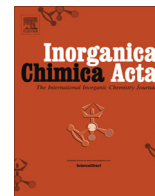




Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Research paper

Structural motifs in heteroleptic copper and cadmium selenites

Stefano Canossa^a, Enrico Bellè^a, Massimiliano Delferro^c, Giovanni Predieri^b, Claudia Graiff^{b,*}^a Dipartimento di Chimica, Università di Parma, Parco Area delle Scienze 17/A, 43124 Parma, Italy^b C.I.R.C.C., Consorzio Interuniversitario Reattività Chimica e Catalisi, Via Celso Ulpiani 27, 70126 Bari, Italy^c Chemical Sciences and Engineering Division, Argonne National Laboratory, 9700 S Cass Avenue, Lemont, IL 60439, USA¹

ARTICLE INFO

Article history:

Received 7 March 2017

Received in revised form 27 April 2017

Accepted 22 May 2017

Available online xxxxx

In honor of Dr. Carlo Mealli for his outstanding contributions in the field of inorganic, organometallic, and cluster chemistry.

Keywords:

Copper

Cadmium

Selenium

Crystal structure

Selenite compound

Selenourea and thiourea cadmium compounds

ABSTRACT

Cu(II) cations in the presence of diamine ligands such as tetramethylethylenediamine (TMEDA) react with Na_2SeO_3 to produce the heteroleptic selenite copper compound of formula $[\text{Cu}_3(\text{TMEDA})_3(\text{SeO}_3)_2(\text{H}_2\text{O})_4](\text{NO}_3)_2$. In the cationic moiety two copper atoms are linked by two selenite anions through the O–Se–O bridge. One of the two bridging selenite anion coordinates to a third copper atom through the third oxygen atom. Reaction of $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ with Na_2SeO_3 in the presence of ligand with softer character such as thiourea $[(\text{NH}_2)_2\text{CS}; \text{tu}]$ or selenourea $[(\text{NH}_2)_2\text{CSe}; \text{tu}]$ in aqueous solution afforded the complex $[\{\text{Cd}(\text{tu})_2\text{SeO}_3\}_2]$, whose structure has been elucidated by X-ray diffraction analysis. It is the first reported example of a molecular cadmium selenite complex. Two cadmium cations stabilized by the coordination of four ancillary thiourea soft ligands, are linked together by two bridging selenite ions through O and O–Se–O bridges. A comparison between the coordination mode of the selenite ion in those cadmium and copper complexes and in inorganic extended CdSeO_3 and hydrated CuSeO_3 phases is also reported.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

The chemistry of inorganic materials containing chalcogen elements (S, Se, Te) oxy-anions in the +4 oxidation state is still of interest in the research community for several reasons. First, it is known that the incorporation of XO_3^{2-} ($\text{X} = \text{S}, \text{Se}, \text{Te}$) anions can lead to non-centrosymmetric structures and consequently those materials display interesting non-linear optical properties [1] ferroelectricity and piezoelectricity [2]. Moreover the presence of the lone pair on the chalcogen atom can be the structure-directing agent towards the formation of crystal structures characterized by the presence of space such as hollows or channels [3]. Actually, the lone pair belonging to the chalcogen (IV) elements can be viewed as “structural scissors” that prevent or inhibit the formation of extended three-dimensional network [4]. In addition, the weakly coordinative capability of the Se(IV) and Te(IV) electron lone pairs has been recently suggested [5] as responsible for supramolecular interaction as observed in the solid state for the anions $[\text{Pd}_{15}(\mu_3\text{-SeO}_3)_{10}(\mu_3\text{-O})_{10}\text{Na}]^{9-}$. Furthermore, when selenite or tellurite

anions act as bridging ligands towards metal atoms they can bring close the transition cationic metals allowing magnetic exchange between paramagnetic centers [6,7].

On the other hand, it has been observed [7] and [8] that by using suitable organic mono or bidentate ligands containing donor soft atoms, such as ethylenediamine (en), tetramethylethylenediamine (TMEDA), thiourea (tu), phenanthroline (phen), bipyridine (bipy), it is possible to obtain novel structures evidencing the presence of discrete oligonuclear transition metal selenite or tellurite complexes which exhibits analogous structural motif of inorganic extended selenite or tellurite phases.

Finally, it has been recently reported [9] that a copper trimesate selenite shows a high robust three dimensional open framework structure, which is retained upon the removal of guest and coordinated little molecules. The porous structure is due to the presence of the lone pair on the chalcogen atom opening the way to the utilization of selenite derivatives in the synthesis of Metal Organic Frameworks (MOFs) or Porous Coordination Polymers (PCPs) [10,11].

