

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (\AA^2)
$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
Os1	0.0000	0.0000	0.0000	0.0238 (2)
C11	0.2577 (1)	0.0244 (1)	-0.0760 (1)	0.0360 (6)
P1	0.0343 (1)	0.1507 (1)	0.0901 (1)	0.0287 (6)
P2	0.0212 (1)	0.2115 (1)	-0.1584 (1)	0.0311 (6)
C1	0.1064 (4)	0.3268 (3)	-0.0266 (3)	0.0413 (28)
C2	0.1454 (3)	0.3310 (3)	-0.1521 (3)	0.0385 (26)
C11	-0.1125 (3)	0.2036 (3)	0.1900 (3)	0.0336 (25)
C12	-0.1016 (4)	0.2347 (3)	0.2828 (3)	0.0440 (30)
C13	-0.2149 (5)	0.2809 (4)	0.3503 (3)	0.0594 (39)
C14	-0.3387 (4)	0.2980 (4)	0.3250 (4)	0.0651 (44)
C15	-0.3484 (4)	0.2736 (4)	0.2307 (4)	0.0631 (46)
C16	-0.2361 (4)	0.2270 (4)	0.1628 (4)	0.0500 (36)
C21	0.1623 (3)	0.1060 (3)	0.1676 (3)	0.0359 (27)
C22	0.3053 (4)	0.1476 (4)	0.1047 (3)	0.0488 (36)
C23	0.4060 (4)	0.1031 (5)	0.1581 (5)	0.0665 (52)
C24	0.3626 (5)	0.0161 (5)	0.2765 (5)	0.0764 (64)
C25	0.2211 (5)	-0.0228 (4)	0.3406 (4)	0.0656 (48)
C26	0.1194 (4)	0.0200 (3)	0.2866 (3)	0.0456 (33)
C31	-0.1373 (3)	0.3014 (3)	-0.1578 (3)	0.0375 (26)
C32	-0.2537 (4)	0.2338 (4)	-0.1589 (3)	0.0469 (32)
C33	-0.3776 (4)	0.2947 (4)	-0.1558 (4)	0.0589 (40)
C34	-0.3882 (5)	0.4238 (5)	-0.1510 (4)	0.0674 (46)
C35	-0.2740 (5)	0.4928 (4)	-0.1498 (4)	0.0633 (43)
C36	-0.1485 (4)	0.4336 (4)	-0.1543 (3)	0.0498 (34)
C41	0.0996 (4)	0.2277 (3)	-0.3123 (3)	0.0383 (26)
C42	0.0510 (5)	0.3154 (4)	-0.4010 (3)	0.0564 (36)
C43	0.1111 (6)	0.3214 (5)	-0.5156 (3)	0.0721 (45)
C44	0.2175 (5)	0.2423 (4)	-0.5438 (3)	0.0661 (40)
C45	0.2666 (4)	0.1557 (4)	-0.4574 (3)	0.0542 (35)
C46	0.2079 (4)	0.1486 (3)	-0.3423 (3)	0.0434 (29)
Cl2S†	0.5340 (4)	0.3950 (4)	0.5889 (2)	0.1906 (51)
C3S‡	0.4164	0.4751	0.5144	0.0600

† Site occupancy refined to 0.928 (6).

‡ Site occupancy refined to 0.464 (3).

Table 2. Geometric parameters (\AA , °)

Os1—C11	2.434 (1)	P1—C21	1.832 (3)
Os1—P1	2.372 (1)	P2—C2	1.833 (3)
Os1—P2	2.348 (1)	P2—C31	1.826 (3)
P1—C1	1.867 (3)	P2—C41	1.831 (3)
P1—C11	1.839 (3)		
C11—Os1—P1	83.1 (1)	C1—P1—C11	97.7 (1)
C11—Os1—P2	85.2 (1)	C1—P1—C21	104.3 (1)
P1—Os1—P2	81.9 (1)	C11—P1—C21	103.3 (1)
Os1—P1—C1	109.0 (1)	C2—P2—C31	104.8 (1)
Os1—P1—C11	123.1 (1)	C2—P2—C41	101.2 (1)
Os1—P1—C21	116.5 (1)	C31—P2—C41	102.8 (1)
Os1—P2—C2	106.4 (1)	P1—C1—C2	113.4 (2)
Os1—P2—C31	117.7 (1)	P2—C2—C1	110.6 (2)
Os1—P2—C41	121.7 (1)		
P1—C1—C2—P2	35.4 (3)		

Crystals were grown by vapour diffusion of Et_2O into a CH_2Cl_2 solution of the compound and mounted in glass capillaries. Five reflections thought to be suffering from extinction were excluded. For the disordered solvent molecule (CH_2Cl_2), isotropic C3S was not refined and no H atoms were included. The remaining H-atom positions were determined from electron-density maps but not refined. Data collection: *Enraf-Nonius Structure Determination Package* (Frenz, 1985). Cell refinement: *Enraf-Nonius Structure Determination Package*. Data reduction: *Enraf-Nonius Structure Determination Package*. Program(s) used to solve structure: *SHELX76* (Sheldrick, 1976). Program(s) used to refine structure: *SHELX76* (Sheldrick, 1976). Molecular graphics: *ORTEPII* (Johnson, 1976).

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71319 (32 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA1057]

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Structures of Two Encapsulated Cobalt(III) Complexes Containing *cyclo*-Triphosphate

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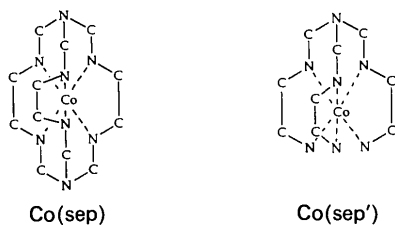
Abstract

The conformational and packing properties of two encapsulated cobalt(III) complexes containing *cyclo*-triphosphate have been investigated. Compound (I),

(1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]icosane)cobalt(III) *cyclo*-triphosphate-water (2/7) has the trivial name cobalt(III) sepulchrate *cyclo*-triphosphate-water (2/7) and chemical formula $[\text{Co}(\text{sep})](\text{P}_3\text{O}_9)\cdot 3.5\text{H}_2\text{O}$. The cation shows an lel_3 geometry very similar to those found in other sepulchrate complexes. The packing motif is given by one-dimensional chains of alternating cations and anions running along the z direction and cross-linked by hydrogen-bonded water molecules. Compound (II) is [tris(aminoethylaminomethyl)amine]tris(ethylenediamine)dicobalt(III) di(*cyclo*-triphosphate) octahydrate, and has the chemical formula $[\text{Co}(\text{sep}')(\text{P}_3\text{O}_9)][\text{Co}(\text{sep}')_{0.72}(\text{en}_3)_{0.28}(\text{P}_3\text{O}_9)]\cdot 8\text{H}_2\text{O}$ (where $\text{sep}' = \text{C}_9\text{H}_{27}\text{N}_7$). Pseudotranslational symmetry is found, perturbed by the substitutional disorder sep'/en_3 . B -centering is therefore simulated involving the anions and water molecules. The crystal packing is similar to that found for compound (I), but the regularity of the chains is broken by the disorder.

Comment

Sepulchrate (sep) and semisepulchrate (sep') are polydentate ligands able to encapsulate metal ions by means of coordination by six amine N atoms.



