Stereochemisty of Rigid Chelate–Metal Complexes. Part 4.† Crystal Structures of Tetra-aquabis(1,10-phenanthroline)strontium(II) Perchlorate– and Tetra-aquabis(1,10-phenanthroline)barium(II) Perchlorate–1,10-Phenanthroline (1/2)

By **Graham Smith** and **Eric J. O'Reilly**, Department of Chemistry, Queensland Institute of Technology, Brisbane, Australia
Colin H. L. Kennard,* Department of Chemistry, University of Queensland, Brisbane, Australia 4067
Allan H. White, Department of Physical and Inorganic Chemistry, University of Western Australia, Nedlands, Western Australia

The crystal structures of the title complexes, $[Sr(phen)_2(OH_2)_4][ClO_4]_2\cdot 2phen$ (1) and $[Ba(phen)_2(OH_2)_4][ClO_4]_2\cdot 2phen$ (2), have been determined by *X*-ray diffraction from diffractometer data and refined by least squares to *R* 0.120(1) and 0.13(2) for 1 423 and 2 478 observed reflections respectively. The two complexes are similar. Crystals are triclinic, space group $P\bar{1}$ with $Z = 1$ in unit cells of dimensions: (1) a = 1 344.4(4), b = 1 268.4(4), c = 706.8(2) pm, α = 99.31(2), β = 92.55(2), γ = 76.21(3)°; (2) a = 1 336.9(1), b = 1 300.3(5), c = 703.2(1) pm, α = 100.01(2), β = 95.15(1), γ = 75.53(2)°. The metal ions have an eight-co-ordinate distorted cube stereochemistry involving four nitrogens from two phenanthroline ligands and four oxygens from water molecules. The *trans*-related phens pack almost parallel to the *ab* plane containing also the metal, while the remaining phen pair, also parallel to *ab* but not bonded to the metal, are merely ' sandwiched ' in the structure halfway between the metal centres, along the *c* axis. The point-group symmetry of the metal complex unit is approximately C_{2h}. There appear to be no bonding forces holding the ' floating ' phens in the structure, the shortest contact, N · · · H–O (to water), being 359 (1) and 378 pm (2). The bonded waters are also independent of the perchlorate anions, the closest contact being 326 and 340 pm. The perchlorate groups are disordered to the extent that the centre of symmetry in the otherwise centric complex is destroyed by a completely dissymmetric tetrahedral arrangement of oxygens.

COMPLEXES of the type $[M(phen)_4][ClO_4]_2\cdot nH_2O$ (M = Mg, Ca, Sr, Ba, Pb, or Mn; n = 0, 2, or 4; phen = 1,10-phenanthroline) have been known for a number of years.[1,2] These complexes were suggested to be eight-co-ordinate with four bidentate phen ligands on the basis of their i.r. spectra, in particular those peaks in the 1 510—1 550 and 700—900 cm^{-1} regions.[3] However, some doubt was placed on these findings in later spectroscopic studies of the same complexes.[4] Consequently a structural analysis was undertaken to ascertain the nature of the metal co-ordination sphere.

Crystals of the tetrahydrate analogues of Sr and Ba, (1) and (2), prepared by the method of Schilt and Taylor,[3] were grown by slow cooling of hot methanol–water solutions in a Dewar flask over several days. The elongated needle crystals were colourless and showed perfect cleavage across the *c* axis. Preliminary *X*-ray examination using both powder and single-crystal techniques indicated that both (1) and (2) were isomorphous. To date, no suitable crystals of the analogues of Mn and Mg have been grown, but *X*-ray powder patterns suggest that they have similar structures to, if not the same as, those of the complexes of Sr and Ba.

EXPERIMENTAL

The structure determination of (1) was carried out using data collected by a 2θ—θ scan, with a Syntex $P\bar{1}$ four-circle diffractometer. A crystal measuring 0.15 × 0.10 × 0.08 mm mounted about the *c* axis was used, and 3 053 reflections [1 423 having $I > 2.5\sigma(I)$] were considered observed up to 2θ 45°. For (2), data were collected using a Hilger and Watts four-circle diffractometer on a crystal measuring 0.38 × 0.25 × 0.12 mm also mounted about the *c* axis. 2 798 Reflections of which 2 478 had $I > 2.5\sigma(I)$ were considered observed up to 2θ 99°.

Crystal Data.—$C_{48}H_{40}Cl_2N_8O_{12}Sr$, (1), M = 1 079.4, Triclinic, a = 1 344.5(4), b = 1 268.4(4), c = 706.8(2) pm, α = 99.31(2), β = 92.55(2), γ = 76.21(3)°, U = 1 155 nm^3, D_m = 1.56, Z = 1, D_c = 1.55, $F(000)$ = 552. Monochro-

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† Part 3, H. S. Preston and C. H. L. Kennard, *J. Chem. Soc.* (*A*), 1969, 2955.

[1] P. Pfeiffer and W. Christeleit, *Z. anorg. Chem.*, 1938, **239**, 133.

[2] P. Pfeiffer and Br. Werdelmann, *Z. anorg. Chem.*, 1950, **261**, 197.

[3] A. A. Schilt and T. C. Taylor, *J. Inorg. Nuclear Chem.*, 1959, **9**, 211.

[4] B. Chiswell and E. J. O'Reilly, *Inorg. Chim. Acta*, 1973, **7**, 707.

matic Mo-K_α radiation: $\lambda = 71.07$ pm; μ(Mo-K_α) = 12.99 cm^{-1}. Space group $P\bar{1}$ (C_i^1, no. 2).

$C_{48}H_{40}BaCl_2N_8O_{12}$, (2), $M = 1\,129.1$, Triclinic, $a = 1\,336.9(1)$, $b = 1\,300.3(5)$, $c = 703.2(1)$ pm, $\alpha = 100.01(2)$, $\beta = 95.15(1)$, $\gamma = 75.53(2)°$, $U = 1\,164$ nm^3, $D_m = 1.60$, $Z = 1$, $D_c = 1.58$, $F(000) = 570$. Nickel-filtered Cu-K_α radiation: $\lambda = 154.18$ pm, μ(Cu-K_α) = 80.74 cm^{-1}. Space group $P\bar{1}$ (C_i^1, no. 2).

