

PS07.00.46 ENANTIOMERIC DISORDER OF AMINO ACID MOIETY IN STRUCTURES OF [Co(III)(EN)₂(AA)]₂, AA=DL-ALANINE, D-LVALINE. E. Suresh, Mohan M. Bhadbhade, Central Salt & Marine Chemicals Research Institute, Bhavnagar-364 002, India

Complexes [Co(III)(en)₂(aa)]₂, where aa= DL-Alanine(1), DL-Valine(2) and DL-Isoleucine(3) were synthesized with the aim to resolve them using suitable chiral reagent. Crystal Data: **1:** Monoclinic C2/c, a=34.091(7), b=6.839(3), c=16.568(6) Å, β=91.44(3)°, V=3887.42 Å³, Z=8, R=0.043, R_w=0.065. **2:** Monoclinic P2₁/n, a=6.777(2), b=7.42(10), c=7.857(2) Å, β=104.91(2)°, V=1838(9) Å³, Z=4, R=0.096, R_w=0.106 (refinement in progress.). **3:** Monoclinic P2₁/n, a=7.732(2), b=20.616(3), c=12.813(4) Å, β=104.91(2)°, V=1838(9) Å³, Z=4, R=0.049, R_w=0.056. The structures were solved by heavy-atom method. Interestingly, C_α carbon and the side chain atoms did not appear in the difference Fourier map clearly in **1** and **2**, whereas the complete molecule could be seen in **3**. Careful examination of Δρ peaks led us to propose a model of enantiomeric disorder for the amino acid moiety alone, with the chiral carbon and the side chain atoms occupying two sites with almost equal occupancy. In all complexes, Co(III) has a distorted octahedral geometry with two ethylenediamine moieties in cis fashion and two vacant sites occupied by the nitrogen and the oxygen atom of the amino acid. The packing patterns will be explained in terms of the size of the side chain which accommodate the disorder in **1** and **2** but not in **3**. Local enantiomeric disorders observed here are, to the best of our knowledge the first to be reported.

PS07.00.47 CRYSTAL STRUCTURES OF URANYL/CALIXARENE COMPLEXES. P. Thuéry and M. Nierlich, CEA/Saclay, SCM, Bat. 125, 91191 Gif-sur-Yvette, France

The interest of calixarene derivatives as 'uranophiles' is well known from solution experiments. However, few actinide complexes of calixarenes have been structurally described: the list is limited to the uranyl (UO₂²⁺) complex of bis(homo-oxa)-p-tertbutylcalix[4]arene and the thorium complex of p-tert-butylcalix[8]arene reported by Harrowfield et al. [1] and the three uranyl complexes here reported.

With p-tert-butylcalix[5]arene, the uranyl ion forms an inclusion complex: the metal ion is surrounded by the five oxygen atoms of the calixarene which is in the cone conformation [2]. A triethylammonium ion is included in the calixarene cavity.

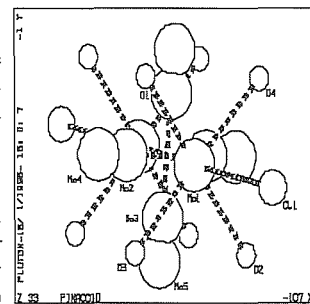
A dimeric species is formed with p-tert-butylcalix[6]arene: two uranyl ions bridge two calixarene moieties, giving rise to an unprecedented assembly type [3]. Uranyl ions are in a nearly regular equatorial square planar environment. An hydronium ion and an acetonitrile molecule are included in each calixarene cavity. Two forms of the binuclear uranyl complex of p-tertbutylcalix[8]arene have been described [4]. The two ions are encompassed by the macrocycle in the pleated loop conformation. Each ion is bonded to four oxygen atoms from the calixarene and to a bridging hydroxyl ion.

1. J.M. Harrowfield, M.I. Ogden and A.H. White: *J. Chem. Soc. Dalton Trans.*, 979 and 2625 (1991).
2. P. Thuéry and M. Nierlich: submitted to *J. Incl. Phenom.*
3. P. Thuéry, M. Lance and M. Nierlich: *Supramol. Chem.*, in press.
4. P. Thuéry, N. Keller, M. Lance, J.D. Vigner and M. Nierlich: *Acta Cryst. C51*, 1570 (1995); *ibid.*: *New J. Chem.* **19**, 619 (1995).

