Zinc and cadmium iodide complexes with (thio)amides: Transformations of formamide complexes and effects of substitution on structure and bonding

Elena V. Savinkina [a,*], Ilya A. Zamilatskov [b], Andrey S. Kuzovlev [a], Dmitry V. Albov [c], Denis V. Golubev [a], Vladimir V. Chernyshev [b,c]

[a] Department of Inorganic Chemistry, Lomonosov University of Fine Chemical Technology, Vernadsky Prospect, 86, Moscow 119571, Russia
[b] Frumkin Institute of Physical Chemistry and Electrochemistry RAS, Leninsky Prospect, 31, Moscow 119071, Russia
[c] Department of Chemistry, Lomonosov Moscow State University, Leninskie Gory, 1–3, Moscow 119991, Russia

ARTICLE INFO

ABSTRACT

Complexes of formamide and dimethylacetamide with cadmium iodide, $[Cd(HCONH_2)_2I_2]$, $[Cd(HCONH_2)_4I_2]$, $[Cd_3(HCONH_2)_2I_6]$, and $[Cd(MeCONMe_2)_6][Cd_2I_6]$ and of 5-acetyl-6-methyl-1,2,3,4-tetrahydropyrimidine-2-thione (MP) with zinc iodide, $[Zn(MP)(H_2O)I_2]$, were synthesized; their crystal structures were studied by X-ray diffraction. Unique transformations of cadmium iodide complexes with formamide were observed. Structural diversity of zinc and cadmium iodide complexes with (thio)amides is discussed in terms of donating ability of the ligands, steric requirements and sizes and polarizing power of the cations.

Published by Elsevier Ltd.

1. Introduction

Metal sulfide, nitride and oxide thin films and nanoparticles are now widely applied in photovoltaics, microelectronics, displays and many other devices [1]. For example, CdS, ZnO, ZnS thin films are applicable for solar cells [2]. A goal of nanochemistry is to develop safe, cost-effective, high-yielding and well-controllable methods of nanoparticle synthesis, where the nature of a precursor plays an important role. Few classes of single source precursors were successful for deposition of good quality metal sulfide, nitride and oxide thin films and nanoparticles; these are metalorganics, carbonyls, hydrides, chlorides and other volatile compounds in gaseous, liquid or solid state [3–5]. A search for new precursors with suitable volatility, solubility and ability to deposit films or nanoparticles with little or no contamination is still an actual task for nanochemistry [6,7].

Metal complexes with amides and ureas and their thio derivatives can serve as promising precursors in preparation of thin films and nanoparticles [8–10]. For example, various zinc and cadmium (alkyl)thiourea complexes as precursors for the synthesis of nano-ZnS and CdS were reported [11,12].

As has been shown by Pentia and coworkers [13], CdS layers prepared from thiourea and different cadmium salts in the same conditions led to the layers with different morphology and properties due to the decreasing of the deposition rate with the cadmium salt anion type in the following sequence: $Cl^- > CH_3COO^- > NO_3^- > SO_4^{2-} > I^-$ [14]. However, the nature of the organic ligand in a precursor should be taken into account too, because it determines the structure of the corresponding complex and, subsequently, affects the quality of the final product.

(Thio)amides and (thio)ureas are also important for biochemistry, since amides form key linkages in natural proteins and polypeptides macromolecules [15], while cyclic thioureas, such as so called "Biginelli compounds", attract significant attention due to their biological activities [16].

* Corresponding author. Tel.: +7 903 7762106; fax: +7 495 4348711.
E-mail address: e.savinkina@mail.ru (E.V. Savinkina).

The general coordination behavior of amides and ureas and their thio derivatives is known for a long time. In the review of Clement et al. [17] on crystal structure data of simple amides and metal complexes containing monodentate amide ligands, structural features were discussed with the use of statistical analysis of a function depending on the degree of alkylation of the amide functional group, the type of metal ion in the amide complex, and the type of binding to the metal ion. To minimize any structural impact caused by inductive effects and changing amide basicity, only formamide and acetamide and their N-alkyl derivatives were discussed. However, more complex ligands are still of interest.

Amazing variability of amide complexes with zinc and cadmium iodides, including molecular, ionic and polymeric compounds was described by us recently [18]. In the present work, we report new results. Structural diversity in zinc and cadmium iodide complexes with (thio)amides is discussed in terms of donating ability of the ligands, steric requirements and sizes and polarizing power of the cations.

2. Experimental

2.1. Materials and methods

All reagents and solvents for the syntheses and analyses were commercially available and used as received without further purifications.

IR spectra were recorded with the Bruker EQUINOX 55/SB (400–4000 cm^{-1}, KBr pellets) spectrometer at room temperature. Raman spectra were excited by a 1064 nm Nd:YAG-laser radiation at room temperature and recorded using a Bruker Fourier-Raman spectrometer RFS 100/S (80–3000 cm^{-1}) with the resolution of 2 cm^{-1}. ^{1}H NMR spectra were recorded at 298 K on a Bruker Advance III 600 spectrometer operating at 600.13 MHz. Spectra were referenced to residual protio-solvent resonances.

2.2. Syntheses

2.2.1. Diiododiformamidecadmium [Cd(HCONH$_2$)$_2$I$_2$] (1)

Cadmium iodide (9.21 g, 25 mmol) and formamide (FA) (2.00 mL, 50 mmol) were dissolved in water (10 mL). The solution was allowed to stay at room temperature for 2 days, while colorless needle-like crystals of 1 precipitated. Attempts to dry the crystals in air resulted in their decomposition. To preserve the crystals, we removed them from the mother liquid and placed in a liquid perfluorinated hydrocarbon, 1-methyldecahydronaphtalene. Yield 86%.

