مجله بلورشناسی و کانی شناسی ایران

سال شانزدهم، شمارهٔ ۴، زمستان ۸۷، از صفحهٔ ۶۴۰ تا ۶۴۵

انجمن بلورشناسی و کانی شناسی ایران

ساختار بلوری کمپلکس پلیمری کادمیم(II) حاصل از ترکیب انتقال پروتون تهیه شده از پی پیرازین و اکسالیک اسید

ژانت سلیمان نژاد[۱]، شبنم هوشمند[۱]، حسین آقابزرگ[۲]، محمد قادرمزی[۳]، جعفر عطار قراملکی[۲]

۱- دانشکده علوم دانشگاه ایلام، ایلام، ایران

۲- دانشکده شیمی دانشگاه تربیت معلم تهران، تهران، ایران

۳ - دانشکده علوم دانشگاه کردستان، سنندج، ایران

پست الکترونیکی: haghabozorg@yahoo.com

(دریافت مقاله ۸۶/۱۲/۲۷ ، نسخه نهایی ۸۷/۹/۲۰)

چکیده: واکنش محلول آبی کادمیم(II) نیترات شش آبه با ترکیب انتقال پروتون $(pipzH_2)(ox)$ که در آن pipz، پی پیرازین و oxH_2، اکسالیک اسید است، منجر به تشکیل کمپلکس پلیمری $(C_2H_6CdO_7)_n$ می‌شود. این کمپلکس در سیستم بلوری تری‌کلینیک و گروه فضایی $P\bar{1}$ با دو مولکول در سلول واحد متبلور می‌شود. پارامترهای سلول واحد برای این کمپلکس عبارت اند از: a = ۵/۹۹۸(۴) Å، b = ۶ /۶۳۴(۵) Å، c = ۸/۴۸۲(۶) Å، α = ۷۴/۶۷۹ °(۱۰)، β = ۷۴/۳۴۸(۱۱)° و γ = ۸۱/۱۱۲(۱۱) °. مقدار R نهایی آن ۰/۰۸۷ برای ۱۳۰۹ بازتاب است. اتم کادمیم(II) به وسیله پنج اتم اکسیژن از یون های اکسالات که به صورت لیگاندهای پل شونده عمل می کنند، و دو اتم اکسیژن از مولکول های آب کوئوردینه شده، احاطه شده و اتم های متصل به فلز، آرایش دو هرمی با قاعده پنج ضلعی واپیچیده را در اطراف یون فلز مرکزی به وجود می آورند. افزون بر آن، یک مولکول آب غیر کوئوردینه نیز در تشکیل کمپلکس شرکت می کند. در این کمپلکس، پیوند های هیدروژنی از نوع O—H···O باعث پایداری ساختار بلوری شده و با متصل کردن اجزای متفاوت به یکدیگر، تشکیل شبکه‌ی سه بعدی اَبَرمولکولی می دهند.

واژه‌های کلیدی: *ترکیب انتقال پروتون، کمپلکس پلیمری کادمیم(II)، پیوندهای هیدروژنی، شیمی اَبَرمولکولی، ساختار مولکولی.*

IRANIAN SOCIETY of CRYSTALLOGRAPHY and MINERALOGY

Vol. 16, No. 4, Winter 1387/2009

IRANIAN JOURNAL of CRYSTALLOGRAPHY and MINERALOGY

Crystal Structure of a Cd(II) Polymeric Complex Obtained from a Proton- Transfer Compound Containing Piperazine and Oxalic Acid

Janet Soleimannejad [1], Shabnam Hooshmand [1], Hossein Aghabozorg[2, 1], Mohammad Ghadermazi [3], Jafar Attar Gharamaleki [2]

1- Department of Chemistry, Ilam University, Ilam, Iran
2- Faculty of Chemistry, Tarbiat Moallem University, Tehran, Iran
3- Department of Chemistry, Faculty of Science, University of Kurdistan, Sanandaj, Iran
Email: haghabozorg@yahoo.com

(Received: 17/3/2008, in revised form: 9/9/2008)

Abstract: The reaction of cadmium(II) nitrate hexahydrate with the proton-transfer compound $(pipzH_2)(ox)$ (where pipz=piperazine and oxH_2=oxalic acid), in aqueous solution leads to the formation of the title polymeric compound $(C_2H_6CdO_7)_n$. This compound crystallizes in the triclinic system, space group $P\bar{1}$ with two formula in the unit cell. The unit cell parameters are: a = 5.998 (4) Å, b = 6.634 (5) Å, c = 8.482 (6) Å, α = 74.679 (10)°, β = 74.348 (11)° and γ = 81.112(11)°. The final R value was 0.087 for 1309 measured reflections. The Cd^{II} ion is seven-coordinated by five O atoms of oxalate ions as tetradentate bridging ligands and two O atoms of coordinated water molecules with distorted pentagonal bipyramid geometry around the central atom. The asymmetric unit also contains one water molecule. The crystal structure is stabilized by O–H···O hydrogen bonds, linking the molecules into a three-dimensional framework, which results in the formation of a supramolecular structure.

