



SHORT COMMUNICATION

Disorder of lattice solvent molecules in the structure of hexaaqua(μ_2 -1,2,4,5-benzenetetracarboxylato)-bis(2,2'-dipyridylamine)dinickel(II) hexahydrate DMSO solvate

DEJAN POLETI^{1*#}, LJILJANA KARANOVIĆ², ALEKSANDAR KREMENOVIĆ² and JELENA ROGAN^{1#}

¹Faculty of Technology and Metallurgy, Karnegijeva 4, 11000 Belgrade and

²Faculty of Mining and Geology, Đušina 7, 11000 Belgrade, Serbia

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Abstract: The crystal structure of the complex $[\text{Ni}_2(\text{btc})(\text{dipya})_2(\text{H}_2\text{O})_6]\cdot 6\text{H}_2\text{O}\cdot \text{DMSO}$ (btc = tetra-anion of 1,2,4,5-benzenetetracarboxylic acid, dipya = 2,2'-dipyridylamine) was refined in the triclinic system, space group $P\bar{1}$, using low temperature (170 K) X-ray diffraction data. The compound consists of binuclear complex entities and lattice solvent molecules making pseudo-layers parallel to the 101 plane and channels parallel to the *b*-axis. The observed structural features were compared with the previously reported results and formula $[\text{Ni}_2(\text{btc})(\text{dipya})_2(\text{H}_2\text{O})_6]\cdot 4\text{H}_2\text{O}$ based on room temperature X-ray diffraction data. A possible arrangement of the disordered lattice solvent molecules located in the structural channels is described and discussed. It is concluded that the layout of these molecules is non-centrosymmetric, although the remaining and main part of the structure is centrosymmetric.

Keywords: nickel(II) complex, 1,2,4,5-benzenetetracarboxylate ion, 2,2'-dipyridylamine, crystal structure, lattice solvent molecules, disorder.

INTRODUCTION

Due to the presence of eight oxygen atoms as potential donor atoms, the tetra-anion of 1,2,4,5-benzenetetracarboxylic acid (btc) is interesting as a ligand suitable for the preparation of inorganic-organic framework structures. In such complexes, btc exhibits a great variety of coordination modes, acting from a simple bidentate ligand bridging two metal centers to a 12-dentate ligand coordinated up to 10 transition metal atoms.^{1–3} As the consequence of the bulkiness of the ligand and the almost free rotation of its COO groups, cavities of different shape and dimensions are characteristic for btc complexes. Some cavities are empty, others are filled by H₂O molecules or different ions. However, complexes with well-defined channels are not so common. Two recent illustrative examples are

* Corresponding author. E-mail: dejan@tmf.bg.ac.yu

Serbian Chemical Society member.

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$\text{K}(\text{H}_3\text{O})[\text{Fe}_2(\text{btc})\text{F}_2]\cdot 3.5\text{H}_2\text{O}$ with small channels filled with K^+ and H_3O^+ ions, as well as H_2O molecules,⁴ and $(\text{H}_3\text{NC}_3\text{H}_6\text{NH}_3)[\text{Cu}(\text{btc})]\cdot 2\text{H}_2\text{O}$ with two channels of different dimensions containing either 1,3-propanediammonium ions or H_2O molecules.⁵

Another example is the title complex having channels that occupy 17 % of the unit cell volume (190 \AA^3) with an effective cross section of about $2 \times 4 \text{ \AA}$. This property classifies the complex as a microporous material and a potential hydrogen storage medium. In fact, the structure of the complex based on single crystal X-ray diffraction data collected at room temperature was published recently with the formula reported as $[\text{Ni}_2(\text{btc})(\text{dipya})_2(\text{H}_2\text{O})_6]\cdot 4\text{H}_2\text{O}$ (dipya=2,2'-dipyridylamine).⁶ However, during that refinement a problem was experienced with the modeling of some disordered solvent molecules present in the channels parallel to the *b*-axis (Fig. 1a). For this reason, the contribution of these molecules to the structural model was removed using the procedure SQUEEZE implemented in the program PLATON.⁷ At the same time, TG analysis also confirmed the presence of additional lattice solvent molecules. To resolve this ambiguity, it was necessary to recollect X-ray diffraction data at a low temperature (170 K), and the results of this new structure determination are reported here.

