Crystal Structures of the Barium Salts of Isonitroso- and of *NN′*-Dimethylisonitroso-malonamide

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The structures of (I) $2Ba[NH_2{\cdot}CO{\cdot}C(NO){\cdot}CO{\cdot}NH_2]_2{\cdot}7H_2O$, and (II) $Ba[MeNH{\cdot}CO{\cdot}C(NO){\cdot}CO{\cdot}NHMe]_2$ have been determined by *X*-ray (heavy-atom) methods from diffractometer data and refined by least squares to *R* 0.10 and 0.038 respectively. Crystals of (I) are tetragonal, space group $P4_12_12$, a = 10.718(3), c = 51.12(3) Å, Z = 8. Crystals of (II) are trigonal, space group $R\bar{3}$, a = 10.966(2) Å, α = 73.34(2)°, Z = 3. (I) comprises pairs of barium atoms 4.763 Å apart and bridged in an infinite polymeric array in the *ab* plane by the ligands, the resulting layers normal to *c* being hydrogen-bonded by interleaving water molecules. The barium atoms are nine- and ten-co-ordinated by an assortment of ligand nitrogen and oxygen atoms and water molecules. (II) comprises centrosymmetric triads of barium atoms disposed in the three-fold axis [Ba ⋯ Ba, 4.2414(7) Å] and bridged by the oxygen atoms of the ligands, the centrosymmetric barium being six-co-ordinate, and the others nine-co-ordinate. A three-dimensional polymer is formed by oxygen bridges.

In conjunction with some concurrent structural studies [1] on the tris(isonitrosomalonamido)ferrate(II) salts, it was considered useful to attempt an accurate definition of the geometry of both the parent ligand, isonitrosomalonamide, and its anion in the uncomplexed form. Attempts to grow crystals of isonitrosomalonamide and its alkali-metal salts were unsuccessful, but considerably more success was obtained with the heavy alkaline-earth metal derivatives, in particular of a number of derivatives of barium. Since it appeared unlikely that in the barium derivatives the anion would exist as an independent species, these derivatives were not generally considered useful. Among the derivatives so obtained, however, two in particular appeared to be of potential interest from the viewpoint of crystal packing, since the crystal symmetry was high and it appeared likely that the lattice might consist of infinite hydrogen-bonded arrays comparable to those found in the iron(II) complex salts, but with different periods imposed by the lattice symmetry. These were the salts $2BaL_2{\cdot}7H_2O$, (I) [HL = isonitrosomalonamide, $NH_2{\cdot}CO{\cdot}C(NOH){\cdot}CO{\cdot}NH_2$], which was found to crystallize in a non-centrosymmetric tetragonal space group, and BaL'_2, (II) [HL′ = *NN′*-dimethylisonitrosomalonamide,, $MeHN{\cdot}CO{\cdot}C(NOH){\cdot}CO{\cdot}NHMe$], which was trigonal. We describe the determination of the crystal structures of these two derivatives.

EXPERIMENTAL

Isonitrosomalonamide and *NN′*-dimethylisonitrosomalonamide were prepared as described in the literature.[1-3] A number of barium derivatives of L and L′ have been obtained, all pale yellow crystalline solids.

(*a*) *With* HL. (i) $BaL_2(HL)_2{\cdot}4H_2O$ was obtained on slowly cooling a solution containing excess of free ligand; (ii) $2BaL_2{\cdot}7H_2O$ (I), by the slow evaporation of a solution containing stoicheiometric quantities of HL and $Ba(OH)_2$ or $BaCO_3$; and (iii) BaL_2 from the slow evaporation of a solution with a slight excess of L^-.

(*b*) *With* HL′. (i) BaL_2' as for (*a*) (ii) but with HL′. Analytical figures for Ba, C, H, and N are given in the Supplementary Publication (see later).

Crystallography.—In both cases, unit-cell dimensions were obtained by a least-squares fit of the angular parameters of 15 high-angle reflections centred in the counter aperture of a Syntex $P\bar{1}$ four-circle diffractometer, unique data sets being gathered by a conventional 2θ—θ scan.

Crystal Data—(I), $C_{12}H_{30}Ba_2N_{12}O_{19}$, M = 903.1, Tetragonal, a = 10.718(3), c = 51.12(3) Å, U = 5 873(4) Å^3, D_m = 2.05(1) g cm^{-3}, Z = 8, D_c = 2.04 g cm^{-3}, $F(000)$ = 3 520. Crystal size 0.19 × 0.09 × 0.06 mm. Cu-K_α radiation (Ni-filtered), λ = 1.541 8 Å. Space group $P4_12_12$ (No. 92, D_4^4). Data corrected for absorption, μ(Cu-K_α) = 213 cm^{-1}; data range $2\theta < 100°$ yielding 1 878 independent reflections, 1 829 with $I > 2\sigma(I)$ being considered observed and used in the structure solution and refinement.

(II), $C_{10}H_{16}BaN_4O_6$, M = 453.6, Trigonal, a = 10.966(2) Å, α = 73.34(2)°, U = 1 179(1) Å^3, D_m = 1.91(1) g cm^{-3}, Z = 3, D_c = 1.92 g cm^{-3}, $F(000)$ = 666. Crystal size:

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[1] C. L. Raston and A. H. White, *J.C.S. Dalton*, to be published.

[2] M. Conrad and A. Schulze, *Ber.*, 1909, 729.

[3] M. A. Whiteley, *J. Chem. Soc.*, 1900, 1040.

polyhedral spheroid *ca.* 0.25 mm dia. Mo-K_α monochromatic radiation, $\lambda = 0.710\ 69$ Å, space group $R\bar{3}$ (No. 148, C_{3i}^2). Data corrected for absorption, $\mu(\text{Mo-}K_\alpha) = 26.4\ \text{cm}^{-1}$, data range $2\theta < 50°$, yielding 1 599 independent reflections of which 1 539 with $I > \sigma(I)$ were considered observed and used in the subsequent refinement.

