$	2.4(1) [109(12)]	1.7(2) [172(13)]
H(3α) · · · O(4)	1.9(1) [152(12)]	1.7(1) [172(13)]
H(3β) · · · $O(2^{VIII})$	1.9(—) [151(—)]	
H(3β) · · · $O(22^{III})$		2.3(1) [146(12)]
H(3β) · · · $O(a^{III})$		2.4(2) [129(11)]
H(4α) · · · $O(14^{IX})$	2.6(—) [113(—)]	2.3(2) [156(15)]
H(4β) · · · $O(c^{X})$	2.3(1) [147(14)]	1.9(2) [164(12)]

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

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

TABLE 3

(*a*) 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 ($n = 1$ or 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*	1	2	1	2
10^4p	1 498	4 162	1 491	4 330
10^4q	9 807	9 070	9 812	8 992
10^4r	−1 254	0 639	−1 229	0 622
s	−0.173 9	1.154	−0.263 6	1.129
σ	0.06	0.06	0.08	0.06
χ^2	142	193	366	231
C(*n*1)	0.09	0.09	0.12	0.09
C(*n*2)	−0.07	−0.04	−0.07	−0.05
N(*n*3)	0.01	−0.03	−0.01	−0.02
C(*n*4)	0.03	0.03	0.03	0.03
N(*n*5)	0.00	0.02	0.02	0.02
C(*n*6)	−0.05	−0.08	−0.09	−0.08
N(0)	0.18	0.22	0.17	0.22
O(*n*2)	−0.23	−0.14	−0.25	−0.12
O(*n*4)	0.04	0.06	0.04	0.06
O(*n*6)	−0.39	−0.35	−0.37	−0.35
M	−0.40	0.07	−0.41	0.04
θ	19.3		20.1	

(*b*) Least-squares 'planes' in the same form defined by (*i*) M, N(0), O(12,22), O(a, c) and (*ii*) the nitrate ligand

	10^4p	10^4q	10^4r	s	σ	χ^2
(*i*)	4 037	9 064	1 246	1.423	0.12	1 474
	4 251	8 970	1 210	1.406	0.12	1 584

[Deviations: M, −0.05, −0.09; N(0), 0.16, 0.17; O(12), −0.08, −0.06; O(22), −0.14, 0.13; O(a), 0.11, 0.12; O(c) 0.00, −0.01]

	10^4p	10^4q	10^4r	s	σ	χ^2
(*ii*)	5 255	8 302	1 860	1.545	0.00	0.24
	5 436	8 211	1 742	1.510	0.00	0.76

[Deviations: All 0.00 except M, 0.20, 0.16]

water molecules. However, considerable differences are found in the geometry and disposition of the nitrate ion, which, in the case of the cobalt derivative, is clearly asymmetrically bidentate, and, as a consequence of the relatively minor increase in stereochemical crowding which occurs on passing to the zinc analogue, becomes almost unidentate; in both cases, metal–nitrate oxygen distances are long, suggesting that the nitrate is weakly bound.

In co-ordinated ions of the planar $[XO_3]^{n-}$ type, systematic variations are often observed in the anion geometry; in these examples, the central-atom–oxygen distances are correlated with the opposed angle. (A good example of such correlation induced by hydrogen-bonding is found elsewhere in this series.[3]) In the present example, the situation is complicated by the somewhat indecisive nature of the nitrate co-ordination to the metal and the interaction of O(b) with nearby hydrogen atoms: it is apparent that the shortest distance within the nitrate, N–O(b), is opposed to the smallest angle [O(a)–N–O(c)]; this angle is found to increase as the co-ordination of O(a) to the metal diminishes on passing from (1) to (2) although this diminution in angle closure may be as much a consequence of the decrease in chelation as of the increase in N–O(a) bond order and corresponding decrease in O(b)–N–O(c). The geometry related to O(c) remains relatively constant [M–O(c), N–O(c), and O(a)–N–O(b)].

As in other structures in the series, the lattice exhibits extensive hydrogen-bonding; this is summarized in Table 2.

[6/060 *Received*, 8*th January*, 1976]

[3] C. L. Raston, A. H. White, and A. C. Willis, Part 8, following paper.