

Oxalatocuprate(II) hexaammincobalt(III) as a precursor of metastable solid solutions in the Co-Cu system

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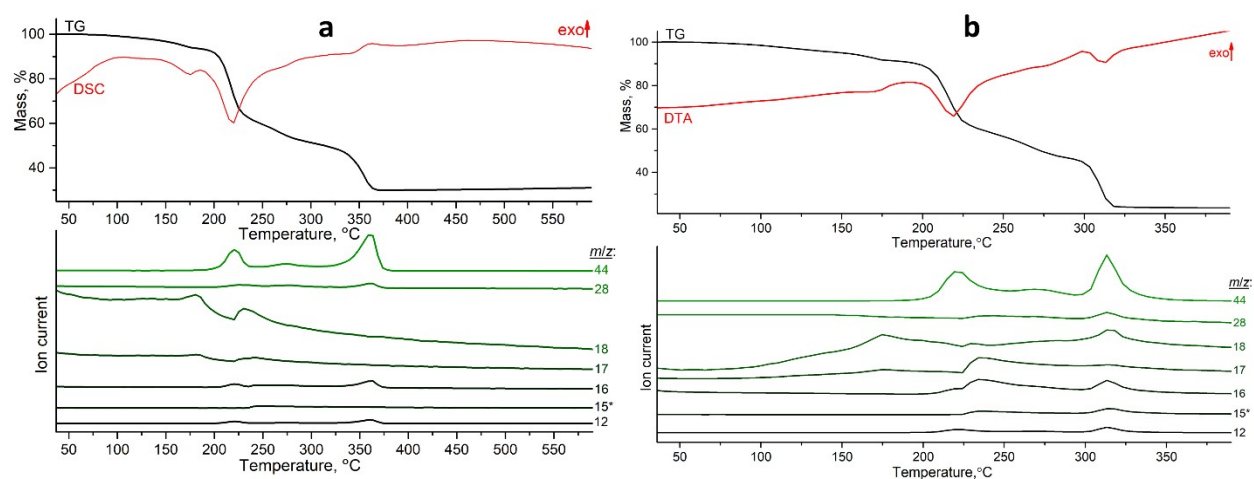


Fig. S1. STA and EGA-MS curves for $[\text{Co}(\text{NH}_3)_6]_2[\text{Cu}(\text{C}_2\text{O}_4)_2]_3 \cdot 4\text{H}_2\text{O}$ in an argon (a) and hydrogen (b) atmosphere, 10 K/min. 15* – data for $m/z=15$ was increased for better visualization.