The X-ray structural aspects of sepulchrate complexes have been studied in previous works (Bacchi, Ferranti & Pelizzi, 1993, and references therein), whereas up to now the X-ray structure of only one tris(aminoethylaminomethyl)amine (semisepulchrate) complex has been determined (Arkowska, Grazynska, Kubiak & Paulus, 1989a), though the structure of a closely related compound is also known (Arkowska, Grazynska, Kubiak & Paulus, 1989b). The short-range geometry of the cation $\text{Co}(\text{sep})^{3+}$ is shown to be quite insensitive to its structural surroundings and the crystal packing is determined mainly by the dimensions and geometry of the counter anions. The semisepulchrate cage is expected to be less rigid as it is much more reactive than the parent sepulchrate molecule. The conformational and packing properties of $[\text{Co}(\text{sep})](\text{P}_3\text{O}_9)\cdot 3.5\text{H}_2\text{O}$ (I) and of $[\text{Co}(\text{sep}')(\text{P}_3\text{O}_9)][\text{Co}(\text{sep}')_{0.72}(\text{en}_3)_{0.28}(\text{P}_3\text{O}_9)]\cdot 8\text{H}_2\text{O}$ (II) are reported here.

Compound (I)

Fig. 1 shows the cation $\text{Co}(\text{sep})^{3+}$ hydrogen bonded to its neighboring anions and water molecules. The

cation shows the common lel_3 conformation approaching D_3 pseudosymmetry. Its molecular geometry has been compared with those found for *rac*- $[\text{Co}(\text{sep})]\text{Cl}_3$ and $[\text{Co}(\text{sep})(\text{ClO}_4)(\text{S}_2\text{O}_3)]$ (Bacchi, Ferranti & Pelizzi, 1993) by performing half-normal probability plot analyses (Abrahams & Keve, 1971) on bond angles and interatomic distances between 1.0 and 9.9 Å for all the non-H atoms. The resulting linear-regression parameters show that there are no significant differences among the three compounds. These results are in accordance with those observed previously, confirming that the sepulchrate cage behaves as an undeformable entity even when inserted in different packing environments, namely one-, two- and three-dimensional strong hydrogen-bonded networks involving Cl^- , $\text{S}_2\text{O}_3^{2-}$ and ClO_4^- , and $\text{P}_3\text{O}_9^{3-}$, respectively.

The anion assumes a twisted boat conformation, with a slight distortion towards boat; the puckering parameters (Nardelli, 1983; following Cremer & Pople, 1975) are $Q_7 = 0.579(8)$ Å, $\theta_2 = 92.2(8)$, $\varphi_2 = 79(1)^\circ$. The unit cell also contains 3.5 water molecules, O10, O11, O12 and O13 (disordered about an inversion center). Each cation interacts with two anions and one water molecule (O11) by means of hydrogen bonds: $\text{N}2 \cdots \text{O}6$, 2.86(1); $\text{N}4 \cdots \text{O}6$, 2.89(1); $\text{N}5 \cdots \text{O}1^{\text{iii}}$, 2.93(1); $\text{N}3 \cdots \text{O}1^{\text{iii}}$, 2.85(2) Å [(iii) = $x, -y - \frac{1}{2}, z - \frac{1}{2}$]; $\text{N}1 \cdots \text{O}11$, 2.96(1); $\text{N}6 \cdots \text{O}11$, 2.83(2) Å. The distortions in the geometry of the $\text{Co}(\text{sep})(\text{P}_3\text{O}_9)_2(\text{H}_2\text{O})$ moiety from ideal D_3 symmetry are of the same type as those found for the $\text{Co}(\text{sep})(\text{Cl}_3)$ moieties in *rac*- $[\text{Co}(\text{sep})](\text{Cl}_3)\cdot \text{H}_2\text{O}$. They are mainly due to the different environments experienced by the three hydrogen acceptors O6, O1 and O11. O6 completes its tetrahedral environment by interacting with the water molecule O12 [$\text{O}6 \cdots \text{O}12$, 2.94(2) Å] and closely approximates the ideal position for D_3 geometry; O1 shows a larger distortion because of the effects of steric repulsion by C6 [$\text{O}1 \cdots \text{C}6^{\text{viii}}$, 3.27(2) Å; (viii) = $x, -y - \frac{1}{2}, z + \frac{1}{2}$]

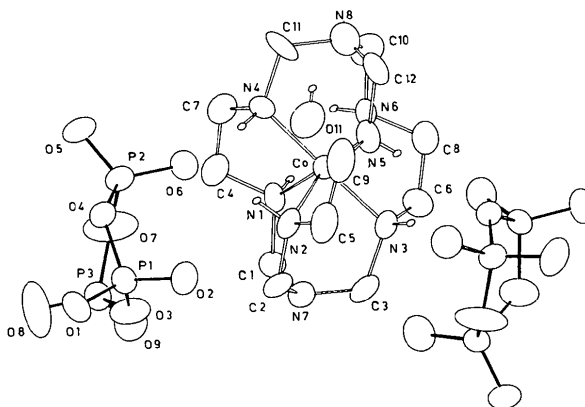


Fig. 1. ORTEP view of compound (I) with 50% probability thermal ellipsoids for the $\text{Co}(\text{sep})(\text{P}_3\text{O}_9)_2(\text{H}_2\text{O})$ moiety. Methylenic H atoms have been omitted.

and the weak hydrogen-bond attraction $C8-H \cdots O1^{iii}$ [$C8 \cdots O1^{iii}$, 3.30 (2) Å; (iii) = $x, -y - \frac{1}{2}, z - \frac{1}{2}$]. The largest deviations from D_3 symmetry are associated with the O11 atom because of its strong hydrogen bonds with the anion $[O11 \cdots O2^{iv}, 2.73$ (1) Å; (iv) = $x, y + 1, z]$ and O10 [$O11 \cdots O10^i, 2.73$ (1) Å; (i) = $-x, y + \frac{1}{2}, -z + \frac{1}{2}$] as these weaken and distort its interactions with the cation. The full list of the hydrogen bonds formed by the cation is given in Table 3. Note that the anionic O atoms also make use of $O \cdots H-C$ interactions to complete their coordination geometry. Considering the direct anion-cation interactions [$O6 \cdots (N2, N4)$ and $O1 \cdots (N3, N5)^{viii}$; (viii) = $x, -y - \frac{1}{2}, z + \frac{1}{2}$], one may identify a zigzag-polymeric one-dimensional connection along the z direction (Fig. 2). The interactions among the subunits [$P_3O_3^{3-} \cdots Co(sep)^{3+}$] are related by the symmetry operations $(x, y, z - \frac{n}{2})$ for n even or $(x, -y - \frac{1}{2}, z - \frac{n}{2})$ for n odd. These chains are cross-linked by hydrogen-bonded water molecules.

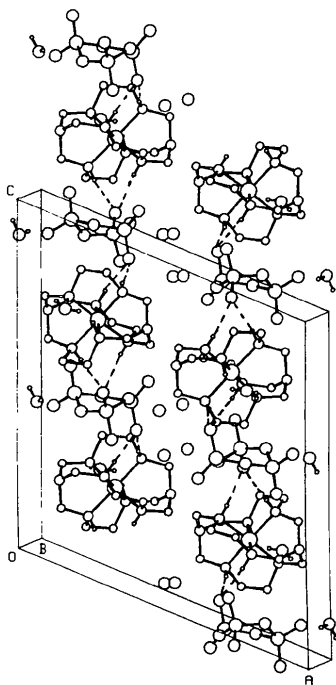


Fig. 2. Crystal packing of compound (I). Methylenic H atoms have been omitted.

