

## Data collection

Rigaku AFC-5R diffractometer  
 $\omega$ - $2\theta$  scans  
 Absorption correction: refined from  $\Delta F$  (Walker & Stuart, 1983)  
 $T_{\min} = 0.817$ ,  $T_{\max} = 0.948$   
 11 132 measured reflections  
 11 132 independent reflections

## Refinement

Refinement on  $F$   
 $R = 0.055$   
 $wR = 0.065$   
 $S = 1.000$   
 6967 reflections  
 683 parameters  
 H-atom parameters not refined  
 $w = 1/[\sigma^2(F_o) + 0.00164|F_o|^2]$

$(\Delta/\sigma)_{\max} = 0.005$   
 $\Delta\rho_{\max} = 0.46 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.63 \text{ e } \text{\AA}^{-3}$   
 Extinction correction: none  
 Scattering factors from *International Tables for Crystallography* (Vol. C)  
 Absolute structure: Flack (1983)  
 Flack parameter = 0.01 (2)

Table 1. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

ZnA—O1A	2.020 (6)	ZnB—O1B	2.030 (6)
ZnA—O2A	2.245 (6)	ZnB—O2B	2.232 (6)
ZnA—O4A	2.015 (6)	ZnB—O4B	2.036 (6)
ZnA—N1A	2.036 (7)	ZnB—N1B	2.027 (7)
ZnA—N2A	2.389 (7)	ZnB—N2B	2.380 (7)
ZnA—N3A	2.070 (7)	ZnB—N3B	2.067 (7)
O1A—ZnA—O2A	93.7 (2)	O1B—ZnB—O2B	93.1 (2)
O1A—ZnA—O4A	101.2 (3)	O1B—ZnB—O4B	101.5 (3)
O1A—ZnA—N1A	84.5 (3)	O1B—ZnB—N1B	84.9 (3)
O1A—ZnA—N2A	155.8 (2)	O1B—ZnB—N2B	155.9 (2)
O1A—ZnA—N3A	109.1 (2)	O1B—ZnB—N3B	109.1 (2)
O2A—ZnA—O4A	160.9 (3)	O2B—ZnB—O4B	161.1 (3)
O2A—ZnA—N1A	92.2 (3)	O2B—ZnB—N1B	92.4 (3)
O2A—ZnA—N2A	71.1 (2)	O2B—ZnB—N2B	70.8 (2)
O2A—ZnA—N3A	84.6 (2)	O2B—ZnB—N3B	84.0 (2)
O4A—ZnA—N1A	100.8 (3)	O4B—ZnB—N1B	100.7 (3)
O4A—ZnA—N2A	98.1 (3)	O4B—ZnB—N2B	98.4 (3)
O4A—ZnA—N3A	79.4 (3)	O4B—ZnB—N3B	79.9 (3)
N1A—ZnA—N2A	77.6 (3)	N1B—ZnB—N2B	78.2 (3)
N1A—ZnA—N3A	166.2 (3)	N1B—ZnB—N3B	165.7 (3)
N2A—ZnA—N3A	88.7 (3)	N2B—ZnB—N3B	87.6 (3)

Table 2. Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ )

D—H...A	D—H	H...A	D...A	D—H...A
O2A—H1...O1B	0.80	1.89	2.562 (8)	141
O2B—H2...O1A	0.86	1.88	2.593 (8)	144

Data collection: *MSCIAFC Diffractometer Control Software* (Molecular Structure Corporation, 1991). Cell refinement: *MSCIAFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1992). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990) and *DIRDIF92* (Beurskens *et al.*, 1992). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA1049). Services for accessing these data are described at the back of the journal.