TABLE 1

Atomic co-ordinates (× 10^4) and isotropic thermal parameters (× 10^3) with estimated standard deviations in parentheses

Complex (1)

Atom	x/a	y/b	z/c	U
Sr	0	0	0	
Cl	2 758(7)	2 467(7)	−3 297(12)	78(3)
O(1)	3 585(14)	1 488(14)	−3 363(39)	64(11)
O(2)	1 926(14)	2 227(21)	−4 541(34)	77(15)
O(3)	2 392(21)	2 832(25)	−1 341(18)	124(18)
O(4)	3 136(21)	3 335(18)	−3 943(45)	128(17)
O(5)	176(13)	905(18)	−6 461(24)	
O(6)	502(12)	1 433(14)	−1 790(26)	
N(11)	2 079(14)	−139(14)	591(27)	
C(21)	2 392(23)	793(25)	1 262(45)	64(9)
C(31)	3 503(26)	663(27)	1 730(48)	75(10)
C(41)	4 182(25)	−321(27)	1 430(48)	74(10)
C(51)	4 568(19)	−2 304(20)	153(37)	63(7)
C(61)	4 271(20)	−3 163(21)	−505(39)	72(8)
C(71)	2 811(25)	−4 066(26)	−1 478(49)	71(10)
C(81)	1 770(23)	−3 953(23)	−1 931(43)	58(8)
C(91)	1 096(23)	−2 895(24)	−1 467(45)	64(9)
N(101)	1 438(13)	−2 019(14)	−802(26)	
C(111)	2 800(16)	−1 148(17)	293(31)	44(6)
C(121)	3 856(19)	−1 208(20)	635(36)	62(7)
C(131)	3 161(17)	−3 176(17)	−866(32)	48(6)
C(141)	2 413(17)	−2 120(17)	−522(32)	46(6)
N(12)	1 806(17)	8 398(18)	4 671(33)	53(7)
C(22)	2 267(24)	9 190(25)	5 325(46)	64(9)
C(32)	3 341(25)	9 006(25)	5 548(47)	65(9)
C(42)	3 971(21)	7 929(23)	5 047(42)	60(7)
C(52)	4 023(19)	5 929(20)	3 851(36)	63(7)
C(62)	3 511(17)	5 168(18)	3 341(32)	51(6)
C(72)	1 852(20)	4 569(21)	2 527(38)	70(8)
C(82)	825(21)	4 884(23)	2 355(40)	81(8)
C(92)	279(26)	5 931(28)	2 749(49)	75(10)
N(102)	807(19)	6 750(20)	3 301(36)	52(7)
C(112)	2 369(16)	7 347(16)	4 205(31)	42(6)
C(122)	3 415(16)	7 075(17)	4 345(31)	44(6)
C(132)	2 432(17)	5 371(18)	3 110(32)	48(6)
C(142)	1 842(17)	6 483(18)	3 501(32)	46(6)

Complex (2)

Atom	x/a	y/b	z/c	U
Ba	0	0	0	
	2 657(4)	2 476(4)	−3 521(8)	50(1)
	2 445(23)	3 554(19)	−2 431(47)	81(16)
	3 543(20)	2 447(36)	−4 614(28)	80(16)
	2 428(20)	3 015(23)	−1 833(21)	274(29)
	2 732(31)	1 566(24)	−2 753(49)	73(15)
	292(10)	1 090(12)	−6 367(21)	
	597(10)	1 529(11)	−1 672(22)	
	2 267(12)	−342(14)	−648(27)	
	2 612(19)	580(20)	1 315(35)	61(6)
	3 675(22)	505(22)	1 786(39)	63(7)
	4 372(24)	−507(24)	1 430(42)	70(8)
	4 696(19)	−2 482(20)	257(35)	60(6)
	4 338(19)	−3 367(20)	−413(36)	63(7)
	2 830(17)	−4 158(18)	−1 535(31)	50(5)
	1 808(21)	−4 033(22)	−1 893(38)	59(7)
	1 145(18)	−2 940(19)	−1 469(33)	49(6)
	1 502(12)	−2 100(13)	−817(25)	
	2 929(15)	−1 323(16)	247(29)	41(5)
	4 036(17)	−1 439(18)	698(33)	51(6)
	3 222(17)	−3 274(17)	−864(32)	49(6)
	2 562(15)	−2 228(16)	−417(29)	38(5)
	1 699(14)	8 315(15)	4 627(26)	44(5)
	2 186(19)	9 113(20)	5 235(35)	61(6)
	3 251(19)	8 959(20)	5 504(35)	60(6)
	3 864(19)	7 917(20)	5 055(35)	56(6)
	3 976(18)	5 989(18)	3 946(32)	55(6)
	3 516(18)	5 179(19)	3 428(34)	55(6)
	1 877(20)	4 581(21)	2 556(37)	65(7)
	843(29)	4 776(30)	2 207(53)	93(10)
	314(21)	5 906(21)	2 564(38)	65(7)
	743(14)	6 690(15)	3 118(26)	52(5)
	2 292(15)	7 317(16)	4 146(29)	40(5)
	3 391(16)	7 102(17)	4 432(30)	43(5)
	2 401(17)	5 377(17)	3 131(32)	49(6)
	1 809(15)	6 449(16)	3 520(28)	38(5)

Anisotropic thermal parameters (× 10^3) with estimated standard deviations in parentheses:

(1)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sr	21(2)	15(2)	29(2)	0(1)	13(1)	4(1)
N(11)	45(13)	32(12)	70(16)	1(10)	−3(11)	8(11)
N(101)	45(13)	46(12)	41(14)	−8(10)	4(10)	4(10)
O(5)	60(15)	21(27)	49(14)	63(16)	−16(12)	5(16)
O(6)	59(13)	70(13)	111(18)	−8(10)	12(12)	37(12)

