are reported by Corbridge (1955). The structure determination was started as part of investigations of the system $CaO-P_2O_5$. Compounds of this system could be useful for medical implantations with respect to the replacement of bones. Special mechanical properties of the compound can be achieved if the preferred direction of crystallization along **c** is supported.

Experimental. Dry calcium dihydrogenphosphate $Ca(H_2PO_4)_2.H_2O$ was melted at 1523 K. Cooling the melt to 1223 K leads to crystals of $Ca(PO_3)_2$, sufficiently large and of good quality. The specimen used for structure determination had dimensions 0·10 × 0·25 × 0·35 mm.

All measurements were performed on a PW 1100 instrument that was rebuilt and equipped with additional facilities (Gomm, 1989). Details of measurements: ω–2θ scan, modified Lehmann–Larsen profile analysis: lattice parameters derived from 46 reflections with $15 < \theta < 18°$; absorption correction by using a modified version of the program *CAMEL JOCKEY* (Flack, 1975) based on empirical ψ-scan data, max. and min. transmission 1·024 (5) and 0·909 (6); intensities collected for $-22 \leq h \leq 22$, $-10 \leq k \leq 10$, $-9 \leq l \leq 9$, $\theta_{max} =$ 27·5°; six standard reflections, no significant variation, 8446 reflections measured, 2113 unique reflections, no unobserved reflections omitted; R_{int} based on F^2 is 0·029. The structure was solved by direct methods and refined by full-matrix least squares based on F^2; weights derived from experimental standard deviations $w^2 = 1/\sigma(F^2)$. In the final stage, anisotropic temperature parameters were used for all atoms; the results are given in Table 1 (coordinates and U_{eq}).[*] The final R values are: $R = 0{\cdot}0395$, $wR = 0{\cdot}057$, $S = 3{\cdot}50$, maximum shift-to-e.s.d. ratio 0·01. Maximum and minimum electron density residuals are $\rho_{max} = 0{\cdot}3$, $\rho_{min} = -0{\cdot}2$ e Å^{-3}, respectively. Extinction corrections were applied according to the Zachariasen (1968) formula; maximum extinction factor was 1·15; form-factor tables from *International Tables for X-ray Crystallography* (1962). All computations were performed on an ATARI 1040 STF computer using the program system *ATARI CRYSTAN*88 (1989).

Discussion. Distances and angles are given in Table 2. Each P atom is surrounded tetrahedrally by O atoms. Two are bridging O atoms to other tetrahedra in the [001] direction. The arrangement of the tetrahedra results in meandering chains parallel to **c** (see Figs. 1 and 2*a*). The distances and angles are in good agreement with those reported in the literature for isolated and bridging O—P values. The chains are connected by the Ca atoms. Ca(01) has coordination number 8; the polyhedron is close to a tetragonal antiprism; the coordination polyhedron for Ca(02) is close to a trigonal prism that is augmented to coordination number 7 by an additional atom (see Fig. 2*b*). It occupies one of the rectangular faces of the prism to form a pyramid, resulting in a capped trigonal prism. The distances and angles are also in good agreement with those in the literature (*International Tables for X-ray Crystallography,* 1962).

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[*] Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51544 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Tetraaqua-di-μ-hydroxo-tetrakis(1,10-phenanthroline)diholmium Tetraperchlorate 1,10-Phenanthroline Solvate (1/2)

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Abstract. $[Ho_2(OH)_2(C_{12}H_8N_2)_4(H_2O)_4](ClO_4)_4.2C_{12}H_8N_2$, $M_r = 1915{\cdot}0$, triclinic, $P\bar{1}$, $a = 11{\cdot}947\ (10)$, $b = 11{\cdot}733\ (10)$, $c = 13{\cdot}084\ (10)$ Å, $\alpha = 99{\cdot}00\ (7)$, $\beta = 95{\cdot}30\ (7)$, $\gamma = 92{\cdot}88\ (8)°$, $V = 1800\ (3)$ Å^3, $Z = 1$, $D_m = 1{\cdot}77$, $D_x = 1{\cdot}767\ (3)$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) =$ 0·71069 Å, $\mu = 2{\cdot}51$ mm^{-1}, $F(000) = 952$, $T =$

