

EXAFS study of copper complexes towards structural characterization of cyano-bridged bimetallic networks.

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Copper salts have been very well known since ancient times for their blue colour. In modern times coordination chemistry concentrates on copper due to liability of its complexes and due to large tendency of bonding to N-donor ligands, like pyrazine, piperazine, DABCO or pyrazole. These bonds allow building coordination networks with different dimensionality. Recently, chemists have concentrated on copper synthesis containing bi- and tri-metallic materials with molecular bridges due to collective phenomena such as magnetic ordering or photoinduced magnetization. [1, 2] One of the promising candidates in this area of research are cyano-bridged octacyanades with different TM ions, e.g. Cu^{II}-L-[TM^V(CN)₈]^{3-/4-} (TM = Mo, W; L = bridging and decorating ligands).

As many of cyano-bridged coordination networks can not be structurally characterized by mean of diffraction, only the EXAFS method seems to be suitable for poorly crystallizing materials. In the first stage we plan to obtain and interpret EXAFS signals for basal copper complexes with known structures. These results will allow determination of the local structure of novel bimetallic coordination networks.

Cu(II) complexes have been synthesized according to published procedure [3-5], using commercially available reagents (pyrazine, piperazine and pyrazole – Sigma Aldrich; copper salts – Idalia). Cu-pyrazole is a simple aromatic ring complex with additional Cu-Cl bonds, Cu pyrazine is a heterocyclic aromatic complex with additional Cu-O bonds, whereas Cu piperazine is non-aromatic organic complex with additional Cu-O bonds.

XAS experiments have been performed in Hasylab, DESY, Hamburg, Germany, at the beamline C1 (CEMO) as an In-house Research Project. EXAFS spectra have been collected at Cu: K edge (8979 eV) at 77K in transmission mode, simultaneously with reference standard (Cu metallic foil).

Results from the XAS measurement for simple copper complexes are presented in Fig. 1. XANES spectra show that Cu valence state, for all investigated samples, is close to 2+. The EXAFS spectra exhibit a dominant peak of the first nearest neighbour shell at 1.9 Å which corresponds to oxygen and/or nitrogen neighbours. The peaks located at about 2.8 Å and 3.8 Å show differences in structure of these materials due to the different ligands applied. Detailed EXAFS analysis of the nearest neighbours' peak show the change of the Cu-N bonding length, according to the measured compound. The shortest Cu-N bonding is observed for Cu pyrazole. For Cu piperazine, the nearest neighbours' peak corresponds to Cu-N and Cu-O bonding. The longest Cu-N bonding is observed for Cu pyrazine. The detailed analysis of XAS results of presented compounds is still under investigation.

To summarize, the EXAFS study confirm information on the local ionic environments in the different copper complexes. The obtained results are promising from the point of view of further analysis and structural description of bimetallic networks and magnetostructural correlations.

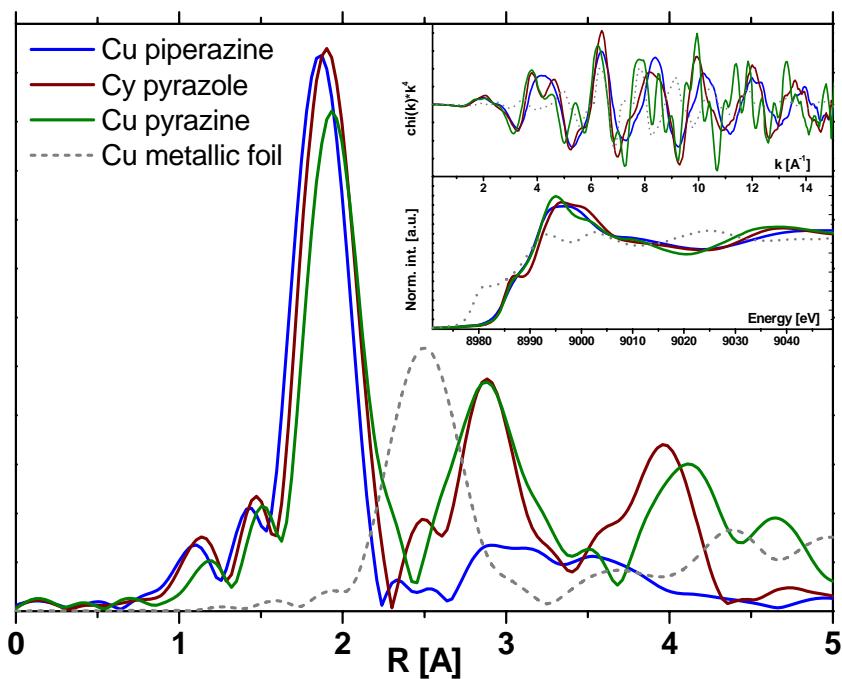


Figure 1. Fourier transforms of the Cu:K edge (EXAFS spectra) for simple copper complexes at 77K. In the inset: the $\chi(k) \cdot k^4$ and XANES spectra at Cu:K edge are presented.

Compound	Cu -N	N_N	Cu-O	N_O	Cu-Cl	N_{Cl}
	Å		Å		Å	
Cu piperazine	2.014	1	1.929	1		
	2.033	1	1.933	1		
			2.388	1		
Cu pyrazole	1.9964	2			2.641	2
	1.9965	2				
Cu pyrazine	2.0805	4	2.301	2		

Table 1. Results of EXAFS fits of Cu nearest ions. Cu-ION and N_{ION} corresponds to the bonding length and number of degeneracy.

References

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