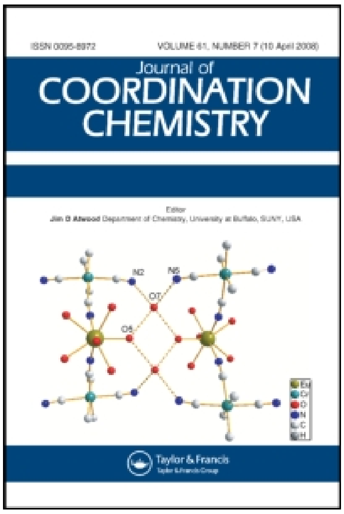
This article was downloaded by:
On: *23 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

One-pot synthesis and crystal structure of diaquabis(hydrazoneglyoxylato)cadmium(II)

S. Yasodhai[a]; V. Gomathi[a]; B. Vinobha[a]; K. Saravanan[b]
[a] Department of Chemistry, Kongunadu Arts and Science College, Coimbatore, Tamil Nadu, India [b] Department of Science and Humanities, Sri Krishna College of Engineering and Technology, Coimbatore, Tamilnadu, India

To cite this Article Yasodhai, S. , Gomathi, V. , Vinobha, B. and Saravanan, K.(2006) 'One-pot synthesis and crystal structure of diaquabis(hydrazoneglyoxylato)cadmium(II)', Journal of Coordination Chemistry, 59: 14, 1615 — 1620

To link to this Article: DOI: 10.1080/00958970500537812

URL: http://dx.doi.org/10.1080/00958970500537812

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Journal of Coordination Chemistry
Vol. 59, No. 14, 20 September 2006, 1615–1620

Taylor & Francis
Taylor & Francis Group

One-pot synthesis and crystal structure of diaquabis(hydrazoneglyoxylato)cadmium(II)

S. YASODHAI*†, V. GOMATHI†, B. VINOBHA† and K. SARAVANAN‡

†Department of Chemistry, Kongunadu Arts and Science College,
Coimbatore 641 029, Tamil Nadu, India
‡Department of Science and Humanities, Sri Krishna College of Engineering and
Technology, Coimbatore 641 008, Tamilnadu, India

(*Received in final form 4 November 2005*)

The mononuclear complex [Cd($H_2NNCHCOO)_2(H_2O)_2$] has been prepared from an aqueous solutions of reactants by one-pot synthesis and is characterized by IR, TG-DTA and single-crystal X-ray diffraction studies. The cadmium ion has distorted octahedral coordination (C_2 symmetry) with two *trans* water molecules and oxygen and nitrogen donors forming two five-membered chelate rings. On heating, the anhydrous complex decomposes in two steps yielding CdO.

Keywords: Cadmium; Glyoxylate; Hydrazone; Crystal structure; Thermal study

1. Introduction

Large numbers of metal hydrazine complexes possessing many interesting structural features have been prepared and characterized. A most intriguing aspect of them is the coordinating ability of hydrazine in the presence of a carboxylate [1–12]. This has opened up a new area of coordination chemistry involving hydrazine complexes with unique properties. In continuation of our studies on the chemistry of hydrazine compounds, we have prepared and a considerable number of metal complexes containing hydrazine and carboxylic acids [8–10, 13–15]. Hydrazones have a particular ability to chelate transition metals [16]. This has invoked further attention due to their anticancer, antitumour and antioxidative activities, among others.

One of the smallest carboxylic acids, glyoxylic acid is is of interest due to the presence of acid and reactive aldehyde groups. It is expected that both functionalities could be utilized and exploited for complex formation with hydrazine. This anticipation is born out by the study reported below. To date, little of the detailed chemistry and structures of hydrazine or hydrazone complexes derived from glyoxylic acid with transition metals has been reported. Other hydrazone complexes are mainly concerned with first row

---

*Corresponding author. Email: suyaso@yahoo.com

ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958970500537812

transition metals. Cadmium, which behaves in a similar way to other divalent first row transition metal ions, has not been studied to any depth. For these reasons, it was considered worthwhile to investigate a cadmium glyoxylatehydrazone complex and the results if this are presented here.