In this paper, pursuing our interest in the chemistry of selenite transition metal complexes we report the synthesis and characterization of two new heteroleptic copper and cadmium selenite of formula $[\text{Cu}_3(\text{TMEDA})_3(\text{SeO}_3)_2(\text{H}_2\text{O})_4](\text{NO}_3)_2$ and $[\{\text{Cd}(\text{tu})_2\text{SeO}_3\}_2]$,

* Corresponding author.

E-mail address: claudia.graiff@unipr.it (C. Graiff).¹ Present address.

respectively. The presence of the ligands (TMEDA and tu) allows the formation of discrete oligonuclear complexes without forming extended coordination network, as formed in the two polymorphs (monoclinic and orthorhombic) $\text{CuSeO}_3 \cdot 2\text{H}_2\text{O}$ and CdSeO_3 . A comparison between the structural motifs observed in the above mentioned compounds and in the extended inorganic phases is also carried out.

2. Experimental section

2.1. General remarks

All manipulations were carried out at room temperature in the air; $(\text{NH}_2)_2\text{CS}$ (thiourea), $(\text{NH}_2)_2\text{CSe}$ (selenourea), tetramethylethylenediamine (TMEDA), $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and Na_2SeO_3 were purchased and used as received (Aldrich). The C, H, N elemental analysis were carried out by using a Carlo Erba EA1108 microanalyzer. FTIR spectra ($4000\text{--}400\text{ cm}^{-1}$) were recorded on a Nicolet Nexus spectrophotometer equipped with a Smart Orbit HATR accessory (diamond or ZnSe).

2.1.1. Preparation of $[\text{Cu}_3(\text{TMEDA})_3(\text{SeO}_3)_2(\text{H}_2\text{O})_4](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ (**1**· H_2O)

A water solution (5 mL) of Na_2SeO_3 (0.115 g, 0.66 mmol) was added dropwise to a water solution (15 mL) containing $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.160 mg, 0.66 mmol) and TMEDA (0.077 g, 0.66 mmol). The blue solution was stirred at room temperature for 1 h. Then the solvent was allowed to evaporate. The solid was redissolved in water and, by slow crystallization using acetone as non-solvent, small amount of blue crystals suitable for X-ray analysis were obtained (Yield 10%), together with very few pale blue ones, which were identified as hydrated inorganic CuSeO_3 salts in two polymorphic phases (see discussion). Anal. Calcd. for: $\text{C}_{18}\text{H}_{58}\text{Cu}_3\text{N}_8\text{O}_{17}\text{Se}_2$ (MW = 1007.26): C 21.46; H 5.80; N 11.12. Found: C 21.07; H 5.55; N 11.09. FTIR (Diamond crystal HATR, cm^{-1}): $\nu = \nu(\text{N-H})$ 3048 cm^{-1} , $\nu(\text{N-O})$ 1307 cm^{-1} , $\nu(\text{Se-O})$ 707 cm^{-1} .

2.1.2. Preparation of $[\{\text{Cd}(\text{tu})_2\text{SeO}_3\}_2] \cdot 2\text{H}_2\text{O}$ (**2**· $2\text{H}_2\text{O}$)

A water solution (5 mL) of Na_2SeO_3 (0.136 g, 0.8 mmol) was added to a water solution (15 mL) of $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (0.205 mg, 0.8 mmol) and thiourea (0.233 g, 3.2 mmol). The resulting mixture was stirred at reflux for 70 min and the colour turned to red-orange and then filtered. The red solid was recognized as selenium. Colourless crystals of **2**· $2\text{H}_2\text{O}$ suitable for X-ray analysis were obtained by slow evaporation of the solvent (Yield 10%). Anal. Calcd. for: $\text{C}_4\text{H}_{20}\text{Cd}_2\text{N}_8\text{O}_8\text{S}_4\text{Se}_2$ (MW = 819.24): C 5.86; H 2.46; N 13.68. Found: C 5.05; H 2.35; N 13.38. FTIR (Diamond crystal HATR, cm^{-1}): $\nu = 3329, 3047, 711$, fingerprint thiourea: 1614, 1506, 1144.

2.1.3. Preparation of $[\{\text{Cd}(\text{su})_2\text{SeO}_3\}_2]$ (**3**)

A water solution (5 mL) of Na_2SeO_3 (0.066 g, 0.4 mmol) was added to a water solution (15 mL) of $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (0.102 mg, 0.4 mmol) and selenourea (0.194 g, 1.6 mmol). The resulting mixture was stirred at room temperature for 30 min and the colour turned to red-orange and then filtered. The red solid was recognized as selenium. By evaporation of the solvent a white microcrystalline powder was obtained (Yield 15%). Anal. Calcd. for: $\text{C}_4\text{H}_{16}\text{Cd}_2\text{N}_8\text{O}_6\text{Se}_6$ (MW = 970.8): C 4.95; H 1.66; N 11.54. Found: C 4.55; H 1.45; N 11.32. FTIR (Diamond crystal HATR, cm^{-1}): $\nu = 3354, 3032, 1635, 1517, 1401, 578$.