(2)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ba	18(1)	26(2)	56(2)	0(1)	10(1)	7(1)
	24(9)	44(11)	64(12)	−6(8)	0(8)	2(9)
	29(9)	44(11)	56(11)	−3(8)	8(8)	10(9)
	34(8)	64(11)	54(10)	10(8)	5(7)	8(8)
	38(8)	54(9)	78(10)	5(7)	14(7)	29(7)

Neither data sets were corrected for absorption. The structure of (1) was solved by the heavy-atom method by placing the Sr at the origin for the space group $P\bar{1}$ to give the location of the non-hydrogen atoms. Refinement was carried out with alternate parts of the phen rings fixed as rigid six-atom groups. In the last few cycles of refinement the rigid-body constraints were removed and the atoms were refined independently. Oxygens of the perchlorate anions, because of their apparent disorder indicated by large temperature factors, were also refined as parts of rigid tetrahedral groups with the Cl–O bond distances fixed at 143(1) pm. This distance was observed in tris-(1,10-phenanthroline)copper(II) perchlorate.[5] Anisotropic thermal parameters of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}kla^*c^* + 2U_{23}klb^*c^*)]$ were used for those atoms in the co-ordination sphere, with the remaining atoms being left isotropic. Scattering factors used were those of the neutral atoms,[6] with the alkaline-earth element being corrected for anomalous dispersion.[7]

In the case of (2), co-ordinates from (1) were confirmed in an initial structure-factor electron-density synthesis to give new co-ordinates which were refined in a similar manner as before. However, three different perchlorate oxygens appeared with the fourth atom being common to both structures. This new set was used in refinement. Because of the high cost, final convergence was not obtained and refinement was stopped at R 0.120 for (1) and 0.130 for (2). A weighting scheme of the type $w = 1.7678/(\sigma^2F_o + 1.2977 \times 10^{-2}F_o^2)$ was used for (1) giving R' 0.128 while unit weights were used for (2). No attempt was made to locate hydrogen atoms in either structure. A final differ-

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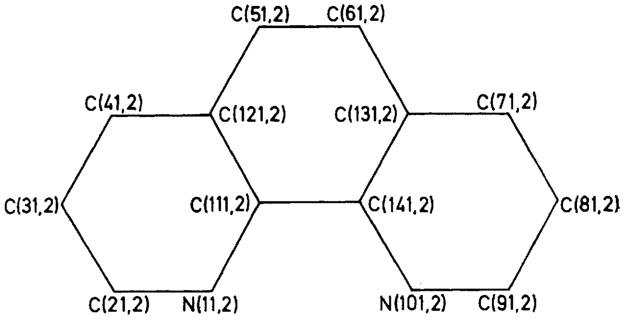
[5] O. P. Anderson, *J.C.S. Dalton*, 1973, 1237.

[6] P. A. Doyle and P. S. Turner, *Acta Cryst.*, 1968, **A24**, 390.

[7] D. T. Cromer and D. Liberman, *J. Chem. Phys.*, 1970, **53**, 1891.

ence Fourier for (1) revealed four significant peaks in the region of the perchlorate groups. These peaks together with the four oxygen atoms of the perchlorate anion were related by an approximate $\bar{1}$ operator. In order to destroy this additional symmetry, the space group $P1$ should have been used. Insertion of all the eight oxygens with site-occupancy factors of 0.5 did not significantly change the R value but it did result in realistic temperature factors for the perchlorate oxygens. Refinement of the site-occupancy factors alone gave R 0.11 for (1). A similar observation (R 0.12) was made for (2). However, for (2) only four of the eight oxygens were common with (1).

Structure amplitudes are listed in Supplementary Publication No. SUP 22009 (27 pp.).* Atomic parameters are given in Table 1. The numbering system for the phenanthrolines is as follows:



Co-ordinated phen is indicated by the last digit being 1, and unco-ordinated phen by 2.

Refinement in the non-centric space group was not attempted although the intensity statistics strongly indicated a non-centric space group, the mean $|E^2 - 1|$ being 0.70 (1) and 0.67 (2). However, it has been previously shown that abnormal probability distributions of intensities may result from the presence of one heavy atom in a triclinic cell ($Z = 1$) containing a number of light atoms.[8,9] It is therefore felt that $P\bar{1}$ is the correct space group, although the costly refinement exercise in the non-centric space group was not attempted because of the large number of atoms and reflections involved.

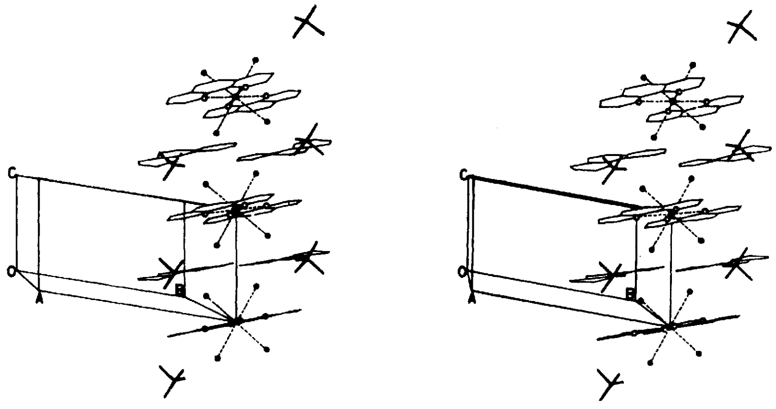


FIGURE 2 Stereoscopic view of the unit cell of $[M(phen)_2(OH_2)_4][ClO_4]_2 \cdot 2phen$ (M = Sr or Ba) viewed down the a axis

