P2—Rh1—P1—O3	117.84 (9)	Rh1—P2—O7—C54	−108.5 (2)
P2—Rh1—P1—O4	−10.32 (10)	O6—P2—O7—C54	27.8 (3)
P2—Rh1—P1—O5	−130.85 (9)	O8—P2—O7—C54	134.1 (2)
O1—Rh1—P1—O3	−57.10 (11)	Rh1—P2—O8—C68	−121.4 (3)
O1—Rh1—P1—O4	174.74 (11)	O6—P2—O8—C68	107.9 (3)
O1—Rh1—P1—O5	54.21 (11)	O7—P2—O8—C68	2.0 (3)
P1—Rh1—P2—O6	−9.44 (10)	Rh1—O1—C1—C2	7.4 (5)
P1—Rh1—P2—O7	118.81 (10)	Rh1—O1—C1—C4	−172.6 (2)
P1—Rh1—P2—O8	−130.27 (10)	Rh1—O2—C3—C2	7.8 (5)
O2—Rh1—P2—O6	176.23 (11)	Rh1—O2—C3—C5	−174.2 (3)
O2—Rh1—P2—O7	−55.52 (12)	P1—O3—C6—C11	123.6 (3)
O2—Rh1—P2—O8	55.40 (11)	P1—O3—C6—C7	−62.1 (3)
P1—Rh1—O1—C1	−176.5 (3)	P1—O4—C20—C21	−70.8 (3)
O2—Rh1—O1—C1	−2.5 (3)	P1—O4—C20—C25	112.4 (3)
P2—Rh1—O2—C3	−179.0 (3)	P1—O5—C34—C39	−102.4 (3)
O1—Rh1—O2—C3	−4.6 (3)	P1—O5—C34—C35	81.5 (4)
Rh1—P1—O3—C6	−104.0 (2)	P2—O6—C40—C45	−71.2 (3)
O4—P1—O3—C6	31.2 (2)	P2—O6—C40—C41	110.2 (3)
O5—P1—O3—C6	137.8 (2)	P2—O7—C54—C59	126.7 (3)
Rh1—P1—O4—C20	−168.32 (17)	P2—O7—C54—C55	−59.7 (4)
O3—P1—O4—C20	56.3 (2)	P2—O8—C68—C731	80.5 (5)
O5—P1—O4—C20	−44.9 (2)	P2—O8—C68—C732	132.8 (4)
Rh1—P1—O5—C34	−127.9 (3)	P2—O8—C68—C69	−82.6 (5)
O3—P1—O5—C34	−2.7 (3)	O1—C1—C2—C3	−5.4 (6)
O4—P1—O5—C34	103.0 (3)	C44—C45—C55—C54	−129.3 (3)
Rh1—P2—O6—C40	−167.26 (17)	C40—C45—C55—C54	50.9 (5)
O7—P2—O6—C40	58.3 (2)	C40—C45—C55—C56	−132.1 (3)
O8—P2—O6—C40	−43.6 (2)	C44—C45—C55—C56	47.7 (4)

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry, as well as a molecular packing diagram, have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55972 (97 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB1032]

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Structures of two Cobalt(III) Sepulchrate Complexes*

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Abstract

The complex (1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]icosane)cobalt(III) perchlorate thiosulfate, [Co(C$_{12}$H$_{30}$N$_8$)](ClO$_4$)(S$_2$O$_3$), crystallizes in the hexagonal space group $P6_322$. Cations and anions occupy special-site positions with the anions disordered as a result of symmetry requirements. Co(sep)$^{3+}$ (sep = C$_{12}$H$_{30}$N$_8$) adopts the optically active D_3 crystallographic geometry. The packing consists of layers of interacting Co(sep)$^{3+}$ and S$_2$O$_3^{2-}$ ions, intercalated by isolated ClO$_4^-$ anions. The second complex, *rac*-(1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]icosane)cobalt trichloride monohydrate, *rac*-Co(C$_{12}$H$_{30}$N$_8$)]Cl$_3$·H$_2$O, crystallizes in the

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* In honour of Professor Antonio Indelli, who passed away untimely in September 1990.

monoclinic space group $P2_1/a$. There are two independent $[Co(sep)]Cl_3·H_2O$ moieties present in the asymmetric unit; the two $Co(sep)^{3+}$ cations have essentially identical conformations, although each one interacts differently with its three corresponding Cl^- anions. The two water molecules contribute to this differentiation, bridging the $[Co(sep)]Cl_3$ moieties in one-dimensional polymeric chains. The geometries of the cations in the two complexes are also identical.

Comment

Sepulchrate (1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]-icosane) complexes are characterized by a rigid ligand cage bonded to the central metal atom by six N donor atoms which cannot leave the coordination sphere, even if the metal oxidation state changes, without breaking covalent N—C or C—C bonds. These capsule constraints (Sargeson, 1979) should allow the chemistry of a number of metal compounds in various oxidation states to be studied whilst keeping their constitution and stereochemistry fixed. The interest of our present work is centred on the structural properties of two Co^{3+} complexes, in particular conformational aspects and packing stereochemistry.