0108-2701/89/040553-04$03.00

Table 1. *Final atomic coordinates and equivalent isotropic thermal parameters*

$$U_{eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*(\mathbf{a}_i.\mathbf{a}_j).$$

	x	y	z	U_{eq}(Å^2)
Ho	0·00028 (3)	0·13614 (3)	0·44725 (2)	0·0322 (2)
Cl1	0·27181 (17)	0·31455 (18)	0·16439 (15)	0·059 (2)
Cl2	0·30986 (18)	0·89984 (18)	0·24956 (15)	0·060 (2)
O11	0·2562 (5)	0·4164 (5)	0·1213 (4)	0·082 (5)
O12	0·3421 (5)	0·2427 (5)	0·1043 (5)	0·095 (5)
O13	0·3255 (6)	0·3424 (6)	0·2676 (4)	0·107 (6)
O14	0·1662 (5)	0·2526 (7)	0·1640 (6)	0·131 (7)
O21	0·1961 (5)	0·8593 (6)	0·2531 (5)	0·095 (5)
O22	0·3729 (6)	0·8065 (7)	0·2630 (6)	0·138 (7)
O23	0·3398 (6)	0·9911 (5)	0·3339 (5)	0·106 (6)
O24	0·3266 (9)	0·9307 (8)	0·1568 (6)	0·188 (10)
OH	0·0631 (3)	−0·0425 (3)	0·4301 (3)	0·037 (3)
O*W*1	−0·0153 (5)	0·3123 (5)	0·3753 (5)	0·051 (4)
O*W*2	0·1559 (5)	0·1550 (6)	0·3477 (5)	0·057 (4)
N1	0·1751 (5)	0·1740 (4)	0·5806 (4)	0·039 (4)
C1A	0·2700 (6)	0·1223 (6)	0·5691 (6)	0·045 (5)
C1B	0·3577 (7)	0·1266 (6)	0·6472 (7)	0·052 (6)
C1C	0·3453 (7)	0·1851 (7)	0·7436 (7)	0·055 (6)
C1D	0·2458 (7)	0·2394 (6)	0·7610 (6)	0·048 (6)
C1E	0·2246 (8)	0·3025 (7)	0·8610 (6)	0·059 (6)
C1F	0·1302 (8)	0·3585 (6)	0·8713 (6)	0·054 (6)
C1G	0·0473 (7)	0·3610 (6)	0·7850 (6)	0·047 (5)
C1H	−0·0471 (8)	0·4264 (7)	0·7911 (6)	0·059 (6)
C1J	−0·1164 (8)	0·4293 (7)	0·7050 (7)	0·060 (6)
C1K	−0·0938 (7)	0·3640 (6)	0·6116 (6)	0·054 (6)
N2	−0·0091 (5)	0·2982 (4)	0·6015 (4)	0·044 (4)
C1L	0·0648 (6)	0·2983 (5)	0·6877 (5)	0·040 (5)
C1M	0·1638 (6)	0·2345 (5)	0·6754 (5)	0·039 (5)
N3	−0·0907 (5)	0·0555 (4)	0·2633 (4)	0·040 (4)
C2A	−0·0327 (7)	−0·0037 (6)	0·1924 (6)	0·048 (6)
C2B	−0·0783 (8)	−0·0440 (7)	0·0912 (6)	0·055 (6)
C2C	−0·1838 (8)	−0·0184 (7)	0·0598 (6)	0·056 (6)
C2D	−0·2477 (7)	0·0423 (6)	0·1301 (6)	0·047 (6)
C2E	−0·3612 (8)	0·0699 (8)	0·1059 (7)	0·063 (7)
C2F	−0·4225 (7)	0·1213 (8)	0·1760 (7)	0·062 (7)
C2G	−0·3765 (6)	0·1493 (6)	0·2840 (6)	0·051 (6)
C2H	−0·4413 (7)	0·1921 (7)	0·3648 (7)	0·059 (6)
C2J	−0·3940 (7)	0·2071 (7)	0·4653 (7)	0·059 (7)
C2K	−0·2838 (7)	0·1850 (6)	0·4851 (6)	0·049 (6)
N4	−0·2153 (4)	0·1503 (4)	0·4128 (4)	0·040 (4)
C2L	−0·2634 (6)	0·1283 (6)	0·3127 (5)	0·038 (5)
C2M	−0·1982 (5)	0·0770 (5)	0·2344 (5)	0·035 (5)
N5	0·8683 (5)	0·3467 (5)	0·1936 (5)	0·054 (4)
C3A	0·9055 (8)	0·2977 (7)	0·1057 (7)	0·062 (7)
C3B	0·8468 (9)	0·2877 (8)	0·0090 (7)	0·068 (7)
C3C	0·7424 (9)	0·3285 (8)	0·0022 (7)	0·073 (7)
C3D	0·6974 (7)	0·3809 (6)	0·0923 (6)	0·054 (6)
C3E	0·5883 (9)	0·4233 (8)	0·0913 (8)	0·073 (8)
C3F	0·5484 (8)	0·4754 (9)	0·1758 (9)	0·078 (8)
C3G	0·6174 (8)	0·4927 (7)	0·2743 (7)	0·063 (7)
C3H	0·5790 (9)	0·5538 (8)	0·3663 (9)	0·080 (8)
C3J	0·6476 (12)	0·5709 (9)	0·4538 (9)	0·092 (9)
C3K	0·7562 (10)	0·5303 (8)	0·4537 (7)	0·082 (8)
N6	0·7929 (6)	0·4689 (5)	0·3717 (5)	0·061 (5)
C3L	0·7254 (6)	0·4515 (6)	0·2816 (6)	0·046 (5)
C3M	0·7650 (6)	0·3902 (6)	0·1870 (6)	0·048 (5)

