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Copper(II) 3,5-Dinitrosalicylate – The Unique System for Co-crystal Formation by Gentle Changes in Preparation Procedure

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Abstract

Reactions of copper(II) salts with 3,5-dinitrosalicylic acid in presence of zinc(II), or manganese(II) salts yield to the complexes (**1**) or (**2**) formation. The composition of complexes found from X-ray structural analysis show that the co-crystals of composition $[Cu_3\{3,5\text{-}(NO_2)_2sal^{2-}\}_2\{3,5\text{-}(NO_2)_2sal^{1-}\}_2(H_2O)_4]_x[Cu\{3,5\text{-}(NO_2)_2sal^{1-}\}_2(H_2O)_2]_{2(1-x)}\cdot 4H_2O$ ($3,5\text{-}(NO_2)_2sal^{z-}$ = 3,5-dinitrosalicylate(z–) anion, x = 0.420(2) for (**1**) and x = 0.225(2) for (**2**)) were obtained. The crystal structures have been determined and refined to $R = 0.042$ ($wR = 0.092$), and $R = 0.039$ ($wR = 0.087$) for complex (**1**) and (**2**), respectively. The complexes crystallizes in monoclinic system, space group $P2_1/c$, and the structure of the complexes comprise of the centrosymmetric trimeric $[Cu_3\{3,5\text{-}(NO_2)_2sal^{2-}\}_2\{3,5\text{-}(NO_2)_2sal^{1-}\}_2(H_2O)_4]$ molecules, that are to the extent *x* replaced by pairs of monomeric $[Cu\{3,5\text{-}(NO_2)_2sal^{1-}\}_2(H_2O)_2]$. The water molecules complete structures by system of different types of hydrogen bonds. The Cu2 atom in $[Cu_3\{3,5\text{-}(NO_2)_2sal^{2-}\}_2\{3,5\text{-}(NO_2)_2sal^{1-}\}_2(H_2O)_4]$ is centrosymmetrically coordinated by two 3,5-dinitrosalicylato dianion thus forming the square planar CuO_4 chromophore. Each of the satellite Cu1 atoms are coordinated by one oxygen atom of bridging 3,5-dinitrosalicylato dianion, two oxygen atoms of chelating 3,5-dinitrosalicylato monoanion (in the phenolato form), and by two water oxygen atoms in the square pyramidal coordination polyhedron. The Cu1 atoms in monomeric molecules are coordinated by one oxygen atom of monodentately coordinated 3,5-dinitrosalicylato monoanion, by two oxygen atoms of chelating 3,5-dinitrosalicylato monoanion, and by two water oxygen atoms to form the square pyramidal coordination polyhedron.

Keywords: copper complex, co-crystal, crystal structure, salicylato ligand

Introduction

The chemistry of copper compounds has been extensively investigated and the relationship between the structure and reactivity, ranging from industrial catalysis to biomedical activity, is of major importance. The ability of salicylic acid to act as an oxygen donor and to form complexes with different metal atoms is well known, but nitro-derivatives of salicylic acids as a donor in solid state coordination compounds has been studied only sporadically (Lajunen LHJ, Kokkonen P, Nissi A and Ruotsalainen H 1984) and study of metal complexes with 3,5-dinitrosalicylic acid in solid state are also rare (Anjaneyulu Y, Rao NVS, Rao RP, Murthy LN and Pisipati VGKM 1986; Anjaneyulu Y, Rao NVS, Rao RP and Pisipati VGKM 1986; Ranford JD, Sadler PJ and Trocher DA 1993). Published data concerning copper(II) 3,5-dinitrosalicylates are not consistent, e.g. proposing dimeric structure formula (Ranford JD, Sadler PJ and Trocher DA 1993) $[\{Cu(Hdns)_2(H_2O)\}_2]\cdot 10H_2O$ for substance showing the effective magnetic moment μ_{eff} = 2.12 B.M. per copper ion at 298 K.