DISCUSSION

The co-ordination spheres about Sr^{2+} and Ba^{2+} consist of four nitrogen and four oxygen atoms (Figures 1 and 2). The nitrogens are from two bidentate phen molecules oriented in *trans* positions across the centre of symmetry. The eight-vertex co-ordination sphere surrounding the metal has $C_{2h}(2/m)$ point-group symmetry, the two-fold axis being perpendicular to the planes containing the chelated phen and the metal [Figure 3(c)]. The oxygens from the four water molecules lie in an approximate plane almost at right angles to the plane containing the phens and the metal. Projections of the co-ordination spheres viewed perpendicular to N(11)–M–N(101) and O(5)–M–O(6) are shown in Figure 3(a) and 3(b) respectively. Bond distances and angles are listed in Table 2(a). The

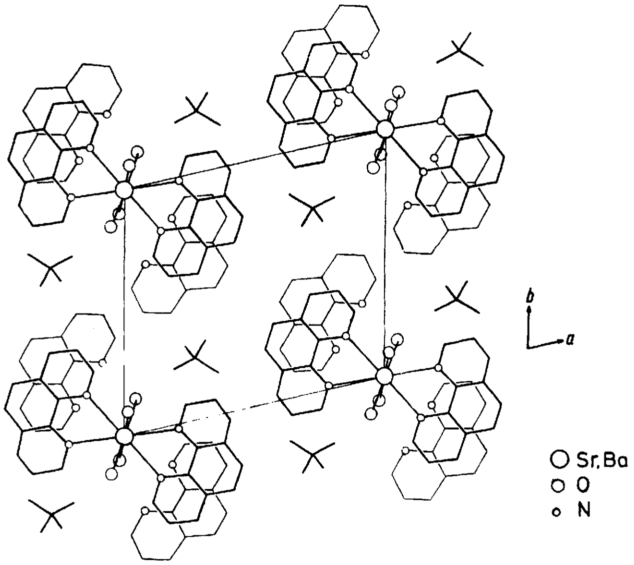


FIGURE 1 Packing in the unit cell of $[M(phen)_2(OH_2)_4][ClO_4]_2 \cdot 2phen$ (M = Sr or Ba) viewed down the c axis

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

[8] G. A. Sim, *Acta Cryst.*, 1958, **11**, 123.

[9] H. Lipson and W. Cochran, 'The Crystalline State. Vol. III: The Determination of Crystal Structures,' G. Bell and Sons, 1966, p. 56.

observed eight-co-ordinate distorted cubic stereochemistry is unusual, although Sr^{2+} and Ba^{2+} exhibit a range of stereochemistries with co-ordination number varying from 7 to 12 (Table 3). However, the first reported example of a distorted cubic arrangement with eight-co-ordination was in bis[tris(2-hydroxyethyl)amine]strontium(II) nitrate[10] but involving six oxygens and two *trans*-located tertiary nitrogens. It is interesting to compare the distances for (1) and (2). The fixed ligand bite (*b*) is constant, as well as the O–N(*r*)

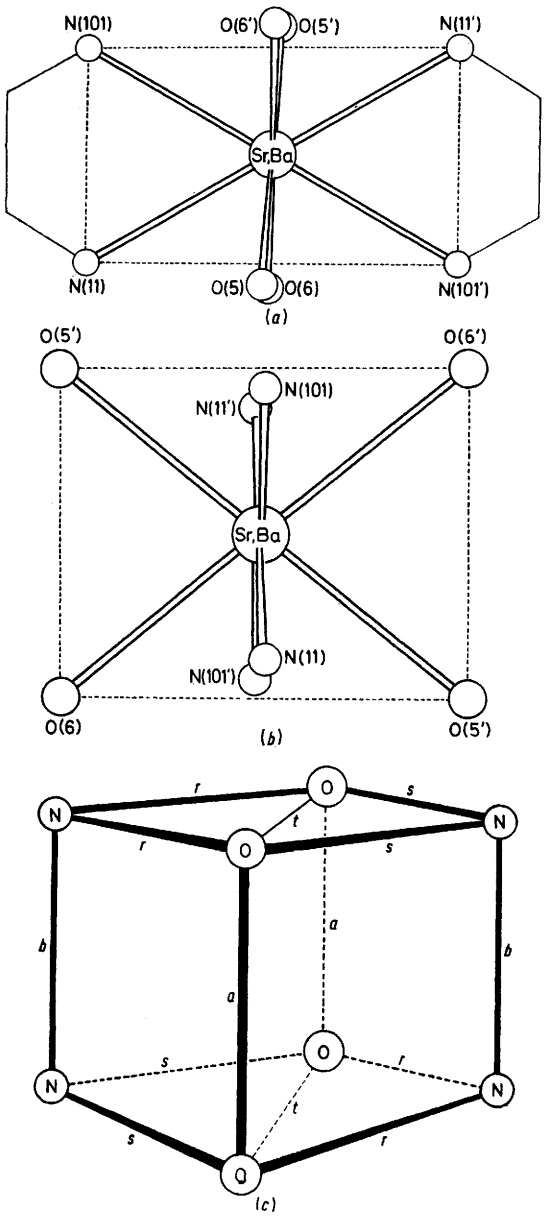

FIGURE 3 Projections of the co-ordination spheres of (1) and (2) viewed: (*a*) perpendicular to the plane of the phen ligands; (*b*) perpendicular to the plane of the water ligands; and (*c*) according to the convention of Hoard and Silverton

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[10] J. C. Voegelle, J. Fischer, and R. Weisse, *Acta Cryst.*, 1973, **B29**, 707.