297 (1) K, final $R = 0{\cdot}0292$ for 3305 reflections. The complex cation is a centrosymmetric dimer in which the two Ho ions are connected through two hydroxo bridges. The remaining coordination sites around each metal ion are occupied by four N atoms and two water molecules.

Introduction. Spectral properties of Ln^{3+}–phenanthroline complexes in anhydrous acetonitrile solution were the subject of a recent paper (Bukietyńska & Pham, 1987). However, the attempt to prepare crystals of the anhydrous holmium complex proved unsuccessful. The title compound crystallizes when a small amount of water is present.

Experimental. The title compound was prepared by mixing a solution of anhydrous $Ho(ClO_4)_3$ in dry acetonitrile with dried phenanthroline. The slow infusion of atmospheric water vapour through a cellophane membrane at room temperature resulted in the formation of well-formed parallelepiped-shaped yellow crystals. A specimen $0{\cdot}2 \times 0{\cdot}3 \times 0{\cdot}5$ mm was cut from a larger crystal. D_m by flotation in $CHBr_3/CHCl_3$. Oscillation and Weissenberg photographs showed the triclinic system and the $P\overline{1}$ space group was successfully assumed. Syntex $P2_1$ diffractometer, Mo $K\alpha$ radiation for lattice parameters (15 reflections, $14 < 2\theta < 27°$), variable $\theta/2\theta$ scan, $4 < 2\theta < 42°$, two standards measured every 50 reflections, relative standard deviation of their average intensity 2·8%. 3884 intensities measured, 3305 with $I \geq 3\sigma(I)$, index range h $0\rightarrow12$, k $-11\rightarrow11$, l $-13\rightarrow12$, no correction for absorption or extinction. Structure was solved with locally modified *XTL/XTLE* programs (Syntex, 1976) and *SHELX76* (Sheldrick, 1976) and refined with locally modified *SHELX76*. Neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974), real and imaginary components of anomalous dispersion included for all non-H atoms. The Ho atoms were located from a Patterson synthesis, the remaining non-H atoms from subsequent difference syntheses; C-bonded H atoms placed geometrically, O-bonded H atoms from difference syntheses. Final blocked-matrix least-squares refinement based on F (non-H atoms anisotropic, hydroxo H atom isotropic, the other H atoms isotropic with constrained positional parameters), the common C—H and O—H distances being refined as additional parameters, $R = 0{\cdot}0292$, $wR = 0{\cdot}0276$, max. $\Delta/\sigma = 0{\cdot}314$, $\Delta\rho$ between $-0{\cdot}71$ and $0{\cdot}49$ e Å^{-3}, the highest peaks around Cl and Ho atoms, $w = 1/\sigma^2(F)$.

Discussion. Final atomic parameters are given in Table 1* and the geometry of the holmium coordination sphere is shown in Table 2, together with averaged bond lengths and angles for the phenanthroline molecules and the perchlorate anions. The structure consists of tetraaqua-di-μ-hydroxo-tetrakis(phenanthroline)diholmium cations, perchlorate anions and free phenanthroline molecules. Each half of the complex cation is related to the other through the inversion centre. The coordination environment of holmium may be described as a distorted square antiprism, with OH, OH^{i}, N3, N4 and *W*1, *W*2, N1, N2 defining the two bases respectively. The distances follow the usual

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, hydrogen bonds and additional interatomic bonds and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51542 (54 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* (°) *of the holmium coordination sphere, together with averaged bond lengths and angles in the phenanthroline molecules and the perchlorate anions*

Ho—Ho^{i}	3·673 (3)	Ho—N1	2·568 (6)
—OH	2·247 (4)	—N2	2·562 (5)
—OH^{i}	2·247 (4)	—N3	2·563 (5)
—O*W*1	2·410 (6)	—N4	2·592 (5)
—O*W*2	2·387 (6)		