Compound (II)

The first data collection gave the cell (I): $a = 13.664$ (2), $b = 11.552$ (2), $c = 14.620$ (2) Å, $\beta = 103.55$ (4)°, $V = 2243.5$ (6) Å³, $Z = 4$ (monoclinic, space group $P2_1/n$). The structure was solved by the heavy-atom technique of *SHELXS86* (Sheldrick, 1986) and refined with *SHELX76* (Sheldrick, 1976) to $R = 7.45\%$ ($S = 3.73$). Substitutional disorder was found for the cation, involving the simultaneous presence of the $Co(sep')^{3+}$ and $Co(en)_3^{3+}$ cations,

with occupancies of 80 and 20%, respectively. Correspondingly, the $P_3O_3^{3-}$ anion showed two conformations, giving a positional disorder. Four water molecules are present in the unit cell. The correlation between the substitutional disorder of the cations and the conformational changes of the anions led us to suspect the presence of two different cationic sites, occupied by $Co(sep')$ and $Co(en)_3$, respectively, and related by a pseudo-translational symmetry which could give relatively strong subcell reflections. In this case the disorder would be due to the overlap of the two images situated erroneously in the subcell. A second cell determination was carried out which revealed the presence of some weak reflections indicating a new cell: $a = 17.494$ (7), $b = 11.548$ (5), $c = 22.21$ (1) Å, $\beta = 93.94$ (1)° [cell (II)]. The matrix $R = [1 \ 0 \ 1/0 \ -1 \ 0/1 \ 0 \ -1]$ transforms cell (I) into cell (II) and the symmetry operations of $P2_1/n$ are changed into those of $P2_1/a$ by $(R^{-1})^T$, where T denotes transposition. R corresponds to a centering operation and it must be stressed that collecting data in the cell (II) primitive reciprocal lattice allows us to detect the $(h + l)$ odd reflections which were neglected by the previous data collection, because in the cell (I) reciprocal lattice they would have non-integer indexes.

A new data collection was performed which led to the following statistics: (1) hkl , $h + l$ odd few observed, systematically weak; (2) $h0l$, h odd absent; (3) $0k0$, k odd absent; (4) $h0l$, $h + l$ odd absent; (5) $h0l$, l odd absent. Group (1) is the pseudo-centering condition which, if completely satisfied, would cause cell (II) to collapse into cell (I); groups (2) and (3) are the typical extinction conditions for $P2_1/a$; groups (4) and (5) are pseudo-extinctions deriving from the pseudo-centering operation which, if performed on the coordinates in $P2_1/a$, simulates $P2_1/c$ and $P2_1/n$ symmetries. So the disordered molecule lying at (x, y, z) in cell (I) can be split into two molecules at (X, Y, Z) and $(X + \frac{1}{2}, Y, Z + \frac{1}{2})$ in cell (II), where $(X \ Y \ Z)^* = (T^{-1})^*(x \ y \ z)^*$. The two molecules must be slightly different to destroy the crystallographic translational symmetry. The coordinates of CoA of cell (II) were obtained by appropriately transforming the coordinates of Co of cell (I) and the coordinates of CoB were obtained by performing the B -centering on the coordinates of CoA. The remaining non-H atoms were located by successive Fourier and ΔF calculations combined with least-squares refinements on F^2 . The final R value, calculated on the observed reflections so it may be compared with the R value from the refinement of cell (I), is 6.54% ($S = 1.336$). The disorder $Co(sep')/Co(en)_3$ does not vanish with the new cell setting, but it is confined to only four sites out of the eight belonging to the pseudo-centered cell, *i.e.* the cationic site at (X, Y, Z) is fully occupied by $Co(sep')^{3+}$ (cation A), while the site at $(X + \frac{1}{2}, Y, Z + \frac{1}{2})$ is occupied by 72% of $Co(sep')^{3+}$ (cation B) and by 28% of $Co(en)_3^{3+}$ (cation B'). The anions show the same distribution where $P_3O_3^{3-}$ (A) has a site occupancy of 100%, while the corresponding pseudo- B -centered anion is disordered

on $P_3O_9^{3-}$ (B), 72%, and (B'), 28%. The simultaneous presence of a B cation and a B' anion is excluded by the distance $O1B' \cdots N7B$ (1.48 Å) being too short. The eight water molecules present in the unit cell are also paired by the pseudo-centering. The approximations of this model leave a non-negligible unexplained electronic density of about $1.4 \text{ e } \text{Å}^{-3}$ in the region of the disordered moieties (1.45 Å from $O1B$), but the residual electronic density is even higher for the refinement in cell (I) ($1.67 \text{ e } \text{Å}^{-3}$, 1.85 Å from Co).

Geometric parameters for compound (II) are reported in Table 5. Fig. 3 shows how the cation A is hydrogen bonded to anions and water molecules and Fig. 4 shows the substitutional disorder involving molecules B and B' . A statistical comparison based on the χ^2 criterion of the positional parameters of the atoms in cations

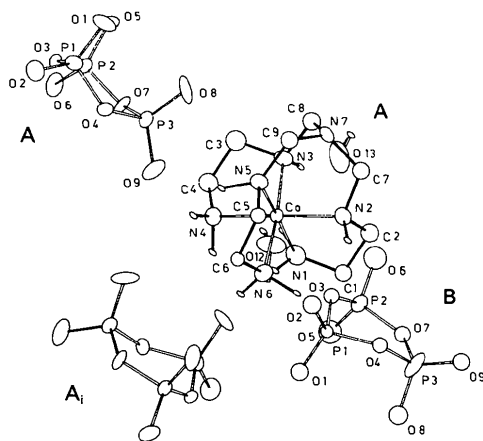


Fig. 3. ORTEP view of compound (II) with 50% probability thermal ellipsoids for cation A hydrogen bonded with surrounding A and B anions and water molecules. Methylenic H atoms have been omitted.

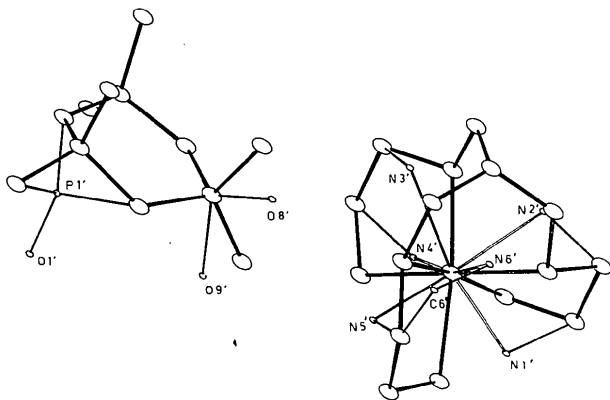


Fig. 4. Overlapped images of molecules B and B' of compound (II). B' atoms with 28% occupancy and relative bonds are labeled and represented with small spheres and light sticks. H atoms have been omitted.

A and B (PARST; Nardelli, 1983) showed that the two cations are not significantly different. A similar comparison has shown that for the anions, the pseudo-centering condition does not hold accurately because of remarkable differences in the Y orthogonal coordinates of the atoms in the A and B anions, if they are superimposed. This suggests that, although much more reactive than the parent sepulchrate compounds, once inserted in a crystalline lattice, semisepulchrate cationic complexes are also relatively rigid.