TABLE 2

(*a*) Bond distances (pm) and angles (°) with estimated standard deviations in parentheses

(*i*) Distances

Complex (1)	
Sr–N(11)	277.6(10)
Sr–N(101)	280.9(9)
Sr–O(5)	260.4(10)
Sr–O(6)	260.1(9)
N(11)–C(21)	136 (2) [138 (2)] *
N(11)–C(111)	140 (3) [136 (2)]
C(21)–C(31)	149 (2) [141 (2)]
C(31)–C(41)	135 (2) [141 (2)]
C(41)–C(121)	133 (3) [140 (2)]
C(121)–C(51)	149 (3) [142 (3)]
C(121)–C(111)	142 (3) [146 (2)]
C(51)–C(61)	126 (3) [135 (3)]
C(61)–C(131)	151 (3) [148 (3)]
C(131)–C(71)	133 (2) [137 (2)]
C(131)–C(141)	146 (3) [142 (2)]
C(71)–C(81)	140 (2) [134 (2)]
C(81)–C(91)	143 (2) [147 (2)]
C(91)–N(101)	131 (2) [130 (2)]
N(101)–C(141)	130 (3) [139 (2)]
C(111)–C(141)	145 (3) [138 (2)]
N(12)–C(22)	131 (2) [135 (2)]
N(12)–C(112)	136 (2) [135 (2)]
C(22)–C(32)	141 (2) [139 (2)]
C(32)–C(42)	142 (2) [140 (2)]
C(42)–C(122)	147 (2) [136 (2)]
C(122)–C(52)	148 (3) [146 (3)]
C(122)–C(112)	137 (3) [143 (2)]
C(52)–C(62)	131 (3) [133 (3)]
C(62)–C(132)	142 (3) [145 (3)]
C(132)–C(72)	142 (3) [138 (2)]
C(132)–C(142)	143 (3) [141 (2)]
C(72)–C(82)	135 (2) [135 (2)]
C(82)–C(92)	135 (2) [145 (2)]
C(92)–N(102)	139 (2) [128 (2)]
N(102)–C(142)	136 (2) [140 (2)]
C(112)–C(142)	145 (3) [142 (2)]
Cl(1)–O(1)	145 (1) [145 (1)]
Cl(1)–O(2)	145 (1) [145 (1)]
Cl(1)–O(3)	145 (1) [145 (1)]
Cl(1)–O(4)	146 (1) [145 (1)]

Complex (2)	
Ba–N(11)	295.6(10)
Ba–N(101)	295.6(10)
Ba–O(5)	274.3(10)
Ba–O(6)	278.3(10)

(*ii*) Angles

(1)	
N(11)–Sr–N(101)	58.9(5)
N(11)–Sr–O(5)	74.5(5)
N(11)–Sr–O(6)	72.2(6)
N(101)–Sr–O(5)	110.6(6)
N(101)–Sr–O(6)	109.5(6)
O(5)–Sr–O(6)	100.2(5)
Sr–N(11)–C(21)	119 (1)
Sr–N(11)–C(111)	122 (1)
Sr–N(101)–C(91)	118 (1)
Sr–N(101)–C(141)	123 (1)
N(11)–C(21)–C(31)	117 (1) [120 (1)]
N(11)–C(111)–C(121)	121 (2) [120 (1)]
N(11)–C(111)–C(141)	117 (2) [121 (1)]
C(21)–C(31)–C(41)	122 (1) [119 (1)]
C(21)–N(11)–C(111)	120 (2) [122 (1)]
C(31)–C(41)–C(121)	119 (1) [122 (1)]
C(41)–C(121)–C(51)	122 (2) [125 (1)]
C(41)–C(121)–C(111)	121 (2) [118 (1)]
C(121)–C(51)–C(61)	123 (2) [123 (2)]
C(121)–C(111)–C(141)	122 (2) [119 (1)]
C(51)–C(61)–C(131)	123 (2) [121 (2)]
C(51)–C(121)–C(111)	117 (2) [118 (1)]
C(61)–C(131)–C(71)	125 (2) [122 (1)]

TABLE 2 (*Continued*)

C(61)–C(131)–C(141)	117 (2) [116 (2)]
C(131)–C(71)–C(81)	120 (1) [120 (1)]
C(131)–C(141)–C(111)	117 (2) [123 (1)]
C(131)–C(141)–N(101)	123 (2) [119 (1)]
C(71)–C(81)–C(91)	118 (1) [118 (1)]
C(81)–C(91)–N(101)	122 (1) [123 (1)]
C(91)–N(101)–C(141)	119 (1) [119 (1)]
N(101)–C(141)–C(111)	120 (2) [118 (1)]
N(12)–C(22)–C(32)	123 (1) [124 (1)]
N(12)–C(112)–C(122)	123 (2) [121 (1)]
N(12)–C(112)–C(142)	119 (2) [119 (1)]
C(22)–C(32)–C(42)	120 (1) [118 (1)]
C(32)–C(42)–C(122)	115 (1) [119 (1)]
C(42)–C(122)–C(52)	118 (2) [122 (1)]
C(42)–C(122)–C(112)	120 (2) [120 (1)]
C(122)–C(52)–C(62)	117 (2) [122 (2)]
C(122)–C(112)–C(142)	119 (2) [120 (1)]
C(52)–C(62)–C(132)	125 (2) [121 (2)]
C(52)–C(122)–C(112)	122 (2) [121 (2)]
C(62)–C(132)–C(72)	126 (2) [124 (1)]
C(62)–C(132)–C(142)	119 (2) [118 (1)]
C(132)–C(72)–C(82)	120 (1) [124 (1)]
C(132)–C(142)–C(112)	119 (2) [121 (1)]
C(132)–C(142)–N(102)	122 (2) [120 (1)]
C(72)–C(82)–C(92)	124 (1) [114 (1)]
C(82)–C(92)–N(102)	118 (1) [126 (1)]
C(92)–N(102)–C(142)	120 (1) [118 (1)]
N(102)–C(142)–C(112)	119 (2) [118 (1)]

(2)	
N(11)–Ba–N(101)	55.1(5)
N(11)–Ba–O(5)	74.8(4)
N(11)–Ba–O(6)	72.7(4)
N(101)–Ba–O(5)	113.2(4)
N(101)–Ba–O(6)	109.9(4)
O(5)–Ba–O(6)	91.0(4)
Ba–N(11)–C(21)	115 (1)
Ba–N(11)–C(111)	123 (1)
Ba–N(101)–C(91)	118 (1)
Ba–N(101)–C(141)	123 (1)

(*b*) Comparative distances (pm) in (1) and (2) represented by the symbols used in Figure 3(*c*). The distances *s* and *t* are made up of two components, N–O(5) and N–O(6), which are considered within experimental error to be equal. Both values are given, together with the mean values (in parentheses)

Distance	Complex	
	(1)	(2)
a	399	394
b	275	274
r	329	326
s	317, 326 (322)	340, 346 (343)
t	442, 445 (444)	470, 476 (473)

* Values for complex (2) are given in square brackets.

and O–O(*a*) distances. The change in metal ionic radius is accommodated only by changes in neighbouring O–N(*s*) and O–O(*t*) distances.

