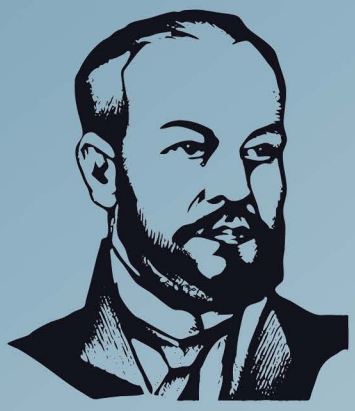
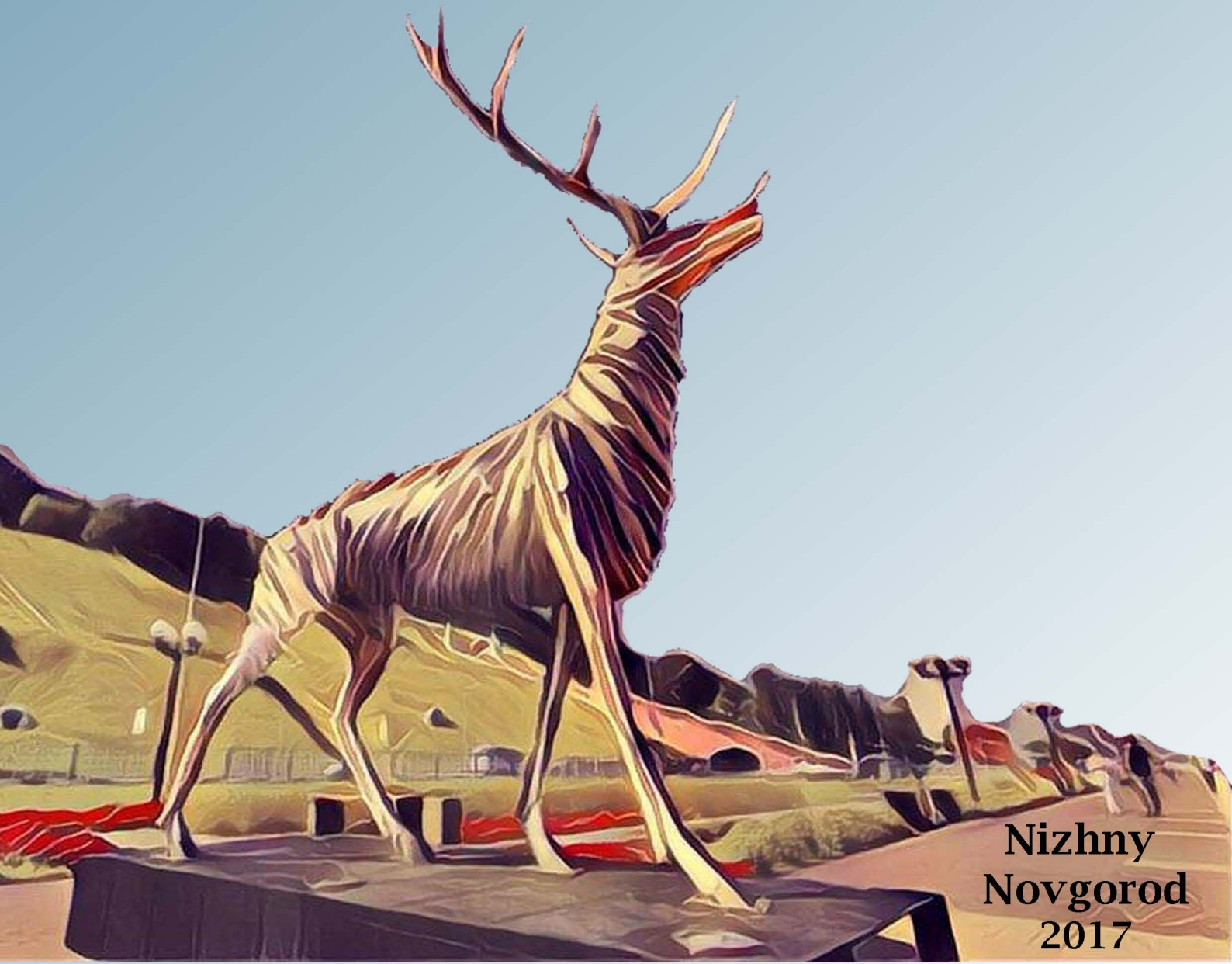