In (1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]icosane)-cobalt(III) perchlorate thiosulfate (I), intensity statistics suggesting the absence of centres of symmetry and systematic absences 000l with l odd limited the possible space groups to $P6_3$ or $P6_322$; a careful check of the equivalences for point groups C_6 and D_6 led us to choose the latter. Patterson interactions revealed the presence of the metal ion on the 32 site at $(\frac{2}{3}, \frac{1}{3}, \frac{3}{4})$, conforming to the potential D_3 geometry of the $Co(sep)^{3+}$ cation (Fig. 1) which also forces N(cap) to lie on the threefold axis at $(\frac{2}{3}, \frac{1}{3}, z)$ with $Z = 2$. The stoichiometry also requires the occupation of sites with the 32 crystallographic symmetry by the ClO_4^- [Cl1 at (0, 0, 0)] and $S_2O_3^{2-}$ [S1 at $(\frac{1}{3}, \frac{2}{3}, \frac{3}{4})$] anions. As the idealized tetrahedral geometry of the anions is not compatible with such a condition, each anion must be disordered over two equivalent positions related by the twofold axes (Figs. 2a,b) with only two independent atoms bonded to the central atom, one on the threefold axis (O1 and S2, respectively, apical), and the other at the general position (x,y,z) (O2 and O3, respectively, equatorial). As a result of symmetry requirements, there are two equivalent apical and six equivalent equatorial atoms. Such disorder hinders satisfactory refinement and is responsible for the rather high final R value . The highest residual peak in the $\Delta\rho$ map (approximately 2 e Å^{-3}) is situated in the sepulchrate cage, at 1.67 Å from the metal ion on the threefold axis. This is possibly the result of further unresolved disorder with position exchange between cations and anions which could account also for the anomalously high anisotropy of C2. The remaining peaks in the $\Delta\rho$ map are lower than 1 e Å^{-3}. This is the only case so far in which the sepulchrate molecule adopts the crystallographic D_3 geometry, an approximate D_3 configuration being the most common among the four sepulchrate complexes reported in the literature, (Mikami, Konno & Saito, 1979; Creaser *et al.*, 1977; Creaser *et al.*, 1982). C_3 crystallographic geometry has also been found for an Ni^{2+} compound (Paik Suh, Shin, Kim & Kim, 1984).

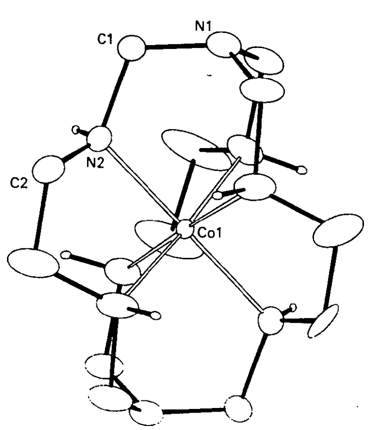


Fig. 1. *ORTEP* diagram of the cation of (I) with 30% probability thermal ellipsoids. Methylene H atoms have been omitted.

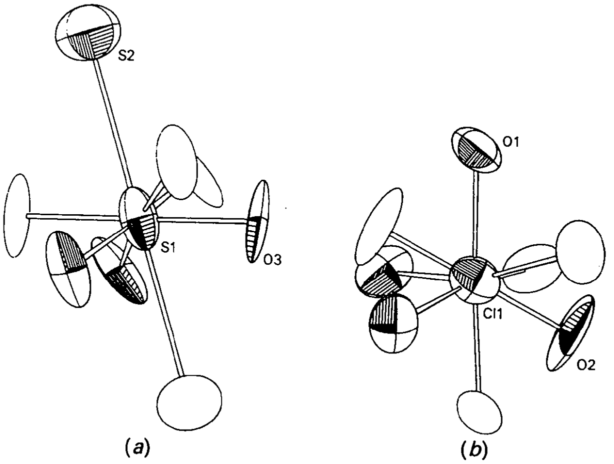
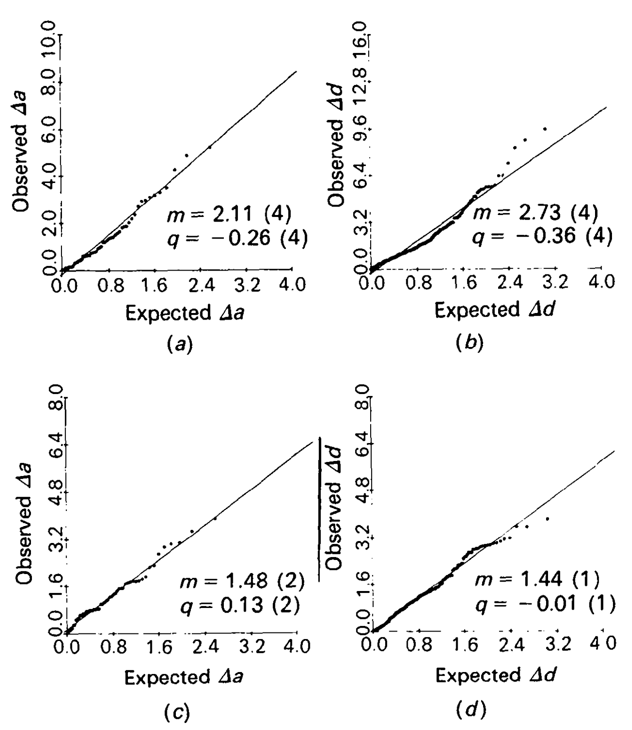


Fig. 2. *ORTEP* diagrams of the disordered (a) ClO_4^- and (b) $S_2O_3^{2-}$ anions of (I). Thermal ellipsoids drawn at 30% probability level, shading indicates one of the two images (see text).

