

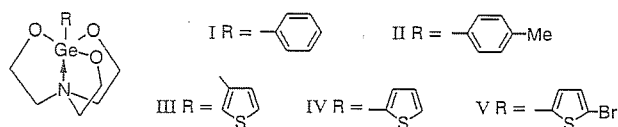
**PS07.00.25 THE STRUCTURE OF ARYL- AND THIENYL-GERMATRANES.** By E. Lukevics, S. Belyakov, A. Kemme, L. Ignatovich, Latvian Institute of Organic Synthesis, Riga, Latvia

The crystals of aryl- (**I**, **II**) and thienylgermatranes (**III-V**) have been obtained to study the influence of a substituent on the pentacoordination of the germanium atom. The compounds **I-V** were prepared by the reaction of  $RGe(OEt)_3$  with triethanolamine.

Their structures were studied by X-ray diffraction method. The crystallographic data for **I-V** are:

	a, Å	b, Å	c, Å	$\beta$ , °	Space group	R-factor
<b>I</b>	15.910	6.661	11.719	90	$P_{na}2_1$ (Z=4)	0.0332
<b>II</b>	13.608	14.012	14.330	99.13	$P2_1/c$ (Z=8)	0.0458
<b>III</b>	8.583	12.494	13.785	127.23	$P2_1/c$ (Z=4)	0.0279
<b>IV</b>	9.478	12.416	12.416	90	$P_{na}2_1$ (Z=4)	0.0479
<b>V</b>	9.544	14.370	9.509	90	$P_{na}2_1$ (Z=4)	0.0495

The values of intramolecular N→Ge donor-acceptor bond lengths for molecules **I-V** are 2.211, 2.209, 2.201, 2.156, 2.175 Å respectively. The crystal structures of **I**, **II**, **IV** are isomorphous to the corresponding silatranes. The structure disorder is observed in the crystals **II** and **V**.



**PS07.00.26 ZIRCONIUM AND HAFNIUM MIXED-LIGAND COMPLEXES WITH ETHYLENEDIAMINETETRAACETATE, FLUORINE AND CARBONATE IONS.** Vadim E. Mistrioukov, Yuri N. Mikhailov, Elena B. Chuklanova, Alexander V. Sergeev, Kurnakov's Institute of General and Inorganic Chemistry of Russian Academy of Sciences.

Zirconium(IV) and hafnium(IV) form with ethylenediaminetetraacetate ion together with fluorine or carbonate ions 8 coordinated complex anions. Complexone, fluorine and carbonate ions can form separately stable complexes with Zr(IV) and Hf(IV), so mixed ligand complex formation was hard to predict.

$(CN_3H_6)_2[Zr(edta)F_2] \cdot 1.5H_2O$  (A),  $(CN_3H_6)_2[Hf(edta)F_2] \cdot H_2O$  (B)  $(CN_3H_6)_2[Zr(edta)CO_3] \cdot 3H_2O$  (C) and  $(CN_3H_6)_2[Hf(edta)CO_3] \cdot 3H_2O$  (D) were obtained from  $[Me(edta)(H_2O)_2]$  intermediate by adding fluorine or carbonate ions. Isolated transparent crystals do not hydrolyse in aqueous solution - that is rare phenomena for Zr and Hf - and may be recrystallized without their composition change.

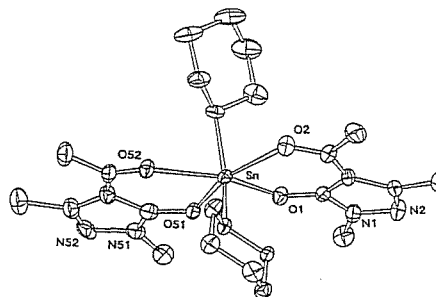
Edta<sup>4-</sup> ion in compounds A - D has closed configuration which could be described as E<sub>g</sub>/R. In  $(CN_3H_6)_2[Zr(edta)F_2] \cdot 1.5H_2O$  and  $(CN_3H_6)_2[Hf(edta)F_2] \cdot H_2O$  oxygen atoms of R-glycine cycles of edta-ion have longer distances to central atom than O atoms of Glycine cycles, two distances from Zr to N atoms are equal, so as from Hf to N. But in Hf complexes Me-N distances are shorter. The main distinction between Zr and Hf complexes is coordinated F-ions participation in H-bonds.

When F ions in complexes A and B are changed to carbonate ion and complexes C and D are obtained, all oxygen atoms of glycine cycles occurs to have same distances to central atom.