The 3,5-dinitrosalicylato moiety could be relatively frequently found in the CCDC System, mostly as ionic salts with different organic cations (e.g. *N*-protonized aminobenzoic acids) and as the structure of free acid solvates. A logical explanation of that could be related to the strong acidity of 3,5-dinitrosalicylic acid Aggett J and Eng Sin Ow 1971) (pK_1 = 0.45, and pK_2 = 7.6). Very interesting 3,5-dinitrosalicylate anion structural feature, maybe related to its acidity, is an existence of all three possible types of anions − the phenolato anion (that is the most frequent in solid state), the carboxylato anion and the presence of 3,5-dinitrosalicylato dianion could be also found (e.g. in the ethylenediamonium 3,5-dinitrosalicylate monohydrate (Smith G, Wermuth UD, Bott BC, Heally PC and White JM 2002)). The presence of both forms (salicylato mono- and di-anion) in one complex molecule – $[Cu_3\{3,5\text{-}(NO_2)_2sal^{2-}\}_2\{3,5\text{-}(NO_2)_2sal^{1-}\}_2(H_2O)_4]\cdot 4H_2O$ (where $3,5\text{-}(NO_2)_2sal^{z-}$ = 3,5-dinitrosalicylate(z–) anion) has been, for the first time, confirmed in our recent study (Valigura D, Melnik M, Koman M, Martiška L, Korabik M, Mrozinski J and Glowiak T 2004; Valigura D, Melnik M, Koman M, Martiška L, Korabik M, Mrozinski J and Glowiak T 2004) by X-ray structure determination.

Homo- and heterometalic polynuclear complexes, especially those containing transition metals, are widely studied for their great variability of properties caused by mutual interactions of metal centers throughout different type of bridging ligands. As part of our study of salicylatocopper(II) complexes we had tried to extend the exploration of the same motif to the formation of mixed metal complexes of $[MCu_2\{3,5\text{-}(NO_2)_2sal^{2-}\}_2\{3,5\text{-}(NO_2)_2sal^{1-}\}_2(H_2O)_4]$ or $[M_2Cu\{3,5\text{-}(NO_2)_2sal^{2-}\}_2\{3,5\text{-}(NO_2)_2sal^{1-}\}_2(H_2O)_4]$ (M = some other

divalent transition metal ion) stoichiometry. Here we report on complexes that have been obtained from experiments where M = Zn, or Mn. They do not contain other metal ion M^{2+}, moreover they are co-crystals of trimeric $[Cu_3\{3,5\text{-}(NO_2)_2sal^{2-}\}_2\{3,5\text{-}(NO_2)_2sal^{1-}\}_2(H_2O)_4]$ and monomeric $[Cu\{3,5\text{-}(NO_2)_2sal^{1-}\}_2(H_2O)_4]$ species giving the compounds of general formula $[Cu_3\{3,5\text{-}(NO_2)_2sal^{2-}\}_2\{3,5\text{-}(NO_2)_2sal^{1-}\}_2(H_2O)_4]_x[Cu_3\{3,5\text{-}(NO_2)_2sal^{1-}\}_2(H_2O)_2]_{2(1-x)}\cdot 4H_2O$, where x = 0.420(2) for complex (**1**) and x = 0.225(2) for complex (**2**). The similar structure to those ones above, but obtained at room temperature, has been recently published by Su & Xu (Su J-R and Xu D-J 2005).

CAUTION: *Metal complexes of 3,5-dinitrosalicylic acid are potentially explosive. Only a small amount of material should be prepared and handled with caution*

Experimental

Preparation of Complexes

Both samples were prepared by similar procedures that differ in used metallic salt and stoichiometries. Complex (**1**; KL-175) was obtained by slow crystallization from the reaction mixture of 0.31 mmol $ZnSO_4$ 1.3 mmol 3,5-$(NO_2)_2$salH and 1.24 mmol $CuSO_4$ in about 250 cm^3 of water, while complex (**2**; KL-180) was obtained from mixture 0.325 mmol $MnSO_4$ 1.37 mmol 3,5-$(NO_2)_2$salH and 0.65 mmol $CuSO_4$ in about 250 cm^3 of water.