The final fractional coordinates for (I) are listed in Table 1 and bond distances and angles in Table 2. The C(cap)—N(cap)—C(cap) angle [114.3(7)°] and the variations in the N(cap)—C(cap)—N(lig)—C(en) bond length [1.45(1), 1.51(1), 1.48(2) Å] are in good agreement with data in the literature cited above, confirming the tendency of N(cap) to assume the geometry typical of a near-sp^2 hybridization. The bite angle [87.1(5)°] and *trans* N(lig)—Co—N(lig) angle [176.0(5)°] in the coordination polyhedron are typical for these chelate systems. It has not been possible to determine unambiguously the absolute configuration of the cation because checks based on *R* values (R_{inv}= 0.0900) and the Flack parameter [x = 0.5(2); calculated from the final coordinates using *SHELXL92* (Sheldrick, 1992)] did not give definitive results. This does not seem to be the result of simple twinning effects as the same results were obtained using data collected for two other different crystals; it is probably caused by the centrosymmetric relations existing among those atoms which occupy 32 and 3 symmetry sites and constitute about 34% of the total electron density inside the unit cell. The tilt angle formed by the C(en)—C(en) direction with the N(cap)—Co—N(cap) threefold crystallographic axis is 5(2)°, indicating that the conformation adopted by the ligand cage is the usual lel_3. This is the most favourable for energetic stabilization of crystal packing because of the hydrogen bonding involving the N—H groups (see below).

The corresponding (+) $\mathrm{Co(sep)Cl_3.\,H_2O}$ enantiomer of *rac*-(1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]icosane)-cobalt(III) trichloride monohydrate (II) has already been studied (Creaser *et al.*, 1977). Complex (II) is racemic and the asymmetric unit contains two independent molecules (*A* and *B*), each comprising a $\mathrm{Co(sep)^{3+}}$ cation associated with three $\mathrm{Cl^-}$ anions (Fig. 3), with two water molecules (O1 and O2) completing the crystal packing. Half-normal probability-plot analyses (Gilli, 1977, following Abrahams & Keve, 1971) of bond angles (Fig. 4*a*) and all bonding and non-bonding distances between non-H atoms in the range 1.0–9.9 Å (Fig. 4*b*) show that there are no substantial differences in the molecular geometries of the cations of *A* and *B*. Similar analyses comparing these cations with the $\mathrm{Co(sep)^{3+}}$ cation of compound (I) gave analogous results (Figs. 4*c*,*d*). This proves that in the title complexes the conformation of the cage is unaffected by the anionic environment which is determined by crystal packing, the ideal symmetry 32 of (I) being closely approximated by the pseudo-D_3 geometry of (II). Final fractional coordinates for (II) are given in Table 1 and bond distances and angles in Table 2. Bite angles and *trans* N(lig)—Co—N(lig) angles [86.1(2) and 175.4(2)°, respectively, averaged over the coordination polyhedra of *A* and *B*] are similar to those found for the analogous compounds cited. Molecules *A* and *B* exhibit the lel_3 geometry, invariant with inversion of absolute configuration, with angles [C(en)—C(en)]∧[N(cap)—Co—N(cap)] ranging from 3.3(3) to 5.2(3)°.



(*a*) (*b*)

(*c*) (*d*)

Fig. 4. Half-normal probability plots comparing (*a*) bond angles for cations *A* and *B* in (II), (*b*) interatomic distances for cations *A* and *B* in (II), (*c*) bond angles for cations of (I) and (II) (molecule *A*) and (*d*) interatomic distances for cations of (I) and (II) (molecule *A*). Best regression lines ($y = mx + q$) and their parameters are also shown.

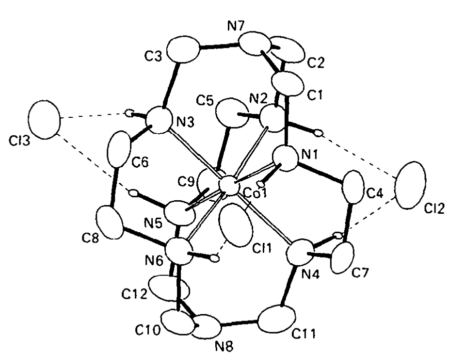


Fig. 3. *ORTEP* diagram of the $\mathrm{[Co(sep)Cl_3]^A}$ moiety of (II) with 50% probability thermal ellipsoids. Dotted lines show N—H···Cl hydrogen bonds. Methylene H atoms have been omitted.