The structures of (I) and (II) were solved by the heavy-atom method. For (I), systematic absences and data established the space group as either $P4_12_12$ (No. 92) or its enantiomer $P4_32_12$ (No. 96); the structure was initially solved in the former.

TABLE 1

(*a*) Atomic fractional cell co-ordinates and thermal parameters ($\times 10^3$ Å^2) for (I), with least-squares estimated standard deviations in parentheses [$(x, y) \times 10^4$ for Ba; for others $\times 10^3$; $(z) \times 10^5$ for Ba, $\times 10^4$ for others]

(*i*) Ba atoms and water molecules

Atom	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ba(1)	7 281(2)	1 940(2)	04 130(4)	14(2)	15(2)	32(1)	−6(1)	−2(1)	2(1)
Ba(2)	9 955(3)	−0 774(2)	89 828(4)	19(2)	19(2)	35(1)	−3(1)	−2(1)	2(1)
O(1)	786(3)	139(3)	−0 124(5)	110(30)	78(25)	70(16)	0(21)	13(19)	−11(18)
O(2)	576(3)	345(3)	0 078(7)	86(31)	89(31)	159(30)	35(22)	−16(26)	2(26)
O(3)	720(3)	231(3)	0 971(5)	68(24)	88(26)	80(17)	−5(19)	8(17)	40(18)
O(4)	911(2)	007(2)	0 393(5)	38(18)	37(18)	92(16)	−14(12)	15(15)	25(16)
O(5)	1 176(3)	−262(3)	0 857(6)	66(24)	43(21)	144(26)	10(17)	17(21)	11(19)
O(6)	1 011(3)	−056(3)	1 449(5)	111(33)	113(33)	75(17)	24(24)	9(20)	−9(19)
O(7)	413(3)	500(8)	0 401(6)	93(30)	79(29)	136(24)	7(20)	−12(23)	−8(25)

(*ii*) Ligands

Atom	*x*	*y*	*z*	*U*	Atom	*x*	*y*	*z*	*U*
O(11)	588(2)	000(3)	0 216(5)	60(8)	O(31)	902(3)	−303(3)	1 057(5)	74(9)
N(11)	434(3)	−135(3)	0 269(6)	55(9)	N(31)	811(4)	−490(4)	1 037(6)	79(12)
C(11)	535(4)	−080(4)	0 369(7)	61(12)	C(31)	846(4)	−385(4)	0 913(7)	83(11)
O(12)	730(3)	−064(3)	0 910(5)	63(8)	O(32)	881(3)	−239(3)	0 300(5)	78(9)
N(12)	679(3)	−041(3)	0 692(5)	52(9)	N(32)	900(4)	−269(4)	0 546(7)	75(11)
C(12)	579(4)	−114(4)	0 602(6)	40(9)	C(32)	830(4)	−373(4)	0 651(6)	40(9)
O(13)	429(3)	−272(3)	0 696(6)	89(10)	O(33)	703(3)	−554(3)	0 593(5)	65(8)
N(13)	592(3)	−252(3)	0 991(6)	63(10)	N(33)	737(4)	−422(3)	0 234(6)	68(10)
C(13)	528(5)	−216(5)	0 767(9)	79(15)	C(33)	746(5)	−448(5)	0 478(9)	88(16)
O(21)	935(3)	331(3)	0 249(5)	72(9)	O(41)	1 224(3)	005(3)	1 061(5)	73(9)
N(21)	1 082(3)	485(4)	0 301(7)	75(11)	N(41)	1 410(4)	118(4)	1 041(7)	78(12)
C(21)	1 010(5)	383(5)	0 395(8)	69(13)	C(41)	1 302(5)	071(5)	0 917(8)	73(14)
O(22)	974(3)	185(3)	0 948(5)	71(9)	O(42)	1 159(3)	040(3)	0 301(5)	68(8)
N(22)	959(4)	229(4)	0 712(6)	66(10)	N(42)	1 184(3)	030(3)	0 548(6)	64(10)
C(22)	1 039(4)	331(4)	0 646(6)	48(10)	C(42)	1 291(4)	094(4)	0 663(3)	49(11)
O(23)	1 204(3)	475(4)	0 750(6)	96(10)	O(43)	1 474(3)	208(3)	0 605(5)	73(9)
N(23)	1 147(3)	332(3)	1 066(6)	64(10)	N(43)	1 346(3)	189(3)	0 238(6)	64(10)
C(23)	1 144(5)	377(5)	0 833(9)	82(15)	C(43)	1 372(5)	174(5)	0 490(8)	72(14)

(*b*) Atom and thermal parameters for (II) [$(x, y, z) \times 10^5$ for Ba; $\times 10^3$ for H; $\times 10^4$ for others]