Instruments

Carbon, hydrogen and nitrogen analyses were carried out on a CHNSO FlashEA^{TM} 1112 Automatic Elemental Analyzer. The copper content was determined by electrolysis of water solution obtained by the sample mineralization with a mixture of sulfuric acid and potassium peroxodisulfate

The electronic spectra (190 – 1100 nm) of the complexes were measured in nujol suspension with a SPECORD 200 (Carl Zeiss Jena) spectrophotometer at room temperature. The infrared spectra (4000–100 cm^{-1}) were recorded on a MAGNA 750 IR (Nicolet) spectrophotometer at room temperature.

Data collection and cell refinement were carried out using Bruker APEXII difractometer installed at a rotating anode source (Mo Kα radiation, λ = 0.71073 Å) using *Bruker AXS* software package (Brucker 2004). The diffraction intensities were corrected for

Lorentz and polarization factors. The structures were solved using *SHELXS-97* (Sheldrick GM 2008) and refined by the full-matrix least-squares procedure with *SHELXL-97* (Sheldrick GM 2008). The multi-scan absorption correction was made by using *SADABS* (Sheldrick GM 1996). Geometrical analyses were performed with *SHELXL-97* (Sheldrick GM 2008). The structures were drawn with *XP* in *SHELXTL* (Sheldrick GM 2008) or with *ORTEP3* (Farrugia LJ 1997).

Results and Discussion

Structure of the Complexes

The atom numbering and the structure of of both complexes (**1**) and (**2**) are illustrated in Figure 1. Both complexes consist of the trimeric $[Cu_3(C_7H_3N_2O_7)_2(C_7H_2N_2O_7)_2(H_2O)_4]$ molecules **A**, monomeric $[Cu(C_7H_2N_2O_7)_2(H_2O)_2]$ ones **B**, or **C** and the water molecules. The complex molecule **A** is centrosymmetric and Cu2 atom is in the centre of symmetry. The square-planar coordination polyhedron of Cu2 atom is formed by centrosymmetrically bonded 3,5-dinitrosalicylate dianions thus forming with Cu2 two six-membered metallocyclic ring with the angle O12–Cu2–O3A of 94.1(1) ^{o}. The carboxylato oxygen atom O12 and the O3 phenolato oxygen atom exhibit the Cu2–O distances of 1.987(2) and 1.815(2) Å, respectively. The other carboxylato oxygen atom of this dianion O11 is bonded to the terminal Cu1 atom with little bit longer Cu1–O11 distance of 1.946(2) Å, thus forming the bridging *syn-anti* bonding mode of the carboxylato group. The terminal Cu1 atom exhibits square pyramidal coordination polyhedron formed by the O11 oxygen atom of the bridging 3,5-dinitrosalicylate dianion, by two oxygen atoms O21 and O23 of the terminal chelating 3,5-dinitrosalicylate monoanion, and by two O2 and O1 oxygen atoms of the water molecules. The terminal chelating 3,5-dinitrosalicylato anion exhibit slightly longer both Cu1–O distances (1.949(2) and 1.904(2) Å, respectively) in comparison to those ones of the Cu2 atom. This elongation is in good relation to the anion charge. The equatorial water molecule exhibit the Cu1–O2 distance 1.922(2) Å, and the apical Cu1–O1 distance is longer (2.339(2) Å). Moreover it is worth to note, that the terminal chelating 3,5-dinitrosalicylato anion is monoanion with proton bonded to O22 carboxylato oxygen atom (phenolato monoanion) similarly as it was found for some salts. This bonding mode of 3,5-dinitrosalicylato anion is rather unique from the transition metal coordination chemistry point of view. Previously published article concerning trimeric complex $[Cu_3\{3,5\text{-}(NO_2)_2sal^{2-}\}_2\{3,5\text{-}(NO_2)_2sal^{1-}\}_2(H_2O)_4]\cdot 4H_2O$ was the first

example of presence of phenolato monoanion of the salicylic acid bonded chelating the 3d transition metal atom, and few other examples of structures containing this type of salicylato anion were tungsten (Kolesnichenko V, Mason MH, Botts JB, Botts AM, Baroni TE, Heppert JA, Rheingold AL, Liable-Sands L and Yap GPA 2001; Baroni TE, Heppert JA, Hodel RR, Kingsborough RP, Morton MD, Rheingold AL and Yap GPA 1996) or molybdenum Edwards CF, Griffith WP, White AJP and Williams DJ 1992) complexes.