RESULTS AND DISCUSSION

Projection of the structure along the *b*-axis and the shape of the molecules of the complex are shown in Figs. 1 and 2, respectively. Two pseudo-layers parallel to the 101 plane, one containing complex units (A) and the other containing solvent molecules only (B), together with channels extending along the *b*-axis, are clearly visible in the crystal packing (Fig. 1a). Within the pseudo-layers A, the complex units are connected by hydrogen bonds and face-to-face π - π stacking interactions, whereas only hydrogen bonds exist within the pseudo-layers B and between pseudo-layers A and B.

In comparison to the room temperature results,⁶ a predictable decrease of the unit cell volume ($\approx 1.4 \%$) and atomic displacement parameters was observed at the low temperature. In addition, one O atom from the uncoordinated COO group, which had a very elongated displacement ellipsoid at room temperature, was found to be split in two nearby positions [Fig. 2; $d(\text{O}101-\text{O}102) = 0.689(8) \text{ \AA}$]. However, in addition to the expected H_2O molecules, one dimethyl sulphoxide, DMSO, molecule (DMSO was present in the reaction mixture as a solvent) with a half occupancy was located in the channels. In this way, as shown by the refinement of the low temperature data, the correct formula of the complex is $[\text{Ni}_2(\text{btc})(\text{dipya})_2(\text{H}_2\text{O})_6]\cdot 6\text{H}_2\text{O}\cdot \text{DMSO}$ and not $[\text{Ni}_2(\text{btc})(\text{dipya})_2(\text{H}_2\text{O})_6]\cdot 4\text{H}_2\text{O}$, as reported previously⁶ for the "squeezed", solvent-free data.

The corrected formula was also confirmed by the results of thermogravimetry, TG (the TG curve was published in ref. 6 as Fig. 5). The first step of dehy-

dration occurred in a nearly horizontal step between 53 and 85 °C with the release of two H₂O molecules (mass loss found 3.6 %, calcd. 3.4 %). Very likely, it concerns two disordered and loosely bound lattice H₂O molecules. Dehydration continued up to 126 °C, when all 12 H₂O molecules were lost (found 21.2 %, calcd. 21.5 %). The DMSO molecule was slowly released between 126 and 292 °C (total mass loss for 12H₂O + DMSO: found 29.3 %, calcd. 30.6 %) when an inflection point on the TG curve was observed. Degradation of the desolvated product continued with the loss of btc ligand up to 430 °C (total mass loss: found 58.6 %, calcd. 58.9 %), with possibly decarboxylation (loss of CO₂) as the first step. Subsequently, the complex showed a slow mass loss and the residue did not reach constant mass up to 700 °C.

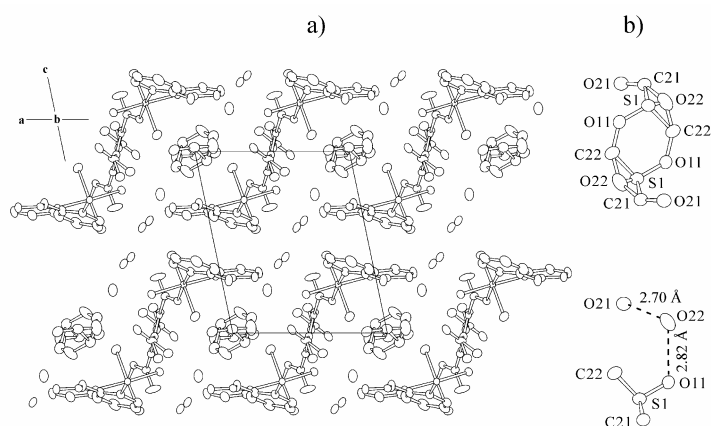


Fig. 1. (a) Crystal packing showing the pseudo-layers of the complex units and lattice solvent molecules, as well as channels extending along the *b*-axis; (b) an enlarged view showing the content of channels as obtained by the crystal structure analysis (top), and a possible arrangement of the disordered H₂O and DMSO molecules (bottom).

