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Syntheses and structures of zinc and cadmium iodide complexes with iodoacetamide

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The crystal structures of the zinc and cadmium iodide complexes with iodoacetamide $[Zn(ICH_2CONH_2)_6][ZnI_4]\cdot ICH_2CONH_2$ and $[Cd(ICH_2CONH_2)_6][Cd_2I_6]$ prepared by the reactions of zinc or cadmium iodide with iodoacetamide in acetonitrile or water, respectively, are studied.

This work continues the systematic study of zinc and cadmium iodide complexation with amides.[1–3] Zinc and cadmium iodides form essentially different complexes with the same ligands. For example, $[Zn(MeCONH_2)_2I_2]$ is a molecular complex in which the Zn atom is four-coordinated with two acetamide ligands bound through their O atoms in a tetrahedral geometry.[2] An analogous cadmium compound is ionic. The structural units of the $[Cd(MeCONH_2)_6][Cd_2I_6]$ complex are the $[Cd(MeCONH_2)_6]^{2+}$ cations and the $[Cd_2I_6]^{2-}$ anions.[3] In the centrosymmetric cation, the Cd atom has an octahedral coordination with six O atoms of acetamide molecules. In the centrosymmetric dimeric anion, the Cd atom is coordinated by the iodine atoms at the tetrahedron vertices with two bridging I atoms and two terminal atoms.

The purpose of the work was to study the structures of zinc and cadmium iodide complexes with iodoacetamide (IAA) **1** and **2**.[†]

Structural units of complex **1** are two centrosymmetric $[Zn(IAA)_6]^{2+}$ cations, $[ZnI_4]^{2-}$ anions and IAA molecules (Figures 1 and 2).[‡] In the cations, the Zn atom has an octahedral coordination with six O atoms of iodoacetamide molecules. In the anion, the Zn atom is coordinated by four I atoms at the tetrahedron vertices. The structure of the cation is stabilised by six intramolecular N–H···O hydrogen bonds. The shortest distance between the iodine atom of the iodoacetamide ligand in the cation and one iodo ligand in the anion is 3.5712(24) Å, indicating weak interhalogen bonding.[4] One more iodo ligand forms two short contacts [3.7074(21) and 3.8031(19) Å] with two iodine atoms of IAA ligands of adjacent complex cations behaving as a bridge. Two other iodo ligands are involved in

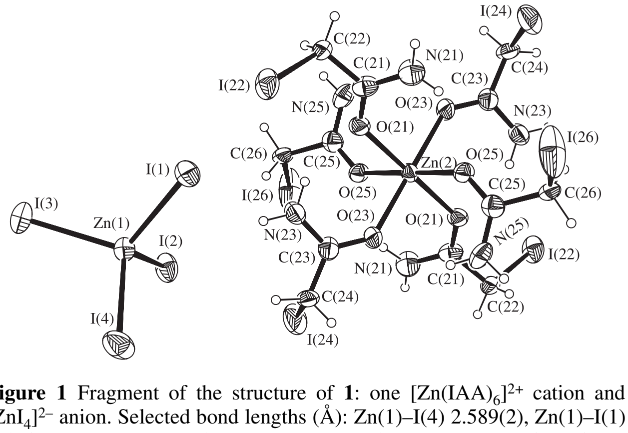

Figure 1 Fragment of the structure of **1**: one $[Zn(IAA)_6]^{2+}$ cation and $[ZnI_4]^{2-}$ anion. Selected bond lengths (Å): Zn(1)–I(4) 2.589(2), Zn(1)–I(1) 2.6057(19), Zn(1)–I(3) 2.607(2), Zn(1)–I(2) 2.618(2), Zn(2)–O(25) 2.052(9), Zn(2)–O(23) 2.080(9), Zn(2)–O(21) 2.095(8); bond angles (°): I(4)–Zn(1)–I(1) 111.54(7), I(4)–Zn(1)–I(3) 106.46(7), I(1)–Zn(1)–I(3) 113.66(7), I(4)–Zn(1)–I(2) 109.16(7), I(1)–Zn(1)–I(2) 108.54(7), I(3)–Zn(1)–I(2) 107.33(7), O(25)–Zn(2)–O(25) 180.0(4), O(25)–Zn(2)–O(23) 95.4(4), O(23)–Zn(2)–O(23) 180.0(6), O(25)–Zn(2)–O(21) 93.2(4), O(23)–Zn(2)–O(21) 91.6(3), O(21)–Zn(2)–O(21) 180.0(5).