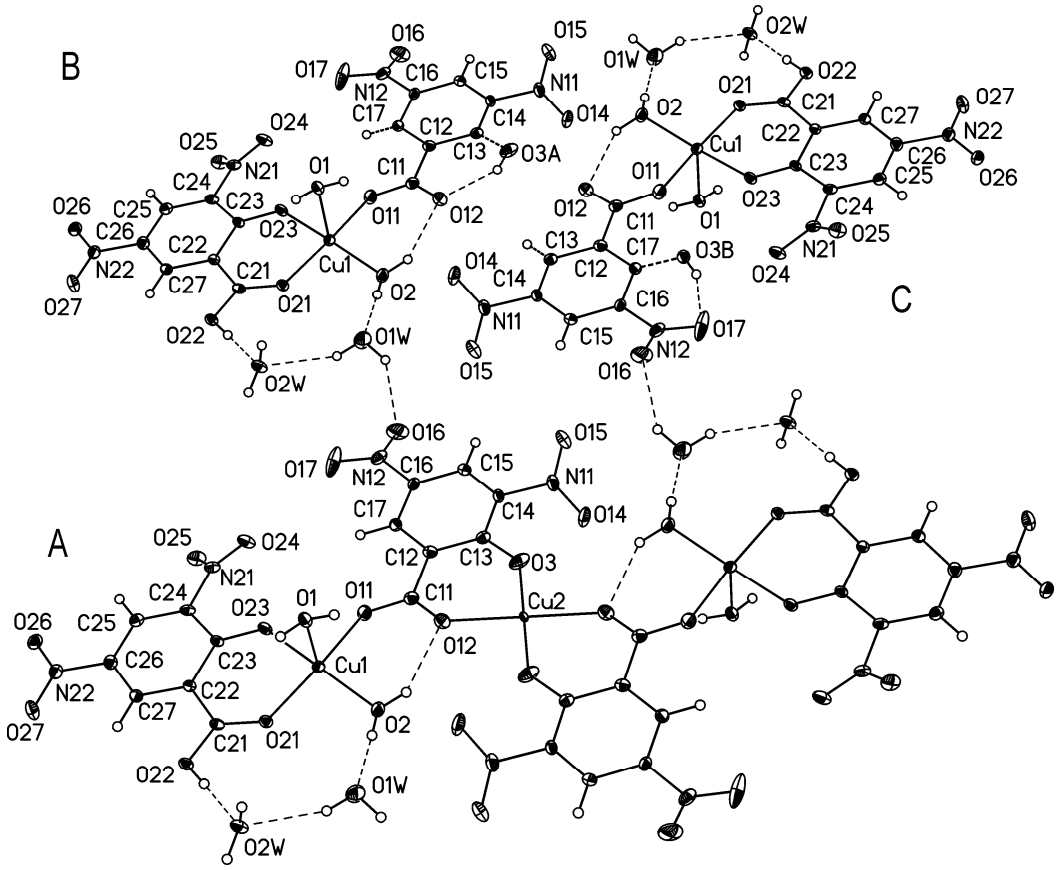

Fig.1. View of the complex (1) with 50% probability displacement ellipsoids A = $[Cu_3(C_7H_3N_2O_7)_2(C_7H_2N_2O_7)_2(H_2O)_4]$ molecule B, C = two disordered orientation of $[Cu(C_7H_2N_2O_7)_2(H_2O)_4]$ molecules and their orientation within the layer