As shown in Fig. 5, a two-dimensional network of hydrogen bonds in (I) holds the cations and thiosulfate anions together in alternating staggered layers. As these ions occupy the *c* [$\mathrm{Co(sep)^{3+}}$] and *d* [$\mathrm{S_2O_3^{2-}}$] sites of the $P6_322$ space group, hexagonal close packing is obtained with a minimum distance between the layers N1···S2 = 3.42(2) Å. The $\mathrm{ClO_4^-}$ ions are intercalated between the layers and occupy the *a* sites whose large dimensions permit the disorder already mentioned (see also Paik Suh, Shin, Kim & Kim, 1984). They interact with the cations through the O1···C2 [3.16(2) Å] and O2···C1 [3.45(3) Å] contacts. Within a layer, each cation binds three thiosulfate anions *via* —N—H···O···$\mathrm{H^i}$—$\mathrm{N^i}$— hydrogen bonds [O···N 3.07(1), 2.95(2) Å]; N and $\mathrm{N^i}$ belong to the same cation and are related by rotation around a twofold crystallographic axis of the 32 site occupied by the metal but are not connected by an —N—C—C—N— ethylenediaminic chain. Each thiosulfate O atom is involved in these interactions and is disordered as described previously, so that the O atom of the —N—H···O···H^i—N^i system oscillates between two equivalent positions, related by a twofold crystallographic axis, of the same anion. As the N—H groups of the metal coordination polyhedron are coupled by N—H···O···H—N bridges, it is also possible to define a chirality for the interactions between the Co(sep)$^{3+}$ cations and $S_2O_3^{2-}$ anions; the absolute configuration of these systems is imposed by the sp^3 geometry of N—H groups which, for a given cation configuration, determines unequivocally the pairs of N atoms for which the N—H directions converge to a potential hydrogen-acceptor atom. It can be shown that the resulting hydrogen-bonding absolute configuration for the present lel_3 pseudo-octahedral moiety is the opposite of that of the MN_6 parent complex.

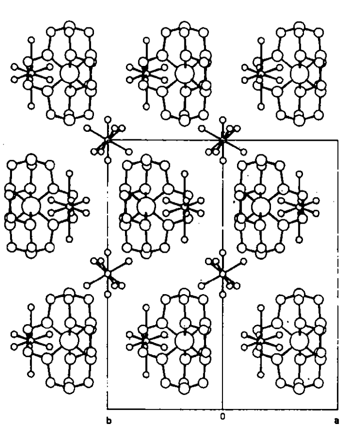


Fig. 5. Crystal packing in (I) viewed along [110]. Anions are represented as disordered moieties; H atoms have been omitted.

In (II), the pseudo-threefold axes N(cap)—Co—N(cap) of molecules A and B make an angle of 118°. The interactions between the anions and cations in $[Co(sep)Cl_3]^A$ and $[Co(sep)Cl_3]^B$ have been compared by analysis of the half-normal probability plot described above; this shows that packing contacts among ionic pairs differ significantly in the two independent molecules (Fig. 6). Three anions link pairs of N—H groups in each cation (Fig. 3, Table 3) and in molecule A there are slightly higher angular deviations of the Co···Cl directions from those of ideal twofold axes. The variation in the N—Cl distances, particularly Cl1 and Cl3, is also higher in molecule A as a result of the Coulombic repulsion Cl1···C9 [($\frac{3}{2} - x, \frac{1}{2} + y, 2 - z$) 3.281(6) Å] and the contact O2···Cl3 [($x, y, z - 1$) 3.176(7) Å], which could be interpreted as a very distorted hydrogen bond (see Table 3).

Water molecules interact very weakly with Cl atoms, generating chains of hydrogen bonds (N—H^A···Cl···H—O—H···Cl···H—N^B)$_n$ which determine a one-dimensional polymeric connection along the z direction (Fig 7). The same motif is found in the (+) enantiomer mentioned above. The stronger O(H_2O)···Cl$^-$ hydrogen bonds in molecule B influence the variation in the average N···Cl$_i$ distances; the smallest value is found for the Cl atom which does not interact with the water molecules (average N—Cl2 distance in B = 3.141 Å) while the greatest value belongs to the Cl atom most involved in water hydrogen bonding (average values of N—Cl1 and N—Cl3 are 3.171 and 3.256 Å, respectively). An analogous trend is found in molecule A in which the variation is smaller because the interactions of the Cl^A atoms with O1 and O2 are weaker (average distances N—Cl2 3.153, N—Cl1 3.157 and N—Cl3 3.216 Å]. For the same reason, the average cation-anion distance relative to the anions involved in hydrogen bonds with water molecules is greater in molecule B (3.214 Å) than in A (3.186 Å). In conclusion, it seems that the main factors distinguishing the geometries of molecules A and B are the angular distortion on Co—Cl directions in A, and the H_2O···Cl hydrogen bonds in B.