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## Oxonium $\Lambda$ -{*N,N'*-bis[2(*S*)-pyrrolidinylmethyl]ethane-1,2-diamine}-*cis*- $\alpha$ -dichloro-cobalt(III) dichloride dihydrate

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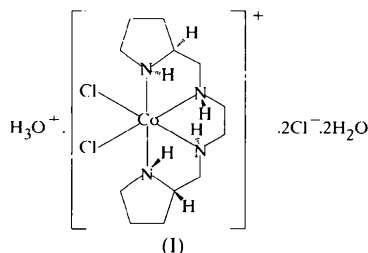
## Abstract

In the complex cation of the title compound, (H<sub>3</sub>O)[CoCl<sub>2</sub>(C<sub>12</sub>H<sub>26</sub>N<sub>4</sub>)]Cl<sub>2</sub>·2H<sub>2</sub>O, the two Cl ligands are in *cis* positions. The complex has a twofold axis and is nearly octahedral. The chiral C atoms possess the *SS* configuration. This configuration may require the secondary amines on the ligand to have the *SS* configuration also, and may be responsible for the ring conformations.

## Comment

Stereospecific *N,N'*-bis[2(*S*)-pyrrolidinylmethyl]ethane-1,2-diamine tetrahydrochloride (*S*-epm-4HCl) has been

prepared in order to synthesize a stereoselective complex, reported as the *Λ-cis-α*-dichlorocobalt(III) complex (Jun & Liu, 1975). Another geometrical isomer, the *trans*-dichlorocobalt(III) complex, has been synthesized and identified by X-ray diffraction (Kim *et al.*, 1998). In the present study, the *S*-epm ligand and its *cis*-dichlorocobalt(III) complex were synthesized by a modified method; the resulting complex, (I), was identified by X-ray diffraction analysis.



The X-ray structure analysis of (I) reveals that the two Cl ligands are in *cis* positions and that all the chiral atoms of the *S*-epm ligand have *SS* configurations. The molecule possesses a twofold axis, which is the line connecting the Co atom and the midpoint of C6—C6' [symmetry code: (i)  $y, x, -z$ ]. Atom O2W, on the twofold axis close to the Cl ligands, may be the O atom of H<sub>3</sub>O<sup>+</sup>, giving an oxidation state of +3 for cobalt, since there are also two Cl<sup>-</sup> counter-anions in the formula unit.

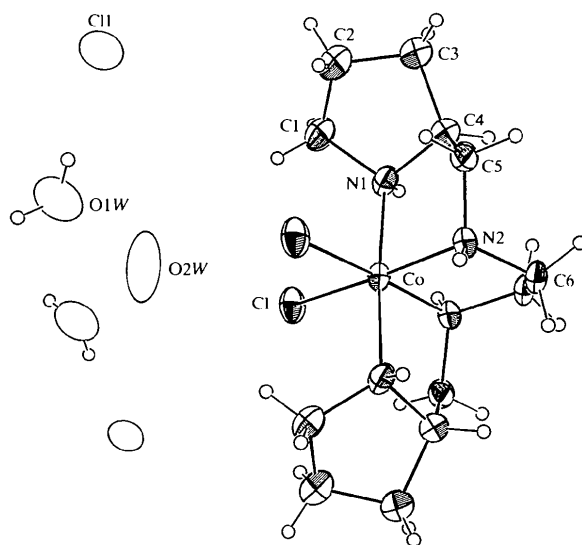


Fig. 1. The molecular structure of the title complex, showing 40% probability displacement ellipsoids.

The coordination geometry about the Co atom is almost octahedral, comprising four N atoms of the *S*-epm ligand and two Cl ligands. The Co—Cl bond

length is 2.260(1) Å, which is similar to that in the *trans*-dichlorocobalt(III) complex of *S*-epm. The Cl—Co—Cl' bond angle is 93.18(7)°. The bond length between Co and N2 of the ethylenediamine fragment [1.959(3) Å] is somewhat shorter than that between Co and N1 of the pyrrolidiny moiety [1.988(4) Å]. A similar situation is found in the *trans*-dichlorocobalt(III) complex. The *SS* configuration of the chiral C atoms may require the secondary amines on the ligand to have the *SS* configuration also, and it may be responsible for the ring conformations, *i.e.* N1—C4—C5—N2, N2—C6—C6'—N2' and N1'—C4'—C5'—N2' with  $\delta$ ,  $\lambda$  and  $\delta$  conformations, respectively.

