## 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 $[Co(NH_3)_5NO_2]XY$ (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 $[Co(NH_3)_5NO_2]XY$ family. We have re-visited phase transition in $[Co(NH_3)_5NO_2]I_2$ at 0.7 GPa [6] using single-crystal X-ray diffraction technique. We have also found high-pressure phase transitions in $[Co(NH_3)_5NO_2]Br_2$ and $[Co(NH3)_5NO_2]BrNO_3$ at 6.8 and 3.0 GPa respectively. In contrast to other studied compounds, phase transition in $[Co(NH_3)_5NO_2]Br_2$ 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 $[Co(NH_3)_5NO_2]XY$ (X, Y = Cl, Br, I, $NO_3$) which are stable in the studied pressure range.

The work was supported by grant from RFBR 14-03-00902.

1) Boldyreva E.V., Sidelnikov A.A., Chupakhin A.P., Lyakhov N.Z., Boldyrev V.V., Proceed. Acad. Sci. USSR 1984, 277, 893-896. 2) Boldyreva E.V., Mol. Cryst. Liq. Cryst. Inc. Non-Lin. Opt. 1994, 242, 17-52. 3) Boldyreva E.V. Coord. Chem. Russ., 2001, 27(5), 323-350. 4) Nath N.K., Panda M.K., Sahoo S.C., Naumov P. CrystEngComm, 2014,16, 1850-1858. 5) Naumov P., Sahoo S.C. , Zakharov B.A., Boldyreva E.V., Angew. Chem. Int. Ed, 2013, 52, 9990-9995. 6) Boldyreva E.V., Ahsbahs H., Uchtmann H., Kascheeva N. E., High Pressure Research, 2000, 17(2), 79-99.

**Keywords:** high pressure, X-ray diffraction, phase transitions, reactivity of solids

## 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 conglomerate[3]), 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 $\beta$ 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 then 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.

1. L. Fábián and C. Pratt Brock, *Acta Crystallographica Section B*, **2010**, *B66*, 94–103 and references therein.2. I. Bernal, S. Watkins, *Acta Crystallographica Section C*, **2015**, *C71*, 216- 221 and references therein.3. R. Bishop, M. L. Scudder, *Crystal Growth & Design*, **2009**, *9*(6), 2890- 2894.

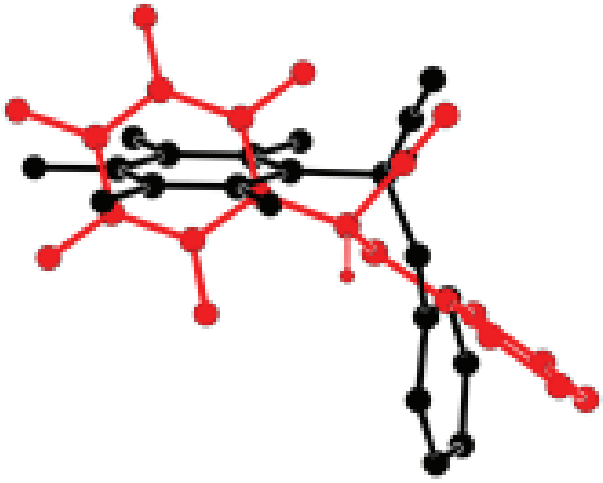

**Figure 1.**

**Keywords:** kryptoracemate, false conglomerate, chiral solids, polymorphysm, intermolecular interactions, halogen bonding, H bonding, π stacking interactions

# MS36-P15 A technique for the comparison and analysis of decorated molecular surfaces

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Molecular surfaces of various types are of immense value in chemistry. Typically, comparison and analysis of such surfaces relies upon human intuition and understanding which is inherently subjective.

We present a technique to describe the shape of the surface, and any associated properties on the surface (so-called decorations) which preserves relative location information while remaining translation and rotation invariant. The technique relies on a spherical harmonic decomposition followed by manipulation of the expansion coefficients in order to generate any number of rotation-invariant descriptors. [1] Although others have employed spherical harmonic decompositions for shape (see [2], [3]), the generation of rotation-invariant descriptors for shape and properties mapped on the surface is new in this context.

Importantly, the technique provides the capability to greatly reduce the amount of information which is invaluable for efficient large-scale algorithmic classification. An example of shape reconstruction is shown Figure 1 dependent only on the highest angular momentum $l_{max}$ of the spherical harmonics used in the process.

The technique will be applied on several sets of decorated Hirshfeld surfaces. Conclusions will be drawn from cluster analysis to objectively examine questions related to, for example, shape and interaction-dependent factors affecting crystal packing; and binding-pocket correlations for drug-search and co-crystallisation applications.

**References**

1. Burel, G. and H. Henocq, *3-DIMENSIONAL INVARIANTS AND THEIR APPLICATION TO OBJECT RECOGNITION.* Signal Processing, 1995. **45**(1): p. 1-22.

2. Morris, R.J., et al., *Real spherical harmonic expansion coefficients as 3D shape descriptors for protein binding pocket and ligand comparisons.* Bioinformatics, 2005. **21**(10): p. 2347-2355.

3. Venkatraman, V., et al. "Potential for Protein Surface Shape Analysis Using Spherical Harmonics and 3D Zernike Descriptors." Cell Biochemistry and Biophysics, 2009. **54**(1-3): 23-32.