



Hydrolysis of hydrazido-oxalic acid leading to the formation of hydrazinium cadmium hydrazido-oxalate/uranium oxalate species with a polymeric structure



Rajendran Selvakumar^a, Steven J. Geib^b, Thatthan Premkumar^{c,*}, Subbiah Govindarajan^{a,*}

^a Department of Chemistry, Bharathiar University, Coimbatore 641 046, Tamilnadu, India

^b Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260, United States

^c The University College and Department of Chemistry, Sungkyunkwan University, Suwon 440-746, South Korea

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ABSTRACT

A series of new metal hydrazido-oxalates with the formula $[M(\text{Hox})_2(\text{H}_2\text{O})_2] \cdot n\text{H}_2\text{O}$, where $M = \text{Co}$ (**1**), Ni (**2**) and Zn (**3**); $\text{Hox} = \text{hydrazido-oxalate}$; $n = 0$ (Co), 1 (Ni) and 5 (Zn), as well as $(\text{N}_2\text{H}_6)_{0.5}[\text{Cd}(\text{Hox})_2]\text{NO}_3$ (**4**) and the hydrazinium uranyl oxalate $(\text{N}_2\text{H}_6)[(\text{UO}_2)_2(\text{C}_2\text{O}_4)_3] \cdot 2\text{H}_2\text{O}$ (**5**) were synthesized. Among the five synthesized compounds, the structures of **1**, **4** and **5** were characterized by single crystal X-ray diffraction. The hydrazinium cation and oxalate anions generated in the synthesis were derived from hydrazido-oxalic acid, which is present in compounds **4** and **5**. The structure of compound **1** consists of an octahedral coordination around cobalt, arising from two chelating (N,O) acid hydrazide ligands, coordinating through the carbonyl oxygen and hydrazinic nitrogen atoms in a *cis*-fashion, and two monodentate water molecules. It is interesting to note that the anionic carboxylate moieties are not involved in the coordination. Unlike cobalt, the anhydrous cadmium compound (**4**) consists of a hydrazinium (+2) cation, nitrate anion and a neutral cadmium hydrazido-oxalate complex. In this complex, the Cd(II) site has a coordination number of eight, comprising of six oxygen atoms and two nitrogen atoms with four adjacent hydrazido-oxalates. Thus, the polyhedral arrangement around the cadmium atoms is connected by hydrazido-oxalate groups to form a 2D framework $[\text{Cd}(\text{Hox})_2]$, with tunnels and a square grid cross-section in two directions which form a cavity at their intersection. The structure of compound **5** consists of a two-dimensional network of uranyl and oxalate ions that form hexagonal rings. Specifically, the oxalate ions are tetradentate, each bridging two uranyl ions which are coordinated by three oxalate groups, and this results in a distorted hexagonal bipyramidal environment for the uranium atoms.

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1. Introduction

Oxalic acid can form two types of acid hydrazides, *viz.* oxalic acid monohydrazide (hydrazido-oxalic acid, $\text{H}_2\text{N}-\text{NH}-\text{CO}-\text{COOH}$; HHox) and oxalyl dihydrazide ($\text{H}_2\text{N}-\text{NH}-\text{CO}-\text{CO}-\text{NH}-\text{NH}_2$). Between the two, the latter dihydrazide has been extensively studied as a ligand owing to its presence in several structures [1–3] due to different hydrogen bonding opportunities in the solid state, leading to abundant polymorphisms [4]. In addition, oxalyl dihydrazide can act as both a neutral and deprotonated multidonor

ligand due to possible amido-imidol tautomerism; this property has been exploited by various researchers in order to synthesize a variety of neutral and/or anionic complexes with interesting biological [5,6] and spectroscopic properties [7,8]. However, despite intense investigations, solid state structures based on oxalyl dihydrazide have not been studied, primarily due to their polymeric nature which can lead to poor solubility in many solvents, including water.