PS07.00.48 ON THE HEAVY ATOM QUANTUM INTERFERENCE SCATTERING PHENOMENA IN DIMOLYBDENUM(II) DIMERS. Boris Udovic, Primoz Segedin, Faculty of Chemistry and Chemical Technology, University of Ljubljana, P.O. Box 537, 61001 Ljubljana, Slovenija

Pyramidally coordinated oxygen atoms freeze and hinder the librational motions of quadruple bonded dimolybdenum(II) dimers inside the prismatic cage of zwitterionic 3,5-diaminobenzoate tetracarboxylate units. De Broglie wavelength $\lambda_{Mo} \sim 1.44$ Å and $\lambda_{Mo} \sim 2.10$ Å were computed

from vibrational spectra at 293 K and assigned to low energy components of the superimposed and periodic motions of molybdenum atoms along the principal dimer axis. The expected quantum interference fringe maxima of interdiffusing and scattering λ_{Mo} waves were confirmed in the Fourier difference maps with observed electron density anomalies on the alternative axes inside and outside the oxygen cage at 293 K. The quantum singularities were refined at the wavelength distances $\lambda_{Mo(2)} = 1.4904(11)$ Å, $\lambda_{Mo(3)} = 1.4901(13)$ Å, $\lambda_{Mo(4)} = 2.09(5)$ Å, $\lambda_{Mo(5)} = 2.08(5)$ Å, from the vibrating molybdenum atoms Mo(1) and Mo(1)(iii) in their potential wells. The occupancy factors of the alternative sites Mo(2) and Mo(3) inside the cage were 3.8% and 4.2%, while outside the cage the alternative sites Mo(4) and Mo(5) were 0.31% and 0.25% respectively. In the prismatic cage the heavy atom random thermal energy, with its related statistical temperature, is converted into a directed kinetic energy with different velocity components which are linked to a rather localized and oriented low temperature by frozen vibrational motions of very cold metal atoms trapped in their quantum well.



PS07.00.49 COMPARISON OF STRUCTURES OF SIX ALKARYLSTANNYL OR ALKYLSTANNYL DITHIOPHOSPHATES. Yao Xinkan, Wang Honggen, Xie Qinglan, Luo Ning, Yang Zhiqiang, Central Laboratory, Nankai University, Tianjin, 300071, China

In various alkarylstannyl and alkylstannyl dithiophosphates the steric hindrance effect clearly play a determinant role in forming four-coordinate or six-coordinate tin species. Triphenylstannyl and tricyclohexylstannyl derivatives are sure to be four-coordinate tin species, and diphenylstannyl or other less-steric-factor alkylstannyl derivatives are sure to be six-coordinate tin species.

These derivatives have been variously studied owing to their functions as fungicides and miticides. Only a few structures of these derivatives were reported. [1-4] We now present x-ray structure analyses of tricyclohexylstannyl (O,O'-di-p-chlorophenyl) dithiophosphate (compound I) and dibutylstannyl (O,O'-p-tolyl) dithiophosphate (compound II). The structural characteristics of these two compounds, along with the other four compounds are summarized in Table 1.

Table 1 Selected Bonds and Local Geometry at Tin

| compd | Sn-S(1) ^a | Sn-S(2) ^b | P-S(1) ^c | P-S(2) ^d | Geometry at Tin | Ref |
|---|----------------------|----------------------|--|---------------------|-----------------|-----|
| I | 2.502(2) | 3.597* | 2.030(3) | 1.914(3) | tetrahedron | |
| II | 2.495(3) | 3.244(4) | 2.029(3) | 1.927(4) | octahedron | |
| | 2.493(2) | 3.228(3) | 2.025(4) | 1.932(4) | | |
| III | 2.458(9) | 5.326* | 2.054(1) | 1.931(1) | tetrahedron | [1] |
| IV | 2.678(1) | 2.689(1) | 2.006(2) | 1.998(2) | octahedron | [2] |
| V | 2.48(2) | 3.334(2) | 2.047(2) | 1.969(2) | octahedron | [3] |
| VI | 2.48(1) | 3.20(1) | 2.04(2) | 1.92(3) | octahedron | [4] |
| | 2.49(1) | 3.23(1) | 2.03(1) | 1.94(1) | | |
| III = (EtO) ₂ P(S)SSnPh ₂ | | | IV = [(PrO) ₂ P(S)S] ₂ SnPh ₂ | | | |
| V = [(MeO) ₂ P(S)S] ₂ Sn(CH ₃) ₂ | | | VI = [(EtO) ₂ P(S)S] ₂ SnPh ₂ | | | |
| a: Sn-S | b: Sn-S | c: P-S | d: P-S | * | no-bonding | |

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- [2] Molloy, K.C., et al, *Inorg. Chem.*, 1980, 19, 2041
- [3] Molloy, K.C., et al, *Inorg. Chem.*, 1981, 20, 2172
- [4] Lieblich, B.W., et al, *Acta Crystallog.*, 1978, B34, 944