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Counter anion dependent symmetry of Cu^{II}–4-amino-1,2,4-triazole polymeric chains

Krzysztof Drabent* and Zbigniew Ciunik

Faculty of Chemistry, University of Wroclaw, 14 F. Joliot-Curie Str., 50-383 Wroclaw, Poland.
E-mail: drab@wchuwr.chem.uni.wroc.pl

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The symmetry changes and length of the symmetry independent part of $[Cu(amtrz)_3]_n^{2+}$ (amtrz = 4-amino-1,2,4-triazole) polymeric chains driven by different anions in crystals with BF_4^- (1), BF_4^-/SiF_6^{2-} (2) and SiF_6^{2-} (3) have been studied by single crystal X-ray method.

A variety of coordination compounds with N^4-substituted 1,2,4-triazoles as a ligand coordinating to first-row transition metal ions have been reported.[1] The interesting magnetic properties of iron(II) and copper(II) compounds with 1,2,4-triazole ligands have been extensively investigated and polynuclear iron(II) 1,2,4-triazole compounds have been found to show spin-crossover behaviour.[2] These ground electronic state related properties depend strongly both on the nature of N^4-substituent of the ligand[3,4] and non-coordinating anion molecule.[5–7] So far no single crystals suitable for X-ray diffraction were obtained for these iron(II) complexes, however structural information deduced from EXAFS (X-ray absorption fine structure) spectroscopy at the iron K edge indicates the presence of linear chains. On the other hand more detailed analysis of these results leads to ambiguous conclusions. For example, the dependence between the Fe–N bond distances and the size of anions suggested by Erenburg *et al.*[7] were not confirmed by Kojima *et al.*[6] It has been assumed that the copper(II) polymers are isostructural with their iron(II) analogues. Crystallographic studies of copper(II) polymeric chains in different anion environments might reveal the nature of cation–anion interactions. However, only two structures of $[Cu(4\text{-}R\text{-}trz)_3]A_2$ type crystals have been presented (both with A = ClO_4^- anions).[8,9] The number of data is limited because single crystals of 1-D polymeric metal(II) 1,2,4-triazoles are generally difficult to obtain due to rapid precipitation of the compounds formed.[4]

Because knowledge of the spatial structure of these polymers seems to be necessary to understand the nature of anion–cation interactions we looked for a useful procedure for growing single crystals of copper(II) analogues. Reaction between amtrz in hot MeCN (0.1 mmol in 10 mL) and an aqueous solution of an appropriate copper salt (0.03 mmol, 2 mL) gave a blue amorphous precipitate. The precipitate was filtered off, washed with 5 mL of MeCN and *immediately*[10] dissolved (at least partially) in water giving a light blue solution. After a few weeks {$[Cu(amtrz)_3](BF_4)_2{\cdot}H_2O$ **1** and $[Cu(amtrz)_3](BF_4)(SiF_6)_{0.5}{\cdot}2H_2O$ **2**} or days {$[Cu(amtrz)_3](SiF_6){\cdot}8/3H_2O$ **3**} well shaped crystals appeared. To obtain **1** the reaction must be carried on in a polyethylene vessel because when glassware is used the mixed anion salt **2** is obtained. It is of note that the synthesis of **2** is reproducible when Pyrex glassware is used. On the other hand, decomposition due to loss of non-coordinated water molecules is observed for compound **3**.† The molecular structures of **1**–**3** were elucidated by X-ray crystallography.‡

The crystals under investigation are composed of linear coordination polymers $[Cu(amtrz)_3]_\infty$ with BF_4 (**1**), BF_4/SiF_6 (**2**) and SiF_6 (**3**) counter ions placed between them as well as different number of water molecules (1, 2 and 8/3, respectively). The μ-N^1,N^2-1,2,4-triazoles act as bidentate ligands bridging copper(II) ions *via* their nitrogen atoms (Fig. 1). The Cu–Cu distances are 3.922 Å in **1**, 3.877 and 3.886 Å in **2**, and 3.855, 3.886 and 3.904 Å in **3**. These values suggest a lack of relation between metal–metal distances and size of counter ion in the crystals. Such a relation was previously postulated for iron(II) triazole complexes on the basis of EXAFS studies.[6]

