

**Experiment title:**

Sustainable chemistry at the synchrotron: Water oxidation by polyoxometallates through the X-ray eye

**Experiment number:**

CH-4078

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BM23

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15

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**Report:**

In terms of water oxidation capability, switchable spin states the unique chance to trigger the catalytic activity by application of an external stimulation. Spin-crossover (SCO) compounds are a representative example of molecular bistability, in which the high-spin (HS) and low-spin (LS) states are in fact interconvertible by external stimuli.<sup>1</sup> Since the first discovery of the SCO phenomenon it has attracted much attention from chemists, biochemists, and physicists, because it offers basically an understanding of ligand field theory. But despite the tremendous insights that have been gained over the past decades into the underlying electronic principles responsible for the occurrence and the specific behavior of spin transition processes, the study of spin crossover complexes is still a highly attractive research field due to their potential application in water splitting.<sup>2</sup>

Especially the molecular mechanisms leading to specific spin crossover behaviour are still not well-understood, since structural (XRD, XAS) and spin-state changes (SQUID, Mößbauer) are measured in two separate of experiments. In a recent experiment we studied a binuclear cobalt complex which shows spin transition from a LS/HS groundstate (50 K, low temperature measurements were carried out at BM01B) to a HS/HS state at higher temperatures and some reference compounds with defined spin states.<sup>3</sup>

The XANES spectra of the SCO complex  $[\{Co^{II}(L-N_4Me_2)\}_2(\mu-bpym^-)](ClO_4)_3 \cdot 2MeCN$  (PS462) at 50 K and ambient temperature show a prepeak at 7702.4 eV and a weak shoulder at around 7712.5 eV. In tetrahedrally coordinated systems the prepeak intensity is usually high, whereas in octahedral coordinated systems the prepeak shows only very low intensities. In accordance to crystal structure data the

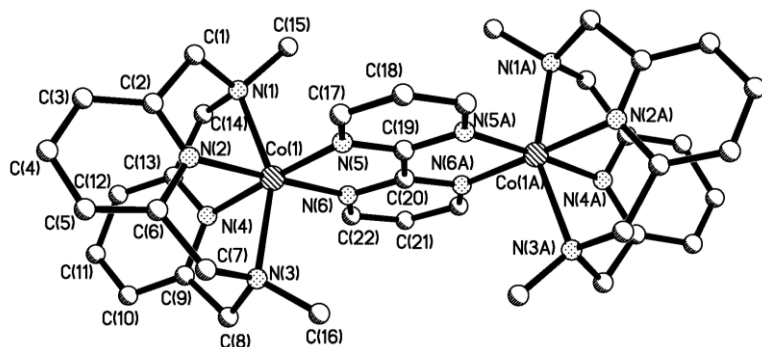


Figure 1: Structure of the binuclear cobalt complex  $[\{Co^{II}(L-N_4Me_2)\}_2(\mu-bpym^-)](ClO_4)_3 \cdot 2MeCN$

binuclear complex exists in an octahedral structure, reflected in the low prepeak intensity. Compared to the spectra of the HS-reference [Co(L-N<sub>4</sub>Me<sub>2</sub>)(pyc)](ClO<sub>4</sub>) (SR-K31), which shows a prepeak at 7701.2 eV and no shoulder and the LS- reference [Co(L-N<sub>4</sub>Me<sub>2</sub>)(bpym)](ClO<sub>4</sub>) (PS453) with a prepeak at around 7701.9 eV and a well pronounced shoulder at 7711.4 eV, the assumption that the binuclear complex exists in a HS/LS