OH—Ho—OH^{i}	70·4 (2)	O*W*1—Ho—N1	105·1 (2)
—O*W*1	146·8 (2)	—N2	73·7 (2)
—O*W*2	77·9 (2)	—N3	79·6 (3)
—N1	80·4 (2)	—N4	76·5 (2)
—N2	134·3 (2)	O*W*2—Ho—N1	74·6 (3)
—N3	80·5 (2)	—N2	115·5 (3)
—N4	116·8 (2)	—N3	78·9 (3)
OH^{i}—Ho—O*W*1	142·4 (2)	—N4	134·5 (2)
—O*W*2	142·9 (2)	N1—Ho—N2	63·8 (2)
—N1	81·4 (2)	—N3	150·0 (2)
—N2	76·7 (2)	—N4	146·7 (2)
—N3	113·3 (2)	N2—Ho—N3	143·0 (2)
—N4	78·7 (2)	—N4	85·7 (2)
O*W*1—Ho—O*W*2	72·4 (3)	N3—Ho—N4	63·2 (2)
		Ho—OH—Ho	109·6 (2)

Symmetry code: (i) $-x$, $-y$, $1-z$.

	Min. value	Max. value	Mean	*n*†
Cl—O	1·349 (8)*	1·423 (7)	1·415 (14)	7
C—N	1·307 (10)	1·366 (9)	1·341 (18)	12
C—C	1·318 (13)	1·462 (11)	1·395 (38)	36
O—Cl—O	105·0 (5)	112·7 (6)	109·4 (19)	8
C—N—C	116·1 (6)	118·3 (6)	117·4 (8)	6
C—C—N	117·8 (6)	125·1 (8)	121·6 (25)	18
C—C—C	117·2 (7)	124·4 (8)	119·9 (19)	42

* Not included in the mean.
† *n* = number of bonds or angles.

pattern observed with lanthanide complexes. The lengths of the Ho—N and Ho—OH bonds found here are very similar to the values for Ho—N and Ho—O bonds in the bis(4-picoline) adduct of 2,2,6,6-tetramethylheptane-3,5-dionatoholmium, Ho(dpm)$_3$(4-pic)$_2$: 2·53 (3) Å and 2·24 (2)–2·30 (2) Å respectively (Horrocks, Sipe & Luber, 1971). The Ho—N distances are, as expected, slightly shorter than those in the EDTA complex (Templeton, Templeton & Zalkin, 1985). It is generally observed that Ln—N bonds involving aromatic N atoms are shorter than those involving aminocarboxylic acids (in complexes with comparable coordination numbers; see *e.g.* Hoard, Lee & Lind, 1965; Al-Karaghouli & Wood, 1968; Hu, Lin, Shen, Xing & Shi, 1986; Sinha, 1976; and many others). The hydroxo bridges are essentially symmetric, the Ho—OH distances being within the observed range (Sinha, 1976). Hydroxo bridges in lanthanide complexes, to the authors' knowledge, have been hitherto observed only in oxyhydroxides LnOOH (Christensen & Hazell, 1972; Christensen & von Heidenstam, 1966). The C—C and C—N bond lengths are within the normal range. The *ORTEP* view (Johnson, 1976) of the complex cation is given in Fig. 1. The Cl—O bonds are normal except for Cl2—O24 which is unusually short, possibly due to slight disorder of the oxygen atom. The complex cation, the perchlorate anions and the unbonded phenanthroline molecules are held together by a moderately elaborate network of hydrogen bonds. The crystal packing is shown in Fig. 2.

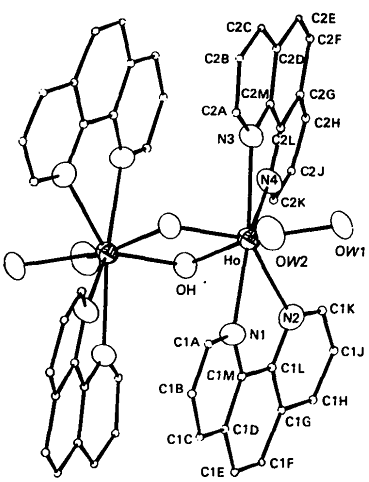

Fig. 1. A view showing the numbering scheme of the complex cation.

