S(3)—C(5)	1.737 (7)	C(12)—C(13)	1.36 (1)
S(4)—C(1)	1.723 (7)	C(13)—C(14)	1.40 (1)
S(4)—C(6)	1.740 (5)	C(15)—C(16)	1.396 (9)
C(1)—C(2)	1.391 (9)	C(15)—C(20)	1.38 (1)
C(3)—C(4)	1.347 (9)	C(16)—C(17)	1.391 (8)
C(3)—C(7)	1.50 (1)	C(17)—C(18)	1.38 (1)
C(4)—C(9)	1.474 (7)	C(18)—C(19)	1.36 (1)
C(5)—C(6)	1.341 (9)	C(19)—C(20)	1.400 (8)
C(5)—C(15)	1.491 (7)		
O(1)—Mo(1)—O(2)	152.7 (2)	O(6)—Mo(2)—O(7)	154.0 (1)
O(1)—Mo(1)—O(3)	84.6 (2)	O(6)—Mo(2)—O(10)	77.2 (1)
O(1)—Mo(1)—O(4)	102.7 (2)	O(7)—Mo(2)—O(10)	76.8 (1)
O(1)—Mo(1)—O(9)	87.7 (2)	O(3)—Mo(3)—O(6)	88.3 (2)
O(1)—Mo(1)—O(10)	76.3 (1)	O(3)—Mo(3)—O(7)	89.2 (2)
O(2)—Mo(1)—O(3)	85.8 (2)	O(3)—Mo(3)—O(8)	103.2 (2)
O(2)—Mo(1)—O(4)	104.3 (2)	O(3)—Mo(3)—O(9)	153.2 (2)
O(2)—Mo(1)—O(9)	89.4 (2)	O(3)—Mo(3)—O(10)	77.5 (1)
O(2)—Mo(1)—O(10)	76.6 (1)	O(6)—Mo(3)—O(7)	152.6 (2)
O(3)—Mo(1)—O(4)	102.4 (2)	O(6)—Mo(3)—O(8)	102.7 (2)
O(3)—Mo(1)—O(9)	153.2 (2)	O(6)—Mo(3)—O(9)	84.9 (2)
O(3)—Mo(1)—O(10)	76.0 (1)	O(6)—Mo(3)—O(10)	76.4 (1)
O(4)—Mo(1)—O(9)	104.4 (2)	O(7)—Mo(3)—O(8)	104.5 (2)
O(4)—Mo(1)—O(10)	178.2 (1)	O(7)—Mo(3)—O(9)	85.1 (2)
O(9)—Mo(1)—O(10)	77.2 (1)	O(7)—Mo(3)—O(10)	76.4 (1)
O(1)—Mo(2)—O(2)	154.2 (1)	O(8)—Mo(3)—O(9)	103.6 (2)
O(1)—Mo(2)—O(5)	104.0 (2)	O(8)—Mo(3)—O(10)	178.9 (2)
O(1)—Mo(2)—O(6)	88.4 (2)	O(9)—Mo(3)—O(10)	75.7 (1)
O(1)—Mo(2)—O(7)	87.6 (2)	Mo(1)—O(1)—Mo(2)	116.3 (2)
O(1)—Mo(2)—O(10)	77.6 (1)	Mo(1)—O(2)—Mo(2)	116.4 (2)
