POLYNUCLEAR CADMIUM COMPOUNDS CONTAINING *cis*-$[Co(en)_2(OH)_2]^+$ LIGANDS

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Dedicated to Dr Karel Mach on the occasion of his 60th birthday.

Polynuclear heterometallic compounds containing cobalt and cadmium were prepared by the reaction of $CdCl_2$ with salts of the *cis*-$[Co(en)_2(H_2O)_2]^{3+}$ cation. X-Ray analyses of the tetranuclear Co_2Cd_2 complex $[Cd_2(\mu\text{-}Cl)Cl_4\{(OH)_2Co(en)_2\}_2]ClO_4$ (**1**) and the polymeric compound $[[Cd(\mu\text{-}Cl)(H_2O)_2\{(OH)_2Co(en)_2\}]Cl_2]_n$ (**2**) confirm that the $[Co(en)_2(OH)_2]^+$ groups act as chelating ligands toward the Cd atoms. The Cd coordination octahedra are connected by a face in **1** and by corners in **2**.
Key words: Polynuclear complexes; Cd complexes; Co complexes; Molecular structures.

Previously we have described the synthesis of a series of heteronuclear metal complexes in which *cis*-$[Co(en)_2(OH)_2]^+$ groups act as chelate ligands toward metal ions[1–4]. The nuclearity and the structures of the products depend on the particular metal ion M^{n+}. Representative examples are the tetranuclear trischelate aluminum(III) complex[4] $[Al\{(OH)_2Co(en)_2\}_3](S_2O_6)_3 \cdot 5\ H_2O$, the trinuclear bischelate copper(II) complex[3] $[Cu\{(OH)_2Co(en)_2\}_2](ClO_4)_4 \cdot 2\ H_2O$ which was rediscovered[5] in 1996, and the dinuclear monochelate platinum(II) complex[3] $[PtCl_2\{(OH)_2Co(en)_2\}]_2[PtCl_4]$. The preparation of a series of trinuclear complexes of the type $[M(H_2O)_2\{(OH)_2Co(en)_2\}_2]X_2 \cdot n\ H_2O$ ($X^{2-} = SO_4^{2-}$ and $S_2O_6^{2-}$) with octahedrally coordinated metal ions M^{2+} was reported by Mori *et al.*[6] and later by Corbin *et al.*[7]. The stability of these compounds was investigated by Cannon and Benjarvongkulchai[8,9]. According to preliminary X-ray crystallographic results the aqua ligands of these complexes are in a *cis* arrangement at the central M atom[10]. In this paper we describe the preparation and molecular structures of the cadmium complexes **1** and **2** containing $[Co(en)_2(OH)_2]^+$ ligands.

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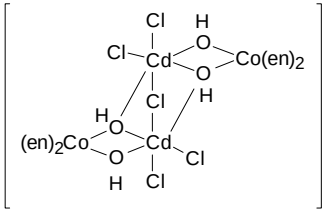
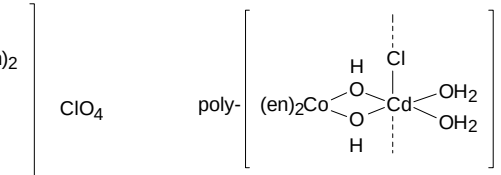


ClO_4

poly-



Cl_2

$[Cd_2(\mu\text{-}Cl)Cl_4\{(OH)_2Co(en)_2\}_2]ClO_4$ (**1**)

$[[Cd(\mu\text{-}Cl)(H_2O)_2\{(OH)_2Co(en)_2\}]Cl_2]_n$ (**2**)

EXPERIMENTAL

Syntheses

Starting materials. The compound *cis*-$[Co(en)_2(H_2O)_2](ClO_4)_3$ was prepared according to ref.[9]; *cis*-$[Co(en)_2(H_2O)_2]Cl_3$ was obtained from the perchlorate salt by ion exchange.

