

(μ -*C-meso*-5,5,7,12,12,14-Hexamethyl-1,4,8,11-tetraazacyclotetradecane-*N*-acetato-1 κ^5 N,N',N'',N''',O:-2 κ O')tetrachloro-1 κ Cl,2 κ^3 Cl-cobalt(III)zinc(II)

Kaliyamoorthy Panneerselvam,^a Tian-Huey Lu,^{a*} Ta-Yung Chi,^b Shu-Fang Tung^c and Chung-Sun Chung^b

^aDepartment of Physics, National Tsing Hua University, Hsinchu, Taiwan 300, Republic of China, ^bDepartment of Chemistry, National Tsing Hua University, Hsinchu, Taiwan 300, Republic of China, and ^cSouthern Instrument Center, National Cheng Kung University, Tainan, Taiwan 701, Republic of China
Correspondence e-mail: thlu@phys.nthu.edu.tw

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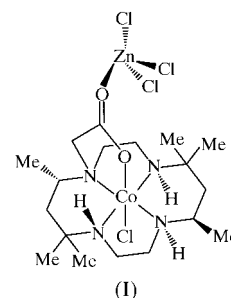
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The crystal structure of the title compound, [CoCl(C₁₈H₃₇N₄O₂){ZnCl₃}], has been determined by X-ray diffraction. *C-meso*-5,5,7,12,12,14-Hexamethyl-1,4,8,11-tetraazacyclotetradecane-*N*-acetate acts as a bridging ligand to coordinate with Co^{III} and Zn^{II} ions. The Co^{III} ion is six-coordinate in a nearly octahedral environment provided by one Cl atom, four N atoms of the bridging ligand, and one O atom. The Zn^{II} ion is four-coordinate in a distorted tetrahedral environment completed by three Cl atoms and an O atom of the bridging ligand.

Comment

Metal complexes of polyaza macrocycles with additional pendant functional groups have attracted interest owing to their diverse applications in fundamental and applied science (Bernhardt & Lawrance, 1990; Kaden, 1993). The coordination behaviour of Ni^{II} and Cu^{II} ions with *C-meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane-*N*-acetate has been studied chemically and crystallographically (Panneerselvam *et al.*, 1998; Xu *et al.*, 1988). In this study, we present the crystal structure of the title compound, (I), to expand the knowledge of this area.

The X-ray structure shows that an asymmetric unit contains two independent molecules (denoted as molecules *A* and *B*). The two molecules have almost identical bond lengths and angles. In both molecules, the *C-meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane-*N*-acetic acid acts as a bridging ligand between the Co^{III} and Zn^{II} ions. The Co^{III} ion is six-coordinate in a nearly octahedral environment provided



by one Cl atom, four N atoms of the bridging ligand, and one O atom. The macrocyclic moiety adopts a conformation in which the two six-membered rings are in a chair form and the two five-membered rings are in a *gauche* form. This combination of these four chelate rings has been found in several similar crystal structures (Clay *et al.*, 1979; Panneerselvam *et al.*, 1998; Tasker & Sklar, 1975). The Co—N distances [1.981 (4)–2.020 (5) Å] are longer than those in the *trans*-dichloro(1,4,8,11-tetraazacyclotetradecane)cobalt(III) cation [1.978 (4) Å; Sosa-Torres & Toscano, 1997] and the [1,4-*N,N'*-bis(carboxymethyl)-1,4,8,11-tetraazacyclotetradecane]cobalt(III) cation [1.969 (4) Å; Ware *et al.*, 1996]. The Co—O distances [1.885 (4) and 1.909 (4) Å] agree with the corresponding values found in the [1,4-*N,N'*-bis(carboxymethyl)-1,4,8,11-tetraazacyclotetradecane]cobalt(III) cation [1.969 (4) Å; Ware *et al.*, 1996]. The Co—Cl distances [2.219 (2) Å for molecule *A* and 2.237 (2) Å for molecule *B*] are shorter than those found in Co^{III} complexes such as chloro(1,5,8,11,14-pentaazacyclohexadecane)cobalt(III) diperchlorate [2.242 (9) Å; Bombieri *et al.*, 1982], chloro(1,4,7,11,14-pentaazacycloheptadecane)cobalt(III) diperchlorate [2.249 (1) Å; Tahirov *et al.*, 1993] and the *trans*-dichloro(1,4,8,11-tetraazacyclotetradecane)cobalt(III) cation [2.252 (1) Å; Sosa-Torres & Toscano, 1997].