The O2W···O1W' distance is 2.415(6) Å, which implies hydrogen bonding.

## Experimental

*N*-Carbobenzoxy-*(S)*-proline was prepared from *(S)*-proline and carbobenzoxy chloride (cbz-Cl), according to the method of Corey *et al.* (1988). *N,N'*-Bis[carbobenzoxy-*(S)*-prolyl]ethane-1,2-diamine was then prepared by mixing cbz-*(S)*-proline and ethane-1,2-diamine in the presence of dicyclohexylcarbodiimide (DCC) as a coupling agent (Kitagawa *et al.*, 1975). Decarbobenzoylation and reduction of the ligand were performed according to the method of Jun & Liu (1975). The *cis*-dichlorocobalt(III) complex was then prepared, also according to the method of Jun & Liu (1975). Analysis for [CoCl<sub>2</sub>(C<sub>12</sub>H<sub>26</sub>N<sub>4</sub>)](H<sub>3</sub>O)Cl<sub>2</sub>·2H<sub>2</sub>O: calculated C 29.89, H 6.90, N 11.62%; found C 30.65, H 6.90, N 11.39%.

## Crystal data

(H<sub>3</sub>O)[CoCl<sub>2</sub>(C<sub>12</sub>H<sub>26</sub>N<sub>4</sub>)]·  
Cl<sub>2</sub>·2H<sub>2</sub>O  
*M<sub>r</sub>* = 482.16  
Tetragonal  
*P*4<sub>3</sub>2<sub>1</sub>2  
*a* = 12.852(2) Å  
*c* = 13.037(3) Å  
*V* = 2153.3(7) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 1.487 Mg m<sup>-3</sup>  
*D<sub>m</sub>* not measured

Mo *K*α radiation  
 $\lambda$  = 0.71073 Å  
Cell parameters from 25  
reflections  
 $\theta$  = 10–18°  
 $\mu$  = 1.311 mm<sup>-1</sup>  
*T* = 293(2) K  
Tetragonal rod  
0.4 × 0.4 × 0.3 mm  
Red-brown

## Data collection

CAD-4 TURBO diffractometer  
 $\omega/2\theta$  scan  
Absorption correction:  
empirical *via* four  $\psi$  scans  
(Fair, 1990)  
*T<sub>min</sub>* = 0.587, *T<sub>max</sub>* = 0.675  
2489 measured reflections  
1651 independent reflections

1562 reflections with  
*I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.052  
 $\theta_{\max}$  = 26.29°  
*h* = -16 → 0  
*k* = -16 → 0  
*l* = -16 → 0  
3 standard reflections  
frequency: 120 min  
intensity decay: 0.02%

## Refinement

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.042  
*wR*(*F*<sup>2</sup>) = 0.088

$\Delta\rho_{\max}$  = 0.340 e Å<sup>-3</sup>  
 $\Delta\rho_{\min}$  = -0.236 e Å<sup>-3</sup>  
Extinction correction: none

S = 1.084

1651 reflections

108 parameters

H atoms: see below

 $w = 1/[\sigma^2(F_o^2) + (0.0428P)^2]$ where  $P = (F_o^2 + 2F_c^2)/3$  $(\Delta/\sigma)_{\max} = 0.001$ 

Scattering factors from

*International Tables for Crystallography* (Vol. C)

Absolute structure:

Flack (1983)

Flack parameter = -0.03 (4)

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Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>)