Atom				U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ba(1)	0	0	0	24.8(6)	24.8(6)	24.8(6)	−6.2(4)	−6.2(4)	−6.2(4)
Ba(2)	17 802(6)	17 802(6)	17 802(6)	24.3(5)	24.3(5)	24.3(5)	−5.7(3)	−5.7(3)	−5.7(3)
C(10)	4 875(7)	−2 833(7)	1 770(8)	47(4)	38(4)	62(5)	−13(3)	−5(4)	−15(3)
C(1)	5 033(5)	−0 639(5)	1 606(5)	33(3)	34(3)	27(3)	−5(2)	−8(2)	−8(2)
N(1)	5 611(5)	−1 853(4)	1 488(5)	30(3)	30(3)	42(3)	−5(2)	−4(2)	−8(2)
O(1)	3 833(3)	−0 301(3)	1 971(4)	23(2)	33(2)	67(3)	−6(2)	−2(2)	−13(2)
C(2)	5 898(5)	0 290(5)	1 322(4)	27(3)	31(3)	22(3)	−6(2)	−4(2)	−4(2)
N(2)	7 191(4)	0 044(4)	0 941(4)	34(2)	35(3)	29(2)	−7(2)	−7(2)	−9(2)
O(2)	7 842(3)	−1 118(3)	0 734(3)	30(2)	33(2)	47(2)	−2(2)	−3(2)	−17(2)
C(3)	5 304(5)	1 655(5)	1 480(5)	26(3)	33(3)	29(3)	−10(2)	−4(2)	−5(2)
N(3)	6 051(5)	2 280(5)	1 732(5)	28(3)	43(3)	77(4)	−5(2)	−14(3)	−25(3)
O(3)	4 180(3)	2 193(3)	1 398(4)	28(2)	34(2)	69(3)	−6(2)	−14(2)	−21(2)
C(30)	5 603(7)	3 631(7)	1 804(9)	44(4)	42(4)	104(7)	−9(3)	−11(4)	−34(4)
H(1)	641(6)	−202(6)	133(6)	6(2)					
H(10a)	532(7)	−347(8)	123(7)	10(3)					
H(10b)	408(6)	−250(6)	149(6)	5(2)					
H(10c)	462(8)	−326(8)	258(8)	10(3)					
H(3)	679(5)	197(5)	168(5)	4(2)					
H(30a)	583(8)	427(8)	067(9)	13(3)					
H(30b)	613(7)	397(7)	220(7)	10(3)					
H(30c)	487(7)	366(7)	228(7)	8(3)					

Both structures were refined by least squares: for (I), the parameters of each ligand were refined as a single matrix, the barium and water oxygen atom parameters being refined as 9 × 9 blocks. Hydrogen atom positions were estimates for the ligands and the bridging water O(4), and included as invariants in the refinement. For (II), full-matrix refinement was used, all hydrogen atoms being located in a difference map and refined. Anisotropic thermal parameters of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} \ldots + 2U_{23}klb^*c^*)]$ were employed for the barium and water oxygens only in (I), the non-hydrogen ligand light atoms being refined isotropically; in (II), all atoms except the hydrogens were refined anisotropically, the latter being refined in the corresponding isotropic form. Refinement converged in each case with no parameter shift $> 0.1\sigma$, the residual R being 0.104 for (I) and 0.037 for (II), with $R' [= (|\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2)^{\frac{1}{2}}]^{-1}$ being 0·116 (I) and 0.040 (II); weighting schemes of the form $w = [\sigma^2(F_o) + n \times 10^{-4}(F_o)^2]^{-1}$ were found appropriate for $n = 6$ and $n = 3$ respectively. The high residuals for (I) are

TABLE 2

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

(*a*) Barium environments

Ba(1)–O(11)	2.75(2)	Ba(2)–O(12)	2.85(3)
Ba(1)–O(21)	2.79(3)	Ba(2)–O(22)	2.84(3)
Ba(1)–N(12)	2.94(3)	Ba(2)–O(31)	2.74(3)
Ba(1)–N(22)	2.93(4)	Ba(2)–O(41)	2.74(3)
Ba(1)–O(1)	2.88(3)	Ba(2)–N(32)	2.90(4)
Ba(1)–O(2)	2.86(4)	Ba(2)–N(42)	2.92(3)
Ba(1)–O(3)	2.88(3)	Ba(2)–O(4)	2.86(2)
Ba(1)–O(4)	2.81(2)	Ba(2)–O(5)	2.78(3)
Ba(1)–O(33$^{\mathrm{I}}$)	2.87(3)	Ba(2)–O(6)	2.86(3)
Ba(1)–O(43$^{\mathrm{II}}$)	2.89(3)	Ba(1) ··· Ba(2)	4.763(4)