Under this assumption, a qualitative explanation can be attempted for the different behavior of cations and anions towards the requirements of pseudo-centering. The substitutional disorder of cations B/B' lowers the lattice symmetry, removing 28% of the B -centering, so causing a distortion in the environment of the B and B' anions. Consequently, the flexible anions modify their conformation to optimize the crystal packing and a larger amount of B -centering is lost for the anionic sites. Nevertheless, a certain similarity in the geometry of anions A and B is maintained: they both show a conformation between chair and half boat, while the anion B' adopts a boat geometry with some half-boat character. The puckering parameters for the anions in cells (I) and (II) are reported in Table 6. The values relative to cell (I) show how the A conformation in (I) is an almost perfect average of A and B conformations in (II), while the anion B' image is essentially independent of the cell choice. The cations A , B and B' show the $1el_3$ conformation and bond distances and angles are typical for these systems. The geometry of the cation A has been compared with that of the common molecular fragment present in the $Co(sep)^{3+}$ cation of $[Co(sep)(ClO_4)(S_2O_3)]$ (which adopts crystallographic D_3 symmetry), to which it is essentially identical. Molecules A and B have similar packing patterns, as shown by the list of selected hydrogen bonds in Table 7. The atoms $O1A$ and $O1B$ are most involved in the anionic interactions with the cations, since they cap the $N4A-N1A-N6A$ and $N4B-N1B-N6B$ faces of the semisepulchrate cage, respectively. With the substitution of cation B for cation B' , the $O1'B'$ atom is pulled towards the $N2'B-N3'B-N6'B'$ hydrogen-bond acceptor system and consequently the conformation of the anion changes remarkably. The packing motif can be described by taking the ionic pairs $[Co(sep') \cdots P_3O_9]^{A,B}$ as the fundamental subunits. Polymeric one-dimensional zigzag A and B chains are generated along the Y direction by the hydrogen-bond interactions among subunits correlated by the operations $(\frac{1}{2} - X + m, Y - \frac{n}{2}, 1 - Z + m)$ for n odd ($m = 0$ for molecule A , $m = 1$ for molecule B) and $(X, Y - \frac{n}{2}, Z)$ for n even. The crystal packing is shown in Fig. 5. The regularity of the B chains is perturbed by the uneven substitution sep'/en_3 , leading to the deformation of B and B' anions as discussed previously. The A chains are linked together by the water molecules $O12, O13, O14, O15$ through a network of hydrogen bonds; the same topology applies for the B chains and $O10, O11, O16,$

O17. The linkages are mainly due to interactions between water molecules and phosphate anions. *A* and *B* chains are directly linked by the $N2^{A,B} \cdots O6^{B,A}$ and $N6^{A,B} \cdots O5^{B,A}$ hydrogen bonds.

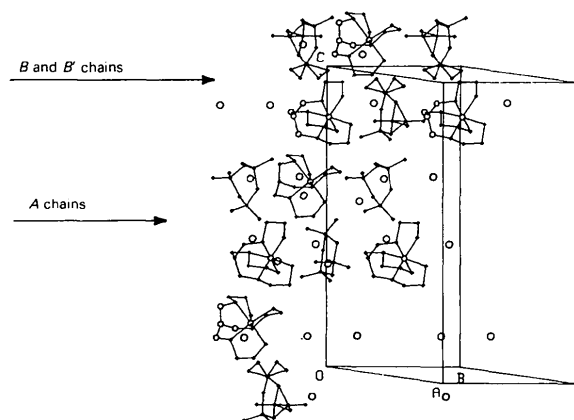


Fig. 5. Crystal packing of compound (II). Empty circles represent atoms N7, C7, C8 and C9 of molecule *B*, with 72% occupancy, water molecules and Co atoms. H atoms have been omitted, as well as atoms with 28% occupancy in cation *B'*.

Experimental

Compound (I)

Crystal data

$[Co(C_{12}H_{30}N_8)](P_3O_9) \cdot 3.5H_2O$	$D_x = 1.6893 \text{ Mg m}^{-3}$
$M_r = 645.32$	Mo $K\alpha$ radiation
Monoclinic	$\lambda = 0.71070 \text{ \AA}$
$P2_1/c$	Cell parameters from 30 reflections
$a = 15.887 (3) \text{ \AA}$	$\theta = 9-17^\circ$
$b = 9.858 (2) \text{ \AA}$	$\mu = 0.9313 \text{ mm}^{-1}$
$c = 17.568 (3) \text{ \AA}$	$T = 293 \text{ K}$
$\beta = 112.75 (2)^\circ$	Irregular prisms
$V = 2537.3 (9) \text{ \AA}^3$	$0.60 \times 0.26 \times 0.23 \text{ mm}$
$Z = 4$	Yellow

Data collection

Siemens AED diffractometer	$\theta_{max} = 23^\circ$
$\omega/2\theta$ scans	$h = -17 \rightarrow 17$
Absorption correction: none	$k = 0 \rightarrow 10$
	$l = 0 \rightarrow 19$
3930 measured reflections	1 standard reflection
3561 independent reflections	monitored every 50 reflections
1847 observed reflections	intensity variation: none
$[I > 1.5\sigma(I)]$	
$R_{int} = 0.0294$	

Refinement

Refinement on F	$(\Delta/\sigma)_{max} = 0.053$
Final $R = 0.0581$	$\Delta\rho_{max} = 0.56 \text{ e \AA}^{-3}$
$wR = 0.0644$	$\Delta\rho_{min} = -0.44 \text{ e \AA}^{-3}$
$S = 3.208$	Extinction correction: none

1768 reflections

458 parameters

All H-atom parameters refined except for H1N, H6N and H2O1

Unit weights applied

Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1986). Program(s) used to refine structure: *SHELX76* (Sheldrick, 1976); *ABSORB* (Ugozzoli, 1987; according to Walker & Stuart, 1983). Molecular graphics: *ORTEP* (Johnson, 1965); *PLUTO* (Motherwell & Clegg, 1976). Software used to prepare material for publication: *PARST* (Nardelli, 1983); *ABRAHAMS* (Gilli, 1977).

Atomic scattering factors from *International Tables for X-ray Crystallography* [1974, Vol. IV, Tables 2.2A, 2.3.1 (Co, P, O, N, C) and 2.2C (H)]

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (\AA^2) for compound (I)

