
The crystals of aryl- (I, II) and thiénylgermatranes (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(OR)₂ with triethanolamine.

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

<table>
<thead>
<tr>
<th></th>
<th>a, Å</th>
<th>b, Å</th>
<th>c, Å</th>
<th>β, °</th>
<th>Space group</th>
<th>R-factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>15.910</td>
<td>6.661</td>
<td>11.719</td>
<td>90°</td>
<td>Pnma(Z=4)</td>
<td>0.0393</td>
</tr>
<tr>
<td>II</td>
<td>13.608</td>
<td>14.012</td>
<td>14.330</td>
<td>99.13°</td>
<td>Pnma(Z=8)</td>
<td>0.0458</td>
</tr>
<tr>
<td>III</td>
<td>8.383</td>
<td>12.494</td>
<td>13.785</td>
<td>127.23°</td>
<td>P2₁/c(Z=8)</td>
<td>0.0279</td>
</tr>
<tr>
<td>IV</td>
<td>9.478</td>
<td>12.416</td>
<td>12.416</td>
<td>90°</td>
<td>Pnma(Z=4)</td>
<td>0.0479</td>
</tr>
<tr>
<td>V</td>
<td>9.544</td>
<td>14.370</td>
<td>9.509</td>
<td>90°</td>
<td>Pnma(Z=4)</td>
<td>0.0485</td>
</tr>
</tbody>
</table>

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 silitranses. The structure disorder is observed in the crystals II and V.

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

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

(C₅H₅)₂[Zr(edta)F₂]·3H₂O(A), (C₅H₅)₂[H(edta)F₂]·2H₂O(B), (C₅H₅)₂[Zr(edta)CO₂]·3H₂O(C) and (C₅H₅)₂[H(edta)CO₂]·3H₂O(D) were obtained from [Me₂edta]·[H₂O] intermediate by adding fluoride 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⁻− ion in compounds A–D has closed configuration which could be described as E,G,R. In (C₅H₅)₂[Zr(edta)F₂]·3H₂O and (C₅H₅)₂[H(edta)F₂]·2H₂O oxygen atoms of R-glycine cycles of edta⁻ ion have longer distances to central atom then O atoms of G 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 β-DIKETONATE LIGANDS. E. Mundorf, F. Caruso, A. Cingolani, F. Marchetti, C. Pettinari, M. Rossi, Department of Chemistry, Vassar College, Poughkeepsie, NY 12601, Istituto di Strutturistica Chimica, CNR, 00016, Monterotondo Stazione (Rome), Italy, Dipartimento di Chimica, Universita' 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-4-acetyl-pyrazolon-5-ato)tin(IV) (monoclinic, C2/c, a = 34.398(10) Å, b = 18.242(7) Å, c = 9.248(3) Å, β = 97.81(3)°) and 2 trans - dibenzyl-bis[1-phenyl-3-methyl-4-methoxyformyl-pyrazolon-5-ato]tin(IV), (monoclinic, P2₁/a, a = 17.329(4) Å, b = 10.555(4) Å, c = 19.174(4) Å, β = 91.07(2)°). 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(3)° for 1 and 164.5(4)° for 2). The factors influencing the structures of these compounds and other related species will be discussed.

PS07.00.28 ISOSTRUCTURAL COMPLEXES EXHIBITING DIFFERENT THERMOCROMIC PHASE TRANSITIONS. Beena Narayanan, Mohan M. Bhardwade, 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 ML₂X₃, where M=Ca,Cu; L=N,N' - Diethylenetriamine(Dieten) and X- anion, but only Cu(Dieten)₂(CIO₄)₂, is studied using variable temperature X-ray methods, revealing 'switching on' of dynamic disorder in the chelate ring at the phase transition (Tc=44°C). Variations in M and X influence Tc significantly; for example Tc for Cu(Dieten)₂(BF₄)₂ (I) is ~24°C whereas for Ni(Dieten)₂(CIO₄)₂ (2) is ~110°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(CIO₄)₂.

Crystal Data:
1 Triclinic P1, a=8.005(1), b=8.619(1), c=9.707(2) Å, V=529.1(4.5) Å³, α=65.73(1), β=66.5(1), γ=63.49(1)°, Z=1; R=0.063 (Rw=0.094).
2: Triclinic P1, a=8.098(3), b=8.853(4), c=9.795(3) Å, α=63.73(4), β=63.31(5), γ=63.54(5)°, V=542.1(5) Å³, Z=1; R=0.094 (Rw=0.107). The M-ion is essentially planar with weak axial interactions, Cu···Br=3.617(3) Å and Ni···CI=3.735(6) Å as observed in case of Cu(Dieten)₂(CIO₄)₂.

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