$$U_{eq} = (1/3)\sum_i \sum_j U^{ij} a^i a^j \cdot a_j$$

	x	y	z	$U_{eq}$
Co	0.15360 (4)	0.15360 (4)	0	0.0273 (2)
Cl	0.15326 (11)	-0.01694 (9)	-0.04214 (10)	0.0430 (3)
N1	0.1274 (3)	0.1889 (3)	-0.1462 (3)	0.0357 (9)
C1	0.0346 (4)	0.1432 (5)	-0.2021 (4)	0.0510 (14)
C2	-0.0334 (5)	0.2343 (5)	-0.2286 (6)	0.075 (2)
C3	0.0399 (4)	0.3235 (4)	-0.2439 (5)	0.0609 (18)
C4	0.1237 (4)	0.3054 (4)	-0.1616 (4)	0.0437 (14)
C5	0.0990 (4)	0.3553 (4)	-0.0621 (4)	0.0408 (13)
N2	0.1596 (3)	0.3043 (3)	0.0218 (3)	0.0291 (8)
C6	0.2695 (3)	0.3394 (4)	0.0311 (4)	0.0342 (11)
Cl1	0.15839 (12)	0.62661 (10)	0.01879 (10)	0.0530 (4)
O1W	-0.2676 (4)	-0.0525 (3)	0.0208 (4)	0.0742 (13)
O2W	-0.0834 (4)	-0.0834 (4)	0	0.139 (4)

Table 2. Selected geometric parameters (Å, °)

Co—N2	1.959 (3)	C2—C3	1.497 (8)
Co—N1 <sup>i</sup>	1.988 (4)	C3—C4	1.538 (7)
Co—Cl	2.2596 (12)	C4—C5	1.482 (7)
N1—C4	1.511 (6)	C5—N2	1.495 (6)
N1—Cl	1.515 (6)	N2—C6	1.488 (5)
Cl—C2	1.501 (8)	C6—C6 <sup>i</sup>	1.508 (9)
N2—Co—N2 <sup>i</sup>	86.8 (2)	N1—Co—Cl <sup>i</sup>	93.95 (12)
N2—Co—N1 <sup>i</sup>	91.12 (16)	N2—Co—Cl	173.91 (12)
N2—Co—N1	85.44 (15)	N2 <sup>i</sup> —Co—Cl	90.26 (11)
N2 <sup>i</sup> —Co—N1	91.12 (16)	N1—Co—Cl	89.30 (12)
N1 <sup>i</sup> —Co—N1	175.3 (2)	Cl <sup>i</sup> —Co—Cl	93.18 (7)
N2—Co—Cl <sup>i</sup>	90.26 (11)		

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

All H atoms of the ligand were placed at calculated positions [ $U(H) = 1.2U_{eq}(\text{attached atom})$ ]. The H atoms of the water molecule were located from the difference Fourier map and refined at fixed positions with  $U(H) = 1.2U_{eq}(O)$ . The oxonium H atoms were not located in the difference Fourier map and were not placed. The final difference Fourier map contained two peaks with heights of  $0.34 \text{ e } \text{Å}^{-3}$  around O2W, but these were not appropriate positions for H atoms.

Data collection: *CAD-4 Software* (Enraf-Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997b). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997a). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1391). Services for accessing these data are described at the back of the journal.

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## A new polymorph of a carbonyliron complex from tetraphenylhexapentaene: bis( $\mu_3, \eta^2, \sigma^2$ -diphenylallenylidene)octa-carbonyltriiron

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### Abstract

The crystal structure of a new polymorphic form of octa-carbonyl- $1\kappa^3C, 2\kappa^3C, 3\kappa^2C$ -bis[ $\mu_3$ -3,3-diphenylallenylidene-1:2 $\kappa^2C^1$ :3(1,2- $\eta^2$ )]-triangulo-triiron(0)(3 Fe—Fe), [Fe<sub>3</sub>(C<sub>15</sub>H<sub>10</sub>)<sub>2</sub>(CO)<sub>8</sub>], has been determined. Reaction of tetraphenylhexapentaene with iron dodecacarbonyl leads to the title complex composed of an Fe<sub>3</sub>(CO)<sub>8</sub> central core bridging two C<sub>3</sub>Ph<sub>2</sub> ligands. The molecule adopts a synclinal conformation of the carbonyl groups in two Fe(CO)<sub>3</sub> groups of the Fe<sub>3</sub> triangle, in contrast to the synperiplanar conformation observed previously.

### Comment

The title compound was first obtained in a pure crystalline form by Zimniak & Jasiobędzki (1975). The same compound was synthesized later according to a sim-