According to Hoard and Silverton,[11] regular polyhedra having triangular faces provide the basis for the stereochemistry of eight-co-ordination so that the cube usually distorts to a dodecahedron or a square antiprism. Most subsequent reviews, based on the occurrence of eight-co-ordinate complexes,[12-15] ignore the possibility of the existence of a cubic arrangement of ligands. One very important property of the metal which governs the ultimate stereochemistry of the complex is the effective metal ionic radius which must be sufficiently large to minimise both ligand–ligand repulsion effects and strain from geometrical constraints imposed by the ligand. For Sr^{2+} and Ba^{2+} with eight-co-ordination, the effective ionic radii are 125 and 142 pm respectively.[16] The observed bond lengths between metal and nitrogen are therefore sufficiently long to separate the C(21) and C(91′) protons on the *trans*-phen ligands by >400 pm, which is sufficient to allow the existence of the rare *trans*-bis(phenanthroline) system. This is in agreement with theoretical calculations.[17] The correlation between the metal–nitrogen distance and the angle subtended at the metal by the phen nitrogen donors has previously been recognized.[18] This must be the case unless there is severe distortion from planarity in the phen ligand. The N(1)–N(10) distances are 274 (1) and 275 pm (2), which, in the absence of an *X*-ray structure determination of phenanthroline hydrate itself, may best be compared with the values for the non-bonded phens in the present structures [277 (1) and 275 pm (2)]. The distances for a range of 15 phen and substituted phen complexes vary from 262 pm in $[(HO)_2CrCr(phen)_2]^{4+}$ (ref. 19) to 278 pm in $[Pd(NO_3)_2(Me_2phen)]$ [20] with a mean of 268 pm. The metal–nitrogen distances in (1) and (2) are, however, without precedence in phen complexes, the largest previously observed being 252 pm in *cis*-$[Hg(phen)_2(SCN)_2]$ [21] where the N–M–N bond angle is 66.3°. This may be compared with the relatively small equivalent angles of 58.9 (1) and 55.1° (2), which, in combination with M–N bond distances of 280 (1) and 296 (2) pm, give close to trigonal-planar (sp^2) bond arrangements about the nitrogen donors. These factors may account for the ease of formation and inherent stability of the complexes of Sr and Ba. Thermogravimetric analysis of (1), for example, indicates the loss of four water molecules between 328 and 353 K with no further weight loss until decomposition commences at *ca.* 473 K.[4]

Deviations of the atoms from the least-squares planes for the co-ordinated and non-bonded rings are listed in SUP 22009. The non-bonded phen rings are very close to being parallel to the co-ordinated phens, the angle between the normals to these planes for (1) and (2) being 2.3 and 2.2° respectively. The phenomenon of a set of 'floating' phen rings sandwiched in the structure with such geometrical regularity is unusual although the structure [22] of $[Ni(pda)_4]Cl_2\cdot 2pda$ contains bonded as well as adducted *o*-phenylenediamines (pda), but with reduced symmetry. In this structure, the unco-ordinated pda is hydrogen-bonded to the bonded pda

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[11] J. L. Hoard and J. V. Silverton, *Inorg. Chem.*, 1963, **2**, 235.

[12] D. L. Kepert, *J. Chem. Soc.*, 1965, 4736.

[13] S. J. Lippard, *Progr. Inorg. Chem.*, 1967, **8**, 109.

[14] E. L. Muetterties and C. M. Wright, *Quart. Rev.*, 1967, **21**, 109.

[15] D. G. Blight and D. L. Kepert, *Inorg. Chem.*, 1972, **11**, 1556.

[16] R. D. Shannon and C. T. Prewitt, *Acta Cryst.*, 1970, **B26**, 1076.

[17] L. H. Berka, W. T. Edwards, and P. A. Christian, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 265.

[18] B. A. Frenz and J. A. Ibers, *Inorg. Chem.*, 1972, **11**, 1109.

[19] J. T. Veal, W. E. Hatfield, and D. J. Hodgson, *Acta Cryst.*, 1973, **B29**, 12.

[20] L. F. Power, *Inorg. Nuclear Chem. Letters*, 1970, **6**, 791.

[21] A. L. Beauchamp, B. Saperas, and R. Rivest, *Canad. J. Chem.*, 1974, **522**, 923.

[22] R. C. Elder, D. Koran, and H. B. Mark, *Inorg. Chem.*, 1974, **13**, 1644.

via amine nitrogens, the contacts being 310 pm. In the present structures there are very long contacts between N(12) and O(5) [359 (1) and 378 pm (2)] which, if interpreted as hydrogen-bonding interactions, might anchor the ' floating ' phenanthroline hydrate *via* the bonded water oxygen. The co-ordinated water molecules have shorter O · · · O contacts with perchlorate oxygens [O(5) · · · O(2), O(6) · · · O(2), O(6) · · · O(3)] varying from 322 to 341 pm which could well be within hydrogen-bonding distances. Basically, however, the perchlorate anions are quite independent as previously indicated by the spectra of the complexes.