The monomeric $[Cu_2\{3,5\text{-}(NO_2)_2sal^{1-}\}_2(H_2O)_2]$ molecules **B**, or **C** could be drawn from the trimeric one simply by removing Cu2 central atom (Cu^{2+} cation) from its position in centre of symmetry together with the protonization of both phenolato groups to saturate charge changes. This virtual procedure gives two monomeric molecules occupying the same place as the trimeric one, and moreover, this simplifies the structure description. The central atoms Cu1 in both monomeric species **B** and **C** are at the same positions as Cu1 atoms in trimeric molecule, coordination polyhedra of Cu1 atoms are the same, thus the distances given above for these parts of trimeric molecules are the same for the monomeric molecules too. However, the formation of two monomeric parts from one trimeric molecule has its

consequence in bonding mode of 3,5-dinitrosalicylato anion. The bridging 3,5-dinitrosalicylato dianion has been changed into monodentately bonded ligand and O3A phenolato oxygen atom must not be oriented toward centre of symmetry and the positional disorder can occur. The occupancy factors O3A/O3B, calculated from X-ray data, were found to be 0.815(5)/0.185(5) for complex (**1**), or 0.747(5)/0.253(5) for complex (**2**). It should be stressed, that greater amount of O3B has been observed for complex containing greater amount of monomeric part, but the relation is not proportional.

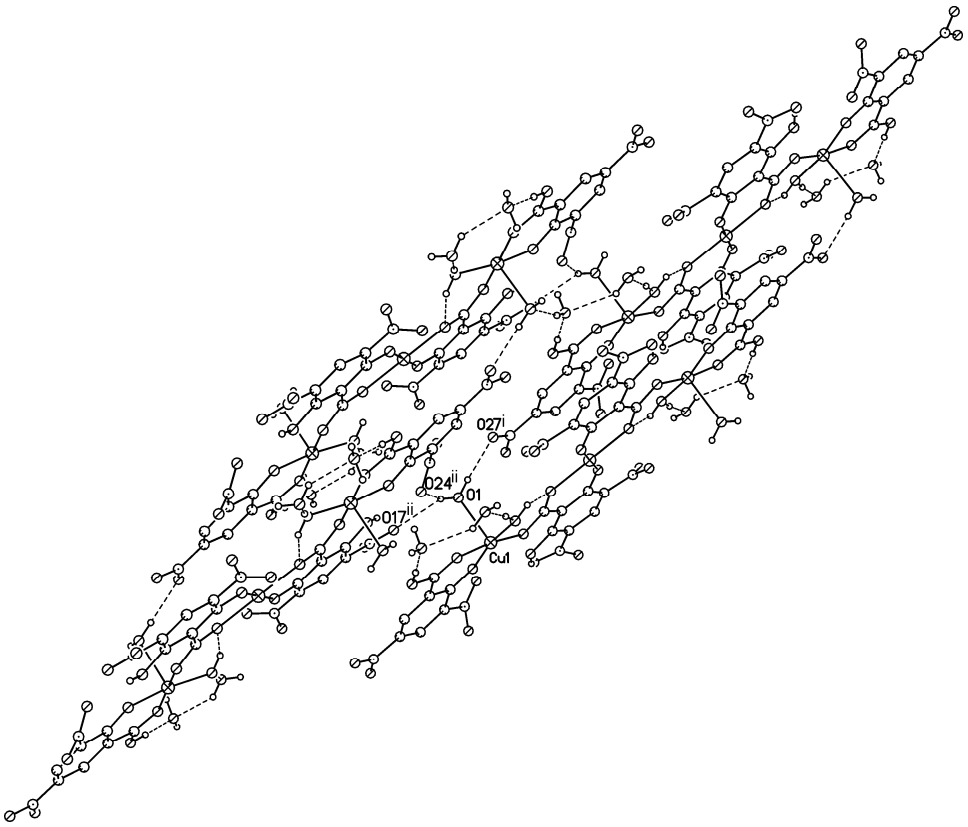

Fig.2. Packing of the complex 1 showing the interlayer hydrogen bonds involving O1 water molecule and the nitro-groups of ligands

On the other hand, higher amount of O3B phenolato orientation is logically explained by possible attraction of phenolic hydrogen atoms that have replaced the copper atom in the centre of symmetry. This disorder has its own consequence on structural data results, because the positition of O3A atom obtained from structure analysis is the superposition of its position in trimeric part **A** and in monomeric one **B** and consequently it could be taken as explanation of rather short Cu2–O3A distance shown above.