μ-Chloro-tetrachlorobis[cis-μ$_3$-hydroxo-μ-hydroxobis(ethylenediamine) cobalt(III)]cadmium perchlorate (**1**). A solution of $[Co(en)_2(H_2O)_2](ClO_4)_3$ (77 mg, 0.15 mmol) in 1 ml water was brought to pH 7.5 by adding a small amount of diluted NaOH. It was then carefully layered over a solution of $CdCl_2 . 2 H_2O$ (33 mg, 0.15 mmol) in 1 ml water avoiding mixing of the solutions. Pink crystals grew within a few hours. Yield 42 mg (60%). For $C_8H_{36}N_8Cd_2Cl_6Co_2O_8$ (927.8) calculated: 10.36% C, 3.91% H, 12.08% N, 24.23% Cd, 12.70% Co; found: 10.44% C, 4.09% H, 11.95% N, 23.72% Cd, 13.13% Co.

Poly[[diaqua{cis-di-μ-hydroxo-bis(ethylenediamine)cobalt(III)}cadmium-μ-chloro]dichloride] (**2**). A solution of $[Co(en)_2(H_2O)_2]Cl_3$ (113 mg, 0.35 mmol) in 1 ml water (pH 8) was carefully layered, avoiding mixing of the solutions, over a solution of $CdCl_2 . 2 H_2O$ (77 mg, 0.35 mmol). Dark pink crystal needles formed slowly within days. Green crystals of *trans*-$[Co(en)_2Cl_2]Cl$ were obtained as a byproduct. The two kinds of crystals were separated manually under a microscope. Yield 32 mg (20%). For $C_4H_{22}N_4CdCl_3CoO_4$ (467.9) calculated: 10.27% C, 4.74% H, 11.97% N, 24.02% Cd, 12.59% Co; found: 10.35% C, 4.44% H, 11.55% N, 24.51% Cd, 12.83% Co.

X-Ray Crystallography

The X-ray measurements were carried out at room temperature on a Philips-PW 1100 single crystal diffractometer using graphite monochromated MoKα radiation (λ = 0.71069 Å). Crystal and structure determination data are summarized in Table I. Lp and in a later stage an empirical absorption correction[11] were applied. The positions of the metals were obtained from E-maps. The positions of the other non-hydrogen atoms were obtained from subsequent Δ*F* syntheses. Hydrogen atoms of the en groups were included at their calculated positions in the F_c-calculations. Their parameters were not refined, however. For both compounds the *R* indices were slightly higher for the other enantiomorphs whose coordinates were determined by changing the signs of the coordinates for all atoms. For the calculations the SHELX76 program[12] system and local programs were used. Final atomic coordinates are given in Tables II and III*.

* Further details concerning the crystal structure analyses are available upon request from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein–Leopoldshafen, by quoting the deposition numbers CSD 391050 (**1**) and CSD 406427 (**2**).

RESULTS AND DISCUSSION

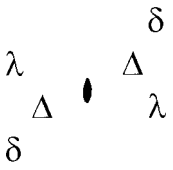
Whereas the reaction of $ZnCl_2$ with $[Co(en)_2(H_2O)_2](ClO_4)_3$ proceeds with the formation of the $ZnCo_3$ complex cation[1] $[Zn\{(OH)_2Co(en)_2\}_3]^{5+}$, the analogous reaction involving $CdCl_2$ yields the Cd_2Co_2 complex **1**. In **1** $[Co(en)_2(OH)_2]^+$ as well as Cl^- ligands are bonded at the Cd atoms. This is in line with the fact that the affinity of Cd(II) towards Cl^- is higher than that of Zn(II). The product **2**, that forms when the reaction is repeated using the chloride $[Co(en)_2(H_2O)_2]Cl_3$ instead of the perchlorate salt, has a completely different structure than that of **1**. Product **2** is a chain polymer. The solubilities of **1** and **2** in water are low. In order to obtain crystals suitable for X-ray diffraction, their formation has to be diffusion-controlled. The crystals obtained are hard and air-stable. The structure of the dinuclear cation **1** is shown in Fig. 1, and a part of the polynuclear cationic complex chain of **2** is depicted in Fig. 2.

