

of Yb and Cu along  $c_z$ . Based on this result and the high resolution transmission electron microscopy images a 3-dimensional model of the superstructure was constructed in space group  $C2$  [1]. Yb was distributed on 336 (4c) sites, 7 (2b) sites and 7 (2a) sites, while Cu was distributed on 1519 (4c) sites. Three different types of Yb co-ordination occur in the structure with their relative abundancies 2:1:1 which is consistent with observed Mössbauer spectra. The Yb sites near the shear planes show Yb - Yb distances of the order of 3.6 Å which are presumably related to the formation of shear planes, and might be of relevance for the interpretation of the magnetic properties. The composition and calculated density of the model are consistent with their observed values. The calculated and observed X-ray structure factors agreed to  $R = 12\%$ . The structure of a related compound  $\text{YbCu}_{3.5}$  can be predicted as having the same topology of plane defects as  $\text{YbCu}_{4.5}$  but with a higher density of occurrence.

[1] R. Cerny, M. François, D. Jaccard, E. Walker, K. Yvon, V. Petricek, I. Cisarova, H.-U. Nissen and R. Wessicken; submitted to *J. Physics: Cond. Matter*

**PS08.01.06 THE STRUCTURE OF COPPER(II) WITH 2-HYDROXYETHYL (PROPYL) IMINE -2-HYDROXY-1-BENZALDEHYDE.** Yu.M. Chumakov, T.J. Malinowski, Institute of Applied Physics, Kishinev, 277028, Moldova, V. I. Tsapkov, N. M. Samus, Moldavian State University, Kishinev, Moldova

The various coordination compounds obtained by the interaction of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  with 2-hydroxyethyl (propyl) imine-2-hydroxy-1-benzaldehyde in function of pH of the medium and the nature of the proton acceptor reagent possess an antiseptic activity, which depends not only of the composition, but of the structure of the complex as well. In order to clarify this dependence the following complex compounds were synthesized and next analyzed by X-ray methods:

$\text{Cu}(\text{HL})\text{NO}_3$  [I],  $\text{Cu}(3\text{-pic})(\text{HL})\text{NO}_3$  [II],  $\text{Cu}(4\text{-pic})(\text{HL})\text{NO}_3$  [III],  $\text{CuL}$  [IV],  $\text{CuL}'$  [V],  $\text{Cu}(\text{Py})(\text{HL})\text{NO}_3$  [VI], where  $\text{H}_2\text{L} = 2\text{HOC}_6\text{H}_4\text{CHN}(\text{CH}_2)_2\text{OH}$ ,  $\text{H}_2\text{L}' = 2\text{HOC}_6\text{H}_4\text{CHN}(\text{CH}_2)_3\text{OH}$ .

It was determined, that the coordination polyhedron around the central atom in the compounds I - III is an extended tetragonal pyramid meanwhile the complex are polymers. The compound II is a dimer. The nitrate group serves in the polymer complexes as bridge-ligand, but in dimers this function fulfil the oxygen atom belonging to the phenol group, the nitrate group is three-dentate in I, monodentate in II and bidentate in III.

In IV the copper atom is coordinated fully by the deprotonated molecule  $\text{H}_2\text{L}$  through the oxygen atoms of phenol and alcohol and by nitrogen of the imine. The tetramer as cubane complex is formed in the complex compound. The surroundings of the central ion in V is a distorted square formed by oxygen atoms of the phenol and alcohol and of the nitrogen of the azometin  $\text{H}_2\text{L}'$ . The fourth corner of the square is occupied by the oxygen atom of the neighbouring complex  $\text{CuL}'$  coupled with the initial complex through the centre of symmetry.

**PS08.01.07 AN INVESTIGATION INTO THE CRYSTAL STRUCTURE AND DISORDER OF  $\text{PbZrO}_3$ .** Corker, D. L., Glazer, A. M., Clarendon Laboratory, Physics Department, Oxford University, England

The following study reports a reinvestigation into the structure of lead zirconate,  $\text{PbZrO}_3$ . Previously reported by Glazer *et al.* (1) in 1993, the crystal structure was determined in space group Pbam and said to exhibit a disorder in the oxygen sites such that the two oxygen substructures A and B were related by:

$$X_A, Y_A, Z_A \Rightarrow X_B, Y_B, Z_B + 0.5$$

This disorder, although agreeing with an earlier single-crystal X-ray diffraction study, disagrees with a neutron powder dif-

fraction analysis by Whatmore, in 1976 (2), where no indications of a disorder could be found.

