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Synthesis and crystal structure of a chloro-bridged dinuclear cadmium(II) complex with 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane

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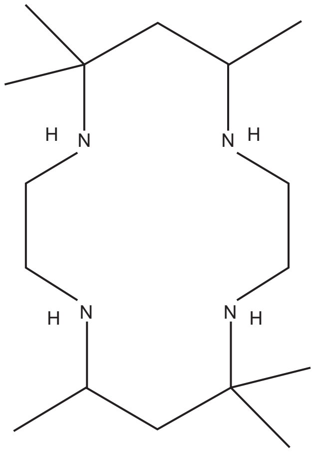
Abstract

The macrocyclic ligand 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (L) reacts with cadmium(II) chloride and excess $NaClO_4$ to give a chloro-bridged dinuclear cadmium(II) complex $[Cd(L)(\mu\text{-}Cl)]_2\cdot 2ClO_4$ (**1**). Each cadmium(II) ion exhibits a distorted octahedral environment with two chloride ligands and four secondary amines of the macrocycle. The compound **1** crystallizes in the orthorhombic system *P*bca with a=14.477(1), b=15.256(2), c=20.500(6) Å, V=4527.6(15) Å^3, Z=4. Cyclic voltammetry of **1** gives one oxidation and two reduced processes.

Keywords: chloro-bridged complex; crystal structure; dinuclear cadmium(II) complex; tetraaza macrocycle.

Introduction

The coordination chemistry of the cadmium(II) complexes has been of great interest due to the increased recognition of its role in biological systems (Marzilli et al., 1980; Taksyama et al., 1996; Strasdeit et al., 1988) and molecular-based materials (Abrahams et al., 1991; Abrahams et al., 1994; Veith et al., 1996; Soma et al., 1994). The number of structurally studied compounds of cadmium(II) with the macrocyclic ligands is, to our knowledge, surprisingly low (Kimura et al., 1990; Bernhardt et al., 1992; Choi et al., 2001): the mononuclear cadmium(II) complexes $[Cd(potc)](ClO_4)_2\cdot H_2O$ (potc=7-(2-pyridyl)-5-oxo-1-,4,8,11-tetraazacyclotetradecane (Kimura et al., 1990) and $[Cd(dttd)](ClO_4)_2$ (dttd=6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane-6,13-diamine) (Bernhardt et al., 1992) exhibit a distorted octahedral geometry. Furthermore, the complex $[Cd(dtda)tp]\cdot 2H_2O$ (dtda=3,14-dimethyl-2,6,13,17-tetraazatricyclo[14,4,0$^{1.18}$,0$^{7.12}$]docosane, tp=terephthalate) shows that the coordination environment of the cadmium ion, is a six-coordinated skew-trapezoidal bipyramidal geometry with four nitrogen atoms of the macrocycle and two carboxylate oxygen atoms of the terephthalate ligand (Choi et al., 2001). On the other hand, the reaction of $CdCl_2$ with 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (L) and excess $NaClO_4$ leads to the chloro-bridged dinuclear cadmium(II) complex $[Cd(L)(\mu\text{-}Cl)]_2\cdot 2ClO_4$ (**1**), and we present its crystal structure here.



Results and discussion

An Oak Ridge Thermal Ellipsoid Plot (ORTEP) (Farrugia, 1997) and crystal packing diagrams of $[Cd(L)(\mu\text{-}Cl)]_2\cdot 2ClO_4$ (**1**) with the atomic numbering scheme are shown in Figures 1 and 2. Selected bond lengths and angles are listed in Table 1. The macrocyclic ligand skeleton of the present compound takes the *trans*-V(*R*,*S*,*S*,*R*) conformation. The crystal structure of **1** exhibits a dinuclear complex in which the cadmium(II) centers are doubly bridged by two chloride ligands, each of which resides at a center of symmetry. Each cadmium(II) ion exhibits a distorted octahedral environment with two chloride ligands and four secondary amines of the macrocycle. The Cd…Cd^i distance within the dinuclear unit is 4.005(18) Å. The four atoms of the Cd_2Cl_2 core lie in the plane, which has a rhomboidal geometry. The core bond angles of Cl(1)-Cd-Cl(1)^i and Cd-Cl(1)-Cd^i angles are 81.3(1) and 98.7(1)°, respectively. The N-Cd-N angles of the six-membered chelate ring are larger than those of the five-membered chelate ring. The average Cd-N distance of 2.378 Å is slightly longer than that found in the cadmium perchlorate complex with 7-(2-pyridyl)-5-oxo-1,4,8,11-tetraazacyclotetradecane [2.315(3) Å] (Kimura et al., 1990), but is similar to that observed for the pendant cadmium perchlorate complex with 6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane-6,13-diamine [2.418(2) Å]

