The structure of the $[(Ph_2SMe)_2.18C6]^{2+}$ component of the 2:1 complex is illustrated in Fig. 1 which includes the atomic-numbering scheme. Fig. 2 shows a space-filling representation of the 2:1 complex corresponding closely to the skeletal view illustrated in Fig. 1, although the positions of the methyl H atoms were not determined: they have been incorporated assuming normal staggered geometries about the $S-CH_3$ bonds.

There is a crystallographic centre of symmetry at the centre of the 18C6 ring which adopts a characteristic all-*gauche* conformation with local pseudo D_{3d} symmetry. The two sulfonium cations approach opposite faces of the macrocycle with the two methyl groups lying on an axis approximately normal (9° to the normal) to the mean plane of the six macrocyclic O atoms: the $S-CH_3$ bonds are inclined at 39° to this plane. This geometry of approach of guest to host is very similar to that observed (Allwood, Crosby, Pears, Stoddart & Williams, 1984) in the structure of $[(PhCOCHPhSMe_2)_2.18C6][PF_6]_2$.

The absence of experimental H-atom positions for the two methyl groups precludes detailed discussion of any hydrogen-bonding interactions. We would expect that the steeply inclined approach of the $S-CH_3$ bonds relative to the mean plane of the macrocycle would result ideally in a two-point $C-H\cdots O$ hydrogen bonding between each methyl group and four of the ether O atoms as observed (Allwood, Crosby, Pears, Stoddart & Williams, 1984) in the structure $[(PhCO-CHPhSMe_2)_2.18C6][PF_6]_2$. Indeed, this is so. The shortest $C(10)\cdots O$ distances in the structure of $[(Ph_2SMe)_2.18C6][Hg_2I_6]$ are 2·93 (1) and 3·29 (1) Å to O(4') and O(7'), respectively. The methyl atom is displaced 1·78 (2) Å from the mean plane of the six O atoms in the macrocycle and the through-the-ring $Me\cdots Me$ distance is 3·61 (5) Å.

An interesting consequence of the tilted approach of the $S-CH_3$ bonds to the plane of the macrocycle is a

fairly close approach [3·52 (2) Å] of S(1) to O(4) [also S(1') to O(4')]. This could be construed as indicating a weak electrostatic interaction between the S atoms which carry formal positive charges and the electronegative O atoms.

The 18C6 molecules are positioned about the crystallographic centres of symmetry at $(\frac{1}{2}, \frac{1}{2}, 0)$ and $(\frac{1}{2}, 0, \frac{1}{2})$.

There are no short intermolecular contacts between the 2:1 complexes and the $[Hg_2I_6]^{2-}$ counterions, which are positioned about the crystallographic centres of symmetry at $(0, 0, 0)$ and $(0, \frac{1}{2}, \frac{1}{2})$. The geometry of the $Hg_2I_6^{2-}$ counterion is similar to those reported (Contreras, Seguel & Hönle, 1980; Beurskens, Bosman & Cras, 1972) for the tetrapropylammonium and 1,2,4-trithiolane-3,5-bis(*N,N*-diethyliminium) di-*μ*-iodo-bis[diiodomercurate(II)] salts.

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Structure and EXAFS of Diaquatetrakis(imidazole)cobalt(II) Dichloride

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Abstract. $[Co(C_3H_4N_2)_4(H_2O)_2]Cl_2$, $M_r = 438·18$, monoclinic, $C2/c$, $a = 12·419$ (2), $b = 11·018$ (2), $c = 15·865$ (3) Å, $\beta = 120·66$ (1)°, $V = 1867·6$ (5) Å^3, $Z = 4$, D_m(flotation, CCl_4/cyclohexane mixture) = 1·553, $D_x = 1·559$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 11·82$ cm^{-1}, $T = 295$ K, $F(000) = 900$, final $R = 0·044$