O(2)—Mo(2)—O(5)	101.8 (2)	Mo(1)—O(3)—Mo(3)	116.5 (2)
O(2)—Mo(2)—O(6)	86.6 (2)	Mo(2)—O(6)—Mo(3)	116.2 (2)
O(2)—Mo(2)—O(7)	85.9 (2)	Mo(2)—O(7)—Mo(3)	116.9 (2)
O(2)—Mo(2)—O(10)	76.6 (1)	Mo(1)—O(9)—Mo(3)	117.0 (2)
O(5)—Mo(2)—O(6)	103.3 (2)	Mo(1)—O(10)—Mo(2)	90.24 (2)
O(5)—Mo(2)—O(7)	102.6 (2)	Mo(1)—O(10)—Mo(3)	90.12 (2)
O(5)—Mo(2)—O(10)	178.3 (2)	Mo(2)—O(10)—Mo(3)	90.03 (2)
C(2)—S(1)—C(3)	95.3 (3)	S(4)—C(6)—C(5)	116.4 (5)
C(2)—S(2)—C(4)	95.6 (3)	S(4)—C(6)—C(8)	115.5 (4)
C(1)—S(3)—C(5)	96.1 (3)	C(5)—C(6)—C(8)	128.0 (5)
C(1)—S(4)—C(6)	95.8 (3)	C(4)—C(9)—C(10)	118.7 (5)
S(3)—C(1)—S(4)	115.0 (4)	C(4)—C(9)—C(14)	122.2 (6)
S(3)—C(1)—C(2)	120.6 (5)	C(10)—C(9)—C(14	119.0 (5)
S(4)—C(1)—C(2)	124.4 (4)	C(9)—C(10)—C(11)	119.8 (6)
S(1)—C(2)—S(2)	115.7 (4)	C(10)—C(11)—C(12)	120.5 (7)
S(1)—C(2)—C(1)	118.9 (4)	C(11)—C(12)—C(13)	120.4 (6)
S(2)—C(2)—C(1)	125.3 (5)	C(12)—C(13)—C(14)	119.8 (7)
S(1)—C(3)—C(4)	117.2 (6)	C(9)—C(14)—C(13)	120.3 (7)
S(1)—C(3)—C(7)	115.3 (4)	C(5)—C(15)—C(16)	119.3 (6)
C(4)—C(3)—C(7)	127.4 (5)	C(5)—C(15)—C(20)	120.0 (6)
S(2)—C(4)—C(3)	116.1 (4)	C(16)—C(15)—C(20)	120.7 (5)
S(2)—C(4)—C(9)	118.1 (5)	C(15)—C(16)—C(17)	119.6 (6)
C(3)—C(4)—C(9)	125.8 (7)	C(16)—C(17)—C(18)	119.2 (7)
S(3)—C(5)—C(6)	116.6 (4)	C(17)—C(18)—C(19)	121.2 (5)
S(3)—C(5)—C(15)	113.7 (5)	C(18)—C(19)—C(20)	120.6 (7)
C(6)—C(5)—C(15)	129.7 (6)	C(15)—C(20)—C(19)	118.7 (7)