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^*$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Co	0.24706 (11)	0.11638 (17)	0.22872 (9)	0.0305 (6)
P1	0.2585 (2)	-0.3956 (3)	0.4653 (2)	0.0364 (14)
P2	0.3202 (2)	-0.1204 (4)	0.5067 (2)	0.0394 (13)
P3	0.1304 (2)	-0.1892 (4)	0.4670 (2)	0.0406 (13)
O1	0.2561 (6)	-0.5064 (9)	0.5207 (5)	0.0523 (42)
O2	0.2798 (6)	-0.4240 (9)	0.3927 (5)	0.0526 (42)
O3	0.1637 (6)	-0.3167 (9)	0.4298 (6)	0.0600 (42)
O4	0.3259 (5)	-0.2809 (8)	0.5224 (5)	0.0361 (34)
O5	0.3765 (6)	-0.0516 (9)	0.5824 (5)	0.0551 (44)
O6	0.3372 (6)	-0.0912 (9)	0.4302 (5)	0.0572 (45)
O7	0.2157 (6)	-0.0908 (10)	0.4845 (7)	0.0837 (53)
O8	0.1204 (8)	-0.2305 (14)	0.5412 (7)	0.1041 (72)
O9	0.0540 (6)	-0.1282 (10)	0.4016 (5)	0.0624 (41)
O10	-0.0250 (6)	0.1190 (10)	0.3777 (5)	0.0630 (44)
N1	0.1533 (7)	0.1878 (9)	0.2653 (6)	0.0351 (42)
N2	0.2252 (7)	-0.0701 (9)	0.2579 (6)	0.0403 (44)
N3	0.1544 (6)	0.0916 (10)	0.1150 (5)	0.0368 (41)
N4	0.3355 (6)	0.1566 (9)	0.3416 (6)	0.0353 (40)
N5	0.3453 (7)	0.0355 (11)	0.2004 (6)	0.0451 (44)
N6	0.2680 (7)	0.2971 (11)	0.1911 (6)	0.0415 (43)
N7	0.0646 (7)	-0.0078 (12)	0.1895 (6)	0.0459 (43)
N8	0.4293 (8)	0.2424 (14)	0.2697 (7)	0.0635 (63)
C1	0.0641 (8)	0.1108 (17)	0.2339 (7)	0.0514 (54)
C2	0.1271 (9)	-0.1079 (15)	0.2366 (7)	0.0513 (55)
C3	0.0677 (8)	0.0174 (14)	0.1099 (7)	0.0463 (55)
C4	0.1954 (9)	0.1996 (13)	0.3575 (8)	0.0492 (60)
C5	0.2727 (12)	-0.1643 (15)	0.2226 (8)	0.0629 (76)
C6	0.1347 (9)	0.2265 (14)	0.0742 (8)	0.0505 (61)
C7	0.2887 (9)	0.2462 (13)	0.3825 (8)	0.0453 (53)
C8	0.2245 (9)	0.2976 (14)	0.0985 (8)	0.0516 (60)
C9	0.3627 (10)	-0.1031 (17)	0.2348 (8)	0.0637 (70)
C10	0.3660 (10)	0.3407 (16)	0.2248 (9)	0.0645 (71)
C11	0.4268 (8)	0.2107 (15)	0.3494 (8)	0.0551 (63)
C12	0.4303 (9)	0.1251 (22)	0.2234 (10)	0.0770 (77)
O11	0.1642 (7)	0.4836 (9)	0.2417 (6)	0.0678 (48)
O12	0.5214 (8)	-0.1638 (13)	0.4429 (7)	0.1036 (66)
O13	0.5366 (11)	0.4374 (19)	0.5872 (12)	0.0589 (93)

Table 2. Geometric parameters (\AA , $^\circ$) for compound (I)

Co—N1	1.97 (1)	N2—C2	1.50 (1)
Co—N2	1.98 (1)	N2—C5	1.48 (2)
Co—N3	1.986 (8)	N3—C3	1.53 (1)
Co—N4	1.977 (8)	N3—C6	1.49 (1)
Co—N5	1.98 (1)	N4—C7	1.50 (1)
Co—N6	1.97 (1)	N4—C11	1.50 (1)
P1—O1	1.47 (1)	N5—C9	1.48 (1)
P1—O2	1.47 (1)	N5—C12	1.53 (2)
P1—O3	1.594 (9)	N6—C8	1.50 (1)
P1—O4	1.613 (8)	N6—C10	1.50 (1)
P2—O4	1.602 (8)	N7—C1	1.41 (2)
P2—O5	1.452 (8)	N7—C2	1.42 (1)

P2—O6	1.50 (1)	N7—C3	1.44 (1)
P2—O7	1.58 (1)	N8—C10	1.40 (1)
P3—O3	1.60 (1)	N8—C11	1.45 (2)
P3—O7	1.60 (1)	N8—C12	1.42 (2)
P3—O8	1.43 (1)	C4—C7	1.45 (1)
P3—O9	1.441 (8)	C5—C9	1.49 (2)
N1—C1	1.51 (1)	C6—C8	1.50 (1)
N1—C4	1.50 (1)		
N5—Co—N6	91.6 (5)	Co—N2—C5	107.9 (8)
N4—Co—N6	90.5 (4)	Co—N2—C2	115.9 (7)
N4—Co—N5	90.5 (4)	C2—N2—C5	113 (1)
N3—Co—N6	85.9 (4)	Co—N3—C6	108.1 (7)
N3—Co—N5	92.7 (4)	Co—N3—C3	114.7 (7)
N3—Co—N4	175.2 (4)	C3—N3—C6	113 (1)
N2—Co—N6	175.5 (4)	Co—N4—C11	116.7 (7)
N2—Co—N5	85.7 (5)	Co—N4—C7	107.8 (7)
N2—Co—N4	93.1 (4)	C7—N4—C11	112.7 (9)
N2—Co—N3	90.6 (4)	Co—N5—C12	114 (1)
N1—Co—N6	91.9 (4)	Co—N5—C9	108.2 (9)
N1—Co—N5	175.2 (4)	C9—N5—C12	115 (1)
N1—Co—N4	86.3 (4)	Co—N6—C10	114.3 (8)
N1—Co—N3	90.7 (4)	Co—N6—C8	107.4 (8)
N1—Co—N2	90.9 (4)	C8—N6—C10	114 (1)
P1—O3—P3	129.5 (7)	C2—N7—C3	114 (1)
P1—O4—P2	127.3 (5)	C1—N7—C3	114 (1)
P2—O7—P3	131.9 (7)	C1—N7—C2	114 (1)
Co—N1—C4	107.6 (8)	C11—N8—C12	113 (1)
Co—N1—C1	115.0 (8)	C10—N8—C12	114 (1)
C1—N1—C4	113 (1)	C10—N8—C11	114 (1)

$$a = 17.494 (7) \text{ \AA}$$

$$b = 11.548 (5) \text{ \AA}$$

$$c = 22.21 (1) \text{ \AA}$$

$$\beta = 93.94 (1)^\circ$$

$$V = 4476 (3) \text{ \AA}^3$$

$$Z = 4$$

$$\mu = 1.057 \text{ mm}^{-1}$$

$$T = 293 \text{ K}$$

Irregular prisms
0.71 × 0.40 × 0.31 mm
Orange

Data collection

Siemens AED diffractometer
 $\omega/2\theta$ scans
Absorption correction:
none
8108 measured reflections
7904 independent reflections
3324 observed reflections
 $[I > 2\sigma(I)]$
 $R_{\text{int}} = 0.0119$

$\theta_{\text{max}} = 25^\circ$
 $h = -20 \rightarrow 20$
 $k = 0 \rightarrow 13$
 $l = 0 \rightarrow 26$
1 standard reflection
monitored every 50
reflections
intensity variation: none

Refinement

Refinement on F^2
 $R[F > 4\sigma(F)] = 0.0654$
 $wR(F^2) = 0.2034$
 $S = 1.336$
7888 reflections
462 parameters
H-atom parameters not refined

Calculated weights
 $w = 1/[\sigma^2(F_o^2) + (0.1180P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = -3.907$
 $\Delta\rho_{\text{max}} = 1.384 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.584 \text{ e \AA}^{-3}$
Extinction correction: none
Atomic scattering factors as
for compound (I)

Table 3. Geometric parameters of the hydrogen bonds formed by the cation (\AA , $^\circ$) of compound (I)

$\sigma(\text{N—H}) = 0.12\text{--}0.16$, $\sigma(\text{C—H}) = 0.12\text{--}0.21 \text{ \AA}$; $\sigma(\text{N—H}\cdots\text{O}) = 11\text{--}15$, $\sigma(\text{C—H}\cdots\text{O}) = 8\text{--}14^\circ$.