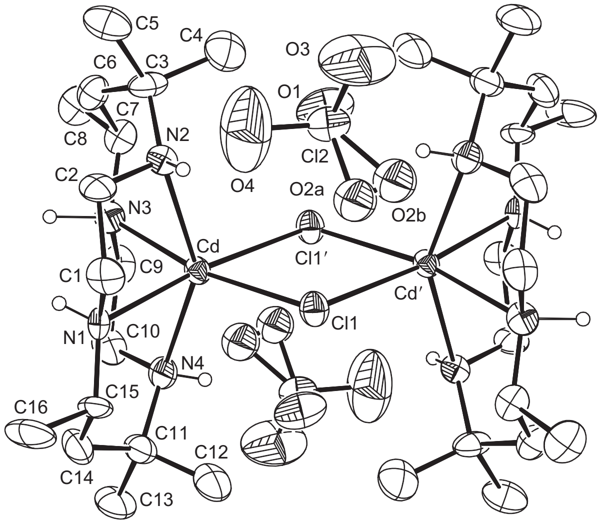


Figure 1 An ORTEP view of $[Cd(L)(\mu\text{-}Cl)]_2\cdot 2ClO_4$ (**1**) with the atomic numbering scheme (30% probability ellipsoids shown).

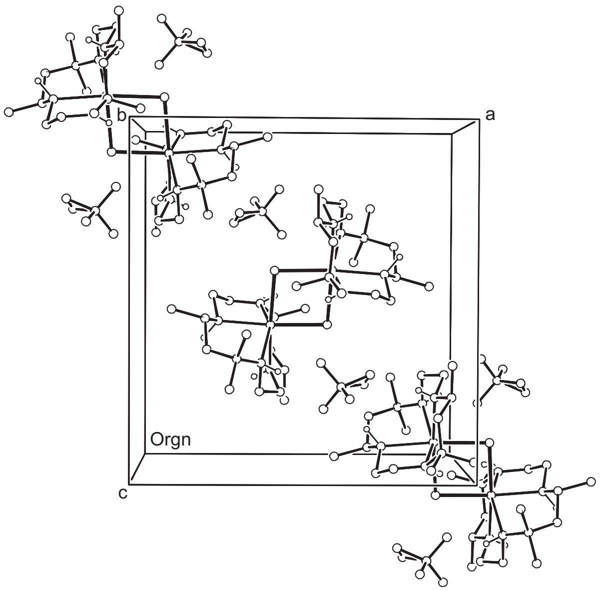


Figure 2 Crystal packing diagram of $[Cd(L)(\mu\text{-}Cl)]_2\cdot 2ClO_4$ (**1**). The hydrogen atoms are omitted for clarity.

(Bernhardt et al., 1992), which has a six-coordinated octahedral geometry.

The IR spectrum of **1** reveals ν(NH) band at 3261/cm associated with secondary amine of the macrocycle. The strong bands at 1086 and 1071/cm are also assigned to the ν(Cl-O) (Nakamoto, 1997). Cyclic voltammogram of **1** in 0.1 m TEAP-DMSO solution is shown in Figure 3. Complex **1** shows one oxidation response on the positive side of Ag/AgCl reference electrode at +0.35 V due to the Cl^-/ClO^- couple which is irreversible in nature. Two reversible and irreversible reduction responses are also observed on the negative side of Ag/AgCl reference electrode at -0.45 and -1.14 V, respectively, which may be assigned to the Cd^{II}/Cd^0 and ClO_4^-/ClO_3^- processes.

Table 1 Selected bond distances (Å) and angles (°) for $[Cd(L)(\mu\text{-}Cl)]_2\cdot 2ClO_4$ (**1**).

Cd-N(1)	2.371(12)	Cd-N(2)	2.431(13)
Cd-N(3)	2.336(14)	Cd-N(4)	2.375(17)
Cd-Cl(1)	2.568(4)	Cd-Cl(1)^i	2.709(4)
Cd…Cd^i	4.005(18)		
N(1)-Cd-N(2)	76.9(4)	N(1)-Cd-N(3)	93.1(5)
N(1)-Cd-N(4)	82.7(5)	N(2)-Cd-N(3)	83.6(4)
N(2)-Cd-N(4)	150.7(5)	N(3)-Cd-N(4)	76.6(6)
N(1)-Cd-Cl(1)	96.1(4)	N(2)-Cd-Cl(1)	93.0(3)
N(3)-Cd-Cl(1)	169.2(3)	N(4)-Cd-Cl(1)	110.2(5)
N(1)-Cd-Cl(1)^i	174.1(4)	N(2)-Cd-Cl(1)^i	108.4(3)
N(3)-Cd-Cl(1)^i	90.0(3)	N(4)-Cd-Cl(1)^i	93.2(4)
Cd-Cl(1)-Cd^i	98.7(1)	Cl(1)-Cd-Cl(1)^i	81.3(1)

Symmetry code: (i) -x+2, -y, -z+1.