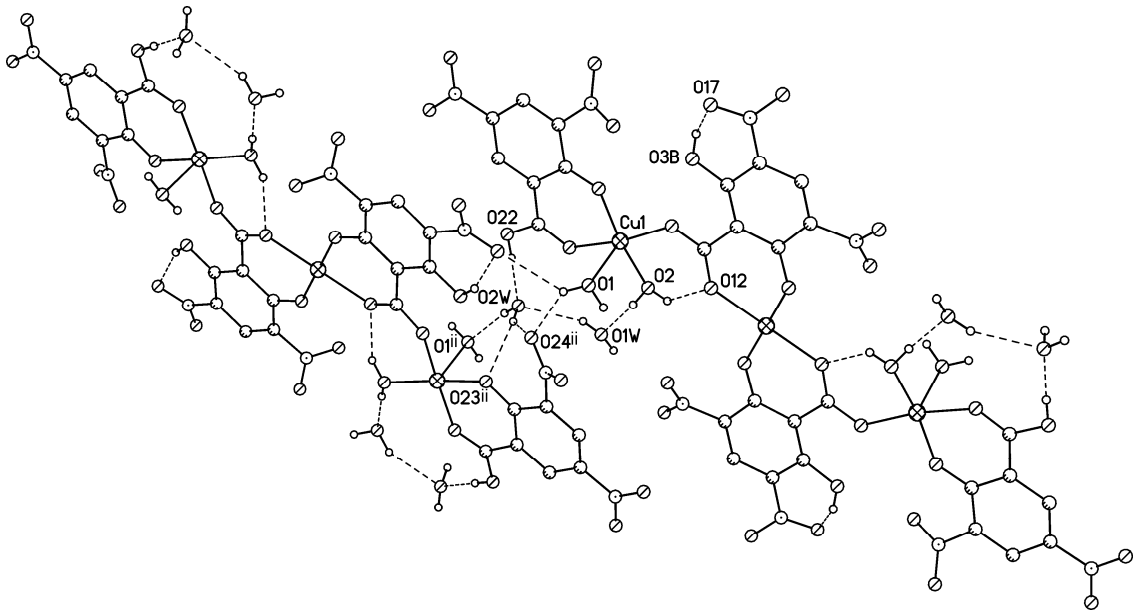

Fig.3. Packing of the complex 1 showing the interlayer hydrogen bonds made by O2W water molecules and O1 water molecule, or O23 phenolato oxygen

There are three types of hydrogen bonds – intramolecular, and two types of intermolecular ones. The intramolecular hydrogen bonds system (Figure 1), that "connects" both 3,5-dinitrosalicylato anions coordinated to Cu1 central atom and in some respect it could be taken as the formation of "chelating" ligand involving both anionic ligands, coordinated water (O2) molecule, and two uncoordinated (O1W and O2W) molecules. This intramoleular system of hydrogen bonds remains the same also for all three molecules **A**, **B** and **C**. The all three planar molecules are within the structure coplanar (Figure 2 and 3) each to other and water molecules containing the O1, O2W and O1W atoms are involved in extending intermolecular hydrogen bonds between the neigbouring trimeric/monomeric molecules. The O1W oxygen atom containing water molecules form intermolecular hydrogen bonds only within the individual plane (Figure 1), while the O2W and O1 water molecules form hydrogen bonds between the planes (Figure 2 and 3). The O1 water molecules are with oxygen atom and both hydrogen atoms involved in the strong hydrogen bonds only within the neigbouring planes, and the relatively short distance Cu1–O1 of 2.339(2) Å (for complex **1**) or 2.344(2) Å (for complex **2**) consequently gives the relatively short distance between the neigbouring planes, about 3.1 Å. This short interplanar distance together with the mutual position of trimeric molecules is probably the reason that there is not enough space for another ligands to be bonded to copper atoms and thus increasing the coordination number of copper atoms.

