conference abstracts

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The determination of crystal structures for non-merohedral twins with the reciprocal lattices not exactly overlapped is not routine task soluble with a normal automated four-circle diffractometer [1]. There may be a problem with cell determination using standard crystallographic software, because the reflections that have contributions from several domains of twins may have bad shapes and macroscopic domains may not be well centered on the goniometer.

Here will be presented determination of crystal structure of the title complex using KM4-CCD four-circle diffractometer and Jana98 [2] software system. The crystals of this complex crystallize in triclinic SG P-1 with a=14.173(3), b=14.488(3), c=14.954(3) Å, α=84.78(2), β=89.73(2), γ=78.03(2)°, Z=2. The presence of pseudo-two-fold axis causes that all crystals grow as twins with twinning matrix:

$$\begin{matrix} 0.0228 & 1.0168 & 0.0037 \\ 0.9767 & -0.0168 & -0.0041 \\ -0.0932 & -0.0865 & -0.9927 \end{matrix}$$

Conventional refinement with SHELXL gives R^1=0.0984 and max. residual difference peak is 2.95 e.Å⁻³, while during refinement of the twinned crystal with JANA98 we obtained significantly better result with R^1=0.0741 and max. residual peak 1.53 eÅ⁻³.

The structure consists of two crystallographically independent molecules. Cu(II) ions adopt a distorted trigonal bipyramidal (**TB**) geometry with three chloride ions in the basal plane. Two protonated H⁺L ions are coordinated in apical positions of **TB** through the N(9) atoms of imidazole rings, while remaining Cl⁻ ion, together with water molecules, are situated outside of the coordination sphere of the central atom. The [Cu(H⁺L)₂Cl₃]⁺ cation is shown in the *figure* below.
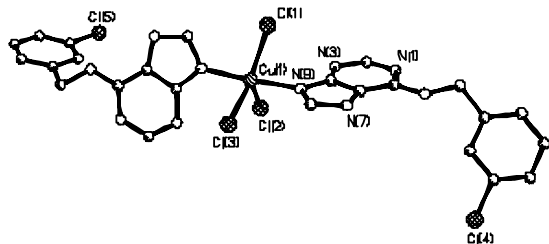
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It is a well-known fact that a traditional structure analysis by X-ray diffraction (XRD) has some limitations (location of light atoms, distinction between elements with close atomic numbers etc). When those problems arise it is useful to carry out neutron diffraction (ND) experiment, but the reactors are not easily accessible for the routine research. However, there is another method allowing to overcome the specified difficulties in most cases. Based on Paulings second rule, bond valence method (BVM) depends not on the scattering factors of the atoms, and operates with their oxidation states. Moreover in some cases BVM is the only way to obtain structural information (e.g. location of O and F which are indistinguishable by neither XRD, nor ND).

Here are some cases where BVM is effective:
1. Location of the light atoms (detection of hydrogen bonds, location of the intercalated atoms, search of migration pathways in solid electrolytes by valence maps etc)
2. Determination of the (average) oxidation state of the site:
   2a. Determination of the oxidation states of the atoms (e.g. in HTSC)
   2b. Determination of the occupancies of the underoccupied sites (solid electrolytes)
   2c. Detection of possible heterovalent substitutions when exact composition is unknown (minerals)
   2d. Determination of the heterovalent ions distribution over inequivalent positions when exact composition is known

The aim of this report was checking of the correctness of BVM in the cases 2b and 2d by the analysis of own and a number of published results of structure refinements by ND.

Also the procedure of bond valence in itself is considered:
- various expressions of «bond valence-bond lengths» relationships ($\exp[(R_{2j}-R_{ij})/b]$, $(R_{ij}/R_1)^{-N}$, k/R_{ij}^{λ})
- different schemes of averaging used for valences calculation for substituted and/or underoccupied sites

The most experimental results are in a good agreement with the calculations of bond valence sums. For the discordant cases the possible reasons of disagreement are discussed.

General conclusion. BVM is a powerful method of crystal structure investigation, capable to replace expensive ND experiments in many cases.