Keywords: *Proton transfer compound, Cadmium (II) polymeric complex, Hydrogen bonds, Supramolecular chemistry, Crystal structure*

Introduction

Intermolecular interactions, such as hydrogen bonding, π-π stacking, ion pairing, hydrophobic interactions and donor-acceptor interactions are famous for making aggregates of molecules. Hydrogen bonding is one of the several types of non-covalent interactions in many organic and inorganic species, which results in aggregation and controls self-assembly, in some cases [1]. In general, molecular association between carboxylic acid and a Lewis base results in more hydrogen bonding association with considerable stability upon a structure-making process. Proton transfer from carboxylic acid to different kinds of amines has been reported [2].

In recent years, our research group has been involved in the study of proton-transfer compounds and their complexes with different metal ions. Continuing our research on proton-transfer systems, we have now found a route to combine a carboxylic acid with an amine and produce some water soluble self-associating ion pair systems, which can react with metal ions and result in different complexes. The resulting compounds, with some remaining sites as electron donors, can coordinate to metal ions. In connection with such self-associated proton-transfer systems, we have previously reported some self-associated proton-transfer systems using pyridine-2,6-dicarboxylic acid ($pydcH_2$) and 1,10-phenanthroline-2,9-dicarboxylic acid ($phendcH_2$) as proton donors and pyridine-2,6-diamine (pyda), creatinine (creat), 1,10-phenanthroline (phen), guanidine (G) and N, N' – diethyl l – 2 – amino – 6 – methyl l - 4 - pyrimidinol (pyrim) as proton acceptors. Some complexes of these systems have been synthesized

and their X-ray crystal structures have been reported [3-5].

Preparation and experiments

The reaction of cadmium(II) nitrate hexahydrate (0.568 mmol, 0.137g in 20 mL H_2O) with the proton-transfer compound piperazinediium oxalate, or ($pipzH_2$)(ox) (1.136 mmol, 0.2g in 20 mL H_2O), in a molar ratio of 1:2 leads to the formation of the title compound until a blue powder precipitated. The resulting powder was dissolved in water to give light blue crystals of the compound after two weeks.

The X-ray data was collected on a Bruker SMART diffractometer (MoK_α radiation, graphite monochromator) at 150(2) K. The crystal data and experimental parameters are given in Table 1. The crystal was solved by direct methods (SHELXS-97) and a refinement was carried out with the full-matrix leasts-squares methods based on F^2 with SHELXL-97. The absorption was performed by means of SADBAs program. Hydrogen atoms were positioned geometrically and refined with a riding model (including torsional freedom for methyl groups), with C–H = 0.95-0.98, and with U(H) constrained to be 1.2 (1.5 for methyl groups) times U_{eq} of the carrier atom. The final R and R_w values are 0.0870 and 0.220 for 1309 measured reflections, respectively.

Table 1. Crystal and experimental data.

Formula: $C_2H_6CdO_7$	
Formula weight: 254.47	
Space Group: $P\bar{1}$	Mo $K\alpha$ radiation
Crystal system: triclinic	Z = 2
a = 5.998 (4) Å	a= 74.679 (10) °
b = 6.634 (5) Å	β = 74.348 (11) °
c = 8.482 (6) Å	γ = 81.112 (11) °
V = 312.1 (4) Å^3	
D_x = 2.707 Mg/m^3	
Absorption coefficient= 3.48 mm^{-1}	
F(000) = 244	
Crystal dimensions (mm) = 0.23 × 0.16 × 0.13	
$R[F^2 > 2\sigma(F^2)]$ = 0.0870	
R_w (F^2)= 0.220	
θ Range for data collection = 2.57 to 27.5°	$-7 \leq h \leq 7$
Goodness-of-fit = 1.029	$-8 \leq k \leq 8$
$(\Delta/\sigma)_{max}$ = 0.000	$-10 \leq l \leq 10$
$(\Delta\rho)_{max}$ = 1.99 e Å^{-3}	
$(\Delta\rho)_{min}$ = –3.10 e Å^{-3}	
Data collection= Bruker smart diffractometer	
Absorption correction: multi-scan SADABS	
No. of reflections collected with $I > 2\sigma(I)$ = 1309, ω scans	
No. of independent reflections = 1381	
No. of parameters = 91	
Measurement: Bruker SMART diffractometer	
Program System: Bruker SAINT	
Structural determination : SHELXL-97 (Sheldrick, 1997)	
Refinement: full-matrix least-squares on F^2	
CCDC 638211 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.	