TABLE I
Crystallographic data for **1** and **2**

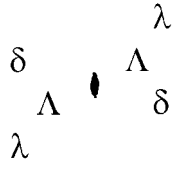
Parameter	**1**	**2**
Formula	$C_8H_{36}N_8Cd_2Cl_6Co_2O_8$	$C_4H_{22}N_4CdCl_3CoO_4$
Crystal dimensions, mm	$0.15 \times 0.2 \times 0.8$	$0.2 \times 0.3 \times 0.6$
μ(MoKα), cm^{-1}	30.9	29.3
Fw	927.83	467.94
Crystal system	orthorhombic	orthorhombic
Space group	*Iba2*	$P2_12_12_1$
a, Å	14.177(2)	8.738(1)
b, Å	15.795(2)	12.083(2)
c, Å	12.478(1)	13.953(2)
Z	4	4
D_o, g cm^{-3}	2.21	2.11
D_c, g cm^{-3}	2.205	2.110
Data collection and refinement $2\theta_{max}$, °	54	54
Unique reflections	1 337	1 842
Observed reflections [$F_o \geq 2\sigma(F_o)$]	1 285	1 778
Parameters refined	154	155
R(*F*)	0.026	0.027
wR(*F*)	0.030	0.031
Residual density, e $Å^{-3}$	0.64	0.62

Selected interatomic distances and angles are listed in Tables IV and V, respectively. The coordination polyhedra about Cd in both compounds are distorted octahedra.

The dinuclear cation **1** possesses crystallographic C_2 symmetry. The following stereochemical symbols give the information about configuration of the cobalt atoms and the conformation of the chelate rings in the cation shown in formula **A** and its enantiomer **B**:



A



B

The Cl3 atom is situated on the twofold rotation axis. The perchlorate anion resides also on a crystallographic 2 axis. Surprisingly it is not disordered. Cation **1** is a scarce example of a heteronuclear compound, in which an OH group of the $[Co(en)_2(OH)_2]^+$ ligand acts as a μ_3-bridge. On the other hand, bridging O atoms with high coordination numbers in dinuclear or polynuclear Cd complexes are not uncommon. As an example we mention the dinuclear pyridine-2 carboxylato complex $[Cd(C_5H_4NCOO)_2]_2$, in which carboxylate oxygen atoms act as μ_2-bridges[13].

The coordination octahedron around Cd is accomplished by three Cl and three O atoms. Two such octahedra share a common face in the dinuclear complex cation. As can be expected, the Cd–Cl(bridge) distance is longer than the Cd–Cl(*exo*) distances

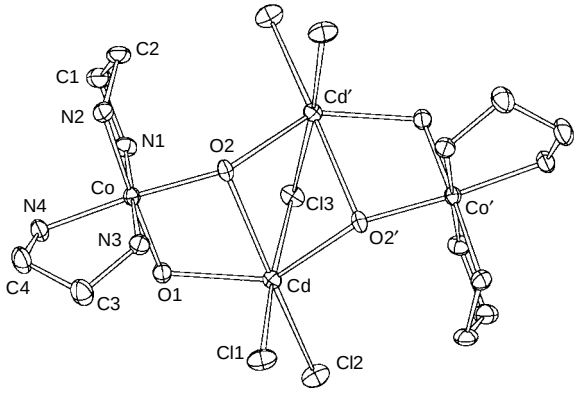


FIG. 1
View of the complex cation of **1** along its twofold symmetry axis

TABLE II
Atomic coordinates and equivalent isotropic temperature factors for **1**