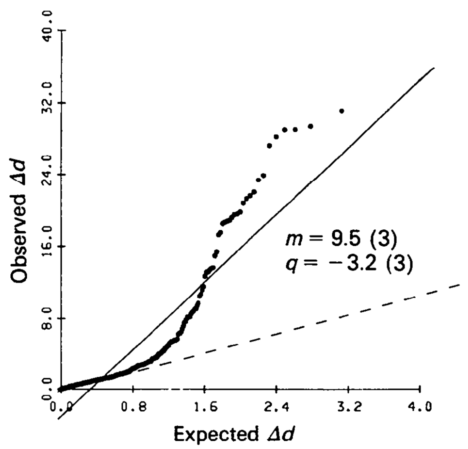


Fig. 6. Half-normal probability plot comparing interactions between cation and anions for molecules A and B of (II). Linear regression parameters are given. The solid line refers to the data shown in this figure and the dotted line to the analysis of interatomic distances for cations A and B (Fig. 4b).

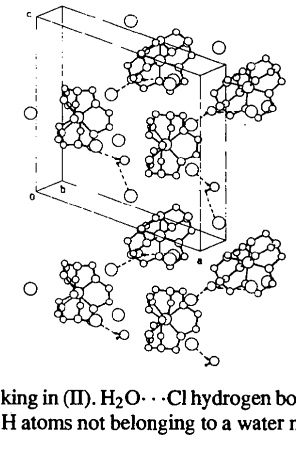


Fig. 7. Crystal packing in (II). H_2O···Cl hydrogen bonds are represented as dotted lines. H atoms not belonging to a water molecule have been omitted.

Experimental

Complex (I)

Crystal data

$[Co(C_{12}H_{30}N_8)]^{3+}.ClO_4^-.S_2O_3^{2-}$
M_r = 556.93
Hexagonal
$P6_322$
a = 8.552 (1) Å
c = 17.064 (2) Å
V = 1080.8 (3) Å^3
Z = 2
D_x = 1.7113 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71070 Å
Cell parameters from 25 reflections
θ = 6.6-12.7°
μ = 1.15 mm^{-1}
T = 293 K
Hexagonal plates
0.59 × 0.58 × 0.21 mm
Yellow

Data collection

Enraf-Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
3792 measured reflections
644 independent reflections
3618 observed reflections [$I>2\sigma(I)$]
R_{int} = 0.030
θ_{max} = 25°

$h = -10 \rightarrow 10$
$k = -10 \rightarrow 10$
$l = 0 \rightarrow 20$
2 orientation standard reflections monitored every 200 reflections
2 intensity standard reflections frequency: 160 min intensity variations: none

Refinement

Refinement on F
Final R = 0.0897
wR = 0.0968
S = 2.49
607 reflections
75 parameters
All H-atom parameters refined for H21, H22 and H2N, only U's refined for H11 and H12
Unit weights applied

$(\Delta/\sigma)_{max}$ = 0.25
$\Delta\rho_{max}$ = 1.92 e Å^{-3}
$\Delta\rho_{min}$ = −0.96 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* [1974, Vol. IV, Tables 2.2A, 2.3.1 (Co, N, C, Cl, O, S) and 2.2C (H)]

Complex (II)

Crystal data

$[Co(C_{12}H_{30}N_8)]^{3+}.3Cl^-.H_2O$
M_r = 469.7
Monoclinic
$P2_1/a$
a = 15.143 (3) Å
b = 18.277 (4) Å
c = 15.191 (3) Å
β = 109.55 (2)°
V = 3962 (1) Å^3
Z = 8
D_x = 1.5750 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71070 Å
Cell parameters from 28 reflections
θ = 14.4-23.4°
μ = 1.29 mm^{-1}
T = 293 K
Irregular prisms
Light orange

Data collection

Philips PW 1100 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North, Phillips & Matthews, 1968)
T_{min} = 1.001, T_{max} = 1.131
6638 measured reflections
6169 independent reflections

4213 observed reflections [$F_o>3.5\sigma(F_o)$]
R_{int} = 0.032
θ_{max} = 24°
$h = -16 \rightarrow 16$
$k = 0 \rightarrow 20$
$l = 0 \rightarrow 16$
1 intensity standard reflection frequency: 90 min intensity variation: none

Refinement

Refinement on F
Final R = 0.0405
wR = 0.0416
S = 2.55
4035 reflections
703 parameters
All H-atom parameters refined
Unit weights applied
$(\Delta/\sigma)_{max}$ = 0.12

$\Delta\rho_{max}$ = 0.72 e Å^{-3}
$\Delta\rho_{min}$ = −0.56 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* [1974, Vol. IV, Tables 2.2A, 2.3.1 (Co, N, C, Cl, O) and 2.2C (H)]