for 1537 observed reflections. The effective magnetic moment is $4 \cdot 86 \; \beta$ ($45 \cdot 07 \times 10^{-24} \, JT^{-1}$, magnetic susceptibility, 295 K). The structure consists of four imidazole rings and two water molecules coordinated to a Co^{II} atom in the basic cationic unit with structural evidence for hydrogen bonding between Cl^- ions, axial water molecules, and N—H groups on two imidazoles. The molecule has inversion symmetry, with the asymmetric unit consisting of two imidazoles (Co—N distances $2 \cdot 103$ and $2 \cdot 169$ Å), and a water (Co—O distance $2 \cdot 171$ Å) to form a slightly distorted octahedral coordination environment. A comparison is made with structural information elucidated from the extended X-ray absorption fine structure (EXAFS).

Introduction. The analysis of the extended X-ray absorption fine structure has recently emerged as a structural tool in the investigation of metalloproteins in non-crystalline form (Lee, Citrin, Eisenberger & Kincaid, 1981). The technique's ability to detect qualitatively the presence of histidyl ligation from third-shell scattering has been established (Felton, Barrow, May, Sowell, Goel, Bunker & Stern, 1982; Bunker, Stern, Blankenship & Parson, 1982), but the quantitative accuracy has been considered only for a few copper complexes of known structure (Co, Scott & Hodgson, 1981). The title compound was prepared in the course of a program to generate a set of model complexes to further investigate and refine the methods for obtaining structural information about imidazole moieties ligated to metals. This is the first reported structure of a tetrakis(imidazole)cobalt(II) species.

Experimental. The compound crystallizes from a 1:2 solution of $CoCl_2.6H_2O$ and imidazole in absolute ethanol upon slow evaporation and exposure to atmospheric moisture. The resulting large, red crystals are stable in air, but decompose upon heating at moderate temperatures. A cleaved crystal, $0 \cdot 58 \times 0 \cdot 48 \times 0 \cdot 41$ mm, was mounted on a glass fiber and coated with epoxy.

Syntex $P2_1$ four-circle diffractometer, graphite monochromator (Bragg 2θ angle $= 12 \cdot 2°$), Mo $K\alpha$ radiation, take-off angle $6 \cdot 75°$; 15 reflections with 2θ values ranging from $19 \cdot 77$ to $30 \cdot 10°$ machine-centered and used in least-squares refinement of lattice parameters; scans of several low-2θ-angle reflections gave peak widths at half-height of less than $0 \cdot 25°$, indicating a satisfactory mosaic spread for the crystal; axial photographs indicated a monoclinic system, rapid scan of intensity data for zero and upper levels yielded systematic absences of $h,k,l \; h + k = 2n + 1$ and $h,0,l \; l = 2n + 1$, consistent only for space groups Cc and $C2/c$, $C2/c$ assumed and used successfully to solve structure; intensity data collected for a complete quadrant ($h \; -14 \rightarrow 12$, $k \; 0 \rightarrow 12$, $l \; 0 \rightarrow 16$) using ω scans, background counts measured at beginning and end of each scan with total background to scan time ratio $T_r = 1 \cdot 0$, no significant variations observed in intensities of three standard reflections $(0,0,10, \; 0,10,0$ and $10,0,0)$ monitored every 97 reflections; total of 1810 reflections, 2θ to $50°$ (max. $\sin\theta/\lambda = 0 \cdot 5947 \, Å^{-1}$), 1537 accepted as statistically above background [$(F > 3\sigma(F)$], no absorption correction; Co and Cl located from Patterson map, solution refined with SHELX76 (Sheldrick, 1976), weighting scheme $w = 1 \cdot 0/[\sigma(F)^2 + 0 \cdot 01F^2]$, function minimized $\sum w(|F_o| - |F_c|)^2$, structure-factor calculations with atomic scattering factors (from International Tables for X-ray Crystallography, 1974) corrected for real and imaginary anomalous-dispersion components, H atoms located but coordinates not refined, final R and wR values $0 \cdot 044$ and $0 \cdot 054$ respectively; max. shift/e.s.d. $= 0 \cdot 129$ for z coordinate of N(11); difference electron density synthesis $\Delta\rho$ max./min. $= 0 \cdot 97/-0 \cdot 91$ e $Å^{-3}$; plots with ORTEPII (Johnson, 1976).

