Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Dichloro{methyl 4-[(1,4,7,10-tetraazacyclododec-1-yl)methyl]benzoate}cobalt(III) methylsulfate

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Key indicators

Single-crystal X-ray study
T = 103 K
Mean σ(C–C) = 0.003 Å
R factor = 0.034
wR factor = 0.098
Data-to-parameter ratio = 19.0

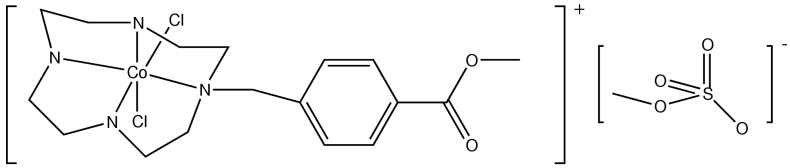
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 29 August 2003
Accepted 10 September 2003
Online 18 September 2003

The title compound, $[CoCl_2(C_{17}H_{28}N_4O_2)](CH_3O_4S)$, is formed from the esterification of the parent benzoic acid complex in refluxing methanol/sulfuric acid. The coordination around cobalt is distorted octahedral, with *cis* chloride ligands.

Comment

Artificial hydrolases based on main-group, lanthanide or transition metal complexes have been developed as non-enzymatic alternatives for the hydrolysis of the phosphodiester bonds in DNA and RNA (Chin, 1991; Kim & Suh, 1994; Williams & Chin, 1996; Williams *et al.*, 1999). It has been suggested that such catalysts may have a significant future impact in gene-cloning, gene-mapping, or therapeutics (Bashkin *et al.*, 1995; Komiyama & Sumaoka, 1996; Hegg & Burstyn, 1998; Komiyama *et al.*, 1999). Cobalt(III), with its high charge density, is a potent candidate for use in hydrolysing phosphodiesters; for example, recently published values for DNA cleavage show that Co^{III} complexes have rate constants of around $2 \times 10^4\ s^{-1}$, which is about three times higher than that for europium(III) salts (Hettich & Schneider, 1997). Although Co^{III} is not stable by itself, in aqueous solutions it can be stabilized by coordinating with donor atoms (usually N) which make strong contributions to the ligand field. These Co^{III}–chelator complexes have been used for mechanistic studies of phosphodiester cleavage for both its efficient hydrolysis rates and kinetic inertness. That is, the complexes promote fast hydrolysis of the phosphodiester bond but are kinetically 'slow' in release of the hydrolysed phosphate (Douglas *et al.*, 1983). The kinetic inertness of the Co^{III} may be overcome (*i.e.* at elevated temperatures), but this property could be an added advantage for sequence-specific disruption of gene function. It has previously been shown that Co^{III} complexes stabilized with ammonium-functionalized cyclen ligands efficiently hydrolyse phosphodiester bonds (Hettich & Schneider, 1997).



(I)

The goal of our research is the design of a simple and effective cobalt(III)-based hydrolysis catalyst, containing a pendant functional group, which would provide a tether for a

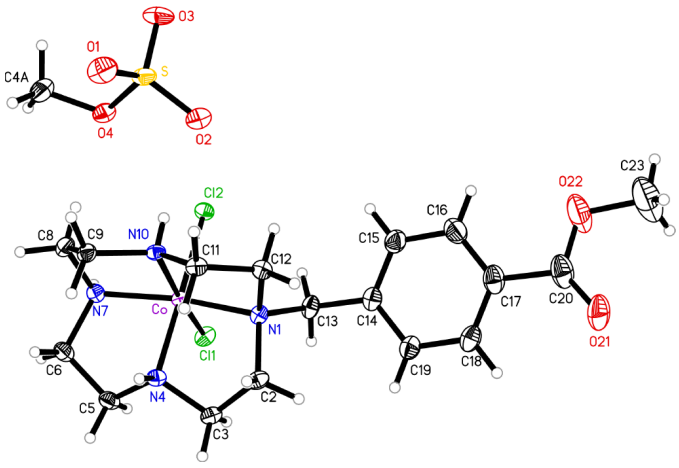


Figure 1
View of (I), showing the labeling of the non-H atoms. Displacement ellipsoids are shown at the 50% probability level.

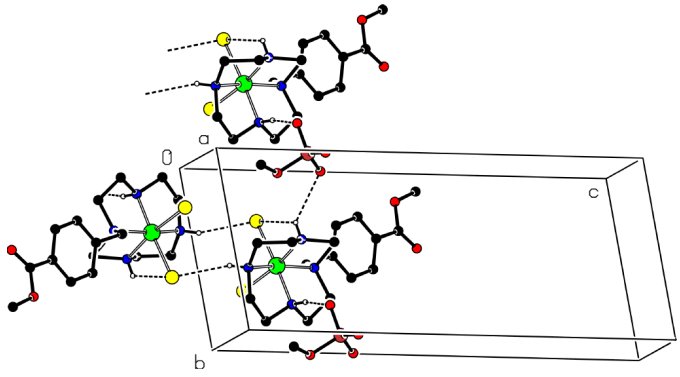


Figure 2
View of a portion of the hydrogen bonding (shown as dashed lines) in the crystal structure of (I). Color codes: green Co, yellow Cl, red O, blue N, black C.