Atom	*x*	*y*	*z*	U_{eq}, Å^2
		Complex cation		
Cd	0.40955(3)	0.57127(3)	0.31340	0.024(1)
Co	0.31580(5)	0.38511(5)	0.24890(9)	0.020(1)
Cl1	0.33356(15)	0.64599(12)	0.14910(16)	0.039(1)
Cl2	0.38201(15)	0.70096(12)	0.42790(16)	0.038(1)
Cl3	0.5	0.5	0.48165(20)	0.032(1)
O1	0.2891(3)	0.4851(3)	0.3295(4)	0.027(2)
O2	0.4440(3)	0.4257(3)	0.2373(4)	0.024(2)
N1	0.3481(4)	0.3296(4)	0.3832(5)	0.030(3)
N2	0.3510(4)	0.2781(4)	0.1829(5)	0.030(3)
N3	0.2858(4)	0.4399(3)	0.1124(5)	0.028(3)
N4	0.1825(4)	0.3535(4)	0.2533(6)	0.030(3)
C1	0.3733(6)	0.2400(5)	0.3676(8)	0.039(4)
C2	0.4143(5)	0.2307(5)	0.2576(7)	0.033(4)
C3	0.1816(6)	0.4477(5)	0.1003(9)	0.045(5)
C4	0.1381(5)	0.3713(6)	0.1469(8)	0.043(5)
		Perchlorate anion		
Cl4	0.0	0.5	0.3859(3)	0.037(1)
O41	0.0795(5)	0.5249(5)	0.3225(11)	0.080(6)
O42	0.0279(6)	0.4311(5)	0.4487(8)	0.084(6)

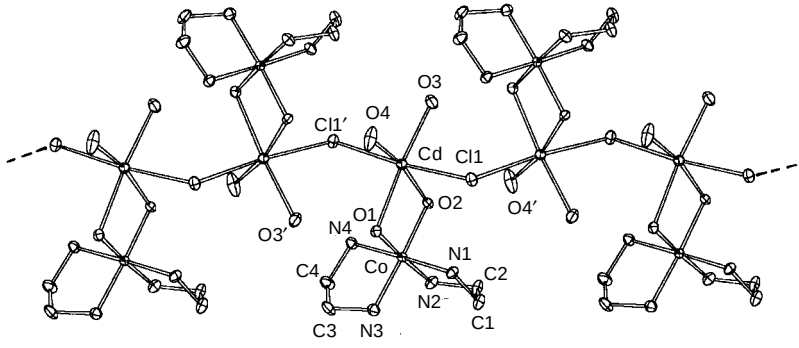


FIG. 2
The macrocation of **2**

(see Table IV). The three independent Cd–O bond distances differ significantly. Again, as can be expected, the Cd–(μ_2-O) distance of 2.19(1) Å is shorter than the Cd–(μ_3-O) distances (2.28(1) and 2.54(1) Å).

The bond angles around Cd deviate considerably from the theoretical 90° angle. The largest and smallest angles are 111.0(1)° and 67.7°; see Table IV. Hydrogen bonds do not seem to play a significant role in this crystal structure. The N…Cl contacts, some of which belong to weak hydrogen bonds, between neighboring cations are longer than 3.23 Å. The closest anion–cation contact is O1…O41 (3.04 Å).

The crystal structure of **2** consists of cationic polymer chains with the repeating unit Cd(μ-Cl)$(H_2O)_2\{(OH)_2Co(en)_2\}$ and surrounding Cl anions. The coordination octahedron around Cd is formed by four O atoms and two Cl atoms. Adjacent octahedra share

TABLE III
Atomic coordinates and equivalent isotropic temperature factors for **2**

Atom	*x*	*y*	*z*	U_{eq}, Å^2
		Complex cation		
Cd	0.50335(5)	0.23976(3)	0.49691(3)	0.021(1)
Co	0.49766(8)	–0.00716(5)	0.40727(4)	0.015(1)
Cl1	0.75561(14)	0.20166(12)	0.59483(10)	0.025(1)
O1	0.4070(4)	0.0657(3)	0.5166(3)	0.020(2)
O2	0.5947(4)	0.1317(3)	0.3752(3)	0.020(2)
O3	0.6153(5)	0.3990(4)	0.4411(4)	0.051(3)
O4	0.3931(5)	0.3136(5)	0.6287(3)	0.056(3)
N1	0.6798(5)	–0.0459(4)	0.4817(3)	0.024(2)
N2	0.6025(5)	–0.0794(4)	0.2994(3)	0.024(2)
N3	0.3919(5)	–0.1423(4)	0.4439(3)	0.024(2)
N4	0.3163(5)	0.0273(4)	0.3312(3)	0.023(2)
C1	0.7734(7)	–0.1262(6)	0.4245(4)	0.031(3)
C2	0.7671(6)	–0.0932(6)	0.3250(4)	0.029(3)
C3	0.2294(7)	–0.1377(6)	0.4124(5)	0.034(3)
C4	0.2251(7)	–0.0760(5)	0.3167(5)	0.032(3)
		Anions		
Cl2	0.5077(2)	0.1256(1)	0.1478(1)	0.034(1)
Cl3	0.4781(2)	–0.1247(1)	0.6719(1)	0.035(1)