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

$$U_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
(I)				
Co1	−0.33333	−0.66667	−0.25000	0.0142 (6)
N1	−0.33333	−0.66667	−0.0750 (7)	0.0438 (40)
N2	−0.1491 (13)	−0.4732 (14)	−0.1833 (5)	0.0466 (42)
C1	−0.1667 (16)	−0.5050 (18)	−0.0956 (6)	0.0508 (56)
C2	−0.1445 (37)	−0.3042 (14)	−0.2068 (6)	0.0978 (83)
Cl1	0.00000	0.00000	0.00000	0.0575 (21)
O1	0.00000	0.00000	0.0769 (15)	0.0671 (139)
O2	0.1219 (30)	−0.0594 (29)	−0.0453 (9)	0.067 (14)
S1	0.33333	−0.33333	−0.25000	0.0499 (21)
S2	0.33333	−0.33333	−0.3744 (7)	0.0839 (50)
O3	0.1899 (20)	−0.4920 (20)	−0.2266 (11)	0.0658 (81)
(II)				
Molecule *A*				
Co1	0.73398 (4)	0.12482 (3)	0.98944 (4)	0.0188 (2)
N1	0.7254 (3)	0.1627 (2)	0.8653 (3)	0.0305 (17)
N2	0.6690 (3)	0.0341 (2)	0.9324 (3)	0.0321 (16)
N3	0.6129 (3)	0.1701 (3)	0.9806 (3)	0.0340 (16)
N4	0.8580 (3)	0.0860 (3)	0.9941 (3)	0.0347 (17)
N5	0.7461 (3)	0.0799 (2)	1.1105 (3)	0.0341 (16)
N6	0.7936 (3)	0.2152 (2)	1.0532 (3)	0.0358 (17)
N7	0.5617 (3)	0.1191 (3)	0.8222 (3)	0.0364 (17)
N8	0.9068 (3)	0.1304 (3)	1.1565 (3)	0.0409 (20)
C1	0.6296 (4)	0.1597 (3)	0.7921 (4)	0.0371 (23)
C2	0.5861 (4)	0.0447 (4)	0.8418 (4)	0.0456 (22)
C3	0.5332 (4)	0.1586 (4)	0.8899 (4)	0.0471 (25)
C4	0.7978 (4)	0.1269 (3)	0.8345 (4)	0.0355 (21)
C5	0.6429 (4)	−0.0057 (3)	1.0070 (4)	0.0358 (21)
C6	0.6302 (4)	0.2493 (3)	1.0037 (4)	0.0407 (24)
C7	0.8846 (4)	0.1250 (3)	0.9196 (4)	0.0387 (22)
C8	0.7211 (4)	0.2536 (3)	1.0841 (4)	0.0416 (24)
C9	0.7264 (4)	0.0008 (3)	1.0952 (4)	0.0400 (22)
C10	0.8868 (4)	0.2041 (4)	1.1330 (4)	0.0494 (24)
C11	0.9334 (4)	0.0879 (4)	1.0885 (5)	0.0514 (26)
C12	0.8390 (4)	0.0930 (4)	1.1889 (4)	0.0476 (21)
Cl1	0.7864 (1)	0.32316 (8)	0.8806 (1)	0.0545 (7)
Cl2	0.8267 (1)	−0.06657 (8)	0.8978 (1)	0.0628 (8)
Cl3	0.5568 (1)	0.1251 (1)	1.1558 (1)	0.0608 (7)
Molecule *B*				
Co1	0.23319 (4)	0.13381 (3)	0.49156 (4)	0.0188 (2)
N1	0.2270 (3)	0.0258 (2)	0.4879 (3)	0.0255 (14)

N2	0.1463 (3)	0.1374 (2)	0.5639 (3)	0.0266 (15)
N3	0.3407 (3)	0.1303 (2)	0.6083 (3)	0.0248 (14)
N4	0.1307 (3)	0.1303 (2)	0.3690 (3)	0.0258 (15)
N5	0.2287 (3)	0.2417 (2)	0.4922 (3)	0.0273 (15)
N6	0.3272 (3)	0.1369 (2)	0.4272 (3)	0.0229 (14)
N7	0.2455 (3)	0.0375 (3)	0.6538 (3)	0.0343 (17)
N8	0.2202 (3)	0.2284 (3)	0.3279 (3)	0.0336 (17)
C1	0.2423 (4)	−0.0117 (3)	0.5800 (4)	0.0329 (21)
C2	0.1605 (4)	0.0793 (3)	0.6374 (4)	0.0388 (23)
C3	0.3293 (4)	0.0815 (3)	0.6847 (4)	0.0331 (21)
C4	0.1373 (4)	0.0038 (3)	0.4151 (4)	0.0333 (19)
C5	0.1491 (4)	0.2129 (3)	0.6009 (4)	0.0377 (22)
C6	0.4250 (3)	0.1106 (3)	0.5841 (3)	0.0297 (20)
C7	0.1241 (4)	0.0540 (3)	0.3342 (4)	0.0316 (20)
C8	0.4201 (3)	0.1538 (3)	0.4985 (4)	0.0294 (19)
C9	0.1499 (4)	0.2645 (3)	0.5253 (4)	0.0384 (23)
C10	0.3043 (4)	0.1855 (3)	0.3428 (4)	0.0326 (20)
C11	0.1357 (4)	0.1864 (3)	0.2985 (4)	0.0347 (22)
C12	0.2261 (4)	0.2787 (3)	0.4021 (4)	0.0384 (21)
Cl1	0.3663 (1)	−0.02676 (9)	0.3837 (1)	0.0462 (6)
Cl2	−0.05614 (9)	0.13642 (9)	0.4175 (1)	0.0430 (5)
Cl3	0.4112 (1)	0.29215 (8)	0.6744 (1)	0.0477 (6)
O1	0.5567 (4)	0.4069 (3)	0.8112 (4)	0.0810 (24)
O2	0.5244 (4)	0.0928 (4)	0.3481 (4)	0.0920 (29)

Table 2. *Geometric parameters* (Å, °)