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

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71484 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: PA1043]

References

Allcock, H. R., Bissell, E. C. & Shawl, E. T. (1973). *Inorg. Chem.* **12**, 2963-2968.

Fettouhi, M., Ouahab, L., Perrin, A., Grandjean, D. & Fabre, J. M. (1991). *Acta Cryst.* C**47**, 2457-2459.

Frenz, B. A. (1985). *Enraf–Nonius SDP-Plus Structure Determination Package*. Version 3.0. Enraf–Nonius, Delft, The Netherlands.

Lindquist, I. (1953). *Ark. Kemi*, **5**, 247-250.

Triki, S., Ouahab, L., Halet, J.-F., Peña, O., Padiou, J., Grandjean, D., Garrigou-Lagrange, C. & Delhaes, P. (1992). *J. Chem. Soc. Dalton Trans.* pp. 1217-1227.

Walker, N. & Stuart, D. (1983). *Acta Cryst.* A**39**, 158-166.

Acta Cryst. (1994). C**50**, 221-224

Barium (Cryptand 222B)$Cl_2.6H_2O$

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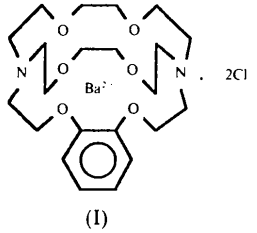
Abstract

In the title compound, (4,7,13,16,21,24-hexaoxa-1,10-diaza-5,6-benzobicyclo[8.8.8]hexacos-5-ene)barium dichloride hexahydrate, $[BaCl_2(C_{22}H_{36}N_2O_6)].6H_2O$, the Ba ion is surrounded by the cryptand molecule (222B) with the arm containing the fused benzene-ring substituent bent towards one of the other two cryptand arms, leaving two slightly larger open faces through which two additional water molecules are coordinated, making a total of ten atoms surrounding the Ba atom. The species could be more accurately represented as $[Ba(222B)(H_2O)_2]^{2+}.2Cl^-.4H_2O$

Comment

Crystals of the barium salt of cryptand 222B were prepared as a preliminary step in the development of a model using a bioconjugate of the 222B ligand, with the intent of exploring its potential in radioimmunotherapy. Previously, we have developed an HPLC (high-performance liquid chromatography) assay (Pettit, Swailes & Peterson, 1989) for studying the components in this system. The molecular structure of the title compound (I) and the labeling of the atoms is shown in Fig. 1.



(I)

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Perhaps the most definitive view of barium cryptand is that deviating slightly from the N(1)-N(10) axis of the molecule, which leaves the three diether strands of the molecule, which link N(1) to N(10), dividing the polar space into three regions. If the cryptand was perfectly symmetric, the three regions might be expected to be equal. The incorporation of the phenyl group as part of one strand causes asymmetry. As a result, one of the two strands lies closer to the unique strand so that there are two angularly wide spaces and one angularly narrow space. The Ba ion is coordinated by two water molecules through these two open areas, in addition to the eight almost equidistant ligand atoms of the cryptand molecule itself. From the polar view, it is clear that the atoms in the arms of the cryptand lie almost in a plane - a characteristic that seems to be common when cryptands stretch to accommodate larger ions. For the lithium, sodium and calcium cases, from the polar point of view, the arms splay out to the sides and appear to be much more relaxed. Quantitatively, this can be expressed by the average deviation of atoms from a plane for each of the cryptand arms: for this Ba^{2+} example, 0.21 and 0.25 Å (Metz, Moras & Weiss, 1973*b*); for Pb^{2+}, 0.24 Å (Metz & Weiss, 1974); for Ca^{2+}, 0.43 Å (Metz, Moras & Weiss, 1973*a*); for Sm^{+3}, 0.43 Å (Burns, 1979); for the Li^+ cryptand (Ward, Rhinebarger & Popov, 1986), the arms deviate too far from planarity for comparison. Another way of distinguishing the coordination differences between a small ion and a large ion, again viewing along the N(1)-N(10) axis, is that the six O atoms are staggered, as if looking down the body diagonal of a cube, for small ions (lithium), and eclipsed for the other extreme (barium).

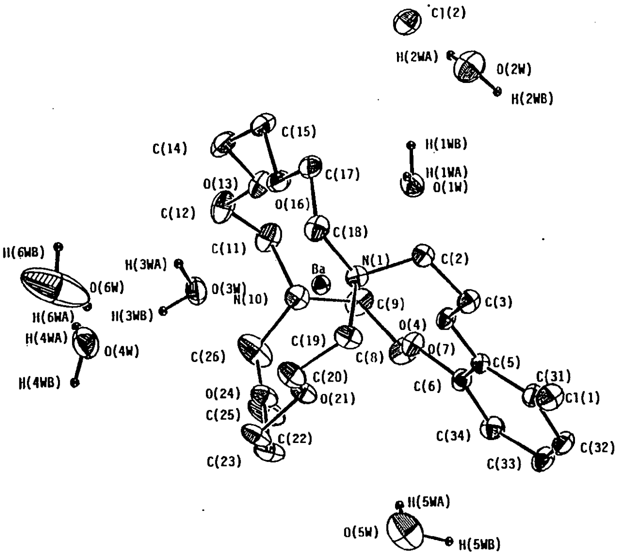

Fig. 1. An *ORTEP* (Johnson, 1965) view of barium cryptand 222B deviating slightly from the N(1)-N(10) direction. Thermal ellipsoids are drawn at the 25% probability level. H atoms are shown only for the water molecules.