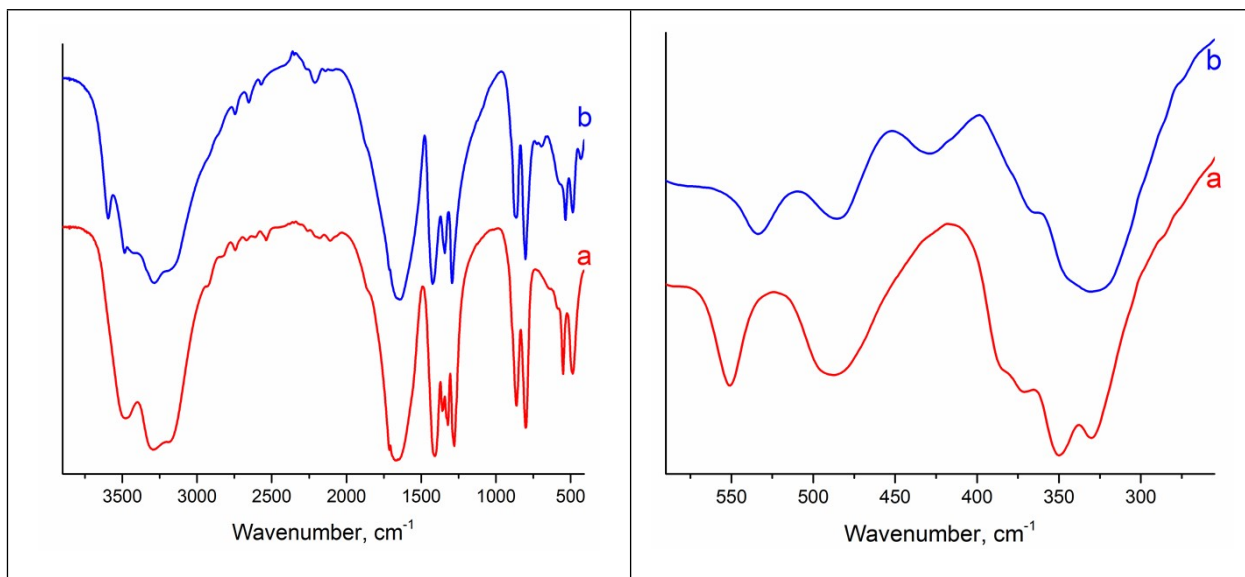


Fig. S2. IR spectra of $[\text{Co}(\text{NH}_3)_6]_2[\text{Cu}(\text{C}_2\text{O}_4)_2]_3 \cdot 4\text{H}_2\text{O}$ (a) and $[\text{Co}(\text{NH}_3)_6]_2[\text{Cu}(\text{C}_2\text{O}_4)_2]_3 \cdot 6\text{H}_2\text{O}$ (b).