(I)

Co1—N2	1.977 (8)	Cl1—O1	1.31 (2)
N1—C1	1.45 (1)	Cl1—O2	1.57 (2)
N2—C1	1.52 (1)	S1—S2	2.12 (1)
N2—C2	1.48 (2)	S1—O3	1.36 (1)
Co1—N2—C2	106.4 (7)	N1—C1—N2	112 (1)
Co1—N2—C1	116.9 (8)	O1—Cl1—O2	119 (1)
C1—N2—C2	113.2 (9)	S2—S1—O3	107.1 (8)

(II)

	A	*B*
Co1—N1	1.972 (5)	1.976 (4)
Co1—N2	1.975 (4)	1.979 (5)
Co1—N3	1.976 (5)	1.967 (3)
Co1—N4	1.986 (5)	1.986 (3)
Co1—N5	1.965 (5)	1.973 (4)
Co1—N6	1.973 (4)	1.980 (5)
N1—C1	1.505 (6)	1.506 (7)
N1—C4	1.481 (8)	1.491 (6)
N2—C2	1.533 (6)	1.503 (7)
N2—C5	1.505 (8)	1.485 (7)
N3—C3	1.512 (6)	1.519 (7)
N3—C6	1.492 (7)	1.486 (7)
N4—C7	1.502 (8)	1.483 (7)
N4—C11	1.505 (7)	1.503 (7)
N5—C9	1.478 (7)	1.501 (8)
N5—C12	1.528 (6)	1.516 (8)
N6—C8	1.504 (9)	1.492 (5)
N6—C10	1.535 (7)	1.502 (7)
N7—C1	1.460 (8)	1.425 (7)
N7—C2	1.415 (8)	1.444 (7)
N7—C3	1.436 (9)	1.441 (7)
N8—C10	1.401 (9)	1.448 (7)
N8—C11	1.452 (9)	1.429 (7)
N8—C12	1.450 (9)	1.434 (8)
C4—C7	1.505 (7)	1.492 (8)
C5—C9	1.508 (7)	1.489 (9)
C6—C8	1.506 (7)	1.502 (8)
N5—Co1—N6	90.3 (2)	90.3 (2)
N4—Co1—N6	90.6 (2)	90.2 (2)
N4—Co1—N5	91.5 (2)	91.1 (2)
N3—Co1—N6	86.8 (2)	86.0 (2)
N3—Co1—N5	91.9 (2)	92.7 (2)
N3—Co1—N4	175.7 (2)	174.6 (2)
N2—Co1—N6	175.6 (2)	174.8 (2)
N2—Co1—N5	86.4 (2)	86.2 (2)
N2—Co1—N4	92.4 (2)	93.8 (2)
N2—Co1—N3	90.4 (2)	90.2 (2)
N1—Co1—N6	92.8 (2)	92.9 (2)
N1—Co1—N5	175.6 (2)	175.6 (2)
N1—Co1—N4	85.3 (2)	85.8 (2)
N1—Co1—N3	91.4 (2)	90.6 (2)
N1—Co1—N2	90.7 (2)	90.9 (2)
Co1—N1—C4	109.2 (3)	108.3 (3)
Co1—N1—C1	115.6 (3)	115.9 (3)
C1—N1—C4	112.4 (4)	112.7 (4)
Co1—N2—C5	107.0 (3)	107.5 (3)
Co1—N2—C2	115.2 (3)	115.6 (4)
C2—N2—C5	113.3 (5)	113.4 (4)
Co1—N3—C6	107.7 (4)	107.8 (3)
Co1—N3—C3	116.2 (4)	115.9 (3)
C3—N3—C6	112.0 (4)	112.0 (4)
Co1—N4—C11	115.6 (4)	115.8 (3)
Co1—N4—C7	107.0 (4)	107.7 (3)
C7—N4—C11	113.4 (5)	113.6 (4)
Co1—N5—C12	116.0 (4)	115.6 (3)
Co1—N5—C9	108.1 (3)	108.2 (3)
C9—N5—C12	111.1 (4)	113.3 (4)
Co1—N6—C10	115.2 (4)	116.1 (3)
Co1—N6—C8	106.4 (4)	107.8 (3)
C8—N6—C10	112.9 (4)	113.0 (4)
C2—N7—C3	116.9 (5)	113.4 (5)
C1—N7—C3	112.4 (5)	113.8 (5)
C1—N7—C2	113.1 (5)	113.9 (4)
C11—N8—C12	112.7 (5)	113.9 (5)
C10—N8—C12	114.9 (5)	113.9 (5)
C10—N8—C11	114.9 (5)	113.9 (5)
N1—C1—N7	113.2 (4)	113.4 (4)
N2—C2—N7	112.9 (5)	113.6 (5)
N3—C3—N7	112.6 (5)	113.0 (4)
N1—C4—C7	105.3 (4)	106.5 (4)
N2—C5—C9	106.1 (5)	107.7 (5)
N3—C6—C8	106.4 (4)	106.8 (4)
N4—C7—C4	106.3 (5)	108.0 (4)
N6—C8—C6	106.6 (5)	106.4 (4)
N5—C9—C5	106.4 (4)	107.1 (5)
N6—C10—N8	113.1 (5)	113.2 (4)
N4—C11—N8	112.8 (5)	113.4 (4)
N5—C12—N8	112.4 (5)	113.5 (4)

