

MS36-P13 High-pressure phase transitions in the family of photosensitive Co(III) complexes

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It is known that mechanical stresses arise during any reaction in solid state. Stresses and strain influence reaction kinetics, reaction course, spatial propagation and sometimes chemical composition of reaction products. It is much easier to study interrelation between chemical reaction and strain in a crystal if the reaction is homogeneous. There are only few examples of homogeneous solid state reactions and one of the best studied examples is reversible nitro-nitrito linkage isomerisation in $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{XY}$ (X, Y = Cl, Br, I, NO_3) complexes. These compounds were extensively studied during the last decades [1-4]. It is therefore very important to know mechanical properties of each crystal structure, in order to interpret and control various photomechanical effects, including the recently studied that could help us to explain mechanism of linkage isomerisation in details and can also help us to understand "photosalient effect" [5].

The aim of the present study was to follow high-pressure behavior of several compounds from $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{XY}$ family. We have re-visited phase transition in $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{I}_2$ at 0.7 GPa [6] using single-crystal X-ray diffraction technique. We have also found high-pressure phase transitions in $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Br}_2$ and $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{BrNO}_3$ at 6.8 and 3.0 GPa respectively. In contrast to other studied compounds, phase transition in $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Br}_2$ was shown to be of single crystal – single crystal type and reversible without crystal breaking. We have also compared the results with high-pressure data for the compounds from the same family $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{XY}$ (X, Y = Cl, Br, I, NO_3) which are stable in the studied pressure range.

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MS36-P14 A Kryptoracemate: a rare example of a racemic solution crystallizing in a Sohnke space group

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A rare outcome of the crystallization of a racemic solution is the formation of a kryptoracemate^{1,2} (also named false conglomerate³), in which a racemic solution produces enantiomorphic crystals which consists, however, of a racemic pair. We were fortunate to come across such well-ordered racemic crystal structure (*kryptorac-1*) crystallizing in the Sohnke space group $P2_12_12_1$ with two independent molecules of opposite chirality in the asymmetric unit which show no pseudosymmetry and which differ significantly with respect to soft conformational degrees of freedom. Our kryptoracemate is particularly interesting, since often the pairs of enantiomers in kryptoracemates have very similar conformations and they show pseudosymmetry.¹ Figure below shows an overlap of the two independent molecules in the asymmetric unit of *kryptorac-1*.

A polymorphic structure of the kryptoracemate crystallizes as a monoclinic twin with β approximately 90° in the centrosymmetric space group $P2_1/c$ (*rac-1*) with two independent molecules of the same chirality in the asymmetric unit and with similar lattice parameters as the kryptoracemate. Powder diffraction performed on bulk material revealed that *rac-1* and *kryptorac-1* co-exist.

Due to its free movement along three different bonds, this class of molecules can adopt several conformations, some of them being more abundant than others. A large number of similar compounds were prepared and structurally characterized. Their conformations, packing, hydrogen and halogen bonding and π stacking interactions are further discussed in order to understand the driving force for the formation of the kryptoracemate.

Note that the Cambridge Structural Database is approaching 745.000 entries (CSD Version 5.36 and the updates, November 2014). Out of them, only a number of approximately 200 credible kryptoracemates were identified.^{1,2} An exhaustive search for this kind of compounds is rather difficult to undertake.

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