Looking along the N(1)-N(10) axis, the torsion angles found in this barium example are $g^+ttg^-ttg^+$ for two of the arms and $g^+ttcttg^+$ for the benzo arm, similar to those reported for the Na^+, K^+, Rb^+ and Cs^+ cryptands (Auffinger & Wipff, 1991). The arrangement is different for Ca^{2+} [$g^-tg^-g^-g^-tg^-$ (Metz, Moras & Weiss, 1973*a*)] and Ba^{2+} cryptands [$g^-ttg^+ttg^-$ (Metz, Moras & Weiss, 1973*b*)].

Experimental

Crystal data

$[BaCl_2(C_{22}H_{36}N_2O_6)].6H_2O$
$M_r = 740.86$
Triclinic
$P\bar{1}$
$a = 11.258$ (4) Å
$b = 12.464$ (5) Å
$c = 13.175$ (4) Å
$\alpha = 84.13$ (3)°
$\beta = 80.95$ (3)°
$\gamma = 62.83$ (3)°
$V = 1623.3$ (11) Å^3
$Z = 2$

$D_x = 1.516$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 20-22°$
$\mu = 1.38$ mm^{-1}
$T = 295$ K
Tabular
0.82 × 0.56 × 0.40 mm
Colorless

Data collection

Enraf-Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical from diffraction data
$T_{min} = 0.92$, $T_{max} = 1.00$
11 625 measured reflections
11 310 independent reflections
10 793 observed reflections [$I > 3\sigma(I)$]

$R_{int} = 0.013$
$\theta_{max} = 25°$
$h = -13 \rightarrow 13$
$k = -14 \rightarrow 14$
$l = -15 \rightarrow 15$
3 standard reflections
frequency: 200 reflections for orientation standards
frequency: 60 min for intensity standards
intensity variation: <2.1%

Refinement

Refinement on F
$R = 0.023$
$wR = 0.038$
$S = 1.12$
5358 reflections
352 parameters
H-atom parameters not refined
Calculated weights $w = 1/[\sigma^2(F) + (0.03F)^2]$

$(\Delta/\sigma)_{max} = 0.09$ (as given by software), actually 0.11
$\Delta\rho_{max} = 0.5$ e Å^{-3}
$\Delta\rho_{min} = -0.1$ e Å^{-3}
Atomic scattering factors from *SDP* software (B. A. Frenz & Associates, Inc., 1982)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Ba	0.19056 (1)	0.22599 (1)	0.23243 (1)	0.02933 (4)
Cl(1)	−0.23884 (6)	0.20297 (6)	−0.09791 (5)	0.0597 (1)
Cl(2)	−0.59934 (9)	−0.25702 (8)	−0.58486 (7)	0.0881 (3)
O(4)	0.1317 (1)	0.1426 (1)	0.0612 (1)	0.0351 (4)
O(7)	0.3508 (1)	0.1728 (1)	0.0381 (1)	0.0409 (4)