Table 3. *Hydrogen-bond distances* (Å) *and angles* (°) *in compound* (II) *involving* Cl *atoms and* N—H *groups or water molecules* O1 *and* O2

	N···Cl	H···Cl	N—H···Cl
Molecule *A*			
N1···Cl1	3.059 (6)	1.89 (7)	170 (6)
N6···Cl1	3.255 (7)	2.32 (8)	142 (6)
N2···Cl2	3.194 (6)	2.23 (6)	169 (5)
N4···Cl2	3.111 (6)	1.99 (7)	160 (5)
N3···Cl3	3.160 (6)	2.10 (9)	155 (6)
N5···Cl3	3.271 (6)	2.30 (10)	163 (7)
Molecule *B*			
N1···Cl1	3.180 (6)	2.39 (6)	170 (5)
N6···Cl1	3.162 (6)	2.34 (5)	165 (5)
N2···Cl2	3.127 (6)	2.260 (5)	172 (5)
N4···Cl2	3.155 (7)	2.42 (6)	173 (5)
N3···Cl3	3.191 (7)	2.36 (6)	157 (5)
N5···Cl3	3.321 (7)	2.64 (4)	172 (5)
	O···Cl	H···Cl	O—H···Cl
Molecule *A*			
O1···Cl1	3.619 (8)	2.88 (9)	163 (9)
O6···Cl3^{i}	3.176 (7)	2.99 (6)	91 (2)
Molecule *B*			
O6···Cl3	3.241 (8)	2.44 (8)	171 (8)
O2···Cl1	3.415 (8)	2.50 (14)	162 (10)

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

The poorly soluble complex (I) was precipitated by adding $Na_2S_2O_3$ and $NaClO_4$ (Rampi Scandola, Scandola & Indelli,

1985) to a solution obtained by treating $Co(en)_3Cl_3$ with CH_2O and NH_3 (Creaser *et al.*, 1982). The data for the cell determination revealed no evidence of twinning. The data were corrected for Lorentz and polarization effects. All non-H atoms were located through Patterson and Fourier techniques. Three H atoms were located by successive least-squares refinements associated with ΔF calculations and the remaining two, H11 and H12, were introduced in idealized positions. An empirical correction for absorption effects was applied (*ABSORB*; Ugozzoli, 1987, following Walker & Stuart, 1983) after the last isotropic refinement ($T_{\min}$ = 0.8998, $T_{\max}$ = 1.1708). Anisotropic thermal parameters were refined for all non-H atoms; H atoms were refined isotropically and held in fixed positions during the last cycles of refinement. Refinements performed with independent data collected using two further different crystals gave comparable results.

Complex (II) was prepared by treating (I) with concentrated HCl and an excess of $NaNO_3$; the resulting $Co(sep)(NO_3)_3$ was dissolved and then eluted on an anionic Cl^- resin giving a solution from which crystals separated after slow evaporation. An empirical absorption correction was performed using three standard reflections. The data were corrected for Lorentz and polarization effects. Patterson interactions revealed the presence of two independent Co atoms; successive least-squares refinements and ΔF calculations enabled the remaining non-H and H atoms to be located. An empirical absorption correction (Walker & Stuart, 1983; Ugozzoli, 1987) was applied after the last isotropic refinement ($T_{\min}$ = 0.8986, $T_{\max}$ = 1.0654). Thermal parameters were refined anisotropically for non-H atoms and isotropically for H atoms; the H atoms were held fixed during the final least-squares cycles.

*SHELX*86 (Sheldrick, 1986) and *SHELX*76 (Sheldrick, 1976) were used for structure solution and refinement and *PARST* (Nardelli, 1983) for geometric calculations. *ORTEP* (Johnson, 1965) and *PLUTO* (Motherwell & Clegg, 1976) were used to produce the drawings. Extensive use was made of the Cambridge Structural Database (Allen, Kennard & Taylor, 1983). Calculations were performed on ENCORE-GOULD-POWERNODE 6040 and ENCORE 91 computers of the Centro di Studio per la Strutturistica Diffrattometrica 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 55841 (40 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL1026]

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Structure of Di-μ-chloro-bis[bis(triphenylphosphine)palladium(II)] Bis(tetrafluoroborate) Acetone Solvate Dihydrate

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Abstract

The structure consists of a palladium dimer with bridging Cl atoms, two tetrafluoroborate anions and two water molecules and one acetone molecule. Each Pd atom in the dimer is surrounded by two Cl and two P atoms, forming a slightly distorted *cis* square-planar configuration.

Comment

Recently we have been using bridged dimers of Pd^{II} as catalysts in homogeneously catalyzed alkene hydration reactions (Ganguly & Roundhill, 1991). During the course of this research we became interested in certain structural features of these bridged dimers such as their intermetallic distances and their dihedral angles between the coordination planes of the Pd centers. Since there have been relatively few structural studies of chloro-bridged dimers of Pd^{II}, we have solved the structure of the title compound.