O(11)–Ba(1)–O(21)	136.1(7)	O(12)–Ba(2)–O(22)	82.2(8)
O(11)–Ba(1)–N(12)	55.6(8)	O(12)–Ba(2)–O(31)	70.9(9)
O(11)–Ba(1)–N(22)	138.4(9)	O(12)–Ba(2)–O(41)	149.9(8)
O(11)–Ba(1)–O(1)	67.3(9)	O(12)–Ba(2)–N(32)	72.8(9)
O(11)–Ba(1)–O(2)	84.0(9)	O(12)–Ba(2)–N(42)	133.7(9)
O(11)–Ba(1)–O(3)	116.7(8)	O(12)–Ba(2)–O(4)	72.7(7)
O(11)–Ba(1)–O(4)	80.1(8)	O(12)–Ba(2)–O(5)	137.3(9)
O(11)–Ba(1)–O(33$^{\mathrm{I}}$)	141.0(8)	O(12)–Ba(2)–O(1)	91.4(9)
O(11)–Ba(1)–O(43$^{\mathrm{II}}$)	69.8(8)	O(22)–Ba(2)–O(31)	144.4(9)
O(21)–Ba(1)–N(12)	137.6(9)	O(22)–Ba(2)–O(41)	73.9(9)
O(21)–Ba(1)–N(22)	54.4(9)	O(22)–Ba(2)–N(33)	137.3(10)
O(21)–Ba(1)–O(1)	69.4(9)	O(22)–Ba(2)–N(42)	74.2(9)
O(21)–Ba(1)–O(2)	88.6(9)	O(22)–Ba(2)–O(4)	75.5(7)
O(21)–Ba(1)–O(3)	104.5(8)	O(22)–Ba(2)–O(5)	104.5(9)
O(21)–Ba(1)–O(4)	79.1(8)	O(22)–Ba(2)–O(6)	80.0(9)
O(21)–Ba(1)–O(33$^{\mathrm{I}}$)	71.0(8)	O(31)–Ba(2)–O(41)	120.8(9)
O(31)–Ba(1)–O(43$^{\mathrm{II}}$)	145.3(9)	O(31)–Ba(2)–N(32)	55.7(9)
N(12)–Ba(1)–N(22)	90.4(9)	O(31)–Ba(2)–N(42)	141.6(4)
N(12)–Ba(1)–O(1)	109.1(9)	O(31)–Ba(2)–O(4)	115.8(8)
N(12)–Ba(1)–O(2)	132.2(9)	O(31)–Ba(2)–O(5)	69.3(9)
N(12)–Ba(1)–O(3)	68.4(9)	O(31)–Ba(2)–O(6)	77.8(9)
N(12)–Ba(1)–O(4)	61.8(8)	O(41)–Ba(2)–N(32)	137.3(10)
N(12)–Ba(1)–O(33$^{\mathrm{I}}$)	129.5(8)	O(41)–Ba(2)–N(42)	56.1(8)
N(12)–Ba(1)–O(43$^{\mathrm{I}}$)	73.3(9)	O(41)–Ba(2)–O(4)	117.5(8)
N(22)–Ba(1)–O(1)	110.0(9)	O(41)–Ba(2)–O(5)	68.1(9)
N(22)–Ba(1)–O(2)	136.0(10)	O(41)–Ba(2)–O(6)	67.0(9)
N(22)–Ba(1)–O(3)	59.5(9)	N(32)–Ba(2)–N(42)	99.9(9)
N(22)–Ba(1)–O(4)	61.4(9)	N(32)–Ba(2)–O(4)	64.2(9)
N(22)–Ba(1)–O(33$^{\mathrm{I}}$)	78.0(9)	N(32)–Ba(2)–O(5)	72.6(10)
N(22)–Ba(1)–O(43$^{\mathrm{II}}$)	127.5(8)	N(32)–Ba(2)–O(6)	133.4(10)
O(1)–Ba(1)–O(2)	70.5(10)	N(42)–Ba(2)–O(4)	63.6(8)
O(1)–Ba(1)–O(3)	168.5(9)	N(42)–Ba(2)–O(5)	75.9(9)
O(1)–Ba(1)–O(4)	70.7(8)	N(42)–Ba(2)–O(6)	121.8(10)
O(1)–Ba(1)–O(33$^{\mathrm{I}}$)	121.2(8)	O(4)–Ba(2)–O(5)	112.8(8)
O(1)–Ba(1)–O(43$^{\mathrm{II}}$)	122.5(9)	O(4)–Ba(2)–O(6)	152.1(9)
O(2)–Ba(1)–O(3)	119.8(9)	O(5)–Ba(2)–O(6)	94.6(10)
O(2)–Ba(1)–O(4)	141.2(9)		
O(2)–Ba(1)–O(33$^{\mathrm{I}}$)	66.8(9)		
O(2)–Ba(1)–O(43$^{\mathrm{II}}$)	68.8(9)		
O(3)–Ba(1)–O(4)	98.9(8)		
O(3)–Ba(1)–O(33$^{\mathrm{I}}$)	63.3(8)		
O(3)–Ba(1)–O(43$^{\mathrm{II}}$)	68.2(8)		
O(4)–Ba(1)–O(33$^{\mathrm{I}}$)	138.7(8)		
O(4)–Ba(1)–O(43$^{\mathrm{II}}$)	134.8(8)		
O(33$^{\mathrm{I}}$)–Ba(1)–O(43$^{\mathrm{II}}$)	75.8(9)		

Ba(1)–O(11)–C(11)	121(2)	Ba(2)–O(14)–N(12)	114(2)
Ba(1)–O(21)–C(21)	125(3)	Ba(2)–O(22)–N(22)	106(2)
Ba(1)–N(12)–O(12)	121(2)	Ba(2)–O(31)–C(31)	127(2)
Ba(1)–N(12)–C(12)	117(2)	Ba(2)–O(41)–C(41)	124(3)
Ba(1)–N(22)–O(22)	122(2)	Ba(2)–N(32)–O(32)	118(3)
Ba(1)–N(22)–C(22)	119(2)	Ba(2)–N(32)–C(32)	120(2)
Ba(1)–O(33$^{\mathrm{I}}$)–C(32$^{\mathrm{I}}$)	128(3)	Ba(2)–N(42)–O(42)	118(2)
Ba(1)–O(43$^{\mathrm{II}}$)–C(43$^{\mathrm{II}}$)	129(3)	Ba(2)–N(42)–C(42)	119(2)
Ba(1) ··· O(4) ··· Ba(2)	114(5)		

(*b*) Intraligand geometries; these are inaccurate, only mean values and σ for a single value are given

N(1)–C(1)	1.38(5)	N(1)–C(1)–O(1)	117(3)
O(1)–C(1)	1.29(5)	N(1)–C(1)–C(2)	120(4)
C(1)–C(2)	1.36(5)	O(1)–C(1)–C(2)	123(4)
C(2)–N(2)	1.43(5)	C(1)–C(2)–N(2)	113(3)
N(2)–O(2)	1.30(4)	C(1)–C(2)–C(3)	126(4)
C(2)–C(3)	1.51(6)	N(2)–C(2)–C(3)	120(3)
C(3)–N(3)	1.32(5)	C(2)–N(2)–O(2)	119(3)
C(3)–O(3)	1.29(5)	C(2)–C(3)–N(3)	118(4)
		C(2)–C(3)–O(3)	116(4)
		N(3)–C(3)–O(3)	124(4)