Results and discussion

Here, the crystal structure of the title complex, (C2H6CdO7) n is reported. The molecular structure is shown in Fig. 1, 2 and selected bond distances and angles are given in Table 1. The final atomic coordinates of non-hydrogen atoms are listed in Table 2. Some selected bond distances, bond angles and torsion angles are given in Table 3. The central Cd(II) ion is coordinated by five O atoms of tetradentate oxalate molecules by bridging their O atoms, with Cd–O bond length ranging from 2.301(8) to 2.382(6) Å. The Cd (1) atom is also coordinated by two O atoms of coordinated water molecules, i.e., Cd (1)–O (5) and Cd (1)–O (6) with Cd–O bond lengths of 2.302(8) and 2.357(7) Å, respectively. These are in agreement with the values reported previously for seven-coordinate cadmium (II) complexes containing pyridine-2,6-dicarboxylate as a ligand [6-7].

The geometry of the complex is distorted pentagonal bipyramidal with two O atoms, O (1) and O (5) (one from bridging oxalate ligand and one from coordinated water molecule), in axial sites. The equatorial positions are occupied by five O (2), O(3), O(4) and O(4)^{i} (i: -*x*+1, -*y*, -*z*+2) of the oxalate ligands, and atom O(6) of the H_2O ligand. The angle O(1)–Cd(1)–O(5) is 174.9 (2)° which is deviated from linearity. With respect to the angles in the equatorial plane, the largest and smallest deviations from the ideal value of 72 are observed for O(4) –Cd(1)-O(2)[69.0(2)°] and O(6)-Cd(1)-O(4)^{i} [80.9(2)°], respectively.

A number of O–H···O hydrogen bonds with D···A distances ranging from 2.706 (10) to 3.032 (12) Å (Table 2) are observed in the crystal structure, producing a chain-like structure (Fig. 3). Therefore hydrogen bonds between carboxylate and water molecules play an important role in stabilizing the crystal structure and construction of the three-dimensionsal framework which results in the formation of a supramolecular structure based on hydrogen bonded network.

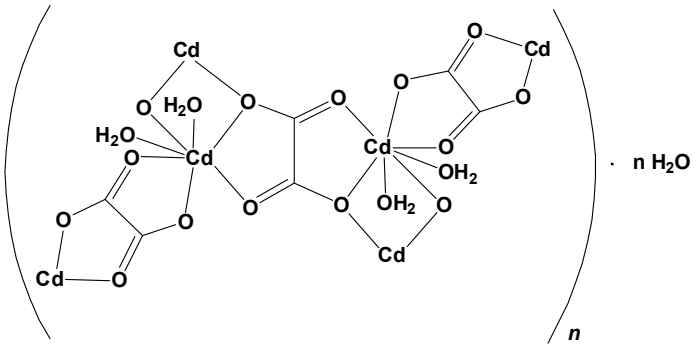

Fig. 1. Chemical structure of the title compound.

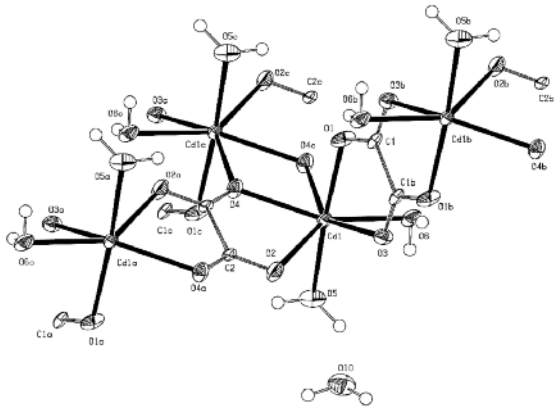

Fig. 2. Molecular structure of polymeric compound $(\underline{C_2H_6CdO_7})_n$ showing the atom numbering scheme. Ellipsoids are drawn at the 50% probability level.

Table 2. Atomic coordinate ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for non-hydrogen atoms.

$$U_{\text{equiv}} = (1/3) \sum_i \left[\sum_j (U^{ij} A_i A_j a_i^* a_j^*) \right],$$

Where A = the real-space cell lengths and a^* = the reciprocal-space cell lengths.

