Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2008, **18**, 92–93
Mendeleev Communications

Reactions of manganese and zinc iodides with formamide in aqueous solution

Elena V. Savinkina,*[a] Ilia A. Zamilatskov,[a] Evgeny A. Buravlev,[a] Dmitry V. Albov[b] and Aslan Yu. Tsivadze[a]

[a] *M. V. Lomonosov Academy of Fine Chemical Technology, 117571 Moscow, Russian Federation. Fax: +7 495 434 8711; e-mail: e.savinkina@mail.ru*
[b] *Department of Chemistry, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation. E-mail: albov@struct.chem.msu.ru*

DOI: 10.1016/j.mencom.2008.03.014

The crystal structures of the products of reactions between manganese and zinc iodides and formamide in aqueous solution, $[Mn(HCOOH)_2(HCOO)_2]$ and $[Zn(HCONH_2)_2I_2]$, were studied.

Formamide forms numerous metal complexes.[1] Zinc formamide complexes are used as intermediates for growing ZnO nanorods[2] or Zn dendrite films.[3] Polarization of formamide carbonyl group with zinc ion is the key stage of enzyme reactions.[4,5] Structures of transition-metal complexes with formamide were studied, such as $CdCl_2{\cdot}2(HCONH_2)$,[6] $M(NO_3)_2{\cdot}2(HCONH_2){\cdot}2H_2O$ (M = Cu, Cd, Co, Mn),[7] $Zn(HCOO)_2{\cdot}2(HCONH_2)$.[8] There are no structural data on transition-metal iodide complexes with formamide.

The purpose of the work was to study reactions of manganese and zinc iodides with formamide and to examine structures of the products.

We found that a reaction of zinc iodide with formamide in aqueous solution under heating resulted in formation of the formate complex $[Zn(H_2O)_2(HCOO)_2]$[9] as a result of formamide hydrolysis. Reaction of zinc iodide with formamide in aqueous solution at room temperature produced crystals of $[Zn(HCONH_2)_2I_2]$ **1**.

We failed to synthesise a formamide complex of manganese iodide in aqueous solution at room temperature. Concentration of a solution containing manganese iodide, formamide and hydroiodic acid resulted in formation of colourless prismatic crystals of $[Mn(HCOOH)_2(HCOO)_2]$ **2**. It is obvious that formic acid and formate ions formed during formamide hydrolysis. Transition-metal cations catalyse amide hydrolysis;[10] probably, manganese is among them.

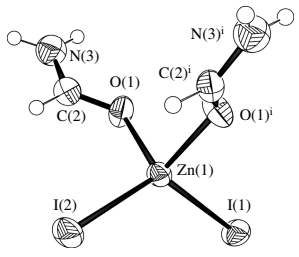

Figure 1 General view of $[Zn(HCONH_2)_2I_2]$. Selected bond lengths (Å): I(1)–Zn(1) 2.5343(17), I(2)–Zn(1) 2.5284(14), Zn(1)–O(1) 2.002(4); bond angles (°): O(1)–Zn(1)–O(1)^i 98.0(3), O(1)–Zn(1)–I(2) 111.59(13), O(1)–Zn(1)–I(1) 104.13(14), I(2)–Zn(3)–I(1) 124.01(5).

Figure 2 A chain in the crystal of $[Zn(HCONH_2)_2I_2]$.

Structure **1**. In the molecular complex $[Zn(HCONH_2)_2I_2]$, the central atom is tetrahedrally coordinated by two iodine atoms and two oxygen atoms from the formamide molecules (Figure 1). The adjacent complexes are linked by double N–H···O hydrogen bonds forming infinite zigzag chains (Figure 2) combined in layers by weak N–H···I hydrogen bonds.†

Structure **2**. There are several reports on syntheses and structures of manganese formate dihydrate[11] and anhydrous manganese formate.[12–14] We have synthesised a different compound. X-ray diffraction analysis showed the layered structure of the crystals of $[Mn(HCOOH)_2(HCOO)_2]$ (Figures 3, 4).† The manganese atom is octahedrally coordinated by six oxygen atoms from two *trans*-arranged formic acid molecules and four bridging formate ions. Structure of the layer in the crystals of **2** is similar to the monoclinic form of $[Cu(HCOOH)_2(HCOO)_2]$.[15] However, layer packing resembles the packing in the orthorhombic form of $[Cu(HCOOH)_2(HCOO)_2]$.[16] The voids in crystals of **2** (~3 Å in diameter) are noticeably smaller than the voids in the crystals of anhydrous manganese formate.[12–14]

† *Crystallographic data for* **1**: at 293(2) K crystals of $C_2H_6I_2N_2O_2Zn$ are orthorhombic, space group *Pnma*, $a = 13.628(7)$, $b = 10.030(5)$ and $c = 7.026(3)$ Å, $V = 960.4(8)$ Å^3, $Z = 4$, $M = 409.26$, $d_{calc} = 2.831$ g cm^{-3}, $\mu(MoK\alpha) = 8.934$ cm^{-1}, $F(000) = 736$. Intensities of 1387 reflections were measured with an Enraf-Nonius CAD-4 diffractometer at 293(2) K [$\lambda(MoK\alpha) = 0.71073$ Å, ω-scans, $2\theta < 55.92°$], and 1221 independent reflections were used in the further refinement. Absorption correction by psi-scans did not give any result.