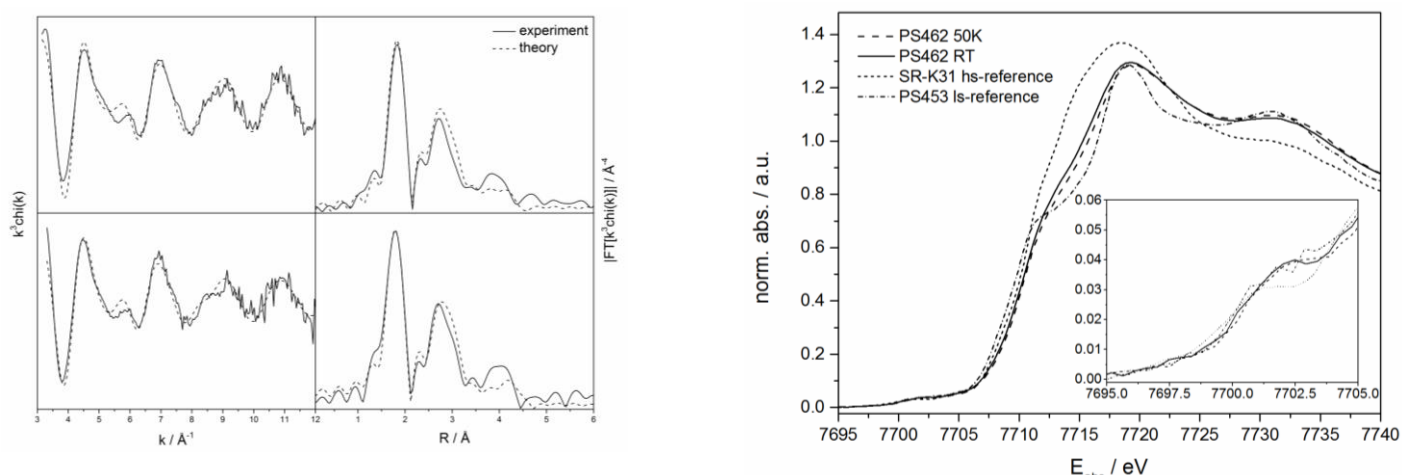


Figure 2: left: EXAFS spectra of the binuclear cobalt complex  $[\{Co^{II}(L-N_4Me_2)_2(\mu-bpym)\}](ClO_4)_3 \cdot 2MeCN$  at 50 K (top) and ambient temperature (bottom; middle:  $k$ ), right: fourier transformation; right: XANES spectra of PS462 at 50 K and ambient temperature and the references SR-K31 (HS) and PS453 (LS)

configuration, with one HS and one LS cobalt centre, resulting from magnetization measurements, is confirmed.

Based on crystal structure data at 110 K EXAFS analysis was carried out to receive detailed structural information. Since this complex contains two cobalt centres the bond lengths of the coordinating atoms in the crystal structure data are only averaged values, so there is no information if one Co-centre exists in HS and the other in LS configuration. According to the XANES spectra and the crystal structure it is obvious that the central ions are surrounded by six nitrogen atoms in an octahedral way in the first coordination sphere. For the EXAFS spectra at 50 K and ambient temperature three nitrogen shells at 1.9 Å; 2.1 Å and 2.2 Å were adjusted. The shell at around 2.2 Å can be assigned to the axial nitrogen atoms whereas the two other shells correspond to the equatorial ones. Compared to the crystal structure the obtained distances are a bit shorter (1.92 Å instead of 1.99 Å) and a bit longer (2.1 Å instead of 2.0 Å) than the averaged ones. If matched with typical Co-N distances for HS and LS systems the bond lengths assort quite well (typical LS Co-N av. 1.94 Å; HS Co-N av. 2.09 Å). As the EXAFS spectra depict only the average of the two cobalt absorbers, it can be concluded that one cobalt centre exists in high-spin and one in low-spin configuration. Additionally, two carbon shells were fitted to the system at around 2.9 Å and 4.4 Å at both temperatures.

Sample	Abs-Bs <sup>a)</sup>	N(Bs) <sup>b)</sup>	R(Abs-Bs) [Å] <sup>c)</sup>	$\sigma$ [Å <sup>-1</sup> ] <sup>d)</sup>	R [%] <sup>e)</sup> $E_f$ [eV] <sup>g)</sup> $A_{fac}$ <sup>h)</sup>
PS462 50K	Co-N	2.6±0.3	1.918±0.019	0.032±0.003	27.76
	Co-N	1.6±0.2	2.074±0.021	0.102±0.010	3.664
	Co-N <sub>Amin</sub>	1.6±0.2	2.228±0.022	0.110±0.011	0.5413
	Co-N		2.861±0.028	0.132±0.013	
	Co-C	14.5±1.5	4.352±0.044	0.132±0.013	
PS462 RT	Co-N	2.2±0.2	1.914±0.019	0.050±0.005	31.23
	Co-N	2.1±0.2	2.063±0.021	0.087±0.009	3.293
	Co-N	2.0±0.2	2.211±0.022	0.112±0.011	0.7662
	Co-N <sub>Amin</sub>	2.0±0.2	2.881±0.029	0.132±0.013	
	Co-C	14.0±1.4	4.394±0.044	0.132±0.013	
	Co-C	8.0±1.2			

Fitted a) Abs=X-ray absorbing atom, Bs=backscattering at 20063 eV number of backscattering atoms, c) distance of absorbing atom to backscattering atom, d) Debye-Waller-like factor, e) fit index, f) reduced  $\chi^2$ , g) Fermi energy, that account for the shift between theory and experiment, h) amplitude reducing factor

[1] P. Gütlich, H.A. Goodwin, *Top. Curr. Chem.* 2004, **233**, 1. [2] J.-F. Letard, P. Guionneau, L. Goux-Capes, *Top. Curr. Chem.* 2004, **235**, 221. [3] H.-J. Krüger, *Coord. Chem. Rev.* **2009**, 253, 2450.