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THE SUPRAMOLECULAR ARRANGEMENT IN THE Ni(II) COMPLEXES OF ISOTHIOSEMICARBAZIDE

S. B. Novaković^a, G. A. Bogdanović^a, V. M. Leovac^c

^a VINČA Institute of Nuclear Sciences, Laboratory of Theoretical Physics and Condensed Matter
Physics, PO Box 522, 11001 Belgrade, Serbia and Montenegro

^b Department of Chemistry, Faculty of Sciences, University of Novi Sad, Trg Dositeja Obradovića 3,
21000 Novi Sad, Serbia and Montenegro

Abstract

The molecules of two complexes $[\text{Ni}(\text{ITSC})_2(\text{H}_2\text{O})_2](\text{tere}) \cdot 2\text{H}_2\text{O}$ and $[\text{Ni}(\text{ITSC})_2(\text{NO}_3)_2]$ (ITSC = S-methylisothiosemicarbazide; tere = terephthalate) tend to associate through the hydrogen bonding interactions into the characteristic 2D blocks separated by the S-methyl moieties. The different coordination mode of the isothiosemicarbazide comparing to thiosemicarbazide (TSC) prevents the formation of the complementary hydrogen bonds with dicarboxylate important for self-assembly of TSC complexes, however in these ITSC the terephthalate anion has role in connection of the blocks and transformation of the 2D into the 3D supramolecular structure. The similar crystal arrangement is found in two earlier reported complexes of Ni(II) with ITSC.

Introduction

Thiosemicarbazide-based ligands and their metal complexes have attracted much attention mainly because of their wide-ranging biological activities, however some of the recent investigations in the field of supramolecular chemistry have been shown that bis(thiosemicarbazide) metal complexes should be also considered as potential building blocks for supramolecular structures [1-4]. In this kind of structures beside thiosemicarbazide (TSC) complex cation some dicarboxylate is present as a counter ion. Since TSC, $\text{N}^1\text{H}_2\text{-N}^2\text{H-C}^3(\text{S})\text{-N}^4\text{H}_2$, behaves as a bidentate ligand coordinated through terminal N^1 and S atoms its remaining N atoms, hydrazine N^2 and thioamide N^4 , form the hydrogen bonding donor pair, suitably oriented for interaction with hydrogen bonding acceptor pair i.e. oxygen atoms of dicarboxylate anion. This complementary hydrogen bonding could be considered as a starting interaction in the processes of self-assembly of bis(TSC) metal complexes with dicarboxylate. In contrast to TSC, S-methylisothiosemicarbazide, $\text{N}^1\text{H}_2\text{-N}^2\text{H-C}^3(\text{S-CH}_3)\text{-N}^4\text{H}_2$, (ITSC) coordinates through terminal N atoms, i.e. it involves N^4 instead of alkylated S atom [5]. This different coordination mode separates the N atoms and excludes the formation of complementary hydrogen bonds with dicarboxylates. Despite to this fact, we found that bis(ITSC) nickel complex with terephthalate exhibit interesting structural features which also deserve investigation from the aspects of supramolecular chemistry. In this work we analyze the supramolecular arrangement of two ITSC complexes, the octahedral $[\text{Ni}(\text{ITSC})_2(\text{NO}_3)_2]$ (**1**) and the product of its reaction with sodium terephthalate, the octahedral $[\text{Ni}(\text{ITSC})_2(\text{H}_2\text{O})_2](\text{tere}) \cdot 2\text{H}_2\text{O}$ (**2**). The crystal structures of these com-

plexes were determined by X-ray analysis. In addition the Cambridge Structural Database (CSD) was searched for other Ni(II) complexes containing this ligand and their structural arrangements compared with those found in complexes **1** and **2**.

Results and Discussion

In the crystal packing of **1** each molecule forms twelve intermolecular hydrogen bonds with four neighboring molecules. Heaving in mind the size of the molecule this is a considerable number of hydrogen interactions. The important fact is that the equatorial part of the molecule contains eight available hydrogen atoms bonded to the nitrogen atoms, while negatively charged axial ligand, poses three oxygen atoms and acts as a strong proton acceptor. The axial ligand of each molecule serves as an acceptor for two hydrogen donors, the hydrazine (N^1) and the thioamide (N^4) atoms, from its neighbor placed in the position: $x+1, y, z$. In this manner the molecules of complex are connected into the chain extended along the a axis. The additional hydrogen interaction between nitrate group and remaining, N^2 -H donor connects these chains into the compact 2D block (A region) in which S-methyl groups of all molecules take the orientation toward the bordering surfaces of the block (Figure 1. (left)). There are no further hydrogen interactions between these molecule aggregates. Since the region with S-methyl groups (B region) represents the weak connection between the blocks, in the case of $[Ni(ITSC)_2(NO_3)_2]$ we can only speak about 2D supramolecular structure. It is interesting to note that the earlier reported octahedral complex $[Ni(ITSC)_2(NO_2)_2]$ [6] shows similar structural behavior. Namely, the molecules of this complex are also organized into the 2D blocks separated by their S-methyl moieties.