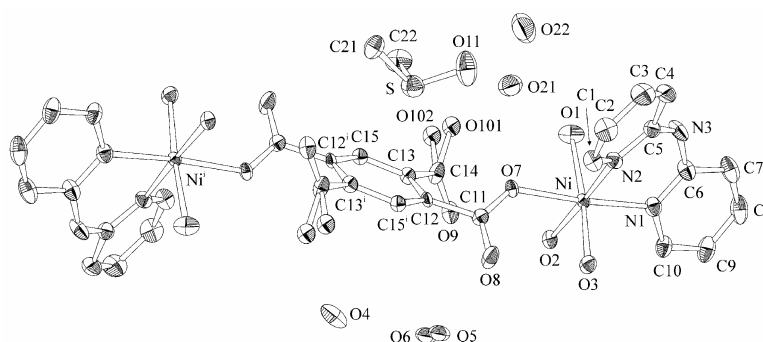


Fig. 2. A view of the centrosymmetric binuclear complex unit with the atomic numbering scheme (displacement ellipsoids are drawn at the 50 % probability level). For the sake of clarity, only the asymmetric part of the lattice solvent molecules is shown and the hydrogen atoms are omitted. Symmetry code: (i) $-x+1, -y+1, -z+2$.

Since the channel solvent molecules (O21, O22 and DMSO) are situated around the symmetry center, they are close to each other (Fig. 1b, top) and cannot co-exist simultaneously, which is in agreement with their half occupancy. Although it was easy to find a plausible layout giving quite reasonable hydrogen bond lengths (dashed lines in Fig. 1b, bottom), this also means that the channel solvent molecules can be allocated over the whole structure in a number of ways. Therefore, this minor part of the structure is non-centrosymmetric, although, as also indicated by the reflection statistics, the remaining and predominant part is centrosymmetric. However, all further attempts to resolve this disorder by refining the structure in space group $P1$ instead of $P\bar{1}$ resulted in higher R -indices and non-positive definite displacement ellipsoids. Very probably, the lack of straightforward conclusions could be related to the diffuse character of the lattice solvent molecules and their negligible contribution to the structural model.

EXPERIMENTAL

The complex was prepared as described previously.⁶ Elemental analysis was performed by standard analytical micromethods. Found (calcd.) %: C, 38.71 (38.27); H, 4.73 (5.02); N 8.18 (8.37). The experimental density was determined at room temperature by the floatation method. TG analysis (30–700 °C range) was performed on a Perkin–Elmer model TGS-2 thermo balance in a dry N₂ atmosphere (flow rate 60 cm³ min⁻¹) at a heating rate of 10 °C min⁻¹.

X-ray diffraction data were collected at 170 K on a STOE IPDS 2 single crystal diffractometer (MoK α radiation, $\lambda = 0.71073$ Å) using a light blue plate-like crystal of approximate dimensions 0.23×0.15×0.06 mm. The data were corrected for Lp and for absorption (integration method, $T_{\min} = 0.8240$, $T_{\max} = 0.9604$). The structure was refined (program SHELXL97)⁸ starting from the known structural model⁶ by the full-matrix least-squares method with anisotropic displacement parameters for all non-H atoms. The hydrogen atoms were treated in three different ways: (a) those connected to C atoms were placed at the geometrically calculated positions and refined using a riding model, (b) those from coordinated and fully occupied H₂O molecules (O1–O4, Fig. 2), as well as the amine H were found in ΔF maps and refined isotropically and (c) the positions of the H atoms from disordered lattice H₂O molecules (O21, O22, O5 and O6, Fig. 2) were determined by comparison of ΔF maps and the positions determined by the Nardelli method.⁹ The latter H atoms are involved in the structural model with all parameters fixed. The refined occupancies of water O5 and O6 atoms [Fig. 2; $d(\text{O5–O6}) = 0.68(3)$ Å] were 0.79(2) and 0.21(2), respectively. Occupancies of DMSO and some other lattice H₂O molecules (O21 and O22, Fig. 2) were tested in independent refinements; in all cases the occupancies were near to 0.5 and the refinement was finished with these values fixed to 0.5. The final results of crystal structure determination are summarized as follows.