O(13)	0.3399 (2)	0.1344 (2)	0.3996 (1)	0.0516 (5)
O(16)	0.0802 (2)	0.1585 (1)	0.4160 (1)	0.0462 (5)
O(21)	−0.0246 (1)	0.4301 (1)	0.1535 (1)	0.0460 (5)
O(24)	0.2233 (1)	0.4319 (1)	0.1605 (1)	0.0507 (5)
O(1*W*)	−0.2984 (2)	0.0304 (1)	−0.2344 (1)	0.0528 (5)
O(2*W*)	−0.1285 (2)	0.2153 (2)	−0.3305 (2)	0.0759 (6)
O(3*W*)	0.0727 (2)	0.3988 (1)	0.3801 (1)	0.0618 (5)
O(4*W*)	0.1100 (2)	−0.4132 (2)	0.4380 (2)	0.0771 (6)
O(5*W*)	0.4941 (3)	0.3987 (2)	−0.1924 (3)	0.1134 (11)
O(6*W*)	0.3519 (3)	0.4987 (3)	0.5025 (4)	0.204 (1)
N(1)	−0.0701 (2)	0.2261 (1)	0.2367 (1)	0.0371 (5)
N(10)	0.4583 (2)	0.2178 (2)	0.2100 (2)	0.0471 (5)
C(2)	−0.0383 (2)	0.1168 (2)	0.1834 (2)	0.0410 (5)
C(3)	0.0189 (2)	0.1154 (2)	0.0715 (2)	0.0426 (5)
C(5)	0.1852 (2)	0.1542 (2)	−0.0387 (2)	0.0344 (5)
C(6)	0.2997 (2)	0.1737 (2)	−0.0511 (2)	0.0370 (5)
C(8)	0.4841 (2)	0.1653 (2)	0.0222 (2)	0.0552 (8)
C(9)	0.5390 (2)	0.1375 (2)	0.1231 (2)	0.0557 (8)
C(11)	0.5225 (2)	0.1595 (3)	0.3034 (2)	0.00597 (8)
C(12)	0.4280 (3)	0.1885 (3)	0.4014 (2)	0.0652 (8)
C(14)	0.2627 (3)	0.1367 (3)	0.4972 (2)	0.0584 (9)
C(15)	0.1703 (3)	0.0847 (2)	0.4875 (2)	0.0561 (8)
C(17)	−0.0225 (2)	0.1239 (2)	0.4107 (2)	0.0522 (6)
C(18)	−0.1232 (2)	0.2166 (2)	0.3454 (2)	0.0518 (6)
C(19)	−0.1699 (2)	0.3361 (2)	0.1883 (2)	0.0507 (6)
C(20)	−0.1524 (2)	0.4463 (2)	0.2040 (2)	0.0536 (8)
C(22)	−0.0118 (2)	0.5392 (2)	0.1529 (2)	0.0591 (8)
C(23)	0.1240 (3)	0.5193 (2)	0.1008 (2)	0.0599 (8)
C(25)	0.3507 (3)	0.4267 (2)	0.1255 (3)	0.0795 (10)
C(26)	0.4510 (2)	0.3396 (2)	0.1936 (3)	0.0793 (10)
C(31)	0.1318 (2)	0.1487 (2)	−0.1246 (2)	0.0432 (6)
C(32)	0.1888 (3)	0.1665 (2)	−0.2225 (2)	0.0522 (8)
C(33)	0.2977 (3)	0.1891 (2)	−0.2340 (2)	0.0547 (8)
C(34)	0.3542 (2)	0.1937 (2)	−0.1481 (2)	0.0469 (6)

Table 2. *Selected geometric parameters* (Å, °)