The Zn^{II} ion is four-coordinate in a distorted tetrahedral environment completed by three Cl atoms and an O atom of the bridging ligand. The Zn—O bond lengths are 2.066 (4) and 2.080 (4) Å, which are shorter than that found in (1,4,8,11-tetraazacyclotetradecane-*N,N',N'',N'''*-dihydrogentetraacetato)zinc(II) tetrahydrate [Zn—O 2.127 (1) Å; Riesen *et al.* 1991], but longer than that found in dichlorobis(pyridine betaine)zinc(II) [Zn—O 1.988 (3) and 1.964 (2) Å; Chen & Mak, 1991]. The average Zn—Cl bond length [2.236 (3) Å] is shorter than that in the [ZnCl₄]²⁻ ion found in bis(2-amino-4,5-dihydro-3*H*⁺-1,3-thiazolium) tetrachlorozincate(II) [2.243 (1)–2.301 (1) Å; Kubiak & Glowiak, 1984].

This crystal structure is stabilized by coordination bonds as well as hydrogen bonds. The hydrogen bonds between the complex cations and chloride anions are detailed in Table 2.

Experimental

Na₃[Co(CO₃)₃]:3H₂O and the ligand *C-meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane-*N*-acetic acid were prepared according to a literature method (Bauer & Drinkard, 1960; Xu *et al.*, 1988). Na₃[Co(CO₃)₃]:3H₂O (1.0 g) and the ligand (1.0 g) were

suspended in water (50 ml). The mixture was heated on a water bath for 2 h. An aliquot of aqueous 12 M HCl (4 ml) was added dropwise to the solution. The solution was heated for a further 30 min, NaClO₄ (4.0 g) was added, and the solution was cooled. The green powder obtained upon cooling was filtered off, washed with ethanol and diethyl ether, and dried in vacuo. The crystals for X-ray analysis were recrystallized from a 1 M ZnCl₂/2 M HCl mixture by slow evaporation.

Crystal data

[CoZnCl₄(C₁₈H₃₇N₄O₂)]
M_r = 607.62
 Triclinic, *P* $\bar{1}$
a = 10.242 (1) Å
b = 10.874 (2) Å
c = 23.168 (5) Å
 α = 92.50 (2)°
 β = 100.39 (2)°
 γ = 97.60 (2)°
V = 2509.6 (8) Å³
Z = 4
D_x = 1.608 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 25 reflections
 θ = 6.06–15.33°
 μ = 2.065 mm⁻¹
T = 293 (2) K
 Pillar, green
 0.28 × 0.18 × 0.11 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.656, *T_{max}* = 0.798
 9300 measured reflections
 8792 independent reflections
 5321 reflections with *I* > 2σ(*I*)
R_{int} = 0.061
 θ_{\max} = 25°
h = -12 → 11
k = 0 → 12
l = -27 → 27
 3 standard reflections
 frequency: 60 min
 intensity decay: 1%