**PS07.00.27 DIORGANOTIN COMPLEXES OF  $\beta$ -DIKETONATE LIGANDS.** E. Mundorff<sup>1</sup>, F. Caruso<sup>2</sup>, A. Cingolani<sup>3</sup>, F. Marchetti<sup>3</sup>, C. Pettinari<sup>3</sup>, M. Rossi<sup>1</sup>. <sup>1</sup>Department of Chemistry, Vassar College, Poughkeepsie, NY 12601, <sup>2</sup>Istituto di Strutturistica Chimica, CNR, 00016, Monterotondo Stazione (Rome), Italy, <sup>3</sup>Dipartimento di Chimica, Università di Camerino, Camerino, Italy.

From our studies on potential diorganotin antitumor compounds, we present the molecular structures of two complexes: **1** *trans* - dicyclohexyl-bis(1,3-dimethyl-4acetyl-pyrazolon-5-ato)tin(IV) [monoclinic,  $C2/c$ ,  $a = 34.398(10)$  Å,  $b = 18.242(7)$  Å,  $c = 9.248(3)$  Å,  $\beta = 97.81(3)^\circ$ ] and **2** *trans* - dibenzyl-bis[1-phenyl-3-methyl-4methoxyformyl-pyrazolon-5-ato)tin(IV), [monoclinic,  $P2_1/n$ ,  $a = 17.329(4)$  Å,  $b = 10.555(3)$  Å,  $c = 19.174(4)$  Å,  $\beta = 91.07(2)^\circ$ . A view of compound **1** is shown.

Both compounds show the metal six-coordinate in a distorted octahedral arrangement known as skewed trapezoidal bipyramidal (STB). A strong deformation of the *trans* diorganotin angle, C-Sn-C, is observed ( $154.6(5)^\circ$  for **1** and  $164.5(4)^\circ$  for **2**). The factors influencing the structures of these compounds and other related species will be discussed.



**PS07.00.28 ISOSTRUCTURAL COMPLEXES EXHIBITING DIFFERENT THERMOCHROMIC PHASE TRANSITIONS.** Beena Narayanan, Mohan M. Bhadbhade, Central Salt and Marine Chemicals Research Inst., Bhavnagar-364002, India

Thermochromic materials are fascinating because of the visible color change during the transition. Much spectroscopic data are available on thermochromic complexes  $ML_2X_2$ , where  $M = Cu, Ni$ ,  $L = N, N$  - Diethylethylenediamine (Dieten) and  $X = \text{anion}$ , but only  $Cu(Dieten)_2(ClO_4)_2$  is studied using variable temperature X-ray methods, revealing 'switching on' of dynamic disorder in the chelate ring at the phase transition ( $T_c \approx 44^\circ C$ ). Variations in M and X influence  $T_c$  significantly; for example  $T_c$  for  $Cu(Dieten)_2(BF_4)_2$  (**1**) is  $\sim 24^\circ C$  whereas for  $Ni(Dieten)_2(ClO_4)_2$  (**2**) is  $\sim 110^\circ C$ . Here, we report structures of **1** and **2** to correlate them with the thermochromic behavior in solid state. Interestingly, **1** and **2** are isostructural with  $Cu(Dieten)_2(ClO_4)_2$ . Crystal Data : **1** Triclinic P1,  $a = 8.005(1)$ ,  $b = 8.619(1)$ ,  $c = 9.707(2)$  Å,  $V = 529.1(4.5)$  Å<sup>3</sup>,  $\alpha = 65.73(1)$ ,  $\beta = 66.5(1)$ ,  $\gamma = 63.49(1)^\circ$ ,  $Z = 1$ ;  $R = 0.063$  ( $R_w = 0.094$ ). **2**: Triclinic.P1,  $a = 8.098(3)$ ,  $b = 8.853(4)$ ,  $c = 9.795(5)$  Å,  $\alpha = 63.73(4)$ ,  $\beta = 63.31(5)$ ,  $\gamma = 63.54(5)^\circ$ ,  $V = 542.1(5.3)$  Å<sup>3</sup>,  $Z = 1$ ;  $R = 0.094$  ( $R_w = 0.107$ ). The M-ion is essentially square planar with weak axial interactions,  $Cu \dots BF_4 [3.617(3)$  Å] and  $Ni \dots ClO_4 [3.733(6)$  Å] as observed in case of  $Cu(Dieten)_2(ClO_4)_2$ .

With remarkable structural similarities, temperature responses of these crystals will be explained in terms of the differences in intermolecular forces.