2.2. X-ray data collection, structure solution and refinement of **1**· H_2O , **2**· $2\text{H}_2\text{O}$, $\text{CuSeO}_3 \cdot 2\text{H}_2\text{O}$ (phase I) and $\text{CuSeO}_3 \cdot 2\text{H}_2\text{O}$ (phase II)

The intensity data of compounds **1**· H_2O , **2**· $2\text{H}_2\text{O}$, $\text{CuSeO}_3 \cdot 2\text{H}_2\text{O}$ (phase I) and $\text{CuSeO}_3 \cdot 2\text{H}_2\text{O}$ (phase II) were collected at room tem-

perature on a Bruker APEX II and on a Bruker AXS Smart 1000 single crystal diffractometers, both equipped with area detector and using a graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$). Crystallographic and experimental details of the structures are summarized in Tables 1 and 2. The structures were solved by direct methods and refined by the full-matrix least-squares technique in the anisotropic approximation using the SHELXS-97 and SHELXL-2014/7 programs [12]. The hydrogen atoms were introduced into the geometrically calculated positions and refined riding on the corresponding parent atoms, excepting the hydrogen atoms of the water molecules from crystallization in **1**· H_2O . The hydrogen atoms of the water molecules in **2**· $2\text{H}_2\text{O}$ were found in the ΔF . Crystallographic data for compounds **1**· H_2O , and **2**· $2\text{H}_2\text{O}$ have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication (CCDC numbers in Tables 1 and 2). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (+44) 1223 336033; e-mail, deposit@ccdc.cam.ac.uk).

3. Results and discussion

Recently [7] we have reacted $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with Na_2SeO_3 in the presence of TMEDA in a water/ethanol mixture obtaining the heteroleptic complex $[\{\text{Ni}(\text{TMEDA})\text{SeO}_3\}_2]$. Single-crystal X-ray diffraction analysis showed that this complex consists of a dinuclear species in which the two nickel atoms are held together by two bridging selenite anions. Knowing that the coordination mode of the selenite group with the capability of build up a discrete dinuclear compound such as $[\{\text{Ni}(\text{TMEDA})\text{SeO}_3\}_2]$ was unusual, we decided to continue this type of investigation by reacting metal (II) cations with Na_2SeO_3 in the presence of TMEDA and different ligands.

3.1. Description of the heteroleptic selenite compound $[\text{Cu}_3(\text{TMEDA})_3(\text{SeO}_3)_2(\text{H}_2\text{O})_4](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ (**1**· H_2O)

In this regard, we tried to reproduce the synthesis of a dinuclear complex, eventually analogous to the Ni one described above, by using copper(II) cations, being however well conscious of the significant differences between the copper and nickel coordination demands. Actually, although we used the same molar ratio adopted for the nickel complex ($\text{Cu}/\text{Se}/\text{TMEDA}$ 1:1:1) we could not obtain any compound corresponding to these molar ratios. The X-ray diffraction analysis of blue crystals, obtained by slow evaporation of acetone solution, revealed that the compound has formula $[\text{Cu}_3(\text{TMEDA})_3(\text{SeO}_3)_2(\text{H}_2\text{O})_4](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ (**1**· H_2O). It is interesting to note that, even if the Cu/TMEDA 1:1 ratio is maintained, the selenite anions were unable to form the dinuclear structure obtained with nickel(II), likely owing to the Jahn-Teller distortions exerted by copper(II) cations. The ORTEP plot of the cationic unit is reported in Fig. 1, together with the atomic labeling scheme. A list of the most important bond distances and angles is collected in Table 3.

Complex **1**· H_2O is a trinuclear compound in which the selenite anions link two copper atoms through O–Se–O bridges, forming a eight-membered ring. One of the selenite anion is also bound to the third copper metal by the third O atom.

Cu1 and Cu2 copper atoms show a distorted squared pyramidal environment, in agreement with the τ parameter defined in [13] ($\tau = 0.12$ and 0.21 for Cu1 and Cu2 respectively). The squared pyramidal coordinations are achieved through the two nitrogen atoms of the TMEDA ligand, two oxygen atoms of the bridging selenite anions and one water molecule, occupying the apical positions; Cu3 copper atom shows also a squared pyramidal

Download English Version:

<https://daneshyari.com/en/article/7750830>

Download Persian Version:

<https://daneshyari.com/article/7750830>

[Daneshyari.com](https://daneshyari.com)