(*c*) Suggested hydrogen-bonding scheme; hydrogen distances (estimated) in parentheses

(*i*) Between layers		
N(11)[H(111)] ··· O(21$^{\mathrm{III}}$)	2.96(4)	(1.97)
N(21)[H(121)] ··· O(11$^{\mathrm{V}}$)	3.00(4)	(2.00)
N(31)[H(131)] ··· O(12$^{\mathrm{IV}}$)	2.97(4)	(2.09)
O(32) ··· O(1$^{\mathrm{VII}}$)	2.93(5)	
O(7) ··· O(2$^{\mathrm{VIII}}$)	2.68(5)	
N(13)[H(113)] ··· O(22$^{\mathrm{IV}}$)	3.03(4)	(2.32)
N(23)[H(123)] ··· O(41$^{\mathrm{VI}}$)	3.00(5)	(2.12)
N(41)[H(141)] ··· O(31$^{\mathrm{VI}}$)	3.00(5)	(2.38)
O(42) ··· O(1$^{\mathrm{VII}}$)	2.88(4)	
O(33) ··· O(6$^{\mathrm{VI}}$)	2.28(4)	
(*ii*) Within layers		
O(4)[H(41)] ··· O(32)	2.69(4)	(1.85)
O(7) ··· O(2)	2.93(5)	
O(3) ··· O(12)	3.17(4)	
O(7) ··· O(23$^{\mathrm{IX}}$)	2.87(5)	
O(13) ··· O(7$^{\mathrm{X}}$)	2.87(5)	
O(4)[H(42)] ··· O(42)	2.72(4)	(1.87)
O(3) ··· O(22)	2.77(4)	
N(43)[H(431)] ··· O(2$^{\mathrm{IX}}$)	3.09(5)	(2.19)
O(23) ··· O(5$^{\mathrm{I}}$)	2.89(5)	
O(13) ··· O(5$^{\mathrm{II}}$)	2.83(5)	

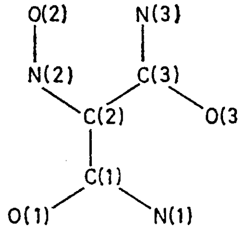
Transformations of the asymmetric unit at x, y, z

I	$x, 1 + y, z$	VI	$\frac{3}{2} - x, y + \frac{1}{2}, \frac{1}{4} - z$
II	$x - 1, y, z$	VII	$y + 1, x - 1, \bar{z}$
III	$y, x - 1, \bar{z}$	VIII	$y, x, \bar{z}$
IV	$\frac{3}{2} - x, y - \frac{1}{2}, \frac{1}{4} - z$	IX	$x + 1, y, z$
V	$y + 1, x, \bar{z}$	X	$x, y - 1, z$

probably a consequence of the high backgrounds due to the fluorescence of the barium irradiated with Cu radiation, the use of which was necessitated by the very long cell dimension. For both structures, neutral-atom scattering factors were used, that for Ba being corrected for anomalous dispersion ($\Delta f'$, $\Delta f''$);[4-6] the parity of (I) was established as that of space group No. 92 rather than No. 96 by changing the sign of $\Delta f''$ and refining to convergence at R 0.130, R' 0.160 [*cf.* 0.118, 0.144] using data with $I > \sigma(I)$.

Structure-factor tables for (I) and (II) are given in Supplementary Publication No. SUP 21731 (21 pp., 1 microfiche).* Computation was carried out on the local CDC 6200 machine using a variant of the '*X*-Ray '72' program system.[7] Final atomic and thermal parameters are given in Table 1.

In (I), O(1) and N(2) are bonded to the same barium atom; however, in addition O(2) and O(3) co-ordinate to adjacent barium atoms. Atom numbering and ligand configuration is as follows:



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* For details see Notice to Authors, No. 7, in *J.C.S. Dalton*, 1975, Index issue.

[4] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[5] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[6] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

[7] '*X*-Ray System,' Technical Report TR 192, Computer Science Centre, University of Maryland, U.S.A., version of June 1972.

TABLE 3

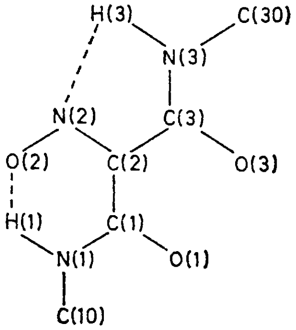
Interatomic distances (Å) and angles (°), with least-squares estimated standard deviations in parentheses, for (II)

