

**MS07.06.06 THE ELASTO-OPTIC EFFECT IN POLY-CRYSTALLINE AGGREGATES.** Alexander Kh. Zilbershtein, Institute of Precambrian Geology & Geochronology, Russia Acad. Sci., St.-Petersburg, Russia

The mutual strain {X} for different elements (parts) of the aggregate may exist, if the temperature  $T_f$  and/or the pressure  $P_f$  of polycrystalline aggregate's formation are not equal to the temperature T and pressure P under study. This mutual strain induces the elasto-optic effect in these elements. The effect may be designed as induced birefringence dN for transparent materials or double reflection dR for strongly absorbing ones. These optical anomalies may be used for determining of the mutual strain {X} and, in turn, for estimation of the unknown values of the  $T_f$  and the  $P_f$ . The latter data are artificial and natural expressions for the dN useful for various problems of a growth of crystals, compounds and aggregates. The expressions for the dN and the dR as a function of the  $T_f$  and the  $P_f$  were obtained. The simple form of the expression for elastoisotropic approximation may be presented as

$$dN = A(B(T_f - T) + C(P - P_f))$$

where the A is the proper combination of the elasto-optic constants for the investigated crystal element of the aggregate; the B (and the C) is the difference between the thermal expansion (and compliances) coefficients for the investigated element and the corresponding neighbouring different element. The unknown parameters of aggregates formation ( $T_f$ ) were obtained for first time, using measured value of the  $\ln N$  and experimentally obtained function  $\ln N(T)$  as well as known values of the T, the P, the B, the C, the  $P_f$  for natural quartz-feldspar and quartz-moissanite aggregates as an example.

**MS07.06.07 HETEROMETALLIC CARBONYL CLUSTERS OF OS, IR, RU, FE AND RH WITH DIVALENT SN, PB AND GE AND THE BULKY LIGANDS -CH(SiMe<sub>3</sub>)<sub>2</sub>, -C<sub>6</sub>H<sub>2</sub>(i-Pr)<sub>3</sub> AND -C<sub>6</sub>H<sub>2</sub>(Ph)<sub>3</sub>.** Christine J. Cardin, David J. Cardin,<sup>1</sup> and Maire A. Convery,<sup>2</sup> Chemistry Department, University of Reading, Whiteknights, Reading, RG6 6AD, U.K.,<sup>1</sup> Chemistry Department, Trinity College, Dublin 2, Ireland<sup>2</sup>

A comparative survey, including some unpublished work, of our structural studies on heterometallic clusters, principally those of Sn(II) with transition metal clusters, will be presented. All clusters have been synthesised in the authors' laboratory, and some have not previously been reported. We find that the SnR<sub>2</sub> moieties, R = CH(SiMe<sub>3</sub>)<sub>2</sub>, -C<sub>6</sub>H<sub>2</sub>(i-Pr)<sub>3</sub> and -C<sub>6</sub>H<sub>2</sub>(Ph)<sub>3</sub> confer kinetic stability on a variety of metal frameworks, electron configurations and unusual geometries.

We also find that the nature of the ligand considerably influences the geometry adopted, and that there is both a characteristic 'bite' and 'twist' for each ligand. In a study of mixed-ligand ruthenium-tin clusters, a very consistent pattern of ligand influences was observed, in which the larger steric effect of the aryl ligand can be distinguished from the larger electronic effect of the alkyl ligand. Limited data are also available on Pb-Ru clusters and on Os-Sn clusters with Sn-amide ligands. Data have been collected using both diffractometer and image plate and a brief comparison of the data collections will be made.