Atom	x	y	z	$U_{(eq)}$
Cd(1)	4506(1)	1894(1)	7937(1)	15(1)
O(1)	5826(14)	-1073(12)	6917(9)	24(2)
O(2)	434(11)	2207(10)	8334(8)	24(1)
O(3)	3789(11)	2490(10)	5258(7)	22(1)
O(4)	2776(10)	-549(10)	10362(7)	20(1)
O(5)	3511(15)	4953(13)	8859(12)	32(2)
O(6)	7768(11)	3568(10)	6140(8)	23(1)
O(10)	604(13)	7570(16)	7027(10)	39(2)
C(1)	5606(14)	-1013(12)	5462(9)	17(1)
C(2)	-676(13)	811(12)	9409(8)	14(1)

Table 3. Selected bond distances (Å), bond angels and torsion angles (°).

Cd(1)–O(1)	2.301 (8)	Cd(1) –O(4)^{i}	2.382 (6)
Cd(1) –O(5)	2.302 (8)	O(1) –C(1)	1.266 (10)
Cd(1) –O(3)	2.346 (6)	O(2) –C(2)	1.244 (10)
Cd(1) –O(4)	2.354 (6)	O(3) –C(1)^{ii}	1.246 (10)
Cd(1) –O(6)	2.357 (7)	O(4) –C(2)^{iii}	1.254 (10)
Cd1) –O(2)	2.358 (7)		
O(1)–Cd(1)–O(5)	174.9 (2)	O(5)–Cd(1)–O(2)	79.3 (3)
O(1)–Cd(1)–O(3)	71.3 (2)	O(3)–Cd(1)–O(2)	73.5 (2)
O(5)–Cd(1)–O(3)	108.9 (3)	O(4)–Cd(1)–O(2)	69.0 (2)
O(1)–Cd(1)–O(4)	82.7 (3)	O(6)–Cd(1)–O(2)	139.4 (2)
O(5)–Cd(1)–O(4)	100.8 (3)	O(1)–Cd(1)–O(4)^{i}	84.0 (2)
O(3)–Cd(1)–O(4)	125.9 (2)	O(5)–Cd(1)–O(4)^{i}	93.8 (3)
O(1)–Cd(1)–O(6)	90.2 (3)	O(3)–Cd(1)–O(4)^{i}	146.4 (2)
O(5)–Cd(1)–O(6)	85.0 (3)	O(4)–Cd(1)–O(4)^{i}	70.7 (2)
O(3)–Cd(1)–O(6)	76.8 (2)	O(6)–Cd(1)–O(4)^{i}	80.9 (2)
O(4)–Cd(1)–O(6)	151.3 (2)	O(2)–Cd(1)–O(4)^{i}	136.8 (2)
O(1)–Cd(1)–O(2)	105.5 (3)	Cd(1)–O(4)–Cd(1)^{i}	109.3 (2)
C(2)–O(2)–Cd(1)	117.9(5)	C(1)^{ii}–O(3)–Cd(1)	116.5 (5)
C(1)–O(1)–Cd(1)	117.2(6)	C(2)^{iii}–O(4)–Cd(1)	118.3 (5)
O(4)–Cd(1)–O(1)–C(1)	132.9 (7)	O(3)–Cd(1)–O(4)–C(2)^{iii}	−37.7 (6)
O(2)–Cd(1)–O(1)–C(1)	67.1 (7)	O(4)^{i}–Cd(1)–O(4)–C(2)^{iii}	175.6 (7)
O(1)–Cd(1)–O(2)–C(2)	64.7 (6)	O(1)–Cd(1)–O(4)–Cd(1)^{i}	86.1 (3)
O(3)–Cd(1)–O(2)–C(2)	129.3 (6)	O(3)–Cd(1)–O(4)–Cd(1)^{i}	146.7 (2)
O(4)–Cd(1)–O(3)–C(1)^{ii}	−65.2 (6)	O(6)–Cd(1)–O(4)–Cd(1)^{i}	9.2 (6)
O(2)–Cd(1)–O(3)–C(1)^{ii}	−112.7 (6)	O(2)–Cd(1)–O(4)–Cd(1)^{i}	−164.2 (3)
O(1)–Cd(1)–O(4)–C(2)^{iii}	−98.2 (6)	O(4)^{i}–Cd(1)–O(4)–Cd(1)^{i}	0.0