The Co $K\alpha$-edge X-ray absorption spectrum of a polycrystalline sample was measured on beam line X-11 at the NSLS facility at Brookhaven National Laboratory. The EXAFS was isolated by cubic-spline fitting to the slowly varying atomic absorption component and normalization of the edge step. The analysis was performed with the standard Fourier filtering technique, and non-linear least-squares fitting (Lee et al., 1981) and ratio methods (Bunker, 1983) with a previously characterized standard.

Discussion. Fig. 1 shows an ORTEPII plot of the molecule as determined by this investigation. Final atomic parameters are reported in Table 1, bond distances and angles in Table 2.* Fig. 2 is a stereopair representation of the contents of the unit cell. The molecular species has an inversion center on the Co, with distinct bond distances for the two imidazoles in the asymmetric unit, Co—N $= 2 \cdot 103$ (2) and $2 \cdot 169$ (2) Å. The rings are planar, with a maximum deviation of $0 \cdot 004$ Å, with the more distant imidazole plane at a dihedral angle of $82 \cdot 3$ (2)° to the plane defined by the Co and the coordinated N atoms. The second ring lies tilted with its plane at $58 \cdot 8$ (2)° to the Co—N plane, and the two equivalent water molecules occupy the remaining positions of the Co atom's nearly octahedral environment at a bond distance equal to the more distant of the N atoms. The Cl^- ions occupy positions characterized (Vainshtein, 1949; Vreugdenhil, Birker, ten Hoedt, Verschoor & Reedijk, 1984) by their hydrogen-bonding interactions with the water molecules [$Cl \cdots H(W)$, $2 \cdot 3$ (1) Å].

The crystal structure can be described as being composed of ribbons of the molecular species connected along the Co–W axes by hydrogen bonding of two equivalent Cl⁻ ions between waters of adjacent cationic units. Parallel ribbons are combined into layers with further hydrogen bonding of each Cl⁻ ion to an imidazole N–H group and possible van der Waals interactions between rings. The three-dimensional structure is built up of alternating layers with perpendicular ribbons. The hydrogen-bonding interaction appears responsible for the aforementioned rotation of one imidazole with respect to the N basal plane; the proton on the imidazole N is brought into closer proximity (2·4 Å) to a Cl⁻ ion than otherwise possible.

For EXAFS analysis, hexakis(imidazole)cobalt(II) nitrate (Prince, Mighell, Reimann & Santoro, 1972), with six equivalent Co–N bond distances [2·160 (1) Å], was used as a standard. E_0 values were chosen at the midpoints of the edge step (7720·0 eV) for conversion to a photoelectron energy scale via $k = 1/\hbar \sqrt{2m(E - E_0)}$. Absorption data, after background removal, were weighted by k^3 and results of several scans were averaged. The first shell of tetrakis-(imidazole)cobalt was analyzed by non-linear least-squares fitting of the filtered EXAFS, in the range $3·5 \le k \le 12·5$ Å⁻¹, to the standard. Results of fits with a single bond distance and with two independent bond distances are summarized in Table 3. With the assumption that the difference in σ^2, the Debye–Waller parameters, between sample and standard is entirely due to the static disorder induced by two different bond lengths for the tetrakis(imidazole) species, the single-scatterer fit with an average first-shell distance and larger σ^2 yields the two distinct bond distances of the two-shell fit. This indicates that the 0·08 Å bond-length difference is resolved. An amplitude ratio and phase difference of the EXAFS contributions of the third shell [N(2),C(2); N(4),C(4)] between the title compound and standard yield an imidazole coordination number of 4·3 (2) at a distance of 4·30 (2) Å [cf. average crystallographic distance, 4·29 (1) Å]. EXAFS and crystallographic results agree.
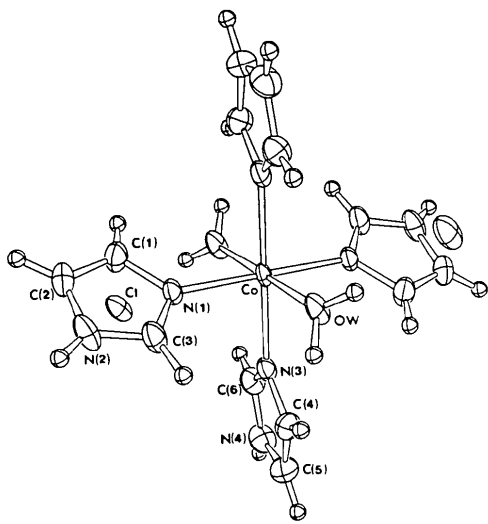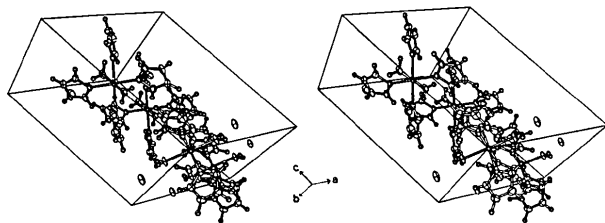
Fig. 1. An *ORTEP*II diagram (Johnson, 1976) of the complex.