2. Experimental

Elemental analyses (CHN) were carried out on a Perkin-Elmer 240B instrument. The cadmium content was estimated by complexometric titration with EDTA. IR spectra (4000–400 cm^{-1}) were recorded in Nicolet Avadar FT spectrophotometer. TG-DTA measurements were performed using a Netzsch Geratebau GMBH thermal analyzer. The complex was prepared by the addition of an aqueous solution (10 cm^3) of glyoxylic acid monohydrate (0.46 g, 5 mmol) and hydrazine hydrate (0.5 cm^3, 10 mmol) to an aqueous solution (10 cm^3) of cadmium nitrate tetrahydrate (0.727 g, 2.5 mmol). The resulting clear solution (pH 4) was set aside for crystallization at room temperature for a day, resulting in the formation of single crystals. These were filtered off, washed with water, alcohol, and ether and dried in air. Yield: 80%. Anal. Calcd for $C_2H_5Cd_{0.5}N_2O_3$ (%): Cd, 35.00; C, 19.10; H, 3.00; N, 18.45. Found: Cd, 35.20; C, 19.12; H, 2.98; N, 18.53.

A crystal fragment of the complex with dimensions $0.20 \times 0.25 \times 0.15$ mm was mounted on an Enaf Nonius MACH3 CAD4 diffractometer using monochromated Mo-Kα radiation at 293 K. Unit cell parameters were obtained by least-squares fit of θ values for several high angle reflections. A total of 1108 reflections was collected up to θ_{max} of 24.96°. The number of independent reflections was 564 with $R(\text{int}) = 0.0232$. Absorption corrections were made by psi-scans. Structure solution (direct methods) and refinement was made using SHELXS and SHELXL programs. The positions of the hydrogen atoms were located using the HFIX instruction. In initial stages of refinement thermal parameters were kept isotropic and after convergence, anisotropic refinement was continued. The final R_1 was 0.0191 ($wR_2 = 0.0475$). Crystal data and refinement details are listed in table 1. Important bond lengths and angles are given in table 2.

3. Results and discussion

An ORTEP diagram of the complex is shown in figure 1. The cadmium atom lies on a centre of symmetry and is bonded to two, symmetry-related, *trans* glyoxylatehydrazone ligands through oxygen and nitrogen donors to form two five-membered chelate rings. Two *trans* water molecules complete the coordination sphere. Bond lengths within the carbonyl groups are typical of M–O–C=O structures. The geometry around cadmium is a distorted octahedron (C_2 symmetry) with Cd–O1 2.260(15), Cd–N1 2.308(3) and Cd–Ow 2.365(2) Å (table 2 and figure 1). With the square plane formed by the two bidentates and water molecules in apical positions, the coordination polyhedron has the typical (4 + 2) arrangement.

Crystal packing involves N–H$\cdots$O and O–H$\cdots$O intermolecular hydrogen bonding. Molecules are interlinked through a zigzag chain of N–H$\cdots$Ow hydrogen bonds along the *b* axis. Parallel chains are connected along the *c* axis through N–H$\cdots$O2 H-bonds

Table 1. Crystal data and structure refinement details for [Cd($H_2NNCHCOO)_2(H_2O)_2$].

Empirical formula	$C_2H_5Cd_{0.5}N_2O_3$
Formula weight	161.28
Temperature (K)	293
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/a$
Unit cell dimensions	
a (Å)	6.851
b (Å)	8.936
c (Å)	7.971
β (°)	90.82
V (Å^3)	487.9
Z	4
D_{Calcd} (Mg m^{-3})	2.195
μ (mm^{-1})	2.257
$F(000)$	316
Crystal size (mm^3)	$0.2 \times 0.25 \times 0.15$
θ range for data collection (°)	2.56–24.96
Limiting indices	$0 \le h \le 8$, $-10 \le k \le 10$, $-1 \le l \le 9$
Reflections collected/unique	1108/564 [R(int) = 0.0232]
Completeness to $\theta = 24.96$ (%)	61.1
Absorption correction	psi-scan
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	564/0/91
Goodness-of-fit on F^2	1.184
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0191$, $wR_2 = 0.0475$
Extinction coefficient	0.088(4)
Largest diff. peak and hole (e Å^{-3})	0.604 and -0.461

Table 2. Significant bond lengths (Å) and angles (°) for Cd($H_2NNCHCOO)_2(H_2O)_2$].