D—H \cdots A	D—H	D \cdots A	D—H \cdots A	Symmetry
N1—H1N \cdots O11	0.88	2.96 (1)	164	
N2—H2N \cdots O6	0.90	2.86 (1)	158	
N3—H3N \cdots O1	0.86	2.85 (2)	159	iii
N5—H5N \cdots O1	0.77	2.93 (1)	174	iii
N4—H4N \cdots O6	0.77	2.89 (1)	170	
N6—H6N \cdots O11	0.96	2.83 (2)	145	
C1—H11 \cdots O9	1.02	3.51 (2)	157	i
C1—H12 \cdots O10	1.23	3.34 (2)	144	
C2—H21 \cdots O9	1.30	3.52 (2)	154	
C2—H22 \cdots O10	1.12	3.37 (2)	142	ii
C3—H31 \cdots O8	1.02	3.31 (2)	152	iii
C4—H41 \cdots O7	0.75	3.57 (2)	159	
C5—H52 \cdots O8	1.01	3.33 (2)	152	iii
C6—H62 \cdots O9	1.12	3.49 (1)	147	i
C7—H71 \cdots O2	0.98	3.26 (2)	125	iv
C7—H72 \cdots O12	1.13	3.46 (2)	137	vii
C8—H81 \cdots O1	0.98	3.30 (2)	142	iii
C8—H82 \cdots O7	0.84	3.49 (1)	143	v
C9—H91 \cdots N8	1.05	3.67 (2)	145	vi
C9—H92 \cdots O12	0.90	3.60 (2)	156	
C10—H102 \cdots O5	0.99	3.31 (2)	134	v
C11—H111 \cdots O5	1.07	3.28 (2)	144	vii
C12—H121 \cdots O13	1.12	3.48 (2)	131	v

Symmetry codes: (i) $-x, y + \frac{1}{2}, -z + \frac{1}{2}$; (ii) $-x, y - \frac{1}{2}, -z + \frac{1}{2}$; (iii) $x, -y - \frac{1}{2}, z - \frac{1}{2}$; (iv) $x, y + 1, z$; (v) $x, -y + \frac{1}{2}, z - \frac{1}{2}$; (vi) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$; (vii) $-x + 1, -y, -z + 1$.

Compound (II)

Crystal data

$[\text{Co}(\text{C}_9\text{H}_{27}\text{N}_7)_{0.72}(\text{C}_6\text{H}_{24}\text{N}_6)_{0.28}][\text{Co}(\text{C}_9\text{H}_{27}\text{N}_7)]\cdot 2(\text{P}_3\text{O}_9)\cdot 8\text{H}_2\text{O}$

$M_r = 1183.75$

Monoclinic

$P2_1/a$

$D_x = 1.7570 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71070 \text{ \AA}$

Cell parameters from 30 reflections

$\theta = 11\text{--}19^\circ$

Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1986). Program(s) used to refine structure: *SHELXL92* (Sheldrick, 1992). Molecular graphics: *ORTEP* (Johnson, 1965); *PLUTO* (Motherwell & Clegg, 1976). Software used to prepare material for publication: *PARST* (Nardelli, 1983); *ABRAHAMS* (Gilli, 1977).

Table 4. Fractional atomic coordinates and equivalent isotropic thermal parameters (\AA^2) for compound (II)

	$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^*$			
	x	y	z	U_{eq}
CoA	0.36734 (9)	0.2629 (1)	0.37774 (7)	0.0146 (5)
PIA	0.0913 (2)	0.1968 (2)	0.6333 (1)	0.0234 (7)
P2A	0.2484 (2)	0.2417 (2)	0.6731 (2)	0.0179 (10)
P3A	0.2004 (2)	0.2291 (2)	0.5448 (1)	0.0197 (8)
O1A	0.0957 (4)	0.0684 (5)	0.6328 (4)	0.0349 (22)
O2A	0.0201 (5)	0.2518 (5)	0.6461 (5)	0.0326 (25)
O3A	0.1579 (5)	0.2488 (4)	0.6786 (4)	0.0195 (20)
O4A	0.1180 (5)	0.2464 (4)	0.5704 (4)	0.0192 (20)
O5A	0.2776 (4)	0.1266 (6)	0.6909 (3)	0.0334 (23)
O6A	0.2840 (4)	0.3426 (6)	0.7044 (3)	0.0299 (22)
O7A	0.2552 (4)	0.2604 (5)	0.6024 (4)	0.0210 (19)
O8A	0.2107 (4)	0.1076 (6)	0.5279 (4)	0.0426 (25)
O9A	0.2102 (4)	0.3188 (7)	0.4991 (3)	0.0404 (24)
N1A	0.4630 (5)	0.3418 (7)	0.3583 (4)	0.0306 (24)
N2A	0.3869 (4)	0.1602 (6)	0.3090 (4)	0.0247 (22)
N3A	0.4213 (5)	0.1572 (6)	0.4353 (4)	0.0269 (23)
N4A	0.3607 (5)	0.3679 (7)	0.4467 (4)	0.0268 (23)
N5A	0.2696 (5)	0.1885 (6)	0.3914 (4)	0.0257 (23)
N6A	0.3084 (4)	0.3745 (7)	0.3268 (4)	0.0257 (23)
N7A	0.3459 (4)	0.0100 (6)	0.3789 (4)	0.0212 (22)
C1A	0.4827 (6)	0.3048 (8)	0.2970 (5)	0.0206 (5)
C2A	0.4668 (6)	0.1776 (8)	0.2940 (5)	0.0224 (12)
C3A	0.4097 (7)	0.1971 (9)	0.4987 (5)	0.0370 (12)
C4A	0.4133 (6)	0.3273 (8)	0.4974 (5)	0.0468 (33)
C5A	0.2106 (7)	0.2325 (8)	0.3438 (6)	0.0436 (31)

