known in molybdates (Magarill & Klevtsova, 1972; Day, Fredrich, Klemperer & Shum, 1977). It does imply, however, that Mo may not have a particularly strong preference for octahedral over tetrahedral coordination, as was originally remarked upon by Kihlborg (1963) in his interpretation of the molybdenum trioxide structure. It may be noted that solutions of molybdenum trioxide in dmso show significant conductivity, Λ_m (for an Mo_3O_9 unit) = 9·6 Ω^{-1} cm^{2}mol^{-1} at 298 K, and 34·1 Ω^{-1} cm^{2}mol^{-1} at 388 K. This raises the possibility that crystallization of the chain polymer may occur by way of ionic species, *viz* $Mo_2O_5(dmso)_n^{2+}$ and MoO_4^{2-}.

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Coordination Chemistry of Alkali and Alkaline-Earth Cations: X-ray Structural Redetermination of Tetraaquabis(1,10-phenanthroline)barium(II) Perchlorate–Bis(1,10-phenanthroline), $[Ba(C_{12}H_8N_2)_2(H_2O)_4](ClO_4)_2.2C_{12}H_8N_2$

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Abstract. $M_r = 1129·1$, triclinic, $P\bar{1}$, $a = 7·026$ (2), $b = 13·003$ (3), $c = 13·361$ (2) Å, $\alpha = 75·51$ (2), $\beta = 84·84$ (2), $\gamma = 80·00$ (2)°, $V = 1162·5$ (4) Å^3, $Z = 1$, $D_m = 1·610$, $D_x = 1·613$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 8·347$ mm^{-1}, $F(000) = 570$, $T = 293$ K, $R = 0·055$ for 3955 unique reflections. Four N atoms from two *o*-phenanthrolines and four O atoms from four water molecules are coordinated to Ba in a distorted cubic arrangement. Two other phenanthrolines are stacked parallel to the coordinated phenanthrolines, slightly offset with one above and one below the plane formed by the coordinated phenanthrolines. The previously reported structure [Smith, O'Reilly, Kennard & White (1977). *J. Chem. Soc. Dalton Trans.* (12), pp. 1184–1190] is confirmed.

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Introduction. The structure of $[Ba(phen)_2(H_2O)_4](ClO_4)_2.2phen$ (phen is 1,10-phenanthroline) was previously determined (Smith, O'Reilly, Kennard & White, 1977) and refined to $R = 0·13$. Our structure, refined to $R = 0·055$, confirms the original determination but has resulted in additional insight concerning the chemistry involved.

In an attempt to understand the biological functions of Na, K, Ca, and Mg (Poonia & Bajaj, 1979; Poonia, 1981), one of the authors (NSP) has been interested in complexation and structural studies of M^{2+}.phen complexes (Vijaywargia, 1983). The complex $[Ba(phen)_2(H_2O)_4](ClO_4)_2.2phen$ which was encountered during these studies had been reported earlier (Pfeiffer & Christeleit, 1938; Schilt & Taylor, 1959) and had been examined crystallographically (Smith, O'Reilly, Kennard & White, 1977). The compound was

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of interest to us because the original authors stated that 'There appear to be no bonding forces holding the 'floating' phen's in the structure, the shortest contact N···H—O (to water), being 378 pm'. Our studies show that there are reasonable H-bonding distances involving the 'floating' phen's at 2·873 and 2·875 Å. However, re-examination of the coordinates in the original paper yield similar H-bonding distances.