(*a*) Barium environments			
(i) Barium (1)			
Ba–O(2^{I})	2.786(4)	O(2^{I})–Ba–O(2^{II})	73.2(1)
(ii) Barium (2)			
Ba–O(1)	2.715(3)	O(1)–Ba–O(2^{V})	132.3(1)
Ba–O(3)	2.693(4)	O(1)–Ba–O(1^{VI})	119.8(1)
Ba–O(2^{III})	2.936(4)	O(1)–Ba–O(3^{VI})	74.6(1)
O(1)–Ba–O(3)	60.8(1)	O(1)–Ba–O(2^{VII})	66.1(1)
O(1)–Ba–O(2^{III})	80.7(1)	O(3)–Ba–O(2^{III})	97.1(1)
O(1)–Ba–O(1^{IV})	119.8(1)	O(3)–Ba–O(2^{V})	115.1(1)
O(1)–Ba–O(3^{IV})	130.6(1)	O(3)–Ba–O(2^{VII})	126.7(1)
Ba(1) · · · Ba(2)	4.214 4(7)	Ba(2^{III})–O(2)–Ba(1^{VIII})	95.6(1)
(*b*) The ligand			
C(10)–N(1)	1.437(9)	C(10)–N(1)–C(1)	121.6(5)
C(1)–N(1)	1.326(7)	N(1)–C(1)–O(1)	121.4(6)
C(1)–O(1)	1.238(6)	O(1)–C(1)–C(2)	121.6(5)
C(1)–C(2)	1.496(8)	N(1)–C(1)–C(2)	117.0(4)
C(2)–N(2)	1.328(6)	C(1)–C(2)–C(3)	119.3(4)
N(2)–O(2)	1.318(5)	C(1)–C(2)–N(2)	127.3(4)
C(2)–C(3)	1.490(7)	N(2)–C(2)–C(3)	113.4(5)
C(3)–O(3)	1.221(6)	C(2)–N(2)–O(2)	119.8(5)
C(3)–N(3)	1.334(9)	C(2)–C(3)–O(3)	122.5(6)
N(3)–C(30)	1.439(9)	C(2)–C(3)–N(3)	117.1(4)
C(10)–H(10a)	0.97(8)	N(3)–C(3)–O(3)	120.4(5)
C(10)–H(10b)	0.95(7)	C(3)–N(3)–C(30)	121.4(6)
C(10)–H(10c)	0.88(7)	N(2)–O(2)–Ba(1)	83.6(3)
C(30)–H(30a)	1.24(8)	N(2)–O(2)–Ba(2)	121.3(3)
C(30)–H(30b)	1.01(9)	C(1)–O(1)–Ba(2)	143.0(3)
C(30)–H(30c)	0.82(7)	C(3)–O(3)–Ba(2)	143.8(4)
N(1)–H(1)	0.82(6)	H(1)–N(1)–C(10)	122(5)
N(3)–H(3)	0.77(5)	H(1)–N(1)–C(1)	115(5)
		H(3)–N(3)–C(3)	118(6)
		H(3)–N(3)–C(30)	119(7)
H(1) · · · O(2)	1.95(7)	O(2) · · · H(1)–N(1)	139(5)
H(3) · · · N(2)	2.36(6)	N(2) · · · H(3)–N(3)	106(6)

Transformations of the asymmetric unit x, y, z:

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

In (II), the ligand adopts a configuration different from that found in (I). O(1) and O(3) now chelate to a barium atom with O(2) co-ordinating and bridging two nearby bariums; N(2) plays no role in co-ordination:



Amide hydrogen atoms have been located and give rise to intramolecular hydrogen bonds as shown (Tables and 3; see later Figure 5).

DISCUSSION

Structure of (I).—The structure comprises polymeric infinite sheets parallel to the *ab* plane, normal to *c*, and linked by hydrogen-bonding interactions from the water molecules. Within each sheet, the basic structural unit is a pair of barium atoms separated by 4.763(4) Å, and their associated ligands. As in the iron derivatives, the ligand conformation is such that O(1) and N(2) can chelate the metal atom in the ligand plane; in the present case, however, the deviations of the barium atoms from the ligand planes are considerable, ranging between 0.47 and 0.80 Å. In addition, O(2) and O(3) provide bridging to adjacent metal atoms. If we consider each barium pair and the associated four chelating ligands, we find that the group has an overall approximate local symmetry, comprising a mirror plane as an approximate bisector of the *ab* plane, parallel to *c* as a strong (non-crystallographically imposed) condition: Ba(1) and Ba(2) lie in the plane and the ligands on either side, ligand (1) generating ligand (2) about Ba(1) and ligand (3) generating ligand (4) about Ba(2). The associated barium–ligand distances are very similar: Ba(1)–N(12), N(22), 2.94(4), 2.93(3); Ba(2)–N(32), N(42), 2.90(4), 2.92(3); Ba(1)–O(11), O(21), 2.75(2), 2.79(2); Ba(2)–O(31), O(41), 2.74(3), 2.74(3) Å. For these groups, in addition, an approximate inversion centre exists between Ba(1) and Ba(2)

TABLE 4

Least-squares planes through the ligands in the form $pX + qY + rZ = s$.* δ, the estimated standard deviation of the defining atoms, and deviations of atoms from the planes are given in Å

(*a*) For (I)

Ligand	(1)	(2)	(3)	(4)
10^4p	−6 076	−6 653	−8 138	−5 369
10^4q	6 575	6 402	5 459	8 172
10^4r	4 455	3 840	1 994	2 095
s	−3.212	−3.852	−8.735	−5.919
σ	0.09	0.05	0.10	0.06
O(1)	−0.13	−0.05	0.17	0.06
N(1)	0.05	0.05	−0.15	−0.04
C(1)	0.00	0.05	0.03	0.03
O(2)	0.08	0.04	−0.04	−0.07
N(2)	0.07	−0.02	−0.13	−0.05
C(2)	0.01	−0.02	−0.02	0.02
O(3)	0.08	−0.01	−0.03	−0.10
N(3)	−0.16	0.04	0.10	0.09
C(3)	−0.01	−0.09	0.10	0.07
Ba(1)	0.78	0.80		
Ba(2)	−1.78	−2.02	0.51	0.47
χ^2	49.3	13.4	63.3	25.4

Angles (°) between planes: (1)–(2) 4.9, (1)–(3) 19.6, (1)–(4) 16.9, (2)–(3) 14.7, (2)–(4) 16.1, (3)–(4) 22.4.