Table 1. Crystal data and structure refinement for (1) and (2)

	1	**2**
Code	KL175	KL180
Chemical formula	$0.42(C_{28}H_{18}Cu_3N_8O_{32})$ $\cdot 1.16(C_{14}H_{10}CuN_4O_{16})$ $\cdot 4H_2O$	$0.225(C_{28}H_{18}Cu_3N_8O_{32})$ $\cdot 1.55(C_{14}H_{10}CuN_4O_{16})$ $\cdot 4H_2O$
M_r	1205.53	1193.53
Cell setting, space group	$P2_1/c$	$P2_1/c$
Temperature (K)	90(1)	90(1)
a (Å)	10.8082(4)	10.8359(8)
b (Å)	14.1158(5)	14.044(1)
c (Å)	13.0974(5)	13.1551(9)
α, β, γ (°)	90	90
β, γ (°)	95.247(1)	95.434(2)
γ (°)	90	90
V (Å^3)	1989.85(13)	1992.9(2)
Z, D_x (Mg m^{-3})	2, 2.012	2, 1.989
Radiation type	Mo Kα	Mo Kα
μ (mm^{-1})	0.71069	0.71069
No of meas./indep./obs. reflections	39519/6123/5821	43129/6030/5828
R_{int}, θ_{max} (°)	0.024, 30.6^o	0.019, 30.5^o
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.042, 0.092, 1.29	0.039, 0.087, 1.31
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.89, –0.70	0.52, –0.58

More detailed comparison of these structuctures with the published structure Su & Xu, with our previously published structure of trimeric complex has no meaning, because Both of them were measured at room temperature while our structure determination has been done at 90 K (See Table 1).

Co-crystal Structure and Formation

As it was mentioned above, the formation of monomeric parts of the co-crystal could be understand as the copper atom replacing by two protons. Consequently the pair of monomeric molecules occupy the same space as one trimeric molecule. A planarity of all complex molecules (**A**, **B** and **C**), with exception of apical O1 atoms and the peripheral nitro-group oxygen atoms are another dominant structural feature of studied complexes that allows stepwise stacking molecules in solid state, thus it allows the co-crystal formation too. The deviations of the oxygen atoms of nitro-groups from the mentioned plane is due to rotation of nitro-groups along the C–N bond and the difference in rotational position of the individual nitro-groups is in connection with another feature of these structures and this is a system of hydrogen bonds. The system of hydrogen bond group together one trimeric molecule with four water molecules or each monomeric molecule with two water molecules in such positions that surface of trimer is similar to surface of pair monomers (Figure 4).