Experimental section

Materials and physical measurements

All chemicals used in syntheses were of reagent grade and were used without further purification. The macrocycle 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (L) was prepared according to the literature method (Hay et al., 1975). IR spectra were recorded with a Perkin-Elmer Paragon 1000 FT-IR spectrophotometer (Perkin Elmer, Waltham, MA 02451, USA) using KBr pellets. Electrochemical measurements were accomplished with a three electrode potentiostat BAS-100BW system (BASi, Kent Avenue, West Lafayette, IN, USA). A 3 mm Pt disk was used as the working electrode. The counter electrode was a coiled Pt wire and a Ag/AgCl electrode was used as a reference electrode. Cyclic voltammetric data were obtained in DMSO solution using 0.1 m tetraethylammonium perchlorate (TEAP) as supporting electrolyte at 20.0±0.1°C. The solution was degassed with high purity N_2 prior to carrying out the electrochemical measurements. Elemental analyses (C, H, N) were performed on a

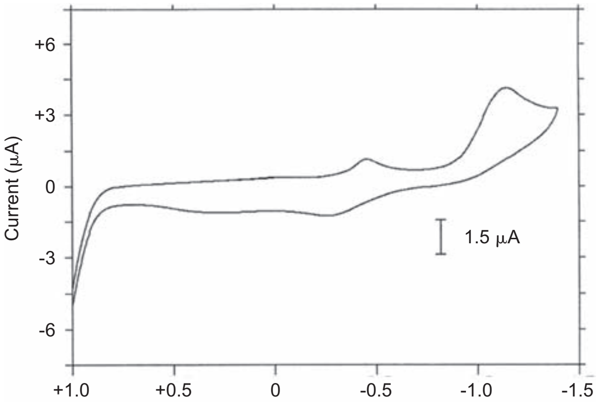


Figure 3 Cyclic voltammogram of $[Cd(L)(\mu\text{-}Cl)]_2\cdot 2ClO_4$ (**1**) in 0.1 M TEAP-DMSO solution at 20.0±0.1°C. The scan rate is 100 mV/s.

Table 2 Crystallographic data for $[Cd(L)(\mu\text{-}Cl)]_2 \cdot 2ClO_4$ (**1**).

Formula	$C_{32}H_{72}Cd_2Cl_4N_8O_8$	Formula weight	1063.58
Crystal system	Orthorhombic	Crystal size (mm)	0.10×0.30×0.30
Space group	*P*bca	*a*, Å	14.477(1)
b, Å	15.256(2)	*c*, Å	20.500(6)
α, °	90.0	β, °	90.0
ϒ, °	90.0	*V*, Å³	4527.6(15)
Z	4	Diffractometer	Enraf-Nonius CAD-4
Temperature (K)	293(2)	μ(Mo-Kα) (/mm)	1.228
F(000)	2192	*D*calc. Mg (/m³)	1.560
Reflns collected	4907	θmax, °	24.96
Reflns unique, R_{int}	3961, 0.1585	Reflns with $I \geq 2\sigma(I)$	1954
R, *wR* (F^2, obs. data)	0.0940, 0.2389	Weighting scheme	$w=1/[\sigma^2(F^2_o)+(0.1963P)^2 +0.0000P]$ where $P=(F^2_o+2F^2_c)/3$
GoF	0.975		
Program used	SHELXS-97 (Sheldrick, 1990)		
	SHELXL-97 (Sheldrick, 1997)	ρ, e/Å³	1.894, -2.271
	ORTEP (Farrugia, 1997)	Deposition number	CCDC798178

Perkin-Elmer CHN-2400 analyzer (Perkin Elmer, Waltham, MA 02451, USA).

Synthesis of $[Cd(L)(\mu\text{-}Cl)]_2 \cdot 2ClO_4$ (1)

To a methanol solution (30 ml) of $CdCl_2$ (183 mg, 1.0 mmol) was added L (284 mg, 1.0 mmol) and the mixture refluxed for 1 h. The solution was allowed to cool at room temperature and filtered to remove the insoluble material. A saturated aqueous solution of excess $NaClO_4$ was added to the filtrate with stirring, and the mixture was stored in a refrigerator until colorless crystals formed. The crystals were filtered, washed with methanol and dried in air. The product was recrystallized from hot water. Yield: 330 mg (62%). Calc. (found) for $C_{32}H_{72}Cl_4Cd_2N_8O_8$: C, 36.13 (36.21); H, 6.82 (6.94); N, 10.54 (10.41)%. IR (KBr/cm): 3261(m), 2963(w), 1487(m), 1450(m), 1366(m), 1262(m), 1165(m), 1086(s), 1071(s), 1023(m), 1008(s), 932(m), 907(w), 851(w), 812(w), 775(w).

X-ray crystallography

All atoms, except all hydrogen atoms and O2 were refined anisotropically. Hydrogen atoms were placed in calculated positions, allowing them to ride on their parent C and N atoms, with U_{iso} (H)=1.2 U_{eq} (C or N). The O2 atom was disordered over two positions and the split atoms, designated as O2a and O2b, were refined isotropically. The final occupancy factors of O2a and O2b are 0.68 and 0.32, respectively. An empirical absorption correction was applied with ϕ-scan (North et al., 1968). The crystallographic data, conditions used for the intensity collection, and some features of the structure refinement are listed in Table 2.

Acknowledgements

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