Crystallographic data for **2**: at 293(2) K crystals of $C_4H_6MnO_8$ are monoclinic, space group *C*2/*c*, $a = 12.722(3)$, $b = 8.5420(11)$ and $c = 8.5010(18)$ Å, $\beta = 93.544(17)°$, $V = 922.1(3)$ Å^3, $Z = 4$, $M = 237.03$, $d_{calc} = 1.707$ g cm^{-3}, $\mu(MoK\alpha) = 1.444$ cm^{-1}, $F(000) = 476$. Intensities of 1655 reflections were measured with an Enraf-Nonius CAD-4 diffractometer at 293(2) K [$\lambda(MoK\alpha) = 0.71073$ Å, ω-scans, $2\theta < 55.92°$], and 1214 independent reflections were used in the further refinement. Absorption correction was made by psi-scans of several reflections.

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 a riding model. Acidic H atom in **2** was refined independently. For **1** and **2**, respectively, the refinement converged to $R_1[I > 2\sigma(I)] = 0.0363$ and 0.0424, GOF = 1.151 and 1.019. All calculations were performed using SHELXS-97 and SHELXL-97.

CCDC 680559 and 680560 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.

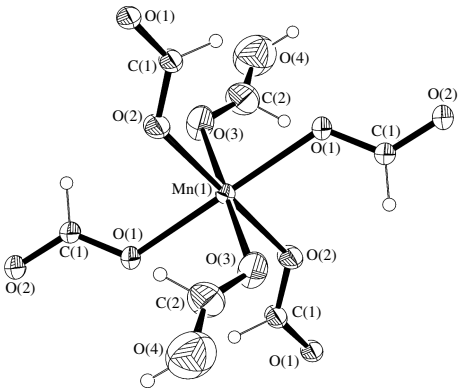

Figure 3 General view of $[Mn(HCOOH)_2(HCOO)_2]$. Selected bond lengths (Å): Mn(1)–O(2) 2.1582(14), Mn(1)–O(1) 2.1611(13), Mn(1)–O(3) 2.2032(16); bond angles (°): O(2)–Mn(1)–O(1) 92.65(5), O(2)–Mn(1)–O(1) 87.35(5).

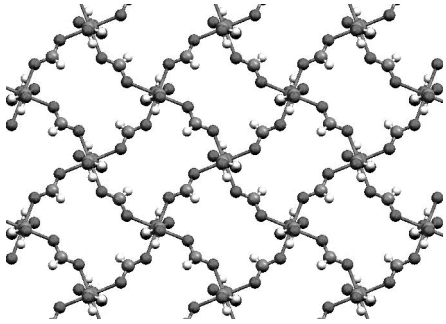

Figure 4 A mesh of the layer in the crystal of $[Mn(HCOOH)_2(HCOO)_2]$.

References

1 N. A. Parpiev, G. V. Tsintsadze, Yu. Ya. Kharitonov, O. F. Khodzhaev and A. Yu. Tsivadze, *Koordinatsionnye soedineniya metallov s formamidom* (*Coordination Compounds of Metals with Formamide*), Fan, Tashkent, 1980 (in Russian).

2 Zh. Zhang, H. Yu, Yu. Wang and M.-Y. Han, *Nanotechnology*, 2006, **17**, 2994.

3 C. M. López and K.-Sh. Choi, *Langmuir*, 2006, **22**, 10625.

4 G. Auerbach, A. Herrmann, A. Bracher, G. Bader, M. Gütlich, M. Fischer, M. Neukamm, M. Garrido-Franco, J. Richardson, H. Nar, R. Huber and A. Bacher, *Proc. Nat. Acad. Sci. USA*, 2000, **97**, 13567.

5 J. Rebelo, G. Auerbach, G. Bader, A. Bracher, H. Nar, C. Hösl, N. Schramek, J. Kaiser, A. Bacher, R. Huber and M. Fischer, *J. Mol. Biol*., 2003, 503.

6 A. Mitschler, J. Fischer and R. Weiss, *Acta Crystallogr*., 1967, **22**, 236.

7 K. K. Palkina, V. T. Orlova, A. Yu. Smolentsev and E. A. Frolova, *Zh. Neorg. Khim*., 2004, **49**, 197 (*Russ. J. Inorg. Chem*., 2004, **49**, 157).

8 S. Fortier and K. A. M. Creber, *Acta Crystallogr., Sect. C*, 1985, **41**, 1763.

9 A. S. Lipton, M. D. Smith, R. D. Adams and P. D. Ellis, *J. Am. Chem. Soc*., 2002, **124**, 410.

10 J. Chin, V. Jubian and K. Mrejen, *J. Chem. Soc., Chem. Commun*., 1990, 1326.

11 M. I. Kay, I. Almodovar and S. F. Kaplan, *Acta Crystallogr., Sect. B*, 1968, **24**, 1312.

12 M. Viertelhaus, H. Henke, C. E. Anson and A. K. Powell, *Eur. J. Inorg. Chem*., 2003, 2283.

13 D. N. Dybtsev, H. Chun, S. H. Yoon, D. Kim and K. Kim, *J. Am. Chem. Soc*., 2005, **126**, 32.

14 Zh. Wang, B. Zhang, H. Fujiwara, H. Kobayashi and M. Kurmoo, *Chem. Commun*., 2004, 417.

15 H. Wang, N. Zhu and H. Fu, *Chinese J. Struct. Chem*., 1985, **4**, 111.

16 N. Lah, P. Šegedin and I. Leban, *Acta Chim. Slov*., 2002, **49**, 251.

Received: 9th July 2007; Com. 07/2978