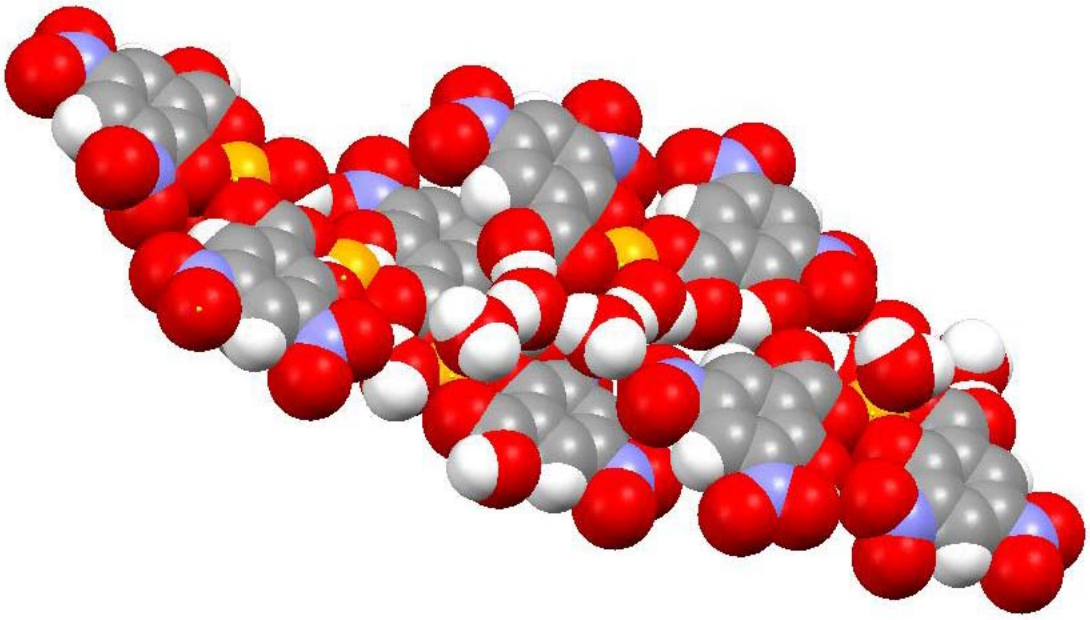

Fig.4. Spacefil model of molecula A (below) and molecules B and C (above) (Copper atoms are shown in dark colour)

The formation of monomeric parts of co-crystal in our system can be better understandable in comparison our synthesis to synthesis of Chinese authors, who reported $[Cu_3\{3,5\text{-}(NO_2)_2sal^{2-}\}_2\{3,5\text{-}(NO_2)_2sal^{1-}\}_2(H_2O)_4]_{0.54}[Cu_2\{3,5\text{-}(NO_2)_2sal^{1-}\}_2(H_2O)_2]_{0.92}\cdot 4H_2O$. The complex of this composition was prepared by adjusting *pH* of reaction mixture to the

neutral solution by addition of sodium hydroxide solution. Higher content of monomeric (protonized) part of co-crystal in our complexes is quite a logical consequence of preparation by using metal sulfates and 3,5 dinitrosalicylic acid without any base. Higher content of protonized monomeric form in co-crystal of (**2**) might be a consequence of the higher M^{2+} : Cu^{2+} ratio that due to complex formation of 3,5-dinitrosalicylato anions with M^{2+} ion increases the acidity of mother liquor. It can be related with higher stability Cu^{2+} 3,5-dinitrosalicylatocomplex that Mn^{2+} or Zn^{2+} 3,5-dinitrosalicylatocomplexes (Lajunen LHJ, Kokkonen P, Nissi A and Ruotsalainen H 1984).

On the other hand it is worth to note, that above explanation of the preparation of different co-crystal by changes *pH*, lets some question unanswered. There is no information in literature concerning the existence of monomeric complex of composition $[Cu_2\{3,5\text{-}(NO_2)_2sal^{1-}\}_2(H_2O)_2]\cdot 2H_2O$. Similarly, there is no information in literature about the composition of crystals during the different stages of crystallization. Rising of the last question is supported by comparison of calculated elemental analysis for both complexes: 27.899 %C, 2.271 %H, 9.295 %N for complex (**1**) and 28.178 %C, 2.327 %H 9.389 %N for complex (**2**). The elemental analysis cannot be used for determination such small differences and similarly there are no spectral techniques suitable for the analysis of such systems and no real differences in properties of both samples have been observed using the instruments given in experimental section. The X-ray structure determination gives the composition of the selected monocrystal and to prove this idea the other crystal taken from the same sample in different stage of crystalization should be taken for structure determination.

Conclusion

In conclusion, we have prepared and characterized two novel molecular complexes $[Cu_3\{3,5\text{-}(NO_2)_2sal^{2-}\}_2\{3,5\text{-}(NO_2)_2sal^{1-}\}_2(H_2O)_4]_{0.420}[Cu_3\{3,5\text{-}(NO_2)_2sal^{1-}\}_2(H_2O)_2]_{1.160}\cdot 4H_2O$ complex (**1**) and complex (**2**) of composition $[Cu_3\{3,5\text{-}(NO_2)_2sal^{2-}\}_2\{3,5\text{-}(NO_2)_2sal^{1-}\}_2(H_2O)_4]_{0.225}[Cu_3\{3,5\text{-}(NO_2)_2sal^{1-}\}_2(H_2O)_2]_{1.550}\cdot 4H_2O$ and the unusual composition was proved by X-ray structure determination. The procedure of co-crystal formation has been analyzed and explained.

Supplementary Material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 676758 (**1**) and CCDC 695711 (**2**). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (internat.) +44 1223/336033; e-mail:deposit@ccdc.cam.ac.uk].

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