Experimental. Synthesis of the complex: Hydrated $Ba(ClO_4)_2$ (0·1 m*M*) and phen (0·4 m*M*) were dissolved in ethanol and allowed to evaporate at room temperature (~ 298 K) until colorless crystals appeared. D_m measured by flotation in 1,2-dibromoethane/benzene. Crystal 0·25 × 0·27 × 0·35 mm. Data collected by diffractometry using a Picker X-ray generator, a Syntex goniostat equipped with an ORTEC counting chain and Krisel Control interface and software. Ni-filtered Cu $K\alpha$ radiation. ω-scan technique. 17 reflections with θ range 21·0 to 29·7° used to measure lattice parameters. Absorption correction by the empirical φ-scan method (North, Phillips & Mathews, 1968) (min. = 1·01, max. = 1·60) incorporating a spherical correction for 2θ dependence (min. = 2·01, max. = 2·46). Max. $(\sin\theta)/\lambda = 0{\cdot}5878$ Å^{-1}. h index ranged from −8 to 8; k from −15 to 15; and l from 0 to 15. Standard reflections 071, 017, and 402; scale factors for intensity variation ranged from 0·993 to 1·038. 3955 unique reflections measured, with 20 reflections less than 2σ. All initial atomic positions determined by the use of a Patterson map. F magnitudes in all least-squares refinements. Parameters refined included x, y, z, U_{ij}, and the overall scale factor. Final R factors obtained were 0·117 (isotropic) and 0·055 (anisotropic); final weighted $R = 0{\cdot}069$ and final $S = 1{\cdot}60$; $w = 1/\sigma^2$. In final refinement cycle max. $\Delta/\sigma = 0{\cdot}9383$, average $\Delta/\sigma = 0{\cdot}07142$. Final difference electron density synthesis yielded a max. height of 1·15 e Å^{-3}, min. height −2·39 e Å^{-3}. Scattering factors for Ba^{2+}, Cl, O, C (Cromer & Mann, 1968), and H (Stewart, Davidson & Simpson, 1965). Ba^{2+} and Cl were corrected for the real part of dispersion (*International Tables for X-ray Crystallography*, 1974). Programs used were of local origin or from *XRAY*76 (Stewart, 1976) and *ORTEP* (Johnson, 1965).

Discussion. The previously reported structure (Smith, O'Reilly, Kennard & White, 1977) is confirmed. The fractional coordinates and corresponding isotropic temperature factors for the asymmetric unit are given in Table 1.* The IUPAC atomic numbering scheme used to label the phenanthrolines is shown in Figs. 1(*a*) and 1(*b*). Fig. 1(*a*) shows bond lengths and angles in the non-coordinated phen 1. Fig. 1(*b*) depicts the bond lengths and angles in the coordinated phen 2. The coordination distances of the N atoms in phen 2 from the Ba^{2+} cation are also shown in Fig. 1(*b*).

Table 1. *Fractional coordinates with e.s.d.'s and isotropic temperature factors* (×10²)

U_{eq} is defined by Willis & Pryor (1975).