suitable support, or further elaboration with soluble units, e.g an oligonucleotide for site-directed cleavage of complementary single-strand DNA or RNA. We synthesized the monofunctionalized cyclen ligand, 4-[1,4,7,10-tetraazacyclotetradec-1-yl]methylbenzoic acid (cycmba) which contains a carboxylic acid moiety, through which further elaboration may be realised. In the course of our studies, we discovered that the cobalt(III) derivative of cycmba undergoes esterification in refluxing, acidified methanol to give the corresponding benzoic acid methyl ester complex (I). Surprisingly, the complex does not crystallize from solution with chloride as the counter-ion, but as the methylsulfate salt. Presumably, this anion arises from mono-esterification of sulfuric acid with methanol (Rodd, 1951).

The geometry around the central cobalt ion is best described as distorted octahedral, with the chloride ions coordinated in a *cis* fashion. The N7—Co—N1, N4—Co—Cl2 and N10—Co—Cl1 angles are 163.90 (7), 177.16 (5)° and 171.96 (5)°, respectively. Theses values are similar to those reported for the related benzoic acid complex dichloro(3-[1,4,7,10-tetraazacyclotetradec-1-yl]methylbenzoic acid)-cobalt(III) chloride [164.89 (11), 172.75 (8)° and 176.69 (9)°; Edwards *et al.*, 1998]. All Co—N and Co—Cl distances are similar to those in the benzoic acid complex, the benzyl-substituted nitrogen–cobalt bond, N1—Co, being the longest [2.0453 (16) Å] and the bond *trans* to N1 (N7—Co) the next longest [1.9868 (17) Å]. All bond lengths and angles within the methylbenzoic acid methyl ester substituent are within expected ranges. While there is no evidence for π-stacking of aromatic rings in the structure, these rings are parallel, with each ring sitting above the carbonyl substituent of an adjacent molecule.

In the crystal structure, pairs of cations form centrosymmetric dimers through N—H···Cl interactions. These dimers are linked, in turn, into chains along the *b* axis by N—H···O hydrogen bonds between cations and anions (see Table 1 and Fig. 2).

Experimental

All reagents and solvents were purchased from commercial sources and used as received. A 50 ml flask was charged with dichloro(4-[1,4,7,10-tetraazacyclotetradec-1-yl]methyl benzoic acid)cobalt(III) chloride (0.114 g, 0.242 mmol) (Knight *et al.*, 2003) and methanol (20 ml). Sulfuric acid (*ca.* 0.2 ml) was added dropwise, and the mixture was refluxed for 4 h. The deep blue–purple solution was allowed to cool to room temperature. After 12 h, purple crystals of (I) were collected by filtration, washed with ether and dried in air. After cooling the filtrate for 5 d at 255 K, a second crop of crystals was obtained. Yield 0.098 g, 72%.

Crystal data

$[Co(C_{17}H_{28}N_4O_2)Cl_2]CH_3O_4S$
M_r = 561.37
Triclinic, $P\overline{1}$
a = 8.0250 (5) Å
b = 8.2310 (5) Å
c = 18.7105 (11) Å
α = 79.067 (1)°
β = 80.884 (1)°
γ = 83.636 (1)°
V = 1193.97 (13) Å^3
Z = 2
D_x = 1.561 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8842 reflections
θ = 2.2–29.0°
μ = 1.07 mm^{-1}
T = 103 (2) K
Prism, purple
0.61 × 0.20 × 0.18 mm

Data collection

Bruker SMART 1000 CCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
T_{min} = 0.695, T_{max} = 0.824
12393 measured reflections
5700 independent reflections
5017 reflections with $I > 2\sigma(I)$
R_{int} = 0.025
θ_{max} = 29.0°
$h = -10 \rightarrow 9$
$k = -11 \rightarrow 10$
$l = -24 \rightarrow 25$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.098
S = 0.96
5700 reflections
300 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0608P)^2 + 0.977P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.89 e Å^{-3}
$\Delta\rho_{min}$ = −0.50 e Å^{-3}

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N4—H4···O3^{i}	0.88 (3)	1.97 (2)	2.836 (2)	166 (2)
N10—H10···O2	0.81 (2)	2.49 (3)	3.111 (2)	134 (2)
N7—H7···Cl2^{ii}	0.86 (3)	2.59 (3)	3.3687 (17)	151 (2)

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

All H atoms bonded to C atoms were placed in calculated positions, with C—H distances ranging from 0.95 to 0.99 Å, and included in the refinement in the riding-model approximation, with U_{iso} = 1.2 (1.5 for methyl) times U_{eq} of the parent atom. H atoms bonded to N atoms were refined independently with isotropic displacement parameters.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2000) and *XPREP* (Bruker, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2000); software used to prepare material for publication: *SHELXTL*.

Crystallographic studies were supported in part by the Office of Naval Research (ONR) and the Naval Research Laboratory (NRL).

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