(*b*) For (II) (atom deviations in square brackets)

Plane (i): C(1), N(1), O(1), C(10), N(2), O(3), C(3)

10^4p	10^4q	10^4r	s	σ	χ^2
3 028	−2 678	9 147	3.365	0.020	101.6

[C(1) −0.02, N(1) 0.00, O(1) −0.02, C(10) 0.02, N(2) 0.02, O(2) −0.02, C(3) 0.02, N(3) 0.55, O(3) −0.42, C(30) 0.53, Ba(2) −0.83, Ba(1) −3.36]

Plane (ii): C(3), N(3), O(3), C(30), C(2)

−1 310	−3 220	9.376	0.3794	0.029	93.7

[C(3) 0.01, N(3) 0.04, O(3) 0.01, C(30) −0.03, C(2) −0.02, N(2) −0.53, O(2) −0.64, Ba(2) 0.78, Ba(1) −0.38]

Angles (°) between planes: (i)–(ii) 25.3

* For (I), $x = ax$, $y = by$, $z = cz$; for (II) x lies parallel to a, z is in the ac plane.

relating Ba(1) to Ba(2) and ligands (1) and (2) to (3) and (4); this relation is only approximate, however, since the ligands about Ba(1) do not lie parallel to those about Ba(2), as evidenced by the different deviations of the Ba atoms from the ligand planes (Table 4). For example: Ba(1) deviates from ligands (1) and (2) by 0.78 and 0.80 Å, while Ba(2) deviates from ligands (3) and (4) by 0.51 and 0.47 Å. The reason for this lies in the fact that in ligands (1) and (2) O(2) occupies two further co-ordination positions about Ba(2) [Ba(2)–O(12), 2.85(3), Ba–O(22), 2.84(3) Å] while O(2) in ligands (3) and (4) has no such function. Oxygen atoms related to O(3) but in adjacent molecules occupy two of the co-ordination positions about Ba(1) at 2.87(3) and 2.89(3) Å on either side of the false mirror. The remaining co-ordination positions about the barium atoms are filled by water molecules all of which lie in the mirror plane. One of these is common to the co-ordination spheres of both Ba(1) and Ba(2), acting as a symmetrical bridge [O(4)–Ba(1), 2.81(2), O(4)–Ba(2), 2.86(2) Å]. There are three more about Ba(1) [Ba(1)–O(1), 2.88(3), Ba–O(2), 2.86(4), and Ba–O(3) 2.88(3)], so that Ba(1) is ten-co-ordinate, while there are two further co-ordinating water molecules about Ba(2) [Ba–O(5), 2.78(3) and Ba–O(6), 2.86(3) Å], so that Ba(2) is nine-co-ordinate.

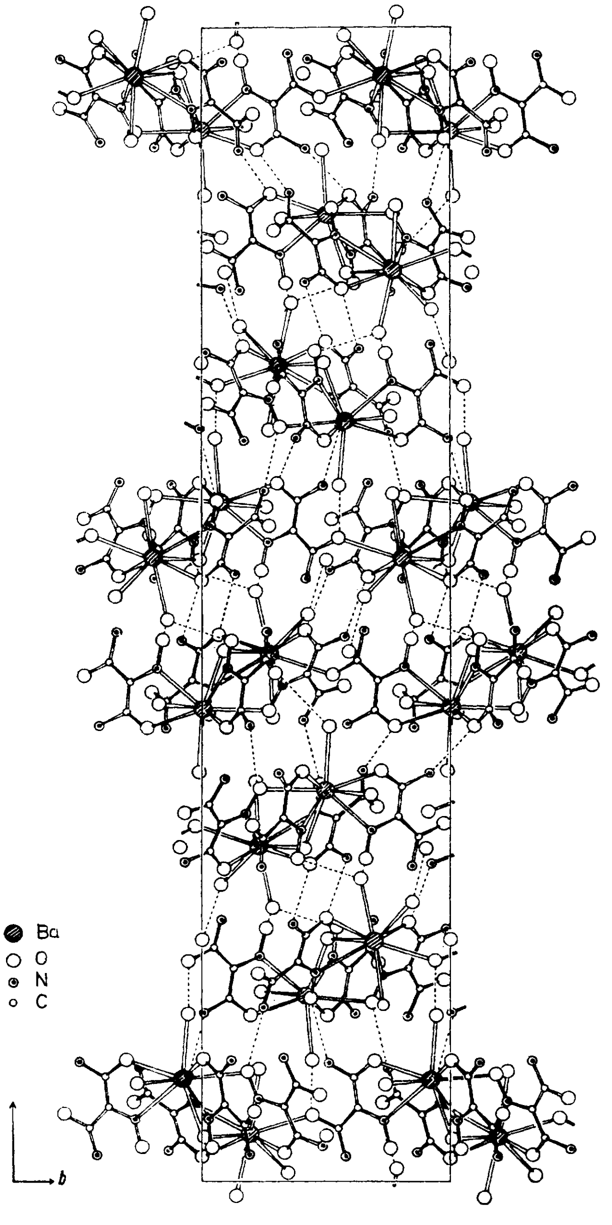


FIGURE 1 Projection of the structure of (I) down *a*, showing the layer structure and probable interlayer hydrogen bonds

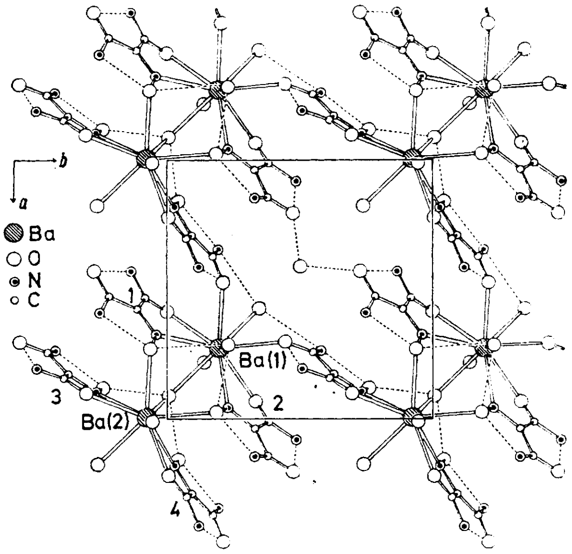


FIGURE 2 Projection of one layer of (I) down *c*, showing the construction of the layer from linked $Ba_2L_4(H_2O)_6$ dimeric units. Probable intralayer hydrogen-bonding is shown. Ligand numbers are given