Empirical formula: C₃₂H₅₀N₆Ni₂O₂₁S; $M_r = 1004.26$; crystal system: triclinic; space group: $P\bar{1}$; unit cell parameters: $a = 9.290(1)$, $b = 10.863(1)$, $c = 11.997(2)$ Å, $\alpha = 67.40(1)$, $\beta = 77.04(1)$, $\gamma = 84.79(1)^\circ$; unit cell volume: $V = 1089.2(3)$ Å³; $Z = 1$; calculated density: $\rho_x = 1.531$ g cm⁻³; experimental density (room temperature): $\rho_m = 1.49(2)$ g cm⁻³; absorption coefficient: $\mu = 0.998$ mm⁻¹; $F(000) = 524$; range for data collection: $1.88^\circ < \theta < 25.35^\circ$; index ranges: $-11 \leq h \leq 11$, $-13 \leq k \leq 13$, $-13 \leq l \leq 14$; reflections collected: 14262; reflections independent: 3980 ($R_{\text{int}} = 0.0800$); number of refined parameters: 344; number of restraints: 11; $S = 1.165$; R indices [$I > 2\sigma(I)$]: $R_1 = 0.0592$, $wR_2 = 0.1065$; R indices (all data): $R_1 = 0.0826$, $wR_2 = 0.1135$; the largest difference peak and hole: 0.99 and -0.46 e Å⁻³.

Supplementary materials

CCDC 627247 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

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ИЗВОД

НЕУРЕЂЕНОСТ МОЛЕКУЛА РАСТВАРАЧА У СТРУКТУРИ ХЕКСААКВА(μ_2 -1,2,4,5-
-БЕНЗЕНТЕТРАКАРБОКСИЛАТО)-БИС(2,2'-ДИПИРИДИЛАМИН)ДИНИКАЛ(II)-
-ХЕКСАХИДРАТА-DMSO СОЛВАТА

ДЕЈАН ПОЛЕТИ¹, ЉИЉАНА КАРАНОВИЋ², АЛЕКСАНДАР КРЕМЕНОВИЋ² и ЈЕЛЕНА РОГАН¹

¹Технолошко-металуршки факултет, Карнегијева 4, 11000 Београд и

²Рударско-геолошки факултет, Бушина 7, 11000 Београд

Кристална структура комплекса $[\text{Ni}_2(\text{btc})(\text{dipa})_2(\text{H}_2\text{O})_6]\cdot 6\text{H}_2\text{O}\cdot \text{DMSO}$ (btc = тетраанјон 1,2,4,5-бензентетракарбоксилне киселине, dipa = 2,2'-дипиридиламин) утањена је у триклиничном систему, просторна група $P\bar{1}$, на основу података добијених рендгенском дифракцијом на ниској температури (170 К). Једињење се састоји од бинуклеарних комплексних јединки и некоординираних молекула растварача, који формирају псеудо-слојеве паралелне равни 101 и канале паралелне *b*-оси. Структурне карактеристике комплекса упоређене су са раније објављеним резултатима и формулом $[\text{Ni}_2(\text{btc})(\text{dipa})_2(\text{H}_2\text{O})_6]\cdot 4\text{H}_2\text{O}$, који су били засновани на подацима прикупљеним на собној температури. У раду је описан и дискутован могући распоред неуређених молекула растварача који се налазе у раније поменутих каналама. Закључено је да распоред тих молекула мора бити нецентросиметричан, иако је преостали и највећи део структуре центросиметричан.

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REFERENCES

1. H. Kumagai, C. J. Kepert, M. Kurmoo, *Inorg. Chem.* **41** (2002) 3410
2. L.-J. Zhang, J.-Q. Xu, Zh. Shi, X.-L. Zhao, T.-G. Wang, *J. Solid State Chem.* **32** (2003) 32
3. H. Kumagai, K. W. Chapman, C. J. Kepert, M. Kurmoo, *Polyhedron* **22** (2003) 1921
4. M. Sonselme, M. Riou-Cavellec, G. Férey, *Solid State Sci.* **4** (2002) 1419
5. D. Poleti, Lj. Karanović, *J. Serb. Chem. Soc.* **70** (2005) 1441
6. J. Rogan, D. Poleti, Lj. Karanović, *Z. Anorg. Allg. Chem.* **632** (2006) 133
7. a) P. v. d. Sluis, A. L. Spek, *Acta Crystallogr.* **A46** (1990) 194; b) A. L. Spek, *Acta Crystallogr.* **A46** (1990) c34
8. G. M. Sheldrick, *Program for the refinement of crystal structures, SHELXL97*, University of Göttingen, Germany, 1997
9. M. Nardelli, *J. Appl. Cryst.* **32** (1999) 563.