[†] *Synthesis of $[Zn(IAA)_6][ZnI_4]\cdot IAA$* **1**. Zinc iodide (1 g, 3.13 mmol) and iodoacetamide (1.15 g, 6.26 mmol) were dissolved in acetonitrile (10 ml) at room temperature and the solution was layered on to a liquid perfluorinated hydrocarbon, 1-methyldecahydronaphthalene (3 ml). In five days the crystals of **1** were formed in 15% yield. The composition of the zinc iodide complex with iodoacetamide (2:7) differs from the composition of the zinc iodide complex with acetamide (1:2).[2] Found (%): Zn, 9.30; C, 9.03; N, 5.09; H, 1.27. Calc. for $[Zn(IAA)_6][ZnI_4]\cdot IAA$ (%): Zn, 9.49; C, 8.69; N, 5.07; H, 1.45.

Synthesis of $[Cd(IAA)_6][Cd_2I_6]$ **2**. Cadmium iodide (1 g, 2.73 mmol) and iodoacetamide (1.01 g, 5.46 mmol) were dissolved in water (10 ml) at room temperature and the solution was layered on to a liquid perfluorinated hydrocarbon, 1-methyldecahydronaphthalene (3 ml). In five days, the crystals of **2** formed in 20% yield. The composition of the cadmium iodide complex with iodoacetamide was the same as for acetamide and propanamide complexes.[3]

[‡] *Crystallographic data for* **1**: at 293(2) K crystals of $C_{14}H_{28}I_{11}N_7O_7Zn_2$ are triclinic, space group $P\bar{1}$, $a = 11.399(4)$, $b = 11.608(3)$, $c = 19.582(5)$ Å, $\alpha = 81.62(2)°$, $\beta = 77.86(3)°$, $\gamma = 61.85(3)°$, $V = 2230.1(11)$ Å^3, $Z = 2$, $M = 1933.07$, $d_{calc} = 2.879$ g cm^{-3}, μ(MoKα) = 8.726 cm^{-1}, $F(000) = 1720$.

Crystallographic data for **2**: at 293(2) K crystals of $C_{12}H_{24}Cd_3I_{12}N_6O_6$ are triclinic, space group $P\bar{1}$, $a = 8.984(4)$, $b = 11.158(5)$, $c = 11.471(5)$ Å, $\alpha = 97.20(2)°$, $\beta = 94.70(3)°$, $\gamma = 96.83(2)°$, $V = 1127.2(8)$ Å^3, $Z = 1$, $M = 2208.37$, $d_{calc} = 3.253$ g cm^{-3}, μ(MoKα) = 9.649 cm^{-1}, $F(000) = 966$.

Intensities of 8752 and 4411 reflections for **1** and **2**, respectively, were measured with an Enraf-Nonius CAD-4 diffractometer at 293(2) K [λ(MoKα) = 0.71072 Å, ω-scans, $2\theta < 51.98°$ and 51.94 for **1** and **2**, respectively].

The structures were solved by a direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic approximation for non-hydrogen atoms. The positions of hydrogen atoms were calculated and refined in an isotropic approximation in a riding model. For **1** and **2**, respectively, the refinement converged to $wR_2 = 0.1868$ and 0.0772, GOF = 0.954 and 1.030 for all independent reflections [$R_1 = 0.0688$ and 0.0497 was calculated against F for 4843 and 3113 observed reflections with $I > 2\sigma(I)$]. All calculations were performed using SHELXS-97 and SHELXL-97.

CCDC 685352 and 685353 contain 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. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2008.

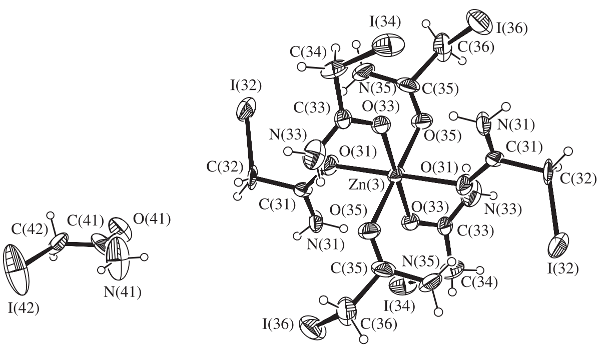

Figure 2 Fragment of the structure of **1**: another $[Zn(IAA)_6]^{2+}$ cation and outer-sphere IAA molecule. Selected bond lengths (Å): Zn(3)–O(33) 2.054(9), Zn(3)–O(31) 2.078(9), Zn(3)–O(35) 2.117(10).

N–H···I and C–H···I contacts with coordinated and outer-sphere IAA molecules.