Fig. 2. An *ORTEP*II stereodrawing of the unit cell.

Table 1. *Fractional coordinates and equivalent isotropic temperature factors* (Å² × 10³)

$$U_{eq} = \tfrac{1}{3}\sum U_{ii}.$$

	x	y	z	U_{eq}
Co	0·0000	0·0000	0·5000	21
Cl	0·41456 (6)	0·09730 (5)	0·57304 (5)	39
N(1)	−0·0668 (2)	0·1333 (2)	0·5569 (1)	27
C(1)	−0·1081 (3)	0·1155 (2)	0·6217 (2)	39
C(2)	−0·1371 (3)	0·2226 (3)	0·6458 (2)	43
N(2)	−0·1148 (2)	0·3079 (2)	0·5946 (2)	40
C(3)	−0·0725 (2)	0·2503 (2)	0·5434 (2)	37
N(3)	−0·1402 (2)	0·0477 (2)	0·3508 (1)	26
C(4)	−0·1380 (2)	0·1362 (2)	0·2907 (2)	33
C(5)	−0·2424 (3)	0·1285 (3)	0·2003 (2)	39
N(4)	−0·3093 (2)	0·0343 (2)	0·2046 (2)	35
C(6)	−0·2451 (3)	−0·0126 (2)	0·2958 (2)	32
OW	0·1275 (2)	0·1300 (2)	0·4944 (1)	35

Table 2. *Interatomic distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Co–N(1)	2·103 (2)	Co–N(3)	2·169 (2)
Co–OW	2·171 (2)	N(1)–C(1)	1·378 (3)
N(1)–C(3)	1·303 (3)	C(1)–C(2)	1·345 (4)
C(2)–N(2)	1·361 (4)	N(2)–C(3)	1·332 (3)
N(3)–C(4)	1·374 (3)	N(3)–C(6)	1·319 (4)
C(4)–C(5)	1·360 (4)	C(5)–N(4)	1·352 (4)
N(4)–C(6)	1·349 (4)		

N(3)–Co–N(1)	91·5 (1)	OW–Co–N(1)	90·7 (1)
OW–Co–N(3)	89·5 (1)	C(1)–N(1)–Co	126·8 (2)
C(3)–N(1)–Co	128·4 (2)	C(3)–N(1)–C(1)	104·7 (2)
C(2)–C(1)–N(1)	110·0 (2)	N(2)–C(2)–C(1)	105·7 (2)
C(3)–N(2)–C(2)	107·4 (2)	N(2)–C(3)–N(1)	112·1 (2)
C(4)–N(3)–Co	129·8 (2)	C(6)–N(3)–Co	124·9 (2)
C(6)–N(3)–C(4)	105·1 (2)	C(5)–C(4)–N(3)	110·0 (2)
N(4)–C(5)–C(4)	105·9 (2)	C(6)–N(4)–C(5)	107·8 (2)
N(4)–C(6)–N(3)	111·1 (2)		

Table 3. *Results of first-shell EXAFS fits of tetrakis-(imidazole)cobalt with a hexakis(imidazole)cobalt standard*

$\Delta\sigma^2$ = difference in Debye–Waller parameters (sample–standard). χ^2 = sum of residuals.