C6A	0.2257 (6)	0.3597 (8)	0.3385 (5)	0.0455 (31)	N3A—C8A	1.50 (1)	N3B—C8B	1.48 (1)
C7A	0.3698 (6)	0.0337 (7)	0.3196 (5)	0.0528 (35)	N4A—C4A	1.48 (1)	N4B—C4B	1.47 (1)
C8A	0.4035 (6)	0.0312 (7)	0.4266 (5)	0.0468 (35)	N5A—C5A	1.51 (1)	N5B—C5B	1.54 (1)
C9A	0.2714 (6)	0.0576 (7)	0.3910 (5)	0.0433 (32)	N5A—C9A	1.51 (1)	N5B—C9B	1.51 (1)
CoB	0.8672 (1)	0.2578 (1)	0.87785 (8)	0.0531 (35)	N6A—C6A	1.50 (1)	N6B—C6B	1.44 (1)
P1B	0.5913 (2)	0.1961 (3)	1.1331 (2)	0.0528 (35)	N7A—C7A	1.43 (1)	N7B—C7B	1.41 (1)
P2B	0.7487 (2)	0.2464 (2)	1.1733 (2)	0.0192 (20)	N7A—C8A	1.43 (1)	N7B—C8B	1.44 (1)
P3B	0.6999 (2)	0.2369 (3)	1.0449 (2)	0.0197 (19)	N7A—C9A	1.46 (1)	N7B—C9B	1.37 (1)
O1B	0.5954 (5)	0.0703 (8)	1.1329 (4)	0.0256 (22)	C1A—C2A	1.50 (1)	C1B—C2B	1.50 (1)
O2B	0.5184 (6)	0.2491 (4)	1.1458 (4)	0.0311 (25)	C3A—C4A	1.50 (1)	C3B—C4B	1.47 (1)
O3B	0.6586 (5)	0.2483 (4)	1.1794 (4)	0.0201 (21)	C5A—C6A	1.50 (1)	C5B—C6B	1.44 (1)
O4B	0.6169 (5)	0.2476 (4)	1.0710 (4)	0.0195 (21)	N5A—CoA—N6A	87.0 (3)	N5B—CoB—N6B	85.9 (4)
O5B	0.7804 (5)	0.1324 (7)	1.1949 (4)	0.0461 (23)	N4A—CoA—N6A	89.3 (3)	N4B—CoB—N6B	87.1 (4)
O6B	0.7820 (5)	0.3502 (8)	1.2034 (4)	0.0465 (24)	N4A—CoA—N5A	92.9 (3)	N4B—CoB—N5B	93.1 (4)
O7B	0.7555 (5)	0.2563 (4)	1.1028 (4)	0.0230 (21)	N3A—CoA—N6A	174.5 (3)	N3B—CoB—N6B	172.9 (4)
O8B	0.7115 (5)	0.1082 (8)	1.0273 (5)	0.0303 (24)	N3A—CoA—N5A	90.7 (3)	N3B—CoB—N5B	93.7 (4)
O9B	0.7099 (5)	0.3170 (7)	0.9982 (4)	0.0237 (22)	N3A—CoA—N4A	85.8 (3)	N3B—CoB—N4B	85.9 (4)
N1B	0.9619 (6)	0.3436 (8)	0.8578 (5)	0.0133 (22)	N2A—CoA—N6A	93.5 (3)	N2B—CoB—N6B	93.8 (4)
N2B	0.8870 (5)	0.1588 (8)	0.8093 (5)	0.0138 (22)	N2A—CoA—N5A	93.2 (3)	N2B—CoB—N5B	93.4 (4)
N3B	0.9228 (5)	0.1583 (8)	0.9352 (4)	0.0138 (22)	N2A—CoA—N4A	173.4 (3)	N2B—CoB—N4B	173.5 (4)
N4B	0.8586 (6)	0.3667 (9)	0.9470 (5)	0.0218 (25)	N2A—CoA—N3A	91.7 (3)	N2B—CoB—N3B	93.3 (4)
N5B	0.7694 (6)	0.1856 (7)	0.8896 (5)	0.0127 (22)	N1A—CoA—N6A	89.4 (3)	N1B—CoB—N6B	87.4 (4)
N6B	0.8063 (6)	0.3748 (9)	0.8265 (5)	0.0220 (26)	N1A—CoA—N5A	176.0 (3)	N1B—CoB—N5B	173.2 (4)
N7B	0.8438 (6)	0.0127 (8)	0.8798 (5)	0.0219 (26)	N1A—CoA—N4A	89.0 (4)	N1B—CoB—N4B	88.1 (4)
C1B	0.9766 (7)	0.3109 (9)	0.7970 (5)	0.0371 (31)	N1A—CoA—N3A	93.0 (3)	N1B—CoB—N3B	93.1 (4)
C2B	0.9696 (6)	0.1811 (8)	0.7948 (5)	0.0259 (25)	N1A—CoA—N2A	85.1 (3)	N1B—CoB—N2B	85.5 (4)
C3B	0.9100 (6)	0.1937 (8)	0.9967 (5)	0.0250 (26)	P1A—O3A—P2A	127.8 (6)	P1B—O3B—P2B	128.3 (5)
C4B	0.9107 (6)	0.3213 (9)	0.9963 (5)	0.0324 (29)	P1A—O4A—P3A	126.0 (5)	P1B—O4B—P3B	126.8 (6)
C5B	0.7099 (7)	0.2428 (7)	0.8444 (6)	0.0304 (32)	P2A—O7A—P3A	132.9 (5)	P2B—O7B—P3B	135.5 (6)
C6B	0.7262 (7)	0.3635 (10)	0.8365 (6)	0.0199 (29)	CoA—N1A—C1A	108.6 (6)	CoB—N1B—C1B	106.3 (7)
C7B	0.8692 (8)	0.0336 (11)	0.8217 (7)	0.0304 (35)	CoA—N2A—C7A	114.3 (5)	CoB—N2B—C7B	111.6 (7)
C8B	0.9026 (9)	0.0344 (12)	0.9270 (7)	0.0391 (40)	CoA—N2A—C2A	108.0 (6)	CoB—N2B—C2B	106.7 (7)
C9B	0.7727 (8)	0.0549 (11)	0.8909 (7)	0.0327 (35)	C2A—N2A—C7A	111.6 (7)	C2B—N2B—C7B	114.3 (9)
P1B'	0.5928 (4)	0.3014 (6)	1.1340 (3)	0.0131 (13)	CoA—N3A—C8A	115.7 (6)	CoB—N3B—C8B	112.9 (8)
O1B'	0.5936 (14)	0.4329 (21)	1.1324 (11)	0.0425 (59)	CoA—N3A—C3A	109.2 (6)	CoB—N3B—C3B	110.4 (7)
O8B'	0.7114 (11)	0.1819 (16)	0.9991 (9)	0.0224 (44)	C3A—N3A—C8A	112.2 (7)	C3B—N3B—C8B	109.6 (9)
O9B'	0.7082 (12)	0.3863 (19)	1.0235 (10)	0.0307 (50)	CoA—N4A—C4A	109.3 (6)	CoB—N4B—C4B	105.8 (7)
N1B'	0.8838 (11)	0.3374 (17)	0.8093 (9)	0.0105 (42)	CoA—N5A—C9A	114.8 (5)	CoB—N5B—C9B	113.5 (7)
N2B'	0.9599 (11)	0.1550 (17)	0.8587 (9)	0.0087 (41)	CoA—N5A—C5A	107.7 (6)	CoB—N5B—C5B	106.8 (7)
N3B'	0.8606 (13)	0.1348 (19)	0.9500 (10)	0.0186 (50)	C5A—N5A—C9A	110.1 (7)	C5B—N5B—C9B	117.5 (8)
N4B'	0.9212 (11)	0.3457 (17)	0.9322 (9)	0.0085 (41)	CoA—N6A—C6A	107.6 (6)	CoB—N6B—C6B	109.4 (8)
N5B'	0.7702 (11)	0.3181 (17)	0.8905 (9)	0.0109 (43)	C8A—N7A—C9A	113.2 (7)	C8B—N7B—C9B	115 (1)
N6B'	0.8030 (13)	0.1183 (20)	0.8296 (10)	0.0212 (52)	C7A—N7A—C9A	114.7 (8)	C7B—N7B—C9B	117 (1)
C6B'	0.7220 (18)	0.1346 (28)	0.8382 (15)	0.0303 (72)	C7A—N7A—C8A	114.3 (8)	C7B—N7B—C8B	112 (1)
O10	0.9159 (4)	0.0631 (7)	0.1507 (4)	0.0352 (51)				
O11	0.9135 (4)	0.4373 (7)	0.1524 (4)	0.0200 (44)				
O12	0.5876 (5)	0.4086 (6)	0.4373 (4)	0.0389 (50)				
O13	0.0780 (5)	0.3818 (8)	0.4276 (4)	0.0219 (45)				
O14	0.4182 (4)	0.0641 (7)	0.6477 (5)	0.0258 (48)				
O15	0.4125 (5)	0.4376 (7)	0.6547 (4)	0.0361 (52)				
O16	1.0872 (5)	0.4022 (7)	0.9375 (4)	0.0495 (57)				
O17	0.5807 (5)	0.3881 (8)	-0.0685 (4)	0.0353 (51)				