Cd–O1	2.2608(15)	N1–N2	1.341(3)
Cd–N1	2.308(3)	C1a–O2a	1.245(3)
Cd–Ow	2.365(2)	C1–C2	1.491(3)
Ow–Hw2	0.74(4)	O1a–C1a	1.270(3)
Ow–Hw1	0.78(5)	N1–C2a	1.276(4)
O1–Cd–O1a	180.0	Cd–Ow–Hw2	118(4)
O1–Cd–N1	73.65(6)	C2a–N1a–N2a	120.6(3)
O1a–Cd–N1	106.35(6)	C2a–N1a–Cd	112.48(16)
N1a–Cd–N1	180.0	N2–N1–Cd	126.86(19)
O1–Cd–Ow	82.95(7)	N1–N2–H2A	118.8(17)
O1a–Cd–Ow	97.05(7)	N1–N2–H2B	118(2)
N1a–Cd–Ow	88.52(10)	H2A–N2–H2B	113(3)
N1–Cd–Ow	91.48(10)	O2a–C1a–O1a	124.29
Owa–Cd–Ow	180.0	O2a–C1a–C2a	117.16(18)
C1a–O1a–Cd	115.08(13)	O1a–C1a–C2a	118.53(19)
N1a–C2a–C1a	120.0(2)		
D–H···A	D···A	H···A	D–H–A
Ow–Hw2···O1#1	2.763(2)	2.06(4)	157(4)
Ow–Hw1···O2#2	2.705(3)	1.95(6)	165(6)
N2–H2A···Owa#3	3.028(3)	2.22(3)	171(2)
N2–H2B···O2#4	2.942(3)	2.18(4)	152(4)

Symmetry codes used are #1: $-x+1, -y, -z+1$; #2: $x-1/2, -y-1/2, z$; #3: $-x+1/2, y+1/2, -z+1$; #4: $-x+1/2, y+1/2, -z$.

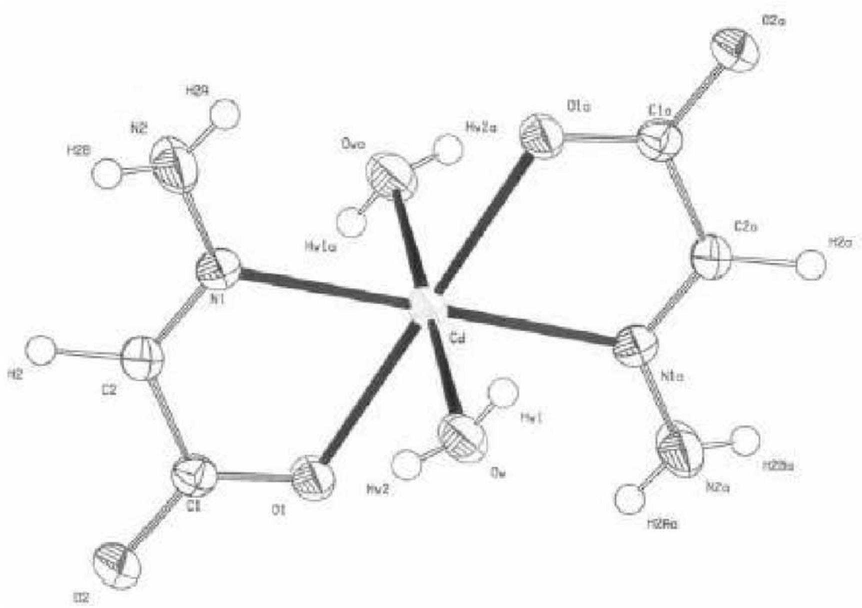


Figure 1. ORTEP diagram of [Cd($H_2NNCHCOO)_2(H_2O)_2$] with the atom numbering scheme.