N	$R(\text{Å})$	$\Delta\sigma^2 \times 10^3$ (Å²)	χ^2
Single-scatterer fit			
6·0 (1)	2·15 (1)	1·3 (1)	0·21
Two-scatterer fit*			
1·7 (2)	2·09 (1)	0	0·15
4·3 (2)	2·18 (1)	0	

* $\Delta\sigma^2$ fixed to 0.

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Dimethylbis(4,4,5,5-tetramethyl-2-thioxo-1,3,2-dioxaphospholane-2-thiolato)tin, (CH₃)₂Sn[SP(S)O₂C₂(CH₃)₄]₂

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Abstract. [Sn(C₆H₁₂O₂PS₂)₂(CH₃)₂], $M_r = 571\cdot3$, orthorhombic, *Pccn*, $a = 16\cdot830$ (9), $b = 11\cdot407$ (5), $c = 12\cdot829$ (9) Å, $V = 2463$ Å³, $Z = 4$, $D_x = 1\cdot541$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0\cdot7107$ Å, $\mu = 1\cdot51$ mm⁻¹, $F(000) = 1160$, $T = 291$ K, final $R = 0\cdot031$ for 1700 observed data [$I > 3\sigma(I)$]. Two anisobidentate dithiophosphate ligands and the two CH₃ groups [C(1)–Sn–C(1ⁱ) 133·9 (2)°] form a heavily distorted octahedron around Sn. The short Sn–S bonds [2·495 (1) Å] and the dative Sn–S bonds [3·130 (1) Å] are in the equatorial plane, each pair being *cis*.

Introduction. Knowledge of structures of organotin dithiophosphates is still rather limited and uncertainty exists mainly regarding the kind of bonding of the dithiophosphato group which is generally considered to act as a bidentate ligand. In fact, Ph₂Sn[SP(S)(OR)₂]₂ (R = isopropyl) consists of *trans* Ph₂Sn units octahedrally coordinated by symmetrically chelating S₂P(OR)₂ ligands (Molloy, Hossain, van der Helm, Zuckerman & Haiduc, 1980), but in Ph₃SnSP(S)-(OEt)₂ the dithiophosphate ligand is monodentate (Molloy, Hossain, van der Helm, Zuckerman &

Haiduc, 1979) and in Ph₂Sn[SP(S)(OEt)₂]₂ apart from a normal covalent Sn–S(1) bond only an additional weak Sn–S(2) bond exists (Liebich & Tomassini, 1978). Of these compounds only Ph₂Sn[SP(S)(OR)₂]₂ (R = isopropyl) has short intermolecular sulfur–sulfur contact distances; it has been termed a 'virtual polymer' (Molloy, Hossain, van der Helm, Zuckerman & Haiduc, 1980).

In a recent paper, from spectroscopic data cyclic dithiophosphate ligands have been proposed to be chelating in diorganotin derivatives of Hdtpl [2-mercapto-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane 2-sulfide, HSP(S)O₂C₂(CH₃)₄] (Rao, Srivastava, Mehrotra, Saraswat & Mason, 1984). We had independently studied analogous organometal dithiophosphates, in part the same, like Me₂Sn(dtpl)₂. From this compound we obtained single crystals and from X-ray diffractometer measurements we can report a more detailed structure.

Experimental. Me₂Sn(dtpl)₂ was obtained from Na(dtpl) (*in situ* from Hdtpl and Na in EtOH) and Me₂SnCl₂ in MeOH after separation of NaCl, con-