Table 5. Geometric parameters (Å, °) for compound (II)

CoA—N1A	1.978 (8)	CoB—N1B	2.01 (1)
CoA—N2A	1.981 (8)	CoB—N2B	1.95 (1)
CoA—N3A	1.962 (8)	CoB—N3B	1.93 (1)
CoA—N4A	1.963 (8)	CoB—N4B	2.00 (1)
CoA—N5A	1.957 (8)	CoB—N5B	1.94 (1)
CoA—N6A	1.960 (8)	CoB—N6B	2.02 (1)
P1A—O1A	1.484 (6)	P1B—O1B	1.455 (9)
P1A—O2A	1.444 (9)	P1B—O2B	1.46 (1)
P1A—O3A	1.603 (8)	P1B—O3B	1.626 (8)
P1A—O4A	1.609 (9)	P1B—O4B	1.594 (9)
P2A—O3A	1.599 (9)	P2B—O3B	1.590 (9)
P2A—O5A	1.469 (7)	P2B—O5B	1.495 (9)
P2A—O6A	1.473 (8)	P2B—O6B	1.474 (9)
P2A—O7A	1.596 (9)	P2B—O7B	1.58 (1)
P3A—O4A	1.598 (9)	P3B—O4B	1.61 (1)
P3A—O7A	1.586 (8)	P3B—O7B	1.575 (9)
P3A—O8A	1.467 (8)	P3B—O8B	1.55 (1)
P3A—O9A	1.469 (8)	P3B—O9B	1.41 (1)
N1A—C1A	1.49 (1)	N1B—C1B	1.44 (1)
N2A—C2A	1.47 (1)	N2B—C2B	1.52 (1)
N2A—C7A	1.51 (1)	N2B—C7B	1.51 (1)
N3A—C3A	1.51 (1)	N3B—C3B	1.46 (1)

Table 6. Puckering coordinates of P₃O₃³⁻ for compounds (I) and (II) [cells (I) and (II)]

	φ_2 (°)	θ_2 (°)	Q_T (Å)
Compound (I)	79 (1)	92.2 (8)	0.579 (8)
Compound (II)			
Cell (I) Molecule A	17 (1)	26.3 (7)	0.435 (5)
B	173.1 (6)	104.4 (7)	0.49 (1)
Cell (II) Molecule A	-18.5 (1)	20.6 (6)	0.448 (4)
B	-12 (1)	33.2 (6)	0.417 (4)
B'	-174.1 (5)	110.4 (5)	0.463 (6)

Table 7. Geometric parameters of the hydrogen bonds formed by the A and B cations (Å, °) of compound (II)

D—H...A	D—H	D...A	D—H...A	Symmetry
N1A—H1NC...O1A	1.02	2.82 (1)	161	v
N1A—H1ND...O12	1.10	2.81 (1)	127	
N2A—H2NA...O6B	1.02	2.88 (1)	150	iv
N3A—H3NA...O13	1.02	2.79 (1)	155	ii
N4A—H4NC...O9A	0.98	3.00 (1)	143	
N4A—H4ND...O1A	1.08	3.04 (1)	165	v
N5A—H5NA...O9A	1.11	3.07 (1)	152	
N6A—H6NC...O5B	1.14	2.94 (1)	143	iv
N6A—H6ND...O1A	1.07	2.90 (1)	150	v
N1B—H1NE...O1B	1.02	2.81 (1)	160	vii
N1B—H1NF...O16	0.89	2.80 (1)	136	
N2B—H2NB...O6A	0.73	2.84 (1)	150	ii
N3B—H3NB...O17	0.77	2.82 (1)	179	vi
N4B—H4NE...O9B	1.02	2.96 (1)	171	
N4B—H4NF...O1B	0.86	3.09 (2)	131	vii

N4B—H4NF...O8B	0.86	3.11 (2)	145	vii
N5B—H5NB...O9B	0.94	3.09 (2)	168	
N6B—H6NE...O1B	1.02	2.94 (1)	160	vii
N6B—H6NF...O5A	0.63 (1)	3.02 (2)	144	ii

Symmetry codes: (i) $x, y, z - 1$; (ii) $x + \frac{1}{2}, -y + \frac{1}{2}, z$; (iii) $-x + 1, -y + 1, -z + 1$; (iv) $x - \frac{1}{2}, -y + \frac{1}{2}, z - 1$; (v) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + 1$; (vi) $x + \frac{1}{2}, -y + \frac{1}{2}, z + 1$; (vii) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + 2$.

Compound (I) was obtained by treating Co(sep)Cl₃ (Bacchi, Ferranti & Pelizzi, 1993) with an equivalent amount of Ag₃P₃O₉ in aqueous solution; AgCl was filtered off and after slow evaporation compound (I) precipitated in crystalline form. The structure was solved and refined with standard procedures; all non-H atoms were refined anisotropically. H atoms were localized by difference Fourier maps and were refined isotropically in a full-matrix least-squares cycle except for H1N, H6N and H2O1 which did not show a steady refinement. All H atoms were held fixed in the last least-squares cycles to achieve a better convergence.

Compound (II) was prepared as for (I): a chloride complex obtained by employing a smaller amount of NH₃ and CH₂O in the step involving the formation of the ligand cage was treated with Ag₃P₃O₉. The observed threshold $I > 2\sigma(I)$ is used only for calculating R_{obs} etc., for comparison with refinements on F . The refinement was performed with anisotropic thermal parameters for the Co, P, N and O atoms of molecule *A*, for the Co, P2, P3 atoms of molecule *B* and for the O atoms of the water molecules. The remaining atoms were refined isotropically. Methylene hydrogens, H1NC, H1NE, H4NE, H6NE, H101, H142, H151, H152 and H172 were introduced in calculated positions; the remaining amine and water H atoms were located by difference Fourier maps and held fixed in successive least-squares calculations. The z and U_{33} parameters are, in general, affected by the largest shift/e.s.d. and, in particular, unstable refinement is observed for the z coordinate of C3 and C4 of both molecules, probably due to the correlation effects introduced by pseudosymmetry.

Extensive use was made of the Cambridge Structural Database. Calculations were performed on Encore-Gould-Powernode 6040 and Encore 91 computers of the Centro di Studio per la Strutturistica Diffraattometrica del CNR, Parma.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71306 (82 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL1051]

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Structure of Dicarboxyl[(8,9,11,12,13,14- η)-12,19-dimethoxy podocarpa-8,11,13-triene]-thiocarbonylchromium(0)

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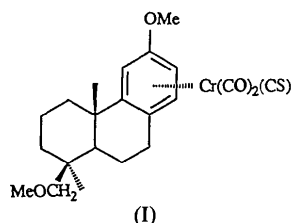
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Abstract

The structure determination of the title compound [dicarbonyl(η^6 -1,2,3,4,4a,9,10,10a-octahydro-6-methoxy-1-methoxymethyl-1,4a-dimethylphenanthrene)-thiocarbonylchromium(0)] establishes that the Cr(CO)₂(CS) moiety binds to the aromatic ring from the side opposite to that of the methyl group on C12, giving the α stereoisomer. The carbonyl and thiocarbonyl groups are oriented approximately halfway between the staggered and eclipsed positions.

Comment

The title compound (I) was prepared during a study of the cyclopentaannulation of diterpenoids mediated by organotransition-metal complexes. In



view of the fact that the preferred conformation of the Cr(CO)₃ moiety in a related diterpenoid tricarbonylchromium complex controlled the regiochemistry of attack of cyano-stabilized carbanions