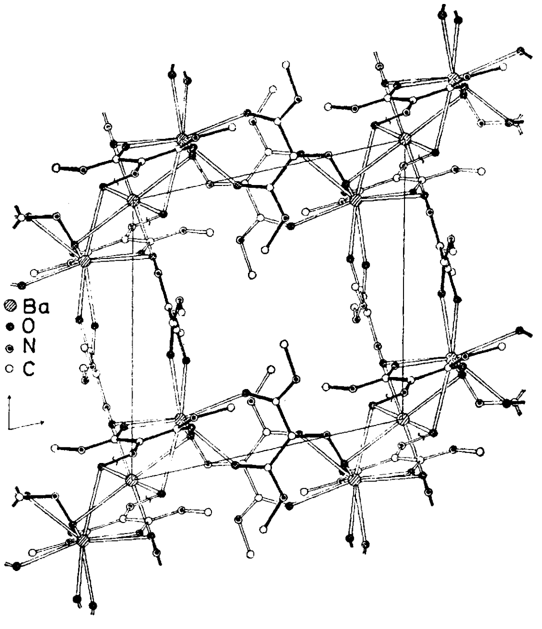


FIGURE 3 Axial projection of (II)

Linking of the dimeric $Ba_2L_4(H_2O)_6$ cluster units into the infinite planar polymer thus takes place by way of the co-ordination of O(3) from ligands (3) and (4) to the Ba(1) atoms of the clusters located on adjacent cell corners. The seventh water molecule fills the vacancy left at the centre of the cell.

The non-location of hydrogen atoms leaves the hydrogen-bonding scheme in some doubt; close contacts are given in Table 2 and depicted in Figures 1 and 2. The layer structure of the complex is consistent with the observation of a facile, almost micaceous cleavage normal to *c*. The ligand geometries are inaccurate and will not be further discussed.

Structure of (II).—Unlike (I), the basic structural unit in (II) is a triad of barium atoms, centrosymmetric about Ba(1) at the origin, with Ba(2) and its inversion image situated 4.2414(7) Å away on either side of it on the three-fold axis. The co-ordination about Ba(2) comprises three equivalent ligands acting as chelates, not through O(1) and N(2), as might have been expected, but through O(1) and O(3). Ba(2) is nine-co-ordinate; about the three-fold axis the three upper co-ordination positions are filled by the three O(3) and the three equatorial positions by the three O(1) from the three chelates. The lower three positions are filled by O(2) from neighbouring ligands; these O(2) atoms in addition bridge to the neighbouring Ba(1) and, because of its centrosymmetric nature, fill the six co-ordination positions about it in a trigonal array. Because of the crosslinking of the O(2) atoms, the crystal is an infinite three-dimensional polymer. As in (I), we find that the barium atoms deviate appreciably from the ligand planes (Table 4); moreover, the ligand itself is not planar but exhibits an appreciable twist of the C(3),N(2),O(2) entity with respect to the remainder of the conjugated skeleton about the C(2)–C(3) bond. A curious angular distortion is found at C(2) [N(2)–C(2)–C(3) 113.4(5)°], and is presumably a consequence of this twist. The ligand geometry is accurate and of interest; however, discussion will be deferred to later papers [8,9] in which its geometry will be compared with those of complexes of similar ligands.

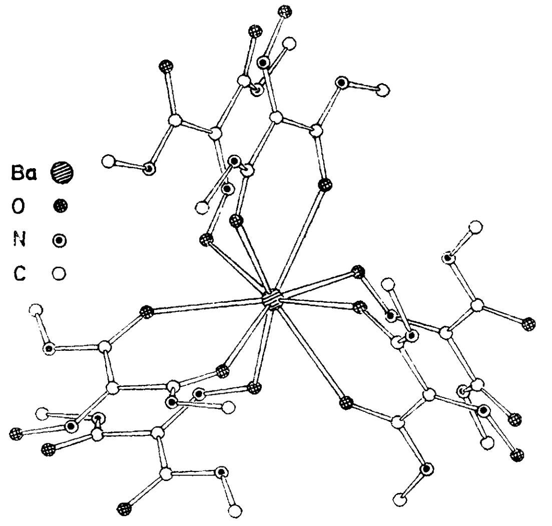


FIGURE 4 Projection of (II) down the three-fold axis

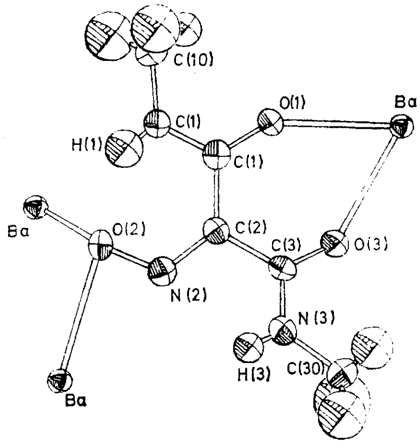


FIGURE 5 Thermal ellipsoids (50%) of the ligand system in (II)

[5/1956 *Received, 7th October*, 1975]

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[8] S. R. Hall, C. L. Raston, and A. H. White, to be published.

[9] M. C. Favas, D. L. Kepert, A. H. White, and A. C. Willis, *J.C.S. Dalton*, in the press.