



	Experiment title: High-pressure crystallography of luminescent coinage-metal coordination complexes - towards the pressure-dependent excited-state dynamics in the solid state	Experiment number: CH-4536
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Report: The aim of the proposed project was to investigate the structure-property relationships of luminescent multicentre transition-metal coordination complexes, namely their structure vs. spectroscopic properties evolution when changing the pressure. Such studies are relevant to designing of new photoelectronic materials of specific properties. Especially interesting here are multicentre coinage-metal systems, in which the short metallophilic contacts considerably affect the nature of the lowest lying emissive states. We have focused on two selected model cases, i.e., Cu(I) and Ag(I) multicentre compounds in the crystalline state. It can be expected that the deformation of the polynuclear core (Ag_2Cu_2 or Cu_4 , respectively) with the increasing pressure will affect the complex geometry (also the crucial $\text{M}\cdots\text{M}$ contacts), and thus shall influence the fluorescence and phosphorescence emission spectra and excited state lifetimes. Combining the ultrafast time-resolved (TR) spectroscopic techniques at different pressure with the crystallographic studies we can scan the space of inter-metal distances and correlate that with the observed spectroscopic phenomena. The studies shall help us to answer the following fundamental questions: (i) What is the actual effect of metal...metal interactions on the spectroscopic properties? (ii) Can we fine-tune these properties by applying specific pressure onto the sample? (iii) Can we correlate the geometrical features with the spectroscopic behaviour?

The high pressure X-ray diffraction experiments were done on the ID27 beamline. All data sets were collected with the monochromatic beam ($\lambda = 0.3738 \text{ \AA}$) with the very small beam size of about $2 \times 2 \mu\text{m}^2$ (FWHM) focused on the sample. We used the round Mar165 CCD detector placed at the approximately 173 mm from the high pressure cell centre. Crystals of both complexes (max. 50 μm of linear size) were placed inside the membrane diamond anvil cells (mDACs), equipped with the Böhler-Almax design diamonds with 500-600 μm collet size. In all the cases the steel gasket was used with the hole drilled to about 250-300 μm diameter. Cells were loaded with He, which acted as pressure transmitting medium. The inside pressure was monitored with the ruby chip fluorescence. Experiments were performed by an omega-step scan rotation mode, with 1° step, in the total angular range from roughly -30° to $+30^\circ$ (this was initially determined as dependent on the current cell and its orientation). We noted the significant sample radiation damage to the

samples, which required constant monitoring of the obtained diffraction patterns, and scanning the different areas of the crystals to minimise the effect. It was only possible to collect reasonable data sets up to 6 - 8 GPa, however, these are of significantly lower quality. Altogether about 40 data sets were collected per each sample. Diffraction images were processed with the CrysAlisPro software (Rigaku Oxford Diffraction), with the instrument geometrical parameters previously optimized for the test sample. Data sets are being currently actively analysed. Refinements of crystal structures are very demanding due to the complexity of the examined structures and low data-to-parameter-number ratios.

Preliminary results for the copper-silver complex indicate the pressure evolution of the metal-metal bond lengths (i.e., Ag...Ag and Ag...Cu) in the complex core at room temperature, which is shown in Figure 1. These findings suggest that between 0 and 1 GPa, there is some shortening of the Ag...Ag contact, but also some elongation or no change of the Ag...Cu distance. In turn, when the pressure gets close to 2 GPa, one can observe further geometry changes leading to more rhombic-like shape (similar to that of the excited state geometry derived previously by the TR Laue experiment and supported by TDDFT QM/MM approach). Such results are in agreement with the time-resolved spectroscopic data collected previously at LENS (Florence, Italy). The change in trend around 2 GPa correlates well with the notable shift of the fluorescence peak observed at this pressure point. Between 0 and 1.5 GPa the emission wavelength is blue-shifted, whereas above 2 GPa it gets red-shifted when compared to that of the 0 GPa reference structure. This is supported with the TDDFT results which indicate that the rhombic core geometry should lead to lower emission energy. It additionally shows the importance of the Ag...Cu contacts. The respective article is under preparation, whereas the data treatment of the second complex is currently underway.

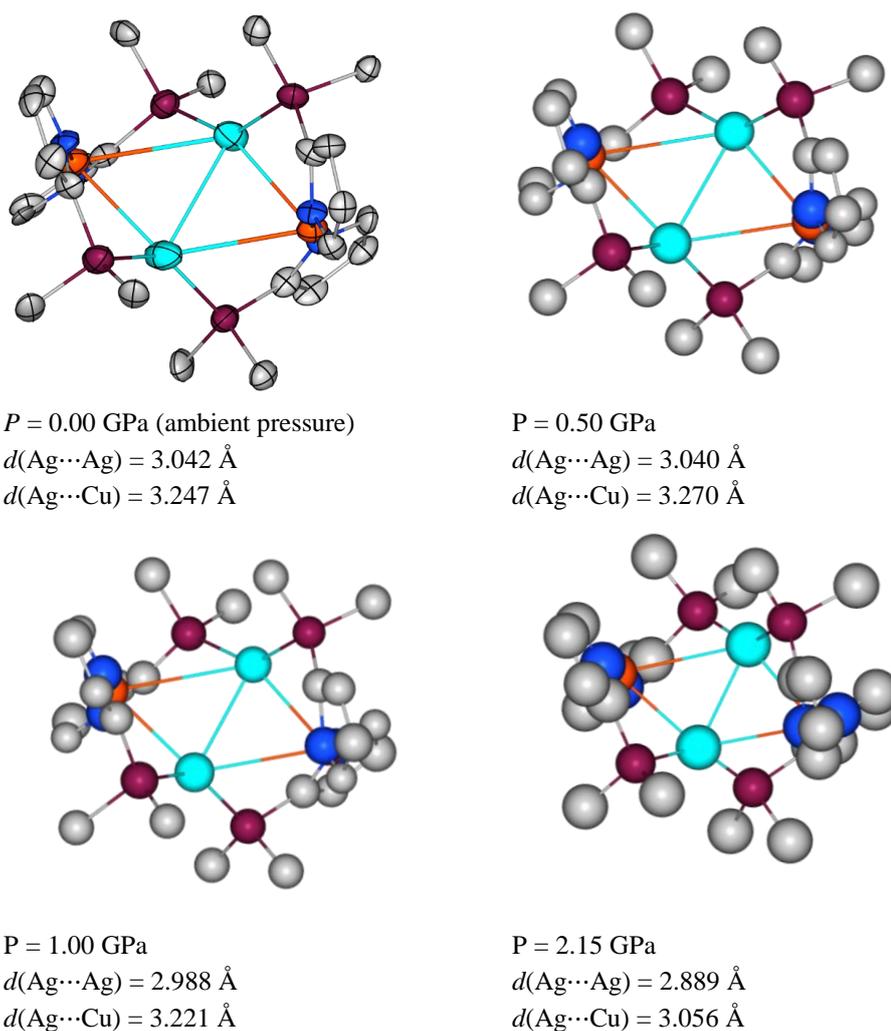


Figure 1. Pressure evolution of the metal core in the Ag_2Cu_2 structures and selected bond.