TABLE 3

Comparison of strontium–oxygen, nitrogen and barium–oxygen, nitrogen distances. Where a range of distances are observed the range is indicated, otherwise average distances are shown. For a comprehensive listing of Sr–O distances from the literature prior to 1972, see footnote *d*

Compound	Co-ordination number and stereochemistry	Bonds involved	Distance (pm)	Ref.
$Sr[O_2CH]_2\cdot 2H_2O$	8, square antiprism	$Sr–OH_2$	265.4 (5)	*a*
		Sr–O (formate)	259.2 (5)	
$Sr[IO_3]_2\cdot H_2O$	9, tricapped trigonal prism	$Sr–OH_2$	253.1 (8)	*b*
		Sr–O (iodate)	260.9 (12)	
$Sr[C_7H_3NO_4]\cdot 4H_2O$	9, monocapped square antiprism	Sr–O (bridge)	261.8 (3)	*c*
		$Sr–OH_2$	271.3 (3)	
		Sr–N	264.0 (3)	
$[Sr\{N(CH_2CH_2OH)_3\}_2][NO_3]_2$	8, distorted cubic	Sr–OH	253.4—259.4 (4)	8
		$Sr–NR_3$	283.0 (4)	
$Sr[S_2O_6]\cdot 4H_2O$	8, very distorted square antiprism	Sr–OS (dithionite)	248—262 (3)	*d*
		$Sr–OH_2$	258—264 (3)	
$Sr[NO_3]_2\cdot 4H_2O$	10, bicapped (one face) distorted Archimedean antiprism	$Sr–OH_2$	265—270 (6)	*e*
		$Sr–ONO_2$ (bridge)	271—280 (3)	
$Sr[MeCO_2][MeCOS]\cdot 4H_2O$	9, very distorted trigonal prism	$Sr–OH_2$	262—275 (1)	*f*
		Sr–O (acetate)	269—272 (1)	
		Sr–O (thioacetate)	269 (1)	
$[Sr\{NH(CONH_2)_2\}_4][ClO_4]_2$	8, distorted square antiprism	Sr–O	249.4 —268.9 (10)	*g*
$Sr[C_4H_2N_3O_4]_2\cdot 4H_2O$	8, bicapped trigonal prism	Sr–O	249.8—264.9 (8)	*h*
		$Sr–OH_2$	251.8—273.5 (7)	
		Sr–N	288.9 (8)	
$Ba[TeO_3]\cdot H_2O$	7, irregular	Ba–O	266.7—278.6 (8)	*i*
$Ba[O_2CC(Me){:}CH_2]_2\cdot H_2O$	9, irregular	$Ba–OH_2$ (bridge)	278—287 (1)	*j*
		Ba–O (methacrylate)	271—290 (1)	
$Ba[S(S_2O_3)_2]\cdot 2H_2O$	9, irregular	Ba–O (sulphonate)	277.3—286.2 (3)	*k*
		$Ba–OH_2$	282.8—292.8 (3)	
$[Ba(OH_2)_3\{S(S_2O_3)_2\}]$	9, irregular	Ba–O (sulphonate)	274.6—290.4 (4)	*l*
		$Ba–OH_2$	280.0—294.0 (4)	
$Ba[Co_2(CN)_{10}]\cdot 13H_2O$	9, 10, Archimedean antiprism	$Ba–OH_2$ (bridge)	290 (1)	*m*
		Ba–N	286 (5)	
$Ba(SCN)_2(cryptate)\cdot H_2O$	10, complex	Ba–N (cryptate)	294.4—300.2 (10)	*n*
		Ba–NCS	287.9, 291.1(10)	
		$Ba–OH_2$	283.8, 288.3 (7)	
		Ba–O (cryptate)	274.2—288.6 (8)	
$Ba(SCN)_2(cryptate)\cdot 2H_2O$	11, complex	Ba–NCS	308.4—317.9 (6)	*o*
		Ba–O	279.6—309.2 (7)	
		$Ba–OH_2$	281.0—287.4 (6)	
		Ba–O (acetate)	272.6 (2)	
$[Ba\{N(CH_2CH_2OH)_3\}_2][O_2CMe]_2$	9, tricapped distorted trigonal prism	$Ba–\overset{H}{O}$	276.1 (4)	*p*
		$Ba–NR_3$	306.8 (5)	
$Ba[C_6H_6O_9S]\cdot 2H_2O$	10, complex	$Ba–OH_2$	286.4 (2)	*q*
		Ba–O (ascorbate)	275.7—306.5 (2)	
$[Ba\{NH(COMe)_2\}_5][ClO_4]_2$	10, distorted bicapped square antiprism	Ba–O	273 (2)—291 (2)	*r*
$Ba[O_2CC(Me){:}CH_2]_2$	8, irregular	Ba–O (bridged)	276.6—303.0 (5)	*s*

[a] J. L. Galigne, *Acta Cryst.*, 1971, **B27**, 2429. [b] A. M. Manotti Lanfredi, M. A. Pellinghelli, A. Tiripicchio, and M. Tiripicchio-Camellini, *Acta Cryst.*, 1972, **B28**, 679. [c] K. J. Palmer, R. Y. Wong, and J. C. Lewis, *Acta Cryst.*, 1972, **B28**, 223. [d] R. N. Hargreaves and E. Stanley, *Z. Krist.*, 1972, **135**, 399. [e] B. Ribar, B. Matkovic, and M. Sljukic, *Z. Krist.*, 1972, **135**, 137. [f] M. M. Borel and M. Ledesert, *Acta Cryst.*, 1975, **B31**, 725. [g] S. Haddad and P. S. Gentile, *Inorg. Chim. Acta*, 1975, **12**, 131. [h] M. Hamelin, *Acta Cryst.*, 1972, **A28**, S91; 1976, **B32**, 367. [i] B. K. Nielsen, R. G. Hazell, and S. E. Rasmussen, *Acta Chem. Scand.*, 1971, **25**, 3037. [j] N. W. Isaacs, J. J. Van der Zee, K. G. Shields, J. V. Tillack, D. H. Wheeler, F. H. Moore, and C. H. L. Kennard, *Cryst. Struct. Comm.*, 1972, **1**, 193. [k] K. Moroy, *Acta Chem. Scand.*, 1972, **26**, 36. [l] K. Moroy, *Acta Chem. Scand.*, 1972, **26**, 45. [m] L. D. Brown, K. N. Raymond, and S. Z. Goldberg, *J. Amer. Chem. Soc.*, 1972, **94**, 7664. [n] B. Metz, D. Moras, and R. Weiss, *Acta Cryst.*, 1973, **B29**, 1382. [o] B. Metz, O. Moras, and R. Weiss, *Acta Cryst.*, 1973, **B29**, 1388. [p] J. C. Voegele, J. C. Thierry, and R. Weiss, *Acta Cryst.*, 1974, **B30**, 70. [q] B. W. McClelland, *Acta Cryst.*, 1974, **B30**, 178. [r] P. S. Gentile, J. White, and S. Haddad, *Inorg. Chim. Acta*, 1975, **13**, 149. [s] C. H. L. Kennard, G. Smith, A. H. White, and T. M. Greaney, *J.C.S. Perkin II*, 1976, 302.