In the crystal packing of **2**, each molecule forms six intermolecular hydrogen interactions. The replacement of the axial nitrate ligand with the molecule of water decrease the number of the hydrogen bonding acceptors, however introduction of the crystal water molecules partly compensate this lack and the molecules are again aggregated into the 2D blocks (A) separated by their S-methyl moieties (B). The important structural difference comparing to above described complex is the incorporation of the terephthalate anion in the B region. The symmetrically disposed COO^- groups of anion bind to the neighboring A blocks through two strong hydrogen bonds transforming the 2D structure of $[Ni(ITSC)_2(H_2O)_2](tere) \cdot 2H_2O$ into 3D supramolecular structure (Figure 1. (right)). The similar structural behavior we also found in the earlier reported square-planar $[Ni(ITSC)_2]Br_2$. In this case the molecules within the block A are mutually interconnected by hydrogen bonds with Br anions. The rest of the Br anions are located in the crystallographically different positions within a B block and form the hydrogen bonds with the complex molecules of the neighboring A blocks.

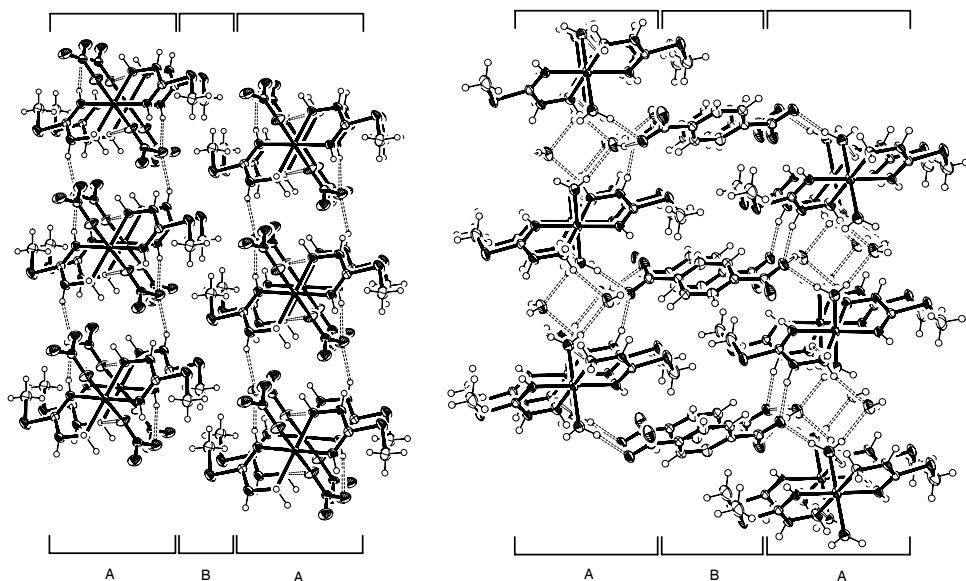


Figure 1. Formation of 2D supramolecular blocks (A region) separated by S-methyl groups (B region) in the crystal packing of complexes **1** (left) and **2** (right).

Conclusion

The Ni(II) complexes of ITSC show an interesting structural arrangement. Their extensive hydrogen interactions aggregate the molecules into the characteristic 2D supramolecular blocks which are separated by S-methyl groups. The dicarboxylate anions introduced to the structure take the place between the S-methyl moieties and bind the neighboring blocks transforming the 2D into the 3D supramolecular structure. The similar behavior in the structural arrangement we also found in two additional, earlier published crystal structures.

References

- [1] J.E.V. Babb, A.D. Burrows, R.W. Harrington, M.F. Mahon, *Polyhedron*, 2003, 22, 673.
- [2] A.D. Burrows, R.W. Harrington, M.F. Mahon, S.J. Teat, *Cryst. Eng. Comm.*, 2002, 22, 539.
- [3] A.D. Burrows, S. Menzer, D.M.P. Mingos, A.J.P. White, D.J. Williams, *J. Chem. Soc., Dalton Trans.*, 1997, 4237.
- [4] A.D. Burrows, R.W. Harrington, M.F. Mahon, *Eur. J. Inorg. Chem.*, 2003, 766-
- [5] G.A. Bogdanović, V.M. Leovac, S.B. Novaković, V.I. Češljević, A. Spasojević-de Bire, *Acta Cryst.*, 2001, C57, 1138.
- [6] P.N. Bourash, M.D. Revenko, Yu.A. Simonov, N.V. Gerbeleu, A.A. Dvorkin, T.I. Malinovskii, *Dokl. Akad. Nauk SSSR*, 1987, 293, 119.
- [7] D.Z. Obadović, V. Divjaković, V.M. Leovac, *Polyhedron*, 1997, 16, 695.