2.2.2. Diiodotetraformamidecadmium [Cd(HCONH$_2$)$_4$I$_2$] (2)

When the crystals of 1 were allowed to stay in the mother liquid for 4 days, they transformed into complex 2. Single crystals of 2 suitable for the X-ray diffraction experiment were obtained from the mixture of cadmium iodide (9.21 g, 25 mmol) and formamide (4.00 mL, 100 mmol) in water (10 mL). Yield 77%.

Reaction between cadmium iodide and formamide without any solvent produced the powdered mixture of 1 (8%) and 2 (92%). The quantitative phase analysis of the mixture was performed with the use of X-ray powder diffraction and two-phase Rietveld refinement [19].

2.2.3. Hexaiododiformamidetricadmium [Cd$_3$(HCONH$_2$)$_2$I$_6$] (3)

We discovered by chance that crystals of 1 decompose in air. After 14 days, some amount of a new phase was found. After 30 days, the amount of the new phase was still insufficient for structural analysis. Only after 90 days the amount of the new phase

– phase 3 – became enough for a structure determination from multi-phase powder sample (Figs. 1 and 2).

2.2.4. Hexakis(dimethylacetamide)cadmium(II) hexaiododicadmate(II) [Cd(C$_4$H$_9$NO)$_6$][Cd$_2$I$_6$] (4)

Cadmium iodide (3.05 g, 8.3 mmol) and dimethylacetamide (1.43 g, 16.6 mmol) were dissolved in water (10 mL). The solution was allowed to stay at room temperature for 21 days, while almost colorless (slightly yellowish) prismatic crystals of 4 precipitated. Yield 96%.

2.2.5. 5-Acetyl-6-methyl-1,2,3,4-tetrahydropyrimidine-2-thione (MP) C$_7$H$_{10}$NOS (5)

Compound 5 was synthesized by the known method [20,21] based on the reaction of α-tosylsubstituted N-alkylthioureas with enolates of α-substituted carbonyl compounds followed by acid-catalyzed dehydration of the obtained 4-hydroxyhexahydropyrimidin-2-thiones.

^{1}H NMR (DMSO-d$_6$) 2.16 (6H, CH$_3$ and CH$_3$C=O), 3.95 (2H, N-CH$_2$), 9.07(1H, NH), 9.93 (1H, NH).

2.2.6. Diiodo(5-acetyl-6-methyl-1,2,3,4-tetrahydropyrimidine-2-thione)aquazinc [Zn(MP)(H$_2$O)I$_2$] (6)

Suspension of 5-acetyl-6-methyl-1,2,3,4-tetrahydropyrimidine-2-thione (114 mg, 0.73 mmol) and zinc iodide (233 mg, 0.73 mmol) in acetone (7 mL) was stirred at room temperature for 30 min. The resulting transparent brownish solution was filtered and the solvent was evaporated at room temperature for 1 day producing white powder, which was dried over P$_2$O$_5$. Yield 97%. M. p. 222 °C (with decomposition).

Elemental *Anal.* Calc. for [Cd(HCONH$_2$)$_2$I$_2$] (456.29): C, 5.25; H, 1.31; N, 6.14. Found: C, 5.35; H, 0.95; N, 6.17%. *Anal.* Calc. for [Cd(HCONH$_2$)$_4$I$_2$] (546.38): C, 8.79; H, 2.21; N, 10.25. Found: C, 8.48; H, 2.21; N, 10.74%. [Cd(C$_4$H$_9$NO)$_6$][Cd$_2$I$_6$] (1621.33): calc. Cd 20.80; found Cd 20.21. [Zn(C$_7$H$_{10}$NOS)(H$_2$O)I$_2$] (439.20): calc. Zn 13.26; found Zn 12.63.

Crystal structures 1–6 were determined by X-ray single-crystal or powder diffraction (Figs. 3–11).

2.2.7. X-ray single-crystal diffraction

Single-crystal X-ray diffraction experiments were carried out on a CAD-4 diffractometer (Nonius BV, Netherlands) at room temperature using graphite monochromated Mo Kα radiation for 1 and 2 and Ag Kα radiation for 4–6. The structures were solved with SHELXS97 [22] and refined with SHELXL97 [22]. All hydrogen atoms were located on a difference Fourier map, then placed in idealized positions (N—H 0.86 Å, C—H 0.93–0.97 Å), and refined as riding with U_{iso}(H) = 1.2 − 1.5U_{eq} of the parent atom. The crystallographic data are summarized in Table 1. Molecular structures of 1, 2, 4–6 drawn with PLATON [23] are shown in Figs. 3, 5 and 8–10, respectively. The polymeric chain in 1 is shown in Fig. 4, prepared with Mercury [24].

2.2.8. X-ray powder diffraction

The powder pattern for 3 was measured at room temperature with a Stoe STADI-P diffractometer (Cu Kα1 radiation, λ = 1.54059 Å, transmission mode). Careful inspection of the measured pattern has shown a presence of diffraction peaks from the crystalline phase 1. All the remaining peaks were successfully indexed in the orthorhombic unit cell with the TREOR90 program [25]. Based on systematic extinctions the space group for 3 was determined to be Pnn2. The unit-cell parameters and space group for 3 were further tested using a two-phases Pawley fit [26], where the positions and intensities of diffraction peaks for 1 were calculated using its known single-crystal structure. The crystal data, data collection and refinement parameters for 3 are given