Unlike oxalyl dihydrazide, the chemistry of oxalic acid monohydrazide is largely unknown, with the exception of a few preliminary accounts of its preparation [9,10]. While HHox can be derived from diethyl oxalate, potassium acetate and alcoholic hydrazine hydrate, the resulting metal complexes have not been studied. We recently performed a series of experiments involving oxamic acid and hydrazine hydrate that resulted in the formation of hydrazido oxalic acid as an unintentional product. We hypothesized that the different functional groups ($-\text{COO}^-$ and $-\text{CO}-\text{NH}-\text{NH}_2$) may bind to metals

* Corresponding authors at: The University College and Department of Chemistry, Sungkyunkwan University, Suwon 440-746, South Korea (T. Premkumar); Department of Chemistry, Bharathiar University, Coimbatore 641 046, Tamilnadu, India (S. Govindarajan).

E-mail addresses: thatthanpremkumar@gmail.com (T. Premkumar), drsgovind@yahoo.co.in (S. Govindarajan).

Table 1
Crystal data and structure refinement for **1**, **4** and **5**.

Empirical formula	C ₄ H ₁₀ CoN ₄ O ₈	C ₄ H ₉ CdN ₆ O ₉	C ₃ H ₃ UNO ₉
Formula weight	301.09	397.57	436.10
Temperature (K)	150(2)	173(2)	203(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	orthorhombic	monoclinic	monoclinic
Space group	<i>Pna</i> 2 ₁	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>Unit cell dimensions</i>			
<i>a</i> (Å)	9.8723(6)	10.6999(5)	5.5420(7)
<i>b</i> (Å)	8.3555(5)	9.4421(4)	19.528(3)
<i>c</i> (Å)	11.8680(7)	11.2283(5)	8.5300(11)
α (°)	90	90	90
β (°)	90	108.9350(10)	102.539(2)
γ (°)	90	90	90
Volume (Å ³)	978.97(1)	1073.00(8)	901.2(2)
<i>Z</i>	4	4	4
Density (calc.) (Mg/m ³)	2.043	2.461	3.214
Absorption coefficient (mm ⁻¹)	1.798	2.103	18.043
<i>F</i> (000)	612	780	772
Crystal size (mm)	0.31 × 0.25 × 0.08	0.12 × 0.12 × 0.12	0.26 × 0.22 × 0.12
Theta range for data collection (°)	2.98–32.56	2.89–32.59	2.09–30.00
Index ranges	–14 ≤ <i>h</i> ≤ 14, –12 ≤ <i>k</i> ≤ 12, –17 ≤ <i>l</i> ≤ 17	–15 ≤ <i>h</i> ≤ 15, –13 ≤ <i>k</i> ≤ 13, –16 ≤ <i>l</i> ≤ 16	–7 ≤ <i>h</i> ≤ 7, –27 ≤ <i>k</i> ≤ 27, –11 ≤ <i>l</i> ≤ 11
Reflections collected	12117	13540	9949
Independent reflections (<i>R</i> _{int})	3478 (0.0137)	3776 (0.0157)	2620 (0.0428)
Completeness to theta = 32.59° (%)	98.9	96.3	99.7
Absorption correction	none	multi-scan	semi-empirical from equivalents
Maximum and minimum transmissions	0.8695 and 0.6056	0.7864 and 0.7864	0.2207 and 0.0889
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	3478/1/195	3776/0/217	2620/1/126
Goodness-of-fit (GOF) on <i>F</i> ²	1.092	0.832	1.979
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0203, <i>wR</i> ₂ = 0.0594	<i>R</i> ₁ = 0.0204, <i>wR</i> ₂ = 0.0735	<i>R</i> ₁ = 0.0598, <i>wR</i> ₂ = 0.2001
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0212, <i>wR</i> ₂ = 0.0533	<i>R</i> ₁ = 0.0217, <i>wR</i> ₂ = 0.0760	<i>R</i> ₁ = 0.0631, <i>wR</i> ₂ = 0.2028
Largest difference in peak and hole (e Å ⁻³)	1.159 and –0.246	1.364 and –0.556	11.299 and –5.725

in different manners, as exhibited by hydrazido carboxylate [11] (–NH₂–NH–COO[–]). Therefore, the present study was aimed at establishing the nature of binding between hydrazido oxalic acid ligands and metal ions such as Co, Ni, Zn, Cd and UO₂.