To investigate this discrepancy further structural analysis is presented. This includes single-crystal X-ray diffraction, at both room and low temperature, and also neutron diffraction, although due to growth problems of large single crystals, the neutron analysis is restricted to that of powders only. If the disorder is false, then explanations of a disorder being exhibited are further cell doublings previously not recognised, twinning or possibly incorrect space group determination. Indeed, there has been much contradicting evidence over the space group determination and whether the structure is truly centrosymmetric. While there has been weak ferroelectricity reported by Dai *et al.* (3) which indicates a non-centrosymmetric space group, Scott and Burns (4), were unable to find neither piezoelectric or pyroelectric effects hence supporting the centrosymmetric classification Pbam.

There is also the possibility that the disorder is simply an artifact of pseudosymmetry. Whatever the space group, one of the main problems in an accurate structure determination is the strong pseudosymmetric character of the Pb and Zr sites and the relatively high scattering factors of the cations to the oxygens. Assuming nothing from previous determinations, an account is given of each of the stages used and pitfalls encountered in investigating all possibilities.

(1) Glazer, A. M., Roleder, K. & Dec, J. (1993). *Acta Cryst.* **B49**, p846

(2) Whatmore, R. PhD thesis, (1975). Univ. of Cambridge, England.

(3) Dai, X., Li, J. & Viehland, D. (1995). *Cond. Matter*, **51**, 5, 2651

(4) Scott, B. A. & Burns, G. (1972). *J. Am. Ceram. Soc.* **55**, 333

**PS08.01.08 CONTRIBUTION TO THE STEREOCHEMISTRY OF MONOVALENT THALLIUM TO OXYGEN ATOMS.** H. Effenberger, Institut für Mineralogie und Kristallographie, Universität Wien, Althanstrabe 14, A-1090 Wien, Austria

For  $\text{Tl}(I)$  atoms two principally different kinds of coordination spheres formed by oxygen atoms are known: (i) The  $\text{Tl}(I)$  atom is strongly covalently bound to a small number of neighbours with short  $\text{Tl}(I)-\text{O}$  bonds. In these cases usually two to four ligands with  $2.50 \text{ \AA} < \text{Tl}(I)-\text{O} < 2.80 \text{ \AA}$  have been found to be arranged at one side of the  $\text{Tl}(I)$  atom. Additional ligands have definitely longer  $\text{Tl}(I)-\text{O}$  bonds starting by  $\text{Tl}(I)-\text{O} > 3.00 \text{ \AA}$ . These coordination figures are in accordance with expectations from the electron configuration of  $\text{Tl}(I)$  atoms with their lone-pair electrons. (ii) The  $\text{Tl}(I)$  atom is coordinated by a large number of O atoms with more or less equal  $\text{Tl}(I)-\text{O}$  bond lengths or at least without larger gap in the distribution of the distances. Regular polyhedra with up to 12 ligands are known. The  $\text{Tl}(I)-\text{O}$  bond lengths as a rule start with larger values as found for the type (i) coordinations. The type (ii)  $\text{Tl}(I)$  atoms sometimes replaces alkali or earth alkali atoms like K, Rb, Cs, and Ca or  $\text{NH}_4$ . It is to be mentioned that transitions between these two principally different kinds of coordination figures are known. A similar crystal chemical behaviour shows e.g.  $\text{Pb}(II)$ .

In connection with an investigation of the geometry of the coordination figures of the  $\text{Tl}(I)$  atoms three  $\text{Tl}(I)$  arsenates have been synthesized hydrothermally and their crystal structures were determined by single crystal X-ray diffraction methods:  $\text{Tl}(I)_3(\text{AsO}_4)$  [ $a = 8.517(3)$ ,  $c = 5.233(2)$  Å, space group  $\text{P}6_3/\text{m}$ ],  $\text{Tl}(I)_2\text{Cu}(I)(\text{AsO}_4)$  [ $a = 6.000(3)$ ,  $b = 5.343(2)$ ,  $c = 8.616(3)$  Å,  $\beta = 98.05(3)^\circ$ , space group  $\text{P}2_1$ ], and  $\text{Tl}(I)\text{Cu}(II)_2(\text{AsO}_4)(\text{AsO}_3\text{OH})$  [ $a = 6.407(2)$ ,  $b = 11.245(5)$ ,  $c = 10.173(4)$  Å,  $\beta = 98.64(2)^\circ$ , space group  $\text{P}2_1/\text{c}$ ]. All these compounds represent type (i) examples. In  $\text{Tl}_3(\text{AsO}_4)$  the  $\text{Tl}(I)-\text{O}$  bond lengths are 2.527, 2.542 and 2.562 Å, in  $\text{Tl}_2\text{Cu}(\text{AsO}_4)$  they are 2.487, 2.565 and 2.778 Å for  $\text{Tl}(I)$  and 2.509, 2.743, 2.749 and 2.847 Å for  $\text{Tl}(II)$ , and in  $\text{TlCu}_2(\text{AsO}_4)(\text{AsO}_3\text{OH})$  they are 2.565 and 2.640 Å, next  $\text{Tl}(I)-\text{O}$  distances are  $\geq 3.0$  Å.