	x	*y*	*z*	U_{eq}(Å²)
Ba^{2+}	0·0	0·0	0·0	3·35
O(1)	0·6335 (8)	0·1125 (5)	0·0291 (4)	6·23
O(2)	0·1637 (8)	0·1525 (4)	0·0597 (4)	4·77
Cl(1)	0·3531 (3)	0·2480 (1)	0·2665 (1)	5·12
O(3)	0·447 (2)	0·246 (1)	0·3555 (8)	11·9
O(4)	0·494 (1)	0·2475 (7)	0·1818 (6)	9·70
O(5)	0·269 (2)	0·1560 (8)	0·278 (1)	11·8
O(6)	0·210 (2)	0·3374 (8)	0·2423 (8)	12·3
O(3*D*)	0·4048	0·1558	0·3478	7·1
O(5*D*)	0·1685	0·2458	0·2324	7·1
O(6*D*)	0·3460	0·3423	0·3035	7·1
N(11)	0·681 (1)	0·6686 (5)	0·0744 (5)	4·88
C(12)	0·736 (2)	0·5862 (7)	0·0319 (6)	6·87
C(13)	0·769 (2)	0·4806 (7)	0·0847 (8)	8·17
C(14)	0·745 (1)	0·4551 (6)	0·1908 (7)	6·25
C(14*A*)	0·685 (1)	0·5385 (6)	0·2410 (6)	4·46
C(15)	0·659 (1)	0·5184 (6)	0·3505 (6)	5·40
C(16)	0·605 (1)	0·6001 (7)	0·3962 (6)	5·25
C(16*A*)	0·560 (1)	0·7085 (6)	0·3379 (5)	4·01
C(17)	0·492 (1)	0·7956 (7)	0·3840 (6)	4·64
C(18)	0·448 (1)	0·8955 (7)	0·3233 (7)	4·96
C(19)	0·469 (1)	0·9117 (6)	0·2160 (6)	4·75
N(110)	0·5361 (9)	0·8321 (5)	0·1691 (5)	4·12
C(110*A*)	0·582 (1)	0·7322 (5)	0·2291 (5)	3·47
C(110*B*)	0·651 (1)	0·6441 (5)	0·1797 (5)	3·84
N(21)	0·0765 (9)	0·7910 (5)	0·1507 (5)	3·91
C(22)	0·146 (1)	0·7032 (6)	0·1157 (6)	4·52
C(23)	0·186 (1)	0·6013 (6)	0·1790 (7)	5·21
C(24)	0·152 (1)	0·5862 (6)	0·2826 (7)	5·30
C(24*A*)	0·081 (1)	0·6752 (6)	0·3227 (6)	4·36
C(25)	0·045 (1)	0·6655 (7)	0·4327 (6)	5·98
C(26)	−0·024 (1)	0·7530 (8)	0·4696 (6)	5·69
C(26*A*)	−0·066 (1)	0·8567 (7)	0·4021 (5)	4·52
C(27)	−0·143 (1)	0·9485 (9)	0·4371 (6)	5·57
C(28)	−0·178 (1)	1·0460 (8)	0·3699 (7)	5·85
C(29)	−0·133 (1)	1·0521 (7)	0·2649 (6)	5·07
N(210)	−0·0628 (9)	0·9682 (5)	0·2255 (5)	4·05
C(210*A*)	−0·029 (1)	0·8702 (6)	0·2941 (5)	3·74
C(210*B*)	0·045 (1)	0·7764 (6)	0·2544 (5)	3·66

Table 2 lists the perchlorate ion bond distances and angles. Perchlorate O atoms O(3), O(5), and O(6) are disordered. The three O atoms, as a group, appear in two different orientations with population parameters of 0·75 and 0·25. The O atoms of one group are located approximately halfway between those of the second group. The O positions with a population parameter of 0·25 were constrained along with the non-disordered O to have the geometry of a perfect tetrahedron during their refinement. O(5) from the perchlorate ion may hydrogen bond to the O(2) (water) at 3·09 Å, as may the non-disordered perchlorate oxygen, O(4), at 3·006 Å to O(1) (water) in an adjacent unit cell.

It appears from our study that N(110) from non-coordinated phen is within hydrogen-bonding distance (2·875 Å) of O(1) (water). The distance from N(11) to an O(2) (water) of an adjacent unit cell is also within hydrogen-bonding limits (2·873 Å).

Re-examination of the coordinates in the original paper yield similar H-bonding distances, 2·90 and

* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39538 (29 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Distances* (Å) *and angles* (°) *in the* ClO_4^- *ion, and the* Ba^{2+} *coordination sphere*

Cl(1)–O(3)	1·41 (1)	Ba^{2+}–O(1)	2·778 (5)
Cl(1)–O(4)	1·438 (8)	Ba^{2+}–O(2)	2·763 (6)
Cl(1)–O(5)	1·39 (1)	Ba^{2+}–N(21)	2·945 (5)
Cl(1)–O(6)	1·39 (1)	Ba^{2+}–N(210)	2·940 (6)
O(3)–Cl(1)–O(4)	108·7 (6)		
O(3)–Cl(1)–O(5)	111·5 (8)		
O(3)–Cl(1)–O(6)	111·7 (8)		
O(4)–Cl(1)–O(5)	106·0 (7)		
O(4)–Cl(1)–O(6)	110·3 (5)		
O(5)–Cl(1)–O(6)	108·3 (8)		