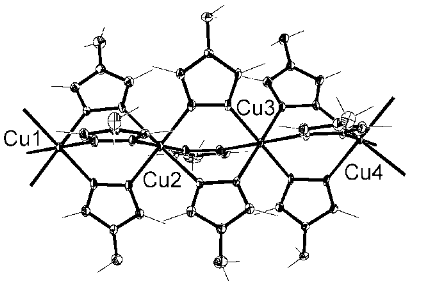

Fig. 1 View of the 1-D coordination polymer in **3**. The anions and water solvate molecules have been omitted for clarity.

In **1**–**3** all copper(II) ions have a distorted (4 + 2), axially elongated octahedral environment (Fig. 2). There are two distinguishable orientations of octahedra along the polymeric chain resulting in alternate *ababa*… order, whereas less regular *abcbab*… order is found for $[Cu(4\text{-}hydroxyethyl\text{-}1,2,4\text{-}triazole)_3](ClO_4)_2{\cdot}3H_2O$.[8] In contrast to **1**–**3**, the latter pattern results from intramolecular hydrogen bonds between neighbouring ligands. The above illustrates very well the distribution of elongation of Cu–N bonds due to the Jahn–Teller effect but this distribution is independent of the size of the counter ions in the crystals. In investigating relations between architectures of the chains and size or charge of counter anions we, however, have found a different interesting phenomenon, neither observed nor even postulated for metal–triazole 1-D polymeric complexes.

The *ababa...* order in **1**–**3** does not reflect the distribution of local symmetry of copper(II) ions. In the present structures copper atoms in the crystals occupy inversion centres ($\bar{1}$) or both

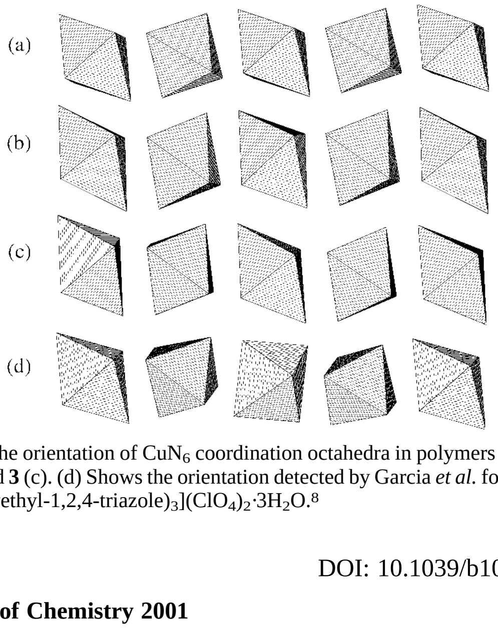

Fig. 2 The orientation of CuN_6 coordination octahedra in polymers of **1** (a), **2** (b) and **3** (c). (d) Shows the orientation detected by Garcia *et al.* for $[Cu(4\text{-}hydroxyethyl\text{-}1,2,4\text{-}triazole)_3](ClO_4)_2{\cdot}3H_2O$.[8]