Ba—O(1*W*$^{\rm i}$)	2.852 (2)	O(1*W*)—O(16$^{\rm i}$)	3.364 (3)
Ba—O(3*W*)	2.760 (2)	O(2*W*)—O(4*W*$^{\rm i}$)	2.792 (3)
Ba—O(4)	2.862 (1)	O(3*W*)—O(4*W*$^{\rm vi}$)	2.759 (3)
Ba—O(7)	2.837 (2)	O(3*W*)—O(4*W*$^{\rm vii}$)	2.864 (3)
Ba—O(13)	2.807 (2)	O(3*W*)—O(13)	3.316 (3)
Ba—O(16)	2.773 (2)	O(3*W*)—O(16)	2.949 (3)
Ba—O(21)	2.836 (2)	O(3*W*)—O(21)	3.266 (3)
Ba—O(24)	2.807 (2)	O(3*W*)—O(24)	3.204 (3)
Ba—N(1)	2.925 (2)	O(4*W*)—O(6*W*$^{\rm viii}$)	2.674 (5)
Ba—N(10)	2.938 (2)	O(4*W*)—O(16$^{\rm vii}$)	3.480 (3)
Cl(1)—O(1*W*)	3.286 (2)	O(6*W*)—O(6*W*$^{\rm ix}$)	3.340 (8)
Cl(1)—O(2*W*)	3.137 (2)	N(1)—C(2)	1.467 (3)
Cl(1)—O(5*W*$^{\rm ii}$)	3.225 (3)	N(1)—C(18)	1.478 (3)
Cl(2)—O(1*W*$^{\rm iii}$)	3.390 (2)	N(1)—C(19)	1.480 (3)
Cl(2)—O(2*W*$^{\rm iii}$)	3.225 (3)	N(10)—C(9)	1.488 (4)
Cl(2)—O(5*W*$^{\rm iv}$)	3.346 (4)	N(10)—C(11)	1.478 (4)
Cl(2)—O(6*W*$^{\rm v}$)	3.392 (4)	N(10)—C(26)	1.477 (4)
Cl(2)—O(6*W*$^{\rm i}$)	3.260 (4)	C(3)—C(2)	1.512 (3)
O(4)—C(3)	1.440 (3)	C(5)—C(31)	1.384 (3)
O(4)—C(5)	1.381 (3)	C(6)—C(5)	1.399 (3)
O(7)—C(6)	1.384 (3)	C(6)—C(34)	1.379 (3)
O(7)—C(8)	1.444 (3)	C(9)—C(8)	1.496 (4)
O(13)—C(12)	1.435 (4)	C(11)—C(12)	1.497 (4)
O(13)—C(14)	1.429 (3)	C(14)—C(15)	1.481 (5)
O(16)—C(15)	1.426 (3)	C(17)—C(18)	1.506 (4)
O(16)—C(17)	1.419 (3)	C(20)—C(19)	1.513 (4)
O(21)—C(20)	1.419 (3)	C(23)—C(22)	1.492 (4)
O(21)—C(22)	1.431 (3)	C(26)—C(25)	1.503 (5)
O(24)—C(23)	1.430 (3)	C(31)—C(32)	1.391 (4)
O(24)—C(25)	1.409 (4)	C(32)—C(33)	1.362 (4)
O(1*W*)—O(4$^{\rm i}$)	3.166 (2)	C(33)—C(34)	1.401 (4)
O(1*W*)—O(13$^{\rm i}$)	3.359 (3)		
C(18)—N(1)—C(19)	108.7 (2)	O(13)—C(12)—C(11)	107.8 (2)
C(18)—N(1)—C(2)	110.2 (2)	C(12)—O(13)—C(14)	112.4 (2)
C(19)—N(1)—C(2)	112.2 (2)	O(13)—C(14)—C(15)	108.9 (2)
C(11)—N(10)—C(26)	109.6 (3)	O(16)—C(15)—C(14)	108.4 (2)
C(11)—N(10)—C(9)	107.3 (2)	C(15)—O(16)—C(17)	112.5 (2)
C(26)—N(10)—C(9)	112.8 (3)	O(16)—C(17)—C(18)	108.7 (2)
N(1)—C(2)—C(3)	115.0 (2)	N(1)—C(18)—C(17)	115.0 (2)
O(4)—C(3)—C(2)	109.9 (2)	N(1)—C(19)—C(20)	111.7 (2)
C(5)—O(4)—C(3)	115.2 (2)	O(21)—C(20)—C(19)	108.5 (2)
O(4)—C(5)—C(6)	116.5 (2)	C(22)—O(21)—C(20)	110.4 (2)
O(4)—C(5)—C(31)	124.0 (2)	O(21)—C(22)—C(23)	109.4 (2)
C(6)—C(5)—C(31)	119.5 (2)	O(24)—C(23)—C(22)	108.5 (2)
O(7)—C(6)—C(5)	116.2 (2)	C(25)—O(24)—C(23)	110.6 (2)
O(7)—C(6)—C(34)	123.7 (2)	O(24)—C(25)—C(26)	109.2 (3)
C(5)—C(6)—C(34)	120.0 (2)	N(10)—C(26)—C(25)	116.7 (3)
C(8)—O(7)—C(6)	114.7 (2)	C(5)—C(31)—C(32)	120.2 (2)
O(7)—C(8)—C(9)	109.1 (2)	C(31)—C(32)—C(33)	120.0 (2)
N(10)—C(9)—C(8)	118.3 (2)	C(32)—C(33)—C(34)	120.7 (2)
N(10)—C(11)—C(12	114.6 (2)	C(6)—C(34)—C(33)	119.4 (3)