2. Experimental

2.1. Materials and methods

All of the chemicals used for the preparation of the ligands and complexes were of analytical grade and were used without further purification. Elemental analyses were carried out with a Perkin Elmer 240B CHN analyzer. IR spectra were recorded with a Shimadzu FTIR 8000 spectrometer, with the samples prepared as KBr pellets. The simultaneous TG-DTA curves were recorded using a Perkin Elmer Pyris Diamond instrument at a heating rate of 10 °C min⁻¹ under air. The hydrazine content of the salts and

Table 2
Selected bond lengths (Å) and angles (°) for compound **1**.

Co–O(8)	2.0495(9)	O(8)–Co–O(7)	178.56(4)
Co–O(7)	2.0611(9)	O(8)–Co–O(4)	89.96(4)
Co–O(4)	2.0843(8)	O(7)–Co–O(4)	89.22(4)
Co–N(1)	2.1094(9)	O(8)–Co–N(1)	91.70(4)
Co–O(1)	2.1520(8)	O(7)–Co–N(1)	89.00(4)
Co–N(3)	2.1686(10)	O(4)–Co–N(1)	174.08(3)
N(1)–N(2)	1.4193(12)	O(8)–Co–O(1)	89.35(3)
N(3)–N(4)	1.4256(13)	O(7)–Co–O(1)	89.57(4)
		O(4)–Co–O(1)	96.61(3)
		N(1)–Co–O(1)	77.73(4)
		O(8)–Co–N(3)	89.07(4)
		O(7)–Co–N(3)	91.91(4)
		O(4)–Co–N(3)	78.01(3)

Table 3
Selected bond lengths (Å) and angles (°) for compound **4**.

Cd–O(6)#1	2.3135(10)	O(6)#1–Cd–O(3)#2	137.98(4)
Cd–O(3)#2	2.3215(11)	O(6)#1–Cd–N(2)#2	150.38(4)
Cd–N(2)#2	2.3584(12)	O(3)#2–Cd–N(2)#2	71.56(4)
Cd–O(4)	2.3897(12)	O(6)#1–Cd–O(4)	91.81(4)
Cd–O(2)	2.4012(11)	O(3)#2–Cd–O(4)	88.58(4)
Cd–N(4)#1	2.4072(13)	N(2)#2–Cd–O(4)	90.91(4)
Cd–O(1)	2.5816(11)	O(6)#1–Cd–O(2)	91.10(4)
Cd–O(5)	2.7342(10)	O(3)#2–Cd–O(2)	92.12(4)
N(1)–N(2)	1.4102(18)	N(2)#2–Cd–O(2)	84.46(4)
N(3)–N(4)	1.4083(17)	O(4)–Cd–O(2)	174.83(4)
		O(6)#1–Cd–N(4)#1	70.04(4)
		O(3)#2–Cd–N(4)#1	151.97(4)
		N(2)#2–Cd–N(4)#1	80.49(4)
		O(4)–Cd–N(4)#1	89.73(4)
		O(2)–Cd–N(4)#1	87.24(4)
		O(6)#1–Cd–O(1)	73.70(4)
		O(3)#2–Cd–O(1)	75.18(4)
		N(2)#2–Cd–O(1)	123.89(4)
		O(4)–Cd–O(1)	132.10(4)

complexes were determined volumetrically using a standard KIO₃ (0.025 M) solution under Andrews' conditions [12]. The metal content in the complexes was estimated by complexometric titration with EDTA [13] after decomposing a known weight of the sample with nitric acid and bringing it to a standard volume.

2.2. Synthesis of hydrazido-oxalic acid

Hydrazido oxalic acid was obtained as pure white polycrystalline solid by adding 2.5 mL (0.005 mol) of 10% hydrazine hydrate to a 30 mL aqueous solution containing 0.445 g (0.005 mol) of

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