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inversion centres and general (1) positions. In **1** all copper atoms are located at inversion centres and the sequence of point symmetries in the chain is $\bar{1},\bar{1},\bar{1},\bar{1},\bar{1}$, *etc.* whereas in **2** consecutive copper(II) ions form the sequence $\bar{1},1,\bar{1},1,\bar{1}$, *etc.*, and in **3** the observed sequence can be described as $\bar{1},1,1,\bar{1},1,1,\bar{1}$, *etc.* Moreover, the symmetry independent parts of the chains have different lengths. The shortest unit, {Cu(amtrz)$_3$Cu}, is observed with BF_4 ions in crystals of **1**, the longest one, {Cu(amtrz)$_3$Cu(amtrz)$_3$Cu(amtrz)$_3$Cu} with SiF_6 ions for **3**, whereas for the anionic BF_4/SiF_6 mixed salt **2**, an intermediate {Cu(amtrz)$_3$Cu(amtrz)$_3$Cu} unit was observed. The different size of non-coordinated anions should also be reflected in the packing of the crystals. Analysis of crystal packing in **1–3** showed that counter ions link polymeric chains *via* N–H$\cdots$F hydrogen bonds and determine the distances between them. Each polymeric chain is surrounded by four chains in **1** and by six chains in **2** and **3**. Perpendicular distances between neighbouring chains are 10.4 and 10.6 Å in **1**, 10.3, 11.3 and 13.3 Å in **2**, and 10.5, 11.4 and 12.3 Å in **3**. The data calculated for mixed anion crystal **2** clearly show that not only do the larger counter ions determine the distances but that the distances are dependent also on the spatial distribution of all anions and water molecules around the rigid polymeric chains and on the parallel displacement of the chains. Detailed analysis of this distribution shows that the symmetry of polymeric chain is dependent on type of counter ions, though this dependence is very complicated. This relation is a function of several factors, namely number of water molecules, charge of counter ions, hydrogen bond systems *etc*. which directly influence the crystal packing as well as the structure of the polymeric chain.

In summary, we conclude that the symmetry and length of independent units of $[Cu(amtrz)_3]_n^{2+}$ polymeric chains is dependent on the type of counter ions present in the crystals. In view of published results of EXAFS studies on similarities between structures of copper(II) and iron(II) complexes with 1,2,4-triazoles[8] the counter ion dependent symmetry of polymeric chains in the latter seems to be a crucial factor in spin-crossover phenomena.

Notes and references

† Anal. for **1**. Calc.: C, 14.20; H, 2.78; N, 33.14. Found: C, 14.15; H, 2.80; N, 33.20. For **2**. Calc.: C, 14.14; H, 3.17; N, 33.01. Found: C, 14.25; H, 2.93; N, 33.32. For **3**. Calc.: C, 15.16; H, 2.97; N, 35.37. Found: C, 15.00; H, 3.00; N, 35.52%. Analysis for **3** corresponds to one water molecule in the formula (see text for discussion).

‡ *Crystal data*: **1**: $C_6H_{14}B_2F_8N_{12}OCu$, M = 507.45, triclinic, space group $P\bar{1}$ (no. 2), a = 7.8433(15), b = 10.5221(14), c = 10.8374(12) Å, α = 76.796(10), β = 77.881(12), γ = 80.354(13)°, V = 844.6(2) Å^3, T = 100 K, Z = 2, μ(Mo-Kα) = 1.409 mm^{-1}, 12363 reflections measured, 4633 unique (R_{int} = 0.0379) which were used in all calculations. The final $wR(F^2)$ was 0.1158 (all data).

2: $C_{12}H_{32}B_2F_{14}N_{24}O_4SiCu_2$, M = 1019.41, triclinic, space group $P\bar{1}$ (no. 2), a = 10.285(2), b = 11.727(2), c = 15.521(3) Å, α = 104.99(3), β = 91.45(3), γ = 103.49(3)°, V = 1751.1(6) Å^3, T = 100 K, Z = 2, μ(Mo-Kα) = 1.389 mm^{-1}, 12688 reflections measured, 8014 unique (R_{int} = 0.0321) which were used in all calculations. The final $wR(F^2)$ was 0.1742 (all data).

3: $C_{18}H_{52}F_{18}N_{36}O_8Si_3Cu_3$, M = 1517.85, triclinic, space group $P\bar{1}$ (no. 2), a = 12.417(2), b = 13.150(3), c = 18.030(4) Å, α = 73.63(3), β = 72.64(3), γ = 70.28(3)°, V = 2590.8(9) Å^3, T = 100 K, Z = 2, μ(Mo-Kα) = 1.436 mm^{-1}, the crystal was mounted in inert oil and transferred to the cold gas stream of the diffractometer, 18608 reflections measured, 11646 unique (R_{int} = 0.0455) which were used in all calculations. The final $wR(F^2)$ was 0.1742 (all data).

CCDC reference numbers 164098–164100. See http://www.rsc.org/suppdata/cc/b1/b101936h/ for crystallographic data in CIF or other electronic format.

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10. The compounds become insoluble after desiccation.