Symmetry codes: (i) $-x, -y, -z$; (ii) $x-1, y, z$; (iii) $-1-x, -y, -1-z$; (iv) $-x, -y, -1-z$; (v) $x-1, y-1, z-1$; (vi) $x, 1+y, z$; (vii) $-x, -y, 1-z$; (viii) $x, y-1, z$; (ix) $1-x, 1-y, 1-z$.

The barium cryptand was prepared by the reaction of equimolar amounts of $BaCl_2.7H_2O$ and 222B in methanol overnight. The dried reaction residue was extracted with dichloromethane and the crude complex recovered by evaporation of the solvent. The complex was crystallized from acetonitrile and sealed in a glass capillary, with its [10$\bar{1}$] direction approximately parallel to the φ axis.

Data collection: *CAD*-4 *Software* (Enraf-Nonius, 1989); scan range (0.8 + 0.35tanθ)°; scan speed 0.8 to 4.0° min^{-1}; background 25% of range, below and above; counting time reflections/background = 2/1.

Structure determination: the structure was determined from Patterson and difference electron-density maps. All the H-atom positions were found from the difference maps, although not initially for some of the water molecules. The chemical analysis of the sample [found: Ba 23.62, Cl 9.14 %; mole ratio Ba/Cl = 2/3] suggested the formula $Ba_2Cl_3(OH).(cryptand)_2$.

Initially, the structure solution was found in the space group $P1$, with two independent Ba atoms and three Cl atoms per cell. The refinement was slow in converging, but the two Ba atoms and the cryptand molecules appeared to be related by a center of symmetry. Two of the Cl atoms were related by a symmetry center and the third was related to a water molecule by a symmetry center. Refining the structure in $P\bar{1}$ gave a solution with a lower R value and rapid convergence. The mean-square atomic displacement for Cl(2) was higher at this stage [$U_{\rm av}$ = 0.062 for Cl(1) and 0.089 Å^2 for Cl(2)], in keeping with the chemical analysis with the occupancy of Cl(2) placed at 0.734 (approximate occupancy for an average of 0.5 Cl and 0.5 O occupancy). The mean-square atomic displacement became $U_{\rm av}$ = 0.062 for Cl(1) and 0.066 Å^2 for Cl(2). (The chemical analysis was performed on an air-dried sample; the crystal for X-ray intensity data was sealed in a glass capillary, since it was noted that left in air the crystals became opaque and eventually broke up. It is reasonable to observe that several of the water molecules found crystallographically have large temperature factors - indistinguishable from partial occupancy.) However, refining the structure with total occupancy for Cl gave the lowest R value (0.023), although the mean-square atomic displacement for Cl(2) was again larger than for Cl(1). The individual crystals may not have an identical chlorine composition and the particular crystal from which the intensity data were obtained may not be typical of the average analysis. In any event, the differences between the atomic coordinates from the two refinement assumptions are minor.

In the final refinement, all non-H atoms were refined anisotropically, the H atoms were kept in fixed positions. The H atoms on the water molecules were kept at the angular positions found from difference maps, with the O—H bond length adjusted to 0.85 Å. The remaining H atoms were placed at calculated positions with C—H = 0.95 Å.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71603 (31 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR1021]

References

Auffinger, P. & Wipff, G. (1991). *J. Am. Chem. Soc.* **113**, 5976-5988.