27th INTERNATIONAL CHUGAEV CONFERENCE ON COORDINATION CHEMISTRY



Nizhny Novgorod
2017

27th International Chugaev Conference on Coordination Chemistry

and

4th Young Conference School "Physicochemical Methods in the Chemistry of Coordination Compounds"

October 2–6, 2017, Nizhny Novgorod

The Conference celebrates the 80th birthday
of Academician Gleb A. Abakumov

BOOK OF ABSTRACTS

Nizhny Novgorod

27th International Chugaev Conference on Coordination Chemistry
4th Conference-School for Young Researchers "Physicochemical Methods in Coordination Chemistry"
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VAN DER WAALS CLATHRATES $(bipy)_3\cdot(SO_2)\cdot(H_2O)$, $(bipy)_2\cdot(SO_2)\cdot(H_2O)_2$ AND $(Bz_3N)_3\cdot(SO_2)$

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Reaction products have been isolated from "sulphur dioxide – 2,2′-bipyridine – water" and "sulphur dioxide – tribenzylamine – water – benzene" systems. Crystallization of 2,2′-bipyridine from aqueous solution containing sulfur(IV) oxide afforded clathrates with the compositions $(bipy)_3\cdot(SO_2)\cdot(H_2O)$ (**1**) and $(bipy)_2\cdot(SO_2)\cdot(H_2O)_2$ (**2**) [1]. X-Ray amorphous guest SO_2 molecules occupy voids in the crystal lattice of 2,2′-bipyridine without distortion of its structure. Van der Waals clathrate with the composition $(Bz_3N)_3\cdot(SO_2)$ (**3**) was obtained for tribenzylamine. Only starting Bz_3N was obtained from "sulphur dioxide – tribenzylamine – water – benzene" system. The isolated compounds were characterized by elemental analyses, X-ray diffraction data, and IR, NMR, and mass spectra.

Thus, compounds **1** and **2** are typical lattice clathrates; the crystal structure of bipy includes SO_2 mono- and dihydrates whose interactions with the host lattice involve only van der Waals forces. Unlike previously described $SO_2\cdot$py adduct in which S←N interaction was detected, clathrates **1** and **2** are the first representatives of molecular compounds formed by sulfur dioxide hydrates and heterocyclic base.

In contrast to the interactions of SO_2 with aminoethanols in water (where oily onium hydrogen sulfites and crystalline sulfite [2] were isolated) and highly basic dihydric aminoguanidine (crystalline onium sulfite monohydrate was formed [3]), neither dissociation of sulfurous acid ($SO_2\cdot H_2O$; $pK_{a1} = 1.86$) nor subsequent protonation of the nitrogen atoms of relatively weakly basic bipyridine ($pK_a = 4.34$) [1] and tribenzylamine ($pK_a = 3.64$) occur in the systems "SO_2 – bipy – H_2O", "SO_2 – Bz_3N – H_2O" and "SO_2 – Bz_3N – H_2O – C_6H_6".

Furthermore, the bipy and Bz_3N crystal lattices don't favor oxidation of SO_2 guest molecules with atmospheric oxygen, which was observed in the systems containing tris(hydroxymethyl)aminomethane, alkylamines, benzylamine, ethylenediamine, morpholine and hexamethylenediamine (mild oxidation product of S(IV) to S(VI), onium sulfates, were isolated and structurally characterized [4]).

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[2] R.E. Khoma, V.O. Gelmboldt, O.V. Shishkin, V.N. Baumer, A.N. Puzan, A.A. Ennan, and I.M. Rakipov, *Russ. J. Inorg. Chem*., **2014**, *59* (6), 541-544. doi10.1134/S0036023614060096
[3] R.E. Khoma, V.O. Gelmboldt, V.N. Baumer, O.V. Shishkin and L.V. Koroeva, *Russ. J. Inorg. Chem*., **2013**, *58*(7), 843-847. doi 10.1134/S0036023613070140
[4] R.E. Khoma, V.O. Gelmboldt, A.A. Ennana, V.N. Baumer, A.N. Puzan, T.V. Koksharova and A.V. Mazepa, *Russ. J. Inorg. Chem*., **2017**, *62*(6), 736–745. doi 10.1134/S0036023617060109

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