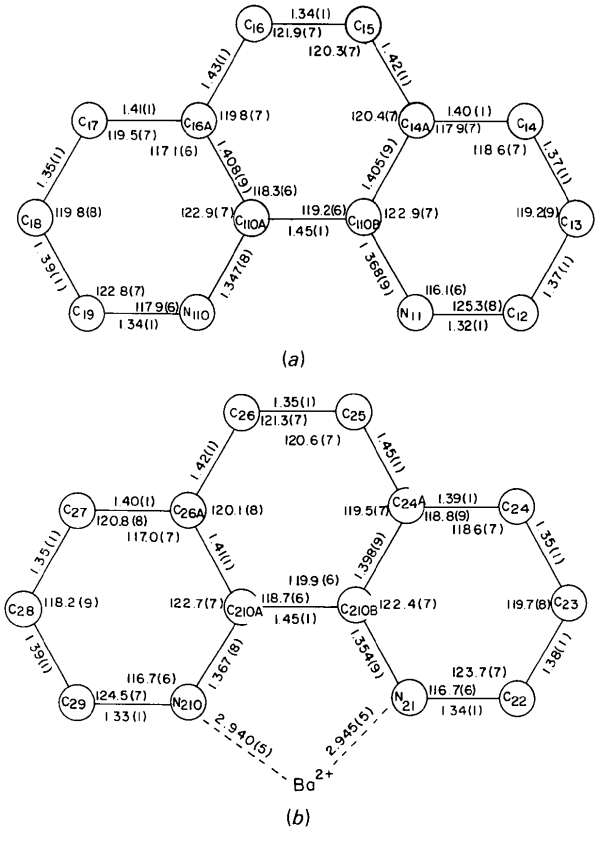

Fig. 1. Bond lengths (Å) and angles (°) in (*a*) phenanthroline 1, and (*b*) phenanthroline 2.

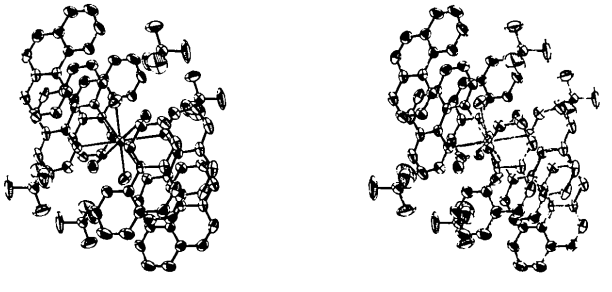

Fig. 2. Stereoview of the contents of a unit cell, with two additional phen's and perchlorate ions from adjacent unit cells.

2·83 Å. The original paper also deals with the isomorphous Sr compound. In the Sr analogue, the shortest N···H–O distance reported is 359 pm. In fact, examination of the original results shows the N···H–O distances in the Sr compound to be 2·88 and 2·87 Å. In the coordinate system reported in the original paper, these distances are between tabulated atoms and atoms transformed by $-x, -y+1, -z$.

The distances in the Ba^{2+} coordination sphere are listed in Table 2. The coordination around Ba^{2+} involves four water molecules [Ba–OH_2, 2·778 (5) to 2·763 (6) Å], and two of the four phen molecules [Ba–N, 2·945 (5) to 2·940 (6) Å].

Least-squares-planes analyses show similar results to the earlier determination. The two differing phen's are almost parallel with an angle of 2·07° between them. The plane formed by the four water O atoms is almost perpendicular (87·1°) to that of the phen's.

In the crystal, the non-coordinated phen is stacked above and slightly offset from the coordinated phen. This packing arrangement yields continuous columns of alternating phen 1 and phen 2 molecules. The contents of the entire unit cell plus one extra non-coordinated phen and one extra perchlorate from the unit cell above and the same extra molecules from the unit cell below are shown in stereo in Fig. 2. The mean distance between the plane of one phen and directly underlying atoms from the other phen molecule (3·45 Å) is in the range expected for normal van der Waals separation between aromatic molecules. Therefore, we believe there to be little, if any, charge transfer between the phen molecules.

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