B. A. Frenz & Associates, Inc. (1982). *SDP Structure Determination Package*. College Station, Texas, USA.

Burns, J. H. (1979). *Inorg. Chem.* **18**, 3044-3047.

Enraf-Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf-Nonius, Delft, The Netherlands.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

Metz, B., Moras, D. & Weiss, R. (1973*a*). *Acta Cryst.* **B29**, 1377-1381.

Metz, B., Moras, D. & Weiss, R. (1973*b*). *Acta Cryst.* **B29**, 1382-1387.

Metz, B. & Weiss, R. (1974). *Inorg. Chem.* **13**, 2094-2098.

Pettit, W. A., Swailes, B. K. & Peterson, R. E. (1989). *J. Chromatogr.* **469**, 440-443.

Ward, D. L., Rhinebarger, R. P. & Popov, A. I. (1986). *Inorg. Chem.* **25**, 2825-2827.

Acta Cryst. (1994). C**50**, 224–226

1,1′-Bis(diphenylphosphine oxide)ferrocene Dihydrate

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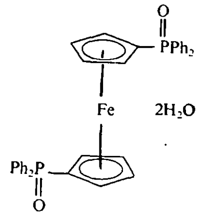
Abstract

The title compound, 1,1′-ferrocenediylbis(diphenylphosphine oxide) dihydrate, $[Fe(C_{17}H_{14}OP)_2].2H_2O$, was obtained by oxidation of bis(diphenylphosphino)ferrocene with trimethylamine oxide. The Fe atom sits on a molecular centre of symmetry and the two Cp rings are planar with a staggered configuration. The two phosphoryl groups are *trans* with respect to the $Fe(Cp)_2$ group.

Comment

In our search for ligands that might play some important part in electronic assistance (Munyejabo, Postel, Bensimon & Roustan, 1993), we became interested in ferrocenyl phosphines and phosphine oxides because of the easily accessible ferrocene–ferricinium redox couple. Ferrocenyl phosphines, because of their peculiarly large bite angle, have been studied extensively but, surprisingly, the structure of 1,1′-bis(diphenylphosphine)ferrocene was published only recently (Casellato, Ajo, Valle, Corain, Longato & Graziani, 1988). Data for the corresponding oxides are rather scarce. The $[CpFe\{CpP(O)Ph_2\}]$ and $[CpFe\{\eta^5\text{-}C_5H_3(CHMeNMe_2)P(O)Ph_2\}]$ monooxides have been obtained through the reaction of ferrocenylphosphines with $[Cp_2Co(CO)_2]$ and were structurally characterized by X-ray analyses (Kim, Lee, Kwon, Uhm, Lee & Byun, 1991). In order to gain further information on this type of phosphoryl ligand, we performed a structural study of 1,1′-bis(diphenylphosphine oxide)ferrocene dihydrate, $Fe[C_5H_4P(O)(C_6H_5)_2]_2.2H_2O$ (1).



(1)

The molecular structure of (1) together with the atom labelling is illustrated in Fig. 1. The Fe atom in (1) lies on a crystallographic inversion centre; the molecule as a whole is centrosymmetric and the asymmetric unit is represented by a half molecule. The distance of the Fe atom from the plane of the cyclopentadienyl ring is 1.66 Å.

In the solid state (1) has a staggered structure. The five-membered rings do not deviate significantly from planarity. The pattern of bond distances within the cyclopentadienyl rings shows substituent-induced geometrical distortions with a mean C—C bond length for the P═O substituted C atoms of 1.426 Å. The adjacent C—C bonds average 1.412 Å, while the unique C—C bond is 1.423 (7) Å.

Bond lengths and angles involving the P atoms compare well with the values reported for the $[CpFe\{CpP(O)Ph_2\}]$ and $[CpFe\{\eta^5\text{-}C_5H_3(CHMeNMe_2)P(O)Ph_2\}]$ monooxides (Kim, Lee, Kwon, Uhm,