

Diacetato(5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-1,8-diene)cobalt(III) triiodide

Shu-Sheng Zhang, Shu-Yan Niu, Gui-Fen Jie, Xue-Mei Li and Kui Jiao*

College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, 266042 Qingdao, Shandong, People's Republic of China

Correspondence e-mail: zhangshush@public.qd.sd.cn

Key indicators

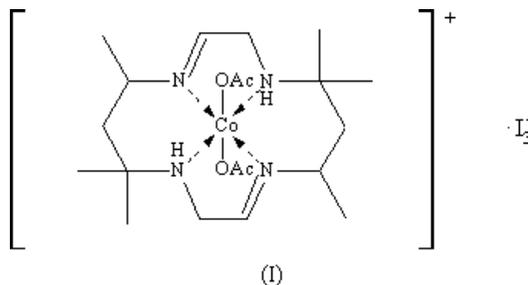
Single-crystal X-ray study
 T = 293 K
 Mean $\sigma(C-C)$ = 0.004 Å
 R factor = 0.028
 wR factor = 0.071
 Data-to-parameter ratio = 18.9

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

In the title compound, $[Co(C_2H_3O_2)_2(C_{16}H_{32}N_4)]I_3$, (I), the Co atom is six-coordinated by four N atoms from the tetradentate cyclotetradecadiene ligand and two O atoms from two acetate ligands. The CoN_4O_2 coordination is octahedral. There are two independent centrosymmetric cations, and the anion lies in a general position.

Comment

There is significant interest in the syntheses and properties of polyazamacrocycles bearing pendant arms. Most such functionalized macrocycles are prepared by elaborate multi-step procedures, with synthesis of partially functionalized macrocycles being more difficult than that of fully functionalized ones. Interest in these molecules and their transition metal complexes has focused on application to catalysis (Collin & Sauvage, 1987), ion selectivity and their use as radio-immunotherapy agents (Cox *et al.*, 1989). In our systematic research on macrocycles and transition metals, we have obtained the title compound, (I).



Compound (I) contains two crystallographically independent $[Co(OAc)_2L]^+$ cations ($L = C_{16}H_{32}N_4$), *A* and *B*, occupying centres of symmetry, and an I_3^- anion in a general position (Fig. 1). The Co atom is six-coordinated by four N atoms from the centrosymmetric 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraaza-1,8-cyclotetradecadiene ligand and two O atoms from two acetate ligands. This CoN_4O_2 coordination geometry is octahedral; the I_3^- anion is outside the coordination sphere, balancing the charge. The four N atoms and the Co atom are coplanar, while the line through the two O atoms is almost perpendicular to the plane, with O—Co—N angles in the ranges 85.63 (1)–94.37 (10) and 84.92 (9)–95.08 (9)° in *A* and *B*, respectively. The Co1—N1 and Co2—N3 bond lengths are 1.950 (2) and 1.935 (2) Å (Table 1), respectively, comparable to the mean Co—N bond length for Schiff base ligands (1.943 Å; Allen *et al.*, 1987). There is a strong intramolecular N—H...O hydrogen bond in each of the cations *A* and *B* (Table 2).

Experimental

Anhydrous ethylenediamine (13.4 ml) and anhydrous ethanol (10 ml) were mixed in a round-bottomed flask, which was cooled in ice, then hydriodic acid (36.3 ml) and acetone (30 ml) were added dropwise. The resulting solution was allowed to stand overnight under these conditions. The resulting solid was separated by filtration under reduced pressure and washed with acetone, and white crystals of the macrocyclic ligand were obtained. This macrocyclic ligand (0.01 mol) and cobalt acetate (0.01 mol) were dissolved completely in anhydrous ethanol (40 ml). After refluxing for 1 h, the mixture was filtered. The filtrate was heated until a solid began to form and was then cooled in ice-water for several hours. The solid product was collected by filtration and recrystallized from anhydrous ethanol, and single crystals suitable for X-ray crystallographic analysis were obtained.