to form a layer. The layers are stacked along *a* and bridged by both O–H· · ·O1 and O–H· · ·O2 H-bonds (figures 2 and 3 view down *b*). In hydrogen bonding, water acts both as donor and acceptor, whereas in the anionic ligand, the NH_2 group acts as a donor and the carboxylate as acceptor. Probable hydrogen bond dimensions are given in table 2; these range between 2.705 and 3.028 Å.

The infrared spectrum of the complex shows a broad band centred at 3383 cm^{-1} and due to the O–H stretch of water; the vibration attributable to the N–H mode is observed at 3129 cm^{-1}. A strong band at 2920 cm^{-1} is assigned to C–H stretching and the azomethine group gives a strong band at 1581 cm^{-1}. The N–N stretch of the hydrazone fragment is observed at 989 cm^{-1}. Asymmetric and symmetric carboxylate stretching modes are seen at 1613 and 1417 cm^{-1}, respectively; the separation, $\Delta\nu$, of 196 cm^{-1} is consistent with unidentate coordination [17].

The combustible nature of hydrazine facilitates the low temperature decomposition of hydrazine complexes and many such precursors have been developed to prepare pure spinel oxide powders containing cadmium [18, 19]. The thermal decomposition of the present complex has been investigated by TG and DTA. Initial decomposition in the temperature range 110–165°C is due to the loss of two water molecules. In DTA, this is observed as a broad endotherm at 130°C and the decomposition temperature suggests that the water molecules are loosely bound to the cadmium ion [20]. The anhydrous compound is stable up to 180°C, then decomposes between 184 and 195°C to yield cadmium carbonate. DTA shows a sudden sharp exotherm at 190°C and weight loss is consistent with the suggested intermediate. Cadmium oxide is the final product at higher temperatures (320–525°C) with two broad exotherms centred at 462 and 496°C. Thermogravimetric data are compatible with the DTA results (calculated percentage weight losses are 11.17, 46.52 and 60.17% for the three steps; observed values are 11.00, 47.10 and 60.00%, respectively).