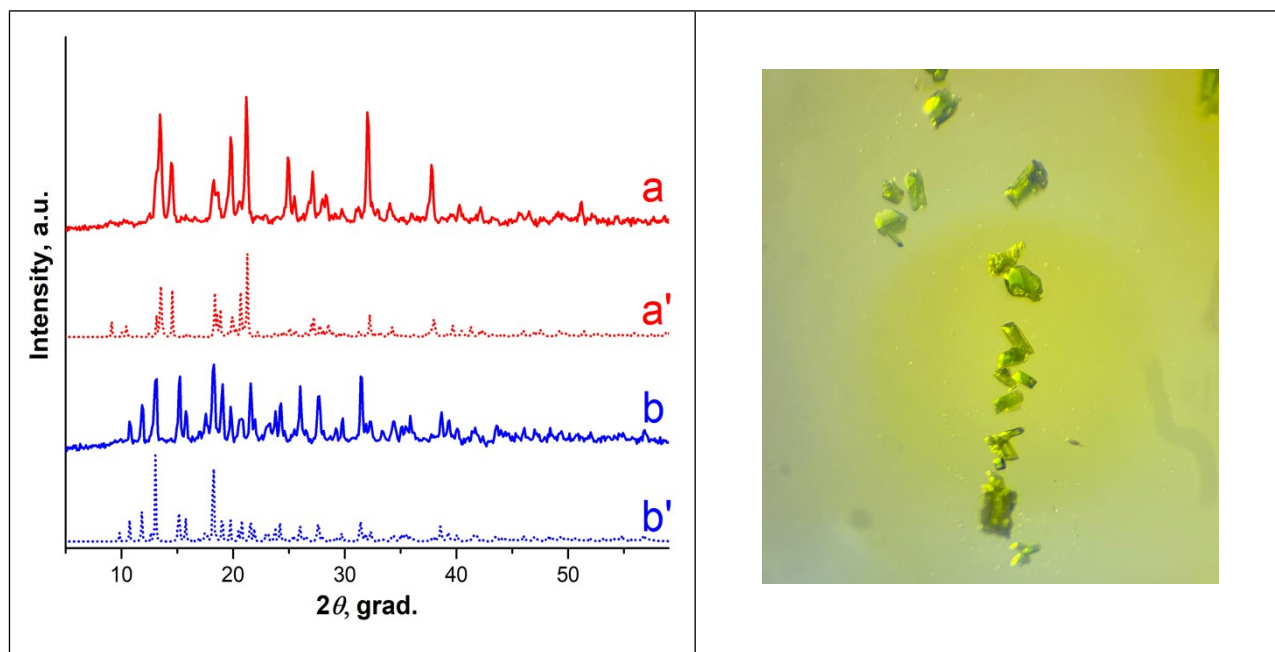


Fig. S3. XRD pattern obtained from the single-crystal data (a' – $[\text{Co}(\text{NH}_3)_6]_2[\text{Cu}(\text{C}_2\text{O}_4)_2]_3 \cdot 4\text{H}_2\text{O}$, b' – $[\text{Co}(\text{NH}_3)_6]_2[\text{Cu}(\text{C}_2\text{O}_4)_2]_3 \cdot 6\text{H}_2\text{O}$) as compared with the powder XRD patterns (a – $[\text{Co}(\text{NH}_3)_6]_2[\text{Cu}(\text{C}_2\text{O}_4)_2]_3 \cdot 4\text{H}_2\text{O}$, b – $[\text{Co}(\text{NH}_3)_6]_2[\text{Cu}(\text{C}_2\text{O}_4)_2]_3 \cdot 6\text{H}_2\text{O}$) (left). A photograph of the crystallites of $[\text{Co}(\text{NH}_3)_6]_2[\text{Cu}(\text{C}_2\text{O}_4)_2]_3 \cdot 6\text{H}_2\text{O}$ (right).

According to UV-Vis spectroscopy, the spectra show three absorption peaks each at 340 nm, 470 nm and 649 nm for $[\text{Co}(\text{NH}_3)_6]_2[\text{Cu}(\text{C}_2\text{O}_4)_2]_3 \cdot 4\text{H}_2\text{O}$ and at 340 nm, 470 nm and 715 nm for $[\text{Co}(\text{NH}_3)_6]_2[\text{Cu}(\text{C}_2\text{O}_4)_2]_3 \cdot 6\text{H}_2\text{O}$ (Fig. S3, ESI). Since the first two absorption maximum of the both DCSs coincides, we assume that it relates to the d-d transitions of Co^{3+} . This assumption is also supported by the literature data.¹ And the third absorption peak relates to the d-d transitions of Cu^{2+} . The shift of the absorption maximum of the second peak for $[\text{Co}(\text{NH}_3)_6]_2[\text{Cu}(\text{C}_2\text{O}_4)_2]_3 \cdot 6\text{H}_2\text{O}$ can be explained by the large number of water molecules in the coordination sphere of Cu.

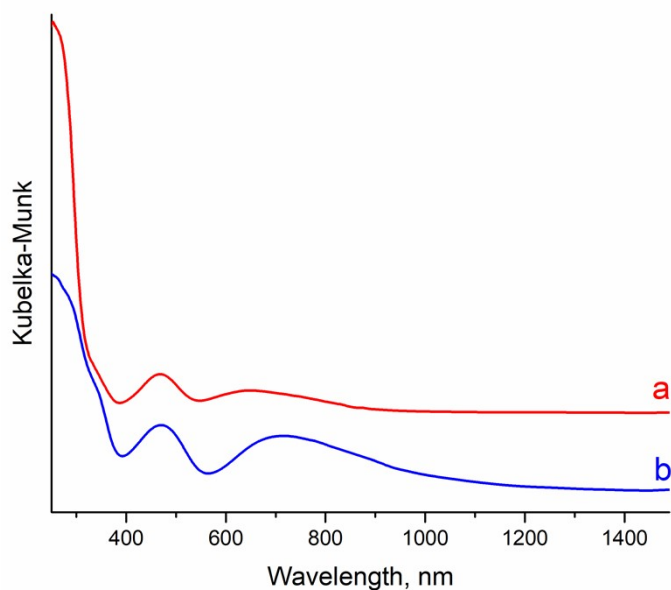


Fig. S4. The absorbance spectra of $[\text{Co}(\text{NH}_3)_6]_2[\text{Cu}(\text{C}_2\text{O}_4)_2]_3 \cdot 4\text{H}_2\text{O}$ (a) and $[\text{Co}(\text{NH}_3)_6]_2[\text{Cu}(\text{C}_2\text{O}_4)_2]_3 \cdot 6\text{H}_2\text{O}$ (b).

¹ A. R. Sotiles, F. Massarotti, J. C. de Oliveira Pires, M. E. F. Ciceri and C. R. B. Parabocz, *Orbital*, 2019, **11**, 348.