**MS07.06.08 Ni<sup>III</sup> COMPLEXES: MAGNETISM CAN LEAD TO WRONG ASSIGNMENT OF TETRACOORDINATED GEOMETRY.** Hartmut Wunderlich, Institut für Anorganische Chemie und Strukturchemie, Heinrich-Heine-Universität, 40225 Düsseldorf, Germany

Tetraordinated Ni<sup>III</sup> complexes reveal frequently planar arrangement of the core, but several crystal structures with tetrahedral or intermediate geometry (dihedral angle at Ni<sup>III</sup> between 0° and 90°) are also reported. By measurement of the magnetic moment the geometry has been assigned corresponding to the relation: paramag-

netism ( $\mu_{\text{eff}} = 3-4$  B.M.) - tetrahedral, diamagnetism - planar. This rule is violated by the compounds **1** and **3a** which are paramagnetic and yet planar complexes. The dependence of the coordination geometry on the type of residues R<sup>1</sup> and R<sup>2</sup> is revealed by a series of crystal structure determinations.

compd.	$\mu_{\text{eff}}$ [BM]	dih. angle [°]
<b>1</b>	3.4	0
<b>2</b>	3.0	82.4
<b>3a</b>	3.3	0
<b>3b</b>	3.3	86.2
<b>4</b>	3.3	81.6
<b>5</b>	diam.	4.5
<b>6</b>	3.1	41.7
<b>7</b>	3.3	68.8

  

R <sup>1</sup> : R <sup>2</sup>	X = O	X = S
i-Pr ; t-Bu	1 <sup>[1]</sup>	2
c-Hex ; t-Bu	3a, 3b <sup>[2]</sup>	4 <sup>[3]</sup>
-CH <sub>2</sub> -CH <sub>2</sub> - ; t-Bu	5	7
-CH <sub>2</sub> -CMe <sub>2</sub> - ; Et	6	6
Et ; t-Bu	7	

  

compd.:	2	5	6	7
a [pm]	1612.3(2)	1337.4(8)	877.4(1)	1730.4(4)
b [pm]	1168.4(2)	1619.7(8)	1233.5(2)	1305.5(3)
c [pm]	1581.5(2)	1281.4(6)	2133.9(3)	1944.4(4)
$\beta$ [°]	90.74(2)	109.20(4)	92.33(1)	105.80(2)
sp.group; Z	P2 <sub>1</sub> /c; 4	P2 <sub>1</sub> /c; 4	P2 <sub>1</sub> /c; 4	P2 <sub>1</sub> /n; 4

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**MS07.06.09 SUPPRESSION OF THE JAHN-TELLER EFFECT IN CHIRAL COPPER(II) AND CHROMIUM(II) OXALATE BRIDGED NETWORK STRUCTURES.** Helmut W. Schmalke, Silvio Decurtins, Rene Pellaux, Mario Graf, Institute for Inorganic Chemistry, University of Zurich, Switzerland

Chiral three-dimensional (3D) framework structures consisting of tris-bipyridyl-metal complexes which function as chiral templates for the collective linking of metal ion centers through bis-chelating oxalate bridges have recently been described [1,2]. These compounds combine fundamental structural interest with potentially useful properties. They may afford supramolecular host-guest materials which can be tailored and functionalized for specific molecular-based magnetic and photophysical properties. Perceiving that the published structural results of the homometallic 3D compounds for the divalent 3d metal ions have been confined so far to Mn(II) and Fe(II), we attempted to prepare and investigate the analogous compounds with Cr(II) and Cu(II). Both, the high-spin d<sup>4</sup> and the d<sup>9</sup> system have in common that their ground state is described by an orbitally degenerate electronic state, <sup>5</sup>E<sub>g</sub> and <sup>2</sup>E<sub>g</sub> (in O<sub>h</sub> symmetry), thus the ions are subject to the Jahn-Teller effect. Whereas for copper(II) systems a lot of supporting data describe the occurrence of a Jahn-Teller distortion, there are substantially fewer data for high-spin chromium(II) [3,4]. For the presented cubic Cu(II) and Cr(II) network structures anisotropic displacement parameters and metal-oxygen distances are compared with the refined tetragonal (P4<sub>1</sub>2<sub>2</sub>) and orthorhombic (P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>) subgroup structures of the Cu(II) compound, and are discussed in relation to the suppressed Jahn-Teller effect.

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