Crystal data

$[\text{Co}(\text{C}_2\text{H}_3\text{O}_2)_2(\text{C}_{16}\text{H}_{32}\text{N}_4)]_3$	$D_x = 1.938 \text{ Mg m}^{-3}$
$M_r = 838.17$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 3657 reflections
$a = 14.807(3) \text{ \AA}$	$\theta = 2.3\text{--}26.2^\circ$
$b = 9.7061(18) \text{ \AA}$	$\mu = 3.85 \text{ mm}^{-1}$
$c = 20.218(4) \text{ \AA}$	$T = 293(2) \text{ K}$
$\beta = 98.589(3)^\circ$	Prism, purple
$V = 2873.2(9) \text{ \AA}^3$	$0.34 \times 0.17 \times 0.07 \text{ mm}$
$Z = 4$	

Data collection

Siemens SMART CCD area detector diffractometer	5656 independent reflections
ω scans	4693 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$R_{\text{int}} = 0.018$
$T_{\text{min}} = 0.351$, $T_{\text{max}} = 0.767$	$\theta_{\text{max}} = 26.2^\circ$
15 682 measured reflections	$h = -18 \rightarrow 12$
	$k = -9 \rightarrow 11$
	$l = -24 \rightarrow 24$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0344P)^2 + 1.6532P]$
$R[F^2 > 2\sigma(F^2)] = 0.028$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.071$	$(\Delta/\sigma)_{\text{max}} = 0.002$
$S = 1.03$	$\Delta\rho_{\text{max}} = 0.66 \text{ e \AA}^{-3}$
5656 reflections	$\Delta\rho_{\text{min}} = -0.40 \text{ e \AA}^{-3}$
300 parameters	
H-atom parameters constrained	

Table 1

Selected geometric parameters (\AA , $^\circ$).

I1—I2	2.9364 (6)	Co1—N2	1.970 (2)
I2—I3	2.9012 (6)	Co2—O2	1.920 (2)
Co1—O1	1.9095 (19)	Co2—N3	1.935 (2)
Co1—N1	1.950 (2)	Co2—N4	1.978 (2)
O1—Co1—N1	92.57 (9)	O2—Co2—N4	86.59 (9)
O1—Co1—N2	86.70 (9)	N1—Co1—N2	94.37 (10)
O2—Co2—N3	91.64 (9)	N3—Co2—N4	95.08 (9)

Table 2

Hydrogen-bonding geometry (\AA , $^\circ$).

$D\cdots H\cdots A$	$D\cdots H$	$H\cdots A$	$D\cdots A$	$D\cdots H\cdots A$
$\text{N2}\cdots\text{H2}\cdots\text{O3}^i$	0.91	1.85	2.716 (3)	159
$\text{N4}\cdots\text{H4}\cdots\text{O4}^{ii}$	0.91	1.85	2.719 (3)	158

Symmetry codes: (i) $3-x, 1-y, 1-z$; (ii) $2-x, -y, 1-z$.

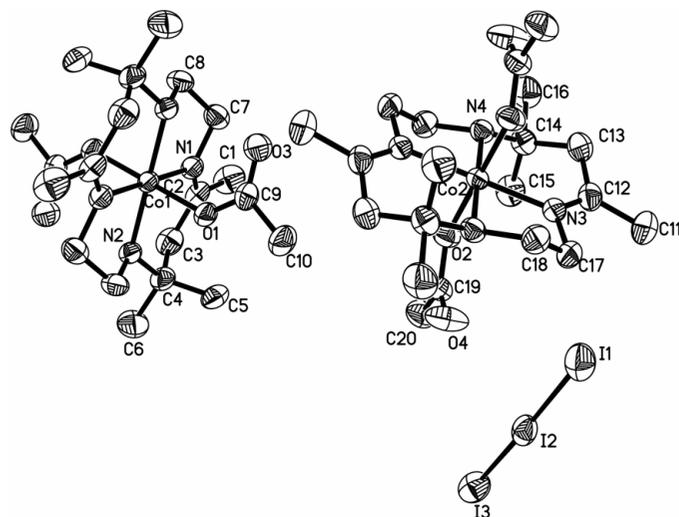


Figure 1

View of (I), showing 50% probability displacement ellipsoids and the atom numbering. H atoms have been omitted for clarity.

All H atoms were positioned geometrically and treated as riding, with C—H and N—H distances of 0.96–0.97 and 0.91 \AA , respectively, and with $U_{\text{iso}}(\text{H}) = 1.2$ or 1.5 (for methyl H atoms) $U_{\text{eq}}(\text{C}, \text{N})$.

Data collection: SMART (Siemens, 1996); cell refinement: SAINT (Siemens, 1996); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Sheldrick, 1997); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL, PARST (Nardelli, 1995) and PLATON (Spek, 2003).

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