In complexes (1) and (2) the ionic radius of the metal ion is not considered to be very critical in the packing since the metal centres are separated by *ca.* 700 pm, the *c* cell dimension. This provides a ' hole ' centred at $(0,0,\frac{1}{2})$. Although a difference Fourier did not indicate any electron density at $(0,0,\frac{1}{2})$, this site may potentially accommodate metal ions of radius even considerably larger than barium. Furthermore, a metal ion at $(0,0,\frac{1}{2})$ would be within bonding distances of at least one of the donor *nitrogens* [N(12)] of the ' floating ' phen molecule and one of the water oxygens [O(6)]. These distances for (1) and (2) are in SUP 22009. The longer distances for O(5) and N(102) are a consequence of rotation of the ' floating ' phen about *c* by *ca.* 20° away from position $(0,0,\frac{1}{2})$. It is therefore thought that the ' floating ' phen is adjacent to a site which could contain another metal ion. This, however, was not observed. Electron-probe analysis of some crystals of (1) and (2) did not reveal the presence of any metal ion which could potentially occupy the vacant site at $(0,0,\frac{1}{2})$, although the presence of trace amounts of Ba^{2+} was observed in (1). It was considered that these ions would be co-ordinated as in (2) and not as occupants of the vacant site at $(0,0,\frac{1}{2})$.

The mean strontium–oxygen, strontium–nitrogen [260.2(10), 279.3(10) pm] and barium–oxygen, barium–nitrogen distances [276.3(10), 295.6(10) pm] are compared with similar bonds involving oxygen and nitrogen in Table 3. The Sr–O distances are comparable with those encountered in similar environments. Few Sr–N distances have been reported but $[Sr\{N(CH_2CH_2OH)_3\}_2][NO_3]_2$ [10] provides the closest comparison (283.0 pm). The Sr–N distance reported in dipicolinatostrontium tetrahydrate (264.0 pm) appears somewhat atypical, although this is probably a consequence of the constraints enforced by the rigid tridentate ligands. The Ba–O and Ba–N distances are within the limits of typical distances shown in the Table. Because of the degree of accuracy of the determinations, bond distances and angles within the phen groups cannot be considered, but they are not significantly abnormal to warrant comment.

Comparison of the bonding systems found in (1) and (2) with other metals has been made. *X*-Ray powder patterns for tetraphenanthroline perchlorates of Mg, Ca, Sr, Ba, Mn, and Pb are compared in Table 4. It may be seen that the analogues of Ca, Sr, and Ba are similar but different from the apparently isostructural compounds of Mg and Mn, while the lead compound shows no similarity to any of the other compounds. Although the structures were refined in $P\bar{1}$, it is felt that the intensity statistics were affected to some extent by the severe rotational disorder present in the perchlorate anions, as well as by the previously mentioned heavy-atom phenomenon. The locations of all the oxygen atoms in the perchlorate anions except O(3) are different from (1) and (2). This brings to light a problem of working with two different crystals of the same structure containing the perchlorate ion where the anion might crystallise by chance in a different manner.

TABLE 4

X-Ray diffraction data (*d* spacings, nm) for the complexes $[M(phen)_4][ClO_4]_2 \cdot nH_2O$ (M = Mg, *n* = 3; M = Ca, *n* = 3; M = Sr, *n* = 4; M = Ba, *n* = 4; M = Mn, *n* = 4; M = Pb, *n* = 0)

Mg [a]		Ca [a]		Sr [b]		Ba [b]		Mn [b]		Pb [b]	
d	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*
				1.30	s						
1.25	s	1.20	s	1.20	s	1.25	s	1.25	s		
										1.10	s
1.05	s	1.00	s	1.00	s	1.05	s	1.05	s	1.00	w
										0.93	s
								0.80	vw	0.83	s
0.77	w	0.75	w					0.70	vw	0.75	w
0.69	vw									0.68	w
		0.65	w	0.65	m	0.65	w			0.64	w
0.62	s					0.63	w	0.65	s		
		0.60	s	0.61	m	0.61	vw			0.60	vw
				0.57	s	0.57	s			0.55	vw
0.53	w			0.54	vw	0.54	vw	0.53	w		
		0.51	m	0.51	s	0.51	s				
		0.49	m	0.49	vw	0.49	vw				
		0.48	m							0.48	vw
0.46	s			0.47	vw	0.47	vw				
										0.45	vw
		0.44	m	0.44	m	0.44	m	0.44	m	0.44	vw
		0.42	m	0.43	m	0.43	m	0.42	m	0.42	vw
0.41	m			0.41	vw	0.41	vw			0.41	vw
		0.40	m	0.40	vw	0.40	vw				
				0.39	vw	0.39	vw				
				0.38	vw	0.38	vw			0.38	w
0.35	s	0.35	s	0.35	s	0.35	s	0.36	s	0.36	vw
0.33	m	0.33	m	0.33	vw	0.33	vw	0.34	m	0.34	m
0.32	m	0.32	m	0.32	vw	0.32	vw	0.32	m	0.32	w
0.31	vw			0.31	vw	0.31	vw	0.31	vw	0.31	w
		0.30	w							0.30	vw

s = Strong, m = medium, w = weak, and vw = very weak.

[a] J. D. Miller and R. H. Prince, *J. Chem. Soc.*, 1965, 3185.

[b] Refs. 3 and 4.

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