The Raman spectrum of **1** (50–300 cm^{-1}) shows two bands at 105 and 156 cm^{-1} assigned to ν_1 and ν_3 vibrations of the $[ZnI_4]^{2-}$ ion, respectively.[5]

The structure of **2** (Figure 3) is similar to $[Cd(MeCONH_2)_6]$-$[Cd_2I_6]$.[3] However, the complexes are not isostructural. The structure of **2** is built of the centrosymmetric $[Cd(IAA)_6]^{2+}$ cations and the centrosymmetric $[Cd_2I_6]^{2-}$ anions. In the cation, the Cd atom is octahedrally coordinated by six O atoms of IAA molecules. In the dimeric anion, the Cd atom is coordinated by two bridging I atoms and two terminal iodine atoms. The structure is stabilised by two intramolecular N–H···O hydrogen bonds. The shortest distance between iodine atoms of the iodoacetamide ligand in the cation and terminal iodo ligands in the anion is 3.8230(17) Å, indicating weak interhalogen bonding.[4] In addition, all terminal I atoms of the anion are involved in the N–H···I short contacts and two of them also participate in the C–H···I contacts.

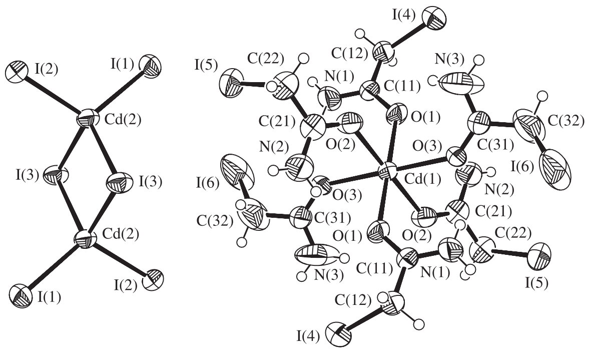

Figure 3 Structure of **2**. Selected bond lengths (Å): Cd(1)–O(2) 2.247(8), Cd(1)–O(3) 2.263(8), Cd(1)–O(1) 2.305(8), Cd(2)–I(1) 2.7192(12), Cd(2)–I(2) 2.7244(12), Cd(2)–I(3) 2.8209(12); bond angles (°): I(1)–Cd(2)–I(2) 112.25(4), I(1)–Cd(2)–I(3) 114.38(4), I(2)–Cd(2)–I(3) 110.95(4), I(3)–Cd(2)–I(3) 98.47(3), Cd(2)–I(3)–Cd(2) 81.53(3), O(2)–Cd(1)–O(2) 180.0(4), O(2)–Cd(1)–O(3) 95.8(3), O(2)–Cd(1)–O(1) 93.5(3), O(3)–Cd(1)–O(1) 90.7(3).

The Raman spectrum of **2** (50–300 cm^{-1}) shows a weak double band at about 100 cm^{-1} and strong bands at 120 and 168 cm^{-1}, which can be assigned to the ν_2 and ν_7 vibrations of the $[Cd_2I_6]^{2-}$ ion, respectively.

Note that the structures of cadmium iodide complexes with acetamide and iodoacetamide are similar, whereas the structure of $[Zn(IAA)_6][ZnI_4]\cdot IAA$ differs drastically from that of $[Zn(MeCONH_2)_2I_2]$. Formation of ionic complexes in the reactions of iodoacetamide with both zinc and cadmium iodides seems to be caused by higher donating ability of the oxygen atom in iodoacetamide as compared to acetamide. As a result, the iodiacetamide ligand substitutes all iodide ions in both compounds and forms complex $[M(IAA)_6]^{2+}$ cations (M = Zn, Cd), in contrast to the molecular complex of zinc iodide with acetamide.

References

1 N. E. Kuz'mina, K. K. Palkina, E. V. Savinkina and I. A. Zamilatskov, *Zh. Neorg. Khim.*, 2005, **50**, 1632 (*Russ. J. Inorg. Chem.*, 2005, **50**, 1521).

2 E. V. Savinkina, E. A. Buravlev, I. A. Zamilatskov and D. V. Albov, *Acta Crystallogr.*, 2007, **E63**, m1094.

3 I. A. Zamilatskov, E. V. Savinkina and D. V. Al'bov, *Koord. Khim.*, 2007, **33**, 407 (*Russ. J. Coord. Chem.*, 2007, **33**, 396).

4 P. H. Svensson and L. Kloo, *Chem. Rev.*, 2003, **103**, 1649.

5 K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, Wiley-Interscience, New York, 1963.

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