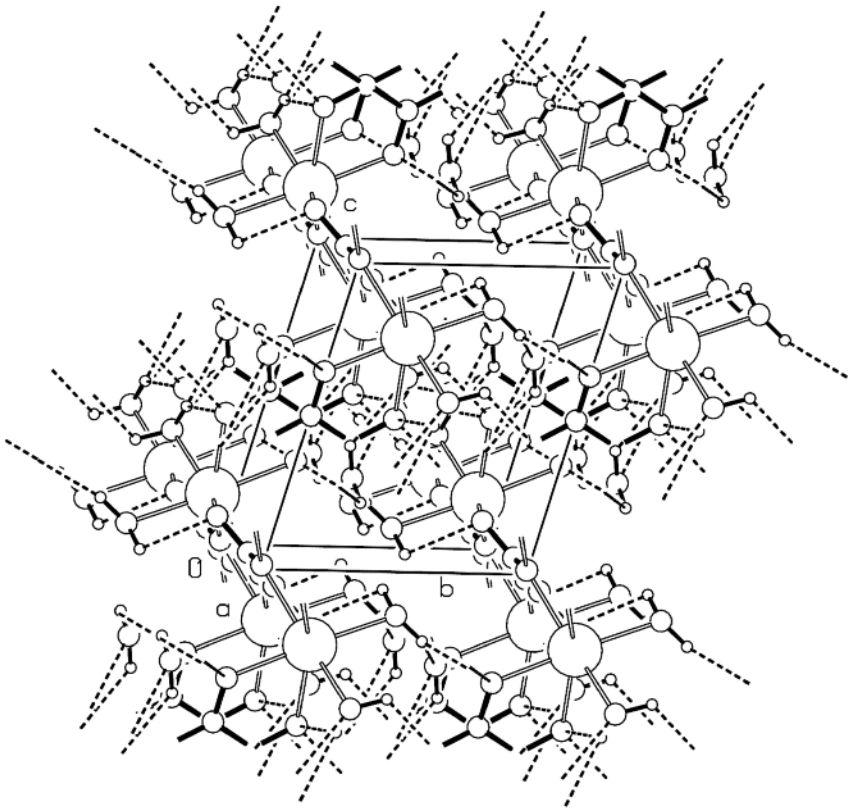

Fig. 3. Unit-cell packing diagram of polymeric compound $(C_2H_6CdO_7)_n$ viewed down the *a* axis. Hydrogen bonds are shown by dashed lines.

References

[1] Aghabozorg H., Ghadermazi M., Attar Gharamaleki J., *"A proton-transfer compound: 1,10-phenanthrolinium–2,4,5-tricarboxybenzoate–2,5-dicarboxybenzene-1,4-dicarboxylate (4/2/1)" Acta Cryst.*, *E62* (2006) o3174-o3176.

[2] Aghabozorg H., Ghasemikhah P., Ghadermazi M., Sheshmani S., *"Piperazinediium bis(pyridine-2,6-dicarboxylato)plumbate(II) dihydrate"*, *Acta Cryst*., *E62* (2006) m2835-m2837.

[3] Aghabozorg H., Aghajani Z., Sharif M. A., *"Bis(2,4,6-triamino-1,3,5-triazin-1-ium) bis(pyridine-2,6-dicarboxylato-κ^3O,N,O')cadmate(II)" Acta Cryst.*, *E62* (2006) m1930-m1932.

[4] Aghabozorg H., Zabihi F., Ghadermazi M., Attar Gharamaleki J., Sheshmani S., *"Piperazinediium bis(pyridine- 2,6 -dicarboxylato) cuprate(II) tetrahydrate", Acta Cryst*., *E62* (2006) m2091-m2093.

[5] Soleimannejad J., Aghabozorg H., Hooshmand S., Ghadermazi M., Attar Gharamaleki J., *"The monoclinic polymorph of catena-poly [[diaquamanganese (II)] - μ-oxalato-κ^4 O^1, O^2 :$O^{1'}$,$O^{2'}$]" Acta Cryst*., E63 (2007) m2389-m2390.

[6] Odoko M., Kusano A., Okabe N., *"Hexaaquabis (μ-pyridine-2,6-dicarboxylato O, N, O':O) dicadmium (II) – pyridine – 2,6-dicarboxylic acid (1/2)"*, *Acta Cryst., E58*, (2002) m25-m27.

[7] Ranjbar, M., Aghabozorg, H., Moghimi, A., *"A seven-coordinate pyridine-2,6-dicarboxylate-bridged cadmium(II) complex, at 110 K*", Acta Cryst., E58 (2002) m304-m306.