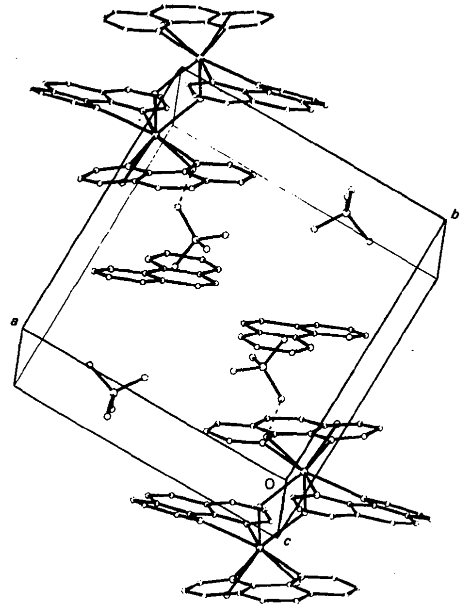

Fig. 2. A view of the crystal structure. The dashed lines represent the hydrogen bonds.

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Structure of the 1:1 Complex of Mercury(II) Saccharinate with 2,2′-Bipyridyl*

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Abstract. $[Hg(C_7H_4NO_3S)_2(C_{10}H_8N_2)]$, $M_r = 721{\cdot}13$, monoclinic, $P2_1/c$, $a = 12{\cdot}238\,(1)$, $b = 14{\cdot}298\,(2)$, $c = 14{\cdot}237\,(3)$ Å, $\beta = 106{\cdot}65\,(1)°$, $V = 2386{\cdot}73$ Å^3, $Z = 4$, D_m (by flotation) $= 1{\cdot}988$, $D_x = 2{\cdot}007$ Mg m^{-3}, $\lambda(\mathrm{Cu}\,K\alpha) = 1{\cdot}54178$ Å, $\mu = 13{\cdot}51$ mm^{-1}, $F(000) = 1392$, room temperature, final $R = 0{\cdot}031$ for 3703 independent observed reflections. The structure is built up of discrete molecules. Hg has a distorted tetrahedral coordination being bonded to two saccharinate N atoms [2·141 (4) and 2·120 (4) Å] and two N atoms belonging to the bipyridyl ligand [2·393 (3) and 2·328 (4) Å]. The N—Hg—N angles in the tetrahedron range from 70·7 (1) to 135·4 (2)°.

Introduction. This investigation is part of our broader research on the complexing properties of *o*-sulfobenzoimide, commonly known as saccharin. So far the crystal structures of sodium and magnesium saccharinates (Jovanovski & Kamenar, 1982), manganese(II) saccharinate (Kamenar & Jovanovski, 1982), mercury(II) saccharinates (Kamenar, Jovanovski & Grdenić, 1982; Jovanovski, Kamenar, Ferguson & Kaitner, 1988) and lead(II) saccharinate (Jovanovski, Hergold-Brundić & Kamenar, 1988) have been studied. In order to extend this investigation to the Hg chelate complexes we have prepared the 1:1 complex of mercury(II) saccharinate with 2,2′-bipyridyl. This is even more interesting because, contrary to the transition-metal complexes, there are not many examples of Hg complexes with chelating N donor ligands. Up to now complexes with such ligands as ethylenediamine (Duplančić, Grdenić, Kamenar, Matković & Sikirica, 1976; Cannas, Cristini & Marongiu, 1976; Grdenić, Sikirica & Vicković, 1977; Cannas, Cristini & Marongiu, 1978), 1,10-phenanthroline (Beauchamp, Saperas & Rivest, 1974; Grdenić, Kamenar & Hergold-Brundić, 1978*b*), 1,8-naphthyridine (Epstein, Dewan, Kepert & White, 1974) and bis(pyrazolyl)alkanes (Cingolani, Lorenzotti, Lobbia, Leonesi, Bonati & Bovio, 1987) have been prepared and structurally characterized. A few different complexes of Hg with 2,2′-bipyridyl as the bidentate ligand are also known (Craig, Farhangi, Graddon & Stephenson, 1974; Canty & Gatehouse, 1976; Grdenić, Kamenar & Hergold-Brundić, 1978*a*; Grdenić, Kamenar & Hergold-Brundić, 1979; Halfpenny, 1982).

Experimental. The complex was prepared by successive addition of an equimolar quantity of 2,2′-bipyridyl to a warm mixture of aqueous solutions of saccharin and mercury(II) acetate. Transparent needle-shaped crystals were obtained by recrystallization from water. Diffraction data collected on a Philips PW 1100 diffractometer, graphite-monochromated Cu $K\alpha$ radiation. Crystal of dimensions 0·33 × 0·09 × 0·07 mm used for measurement of unit-cell parameters

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* Saccharin is 1,2-benzisothiazol-3(2*H*)-one 1,1-dioxide.

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