common corners. The polymer chains run parallel to the crystallographic *a* axis. They have 2_1 symmetry. The arrangement of the $Co(en)_2(OH)_2$ fragment which belongs to the chain shown in Fig. 2, is characterized by the stereochemical symbol $\Delta\lambda_2$. Inspection of the close contacts in **2** shows that there is one intra-chain hydrogen bond between each of the O atoms of the $Co(en)_2(OH)_2$ group and a water ligand at a neighboring Cd atom (see Table V). These hydrogen bonds evidently contribute to the stability of the cationic chain. Additional hydrogen bonds exist between amine nitrogens and the bridging as well as the ionic Cl atoms.

TABLE IV
Selected bond lengths (Å) and angles (°) of **1**. A prime refers to the atomic position $1 - x$, $1 - y$, z

Atoms	Bond lengths	Atoms	Bond angles
Cd–O1	2.192(5)	O1–Cd–O2	67.7(2)
Cd–O2	2.536(5)	O1–Cd–O2′	139.4(2)
Cd–O2′	2.284(5)	O1–Cd–Cl1	91.8(1)
Cd–Cl1	2.599(2)	O1–Cd–Cl2	109.3(1)
Cd–Cl2	2.528(2)	O1–Cd–Cl3	92.3(1)
Cd–Cl3	2.705(2)	O2–Cd–O2′	71.9(2)
Co–O1	1.910(5)	O2–Cd–Cl1	101.3(1)
Co–O2	1.932(5)	O2–Cd–Cl2	167.5(1)
Co–N1	1.946(6)	O2–Cd–Cl3	79.7(1)
Co–N2	1.946(6)	O2′–Cd–Cl1	92.2(1)
Co–N3	1.957(6)	O2′–Cd–Cl2	111.0(1)
Co–N4	1.956(6)	O2′–Cd–Cl3	84.3(1)
Cd...Co	3.326(2)	Cl1–Cd–Cl2	90.8(1)
		Cl1–Cd–Cl3	175.9(1)
		Cl2–Cd–Cl3	88.4(1)
		Co–O1–Cd	108.1(2)
		Co–O2–Cd	95.2(2)
		O1–Co–O2	87.2(2)
		O1–Co–N2	172.8(2)
		O2–Co–N4	174.7(2)
		N1–Co–N3	178.7(3)

TABLE V
Selected bond lengths (Å) and angles (°) of **2**. A prime refers to the atomic position $-1/2 + x$, $1/2 - y$, $1 - z$. A star refers to $1/2 + x$, $1/2 - y$, $1 - z$

Atoms	Bond lengths	Atoms	Bond angles
Cd–O1	2.282(4)	O1–Cd–O2	72.1(1)
Cd–O2	2.286(4)	O1–Cd–O3	166.2(2)
Cd–O3	2.295(5)	O1–Cd–O4	96.2(2)
Cd–O4	2.259(5)	O2–Cd–O3	94.5(2)
Cd–Cl1	2.634(2)	O2–Cd–O4	168.2(2)
Cd–Cl1′	2.613(2)	Cl1–Cd–Cl1′	174.2(1)
Co–O1	1.931(4)	O1–Co–O2	88.1(2)
Co–O2	1.933(4)	O1–Co–N2	176.4(2)
Co–N1	1.957(5)	O2–Co–N3	176.8(2)
Co–N2	1.966(5)	N1–Co–N4	178.3(2)
Co–N3	1.944(5)		
Co–N4	1.953(5)		
Cd...Co	3.235(1)		
O1...O3′	2.65(1)		
O2...O4*	2.69(1)		

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