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.052
wR (*F*²) = 0.131
S = 0.932
 8792 reflections
 541 parameters
 H-atom parameters constrained
w = 1/[σ²(*F_o*²) + (0.0689*P*)²]
 where *P* = (*F_o*² + 2*F_c*²)/3
 (Δ/σ)_{max} = 0.002
 Δρ_{max} = 0.86 e Å⁻³
 Δρ_{min} = -0.68 e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Co1A—O1A	1.909 (4)	Co1B—O1B	1.885 (4)
Co1A—N3A	1.983 (4)	Co1B—N3B	1.981 (4)
Co1A—N2A	2.004 (4)	Co1B—N2B	2.016 (5)
Co1A—N4A	2.006 (5)	Co1B—N1B	2.018 (4)
Co1A—N1A	2.012 (4)	Co1B—N4B	2.020 (5)
Co1A—Cl1A	2.219 (2)	Co1B—Cl1B	2.237 (2)
Zn1A—O2A	2.066 (4)	Zn1B—O2B	2.080 (4)
Zn1A—Cl4A	2.229 (2)	Zn1B—Cl4B	2.211 (2)
Zn1A—Cl2A	2.237 (2)	Zn1B—Cl2B	2.237 (2)
Zn1A—Cl3A	2.247 (2)	Zn1B—Cl3B	2.254 (2)
O1A—Co1A—N3A	90.8 (2)	Cl4A—Zn1A—Cl3A	120.0 (1)
O1A—Co1A—N2A	86.2 (2)	Cl2A—Zn1A—Cl3A	108.6 (1)
N3A—Co1A—N2A	85.7 (2)	O1B—Co1B—N3B	88.9 (2)
O1A—Co1A—N4A	95.5 (2)	O1B—Co1B—N2B	87.7 (2)
N3A—Co1A—N4A	93.3 (2)	N3B—Co1B—N2B	85.7 (2)
N2A—Co1A—N4A	178.0 (2)	O1B—Co1B—N1B	85.5 (2)
O1A—Co1A—N1A	86.0 (2)	N3B—Co1B—N1B	174.2 (2)
N3A—Co1A—N1A	176.6 (2)	N2B—Co1B—N1B	93.1 (2)
N2A—Co1A—N1A	95.4 (2)	O1B—Co1B—N4B	91.9 (2)
N4A—Co1A—N1A	85.8 (2)	N3B—Co1B—N4B	94.6 (2)
O1A—Co1A—Cl1A	178.3 (1)	N2B—Co1B—N4B	179.4 (2)
N3A—Co1A—Cl1A	88.0 (1)	N1B—Co1B—N4B	86.5 (2)
N2A—Co1A—Cl1A	92.6 (1)	O1B—Co1B—Cl1B	176.8 (1)
N4A—Co1A—Cl1A	85.7 (2)	N3B—Co1B—Cl1B	88.8 (1)
N1A—Co1A—Cl1A	95.2 (1)	N2B—Co1B—Cl1B	94.3 (1)
O2A—Zn1A—Cl4A	104.8 (2)	N1B—Co1B—Cl1B	96.9 (1)
O2A—Zn1A—Cl2A	103.8 (1)	N4B—Co1B—Cl1B	86.1 (2)
Cl4A—Zn1A—Cl2A	114.4 (1)	O2B—Zn1B—Cl4B	99.7 (1)
O2A—Zn1A—Cl3A	103.3 (1)	O2B—Zn1B—Cl2B	114.6 (1)

Cl4B—Zn1B—Cl2B	116.7 (1)	Cl4B—Zn1B—Cl3B	116.8 (1)
O2B—Zn1B—Cl3B	98.8 (1)	Cl2B—Zn1B—Cl3B	108.7 (1)

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N2A—H1A...Cl3A	0.91	2.53	3.406 (5)	160
N3A—H2A...Cl2B	0.91	2.88	3.608 (5)	138
N3A—H2A...Cl1A	0.91	2.54	2.923 (5)	106
N4A—H3A...Cl1A	0.91	2.43	2.878 (5)	111
N2B—H1B...Cl3B	0.91	2.53	3.420 (5)	167
N3B—H2B...Cl1B	0.91	2.58	2.957 (5)	105
N3B—H2B...Cl3A ⁱ	0.91	2.73	3.454 (5)	137
N4B—H3B...Cl4B ⁱ	0.91	2.87	3.599 (5)	139
N4B—H3B...Cl1B	0.91	2.47	2.911 (5)	110

Symmetry code: (i) *x*, 1 + *y*, *z*.

The maximum 2θ for data collection is 50°. The data collection would not go beyond this limit, because the crystal quality was not good. The H atoms were fixed geometrically and refined with constraint.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *NRCVAX* (Gabe *et al.*, 1989); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985); program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993); molecular graphics: *NRCVAX* (Gabe *et al.*, 1989); software used to prepare material for publication: *SHELXL93*.

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