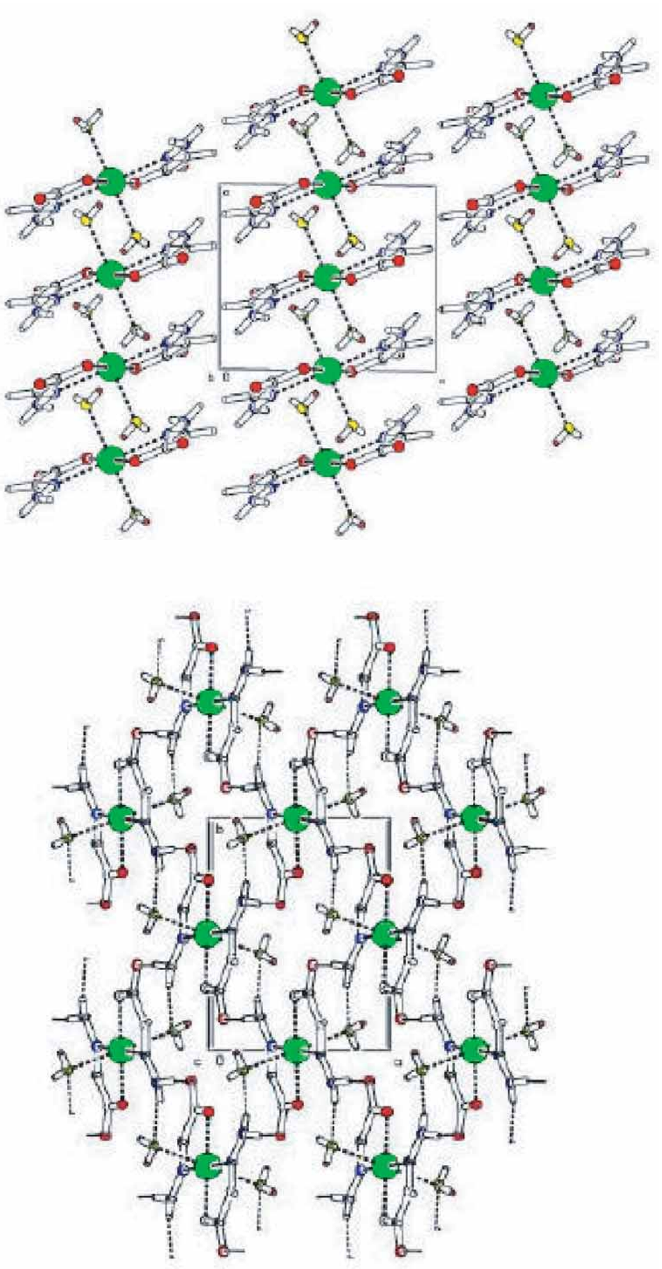


Figure 2. Packing of $[Cd(H_2NNCHCOO)_2(H_2O)_2]$ viewed down the *b* axis (upper) and the *c* axis (lower).

Supplementary data

Other crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, code number CCDC 275957.

Acknowledgements

The authors thank Dr R.K. Rajaram, School of Physics, Madurai Kamaraj University, Madurai for collecting the single-crystal data.

References

[1] K.C. Patil, D. Gajapathy, K. Kishore. *Thermochim. Acta*, **52**, 113 (1982).
[2] P. Ravindranathan, K.C. Patil. *Thermochim. Acta*, **71**, 53 (1983).
[3] D. Gajapathy, S. Govindarajan, K.C. Patil, H. Manohar. *Polyhedron*, **2**, 865 (1983).
[4] B.N. Sivasankar, S. Govindarajan. *Synth. React. Inorg. Met.-Org. Chem.*, **24**, 1573 (1994).
[5] E.R. Jiji, K.K. Aravindakshan. *J. Therm. Anal.*, **44**, 65 (1995).
[6] V. Jordanovska, R. Trojko. *Thermochim. Acta*, **258**, 205 (1995).
[7] K. Kuppusamy, B.N. Sivasankar, S. Govindarajan. *Thermochim. Acta*, **295**, 251 (1995).
[8] S. Yasodhai, S. Govindarajan. *Synth. React. Inorg. Met.-Org. Chem.*, **29**, 919 (1999).
[9] S. Yasodhai, T. Sivakumar, S. Govindarajan. *Thermochim. Acta*, **338**, 57 (1999).
[10] S. Yasodhai, S. Govindarajan. *Synth. React. Inorg. Met.-Org. Chem.*, **30**, 745 (2000).
[11] T. Premkumar, S. Govindarajan. *Thermochim. Acta*, **386**, 35 (2002).
[12] K. Saravanan, S. Govindarajan. *J. Therm. Anal. Cal.*, **73**, 951 (2003).
[13] S. Yasodhai, S. Govindarajan. *Indian J. Chem.*, **38A**, 1244 (1999).
[14] S. Yasodhai, S. Govindarajan. *J. Therm. Anal. Cal.*, **62**, 737 (2000).
[15] S. Yasodhai, S. Govindarajan. *J. Therm. Anal. Cal.*, **67**, 679 (2002).
[16] Z. Yang, R. Yang, K. Yu. *Polyhedron*, **15**, 3749 (1996).
[17] K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds* (Wiley-Interscience, New York, 1962).
[18] B.N. Sivasankar, S. Govindarajan. *Z. Naturforsch.*, **49b**, 950 (1994).
[19] K.C. Patil, M.M.A. Sekar. *Int. J. Self-Propagating High-Temp. Synth.*, **3**, 181 (1994).
[20] S. Govindarajan, K.C. Patil, H. Manohar, P.E. Werner. *J. Chem. Soc., Dalton Trans.*, 119 (1986).