

important to recognise that the use of two completely different types of basis set to describe these large organotin systems minimises errors associated with basis set-specific artifacts. The 3-21G basis set is a split valence descriptor, while the LanL2DZ basis set utilises a double zeta description for first row elements and an effective core potential (ECP) for heavier atoms. Calculated gas-phase stabilisation energies range from 400-1200 kJ mol⁻¹, depending on the system under study. More significantly, predicted stabilisation energies from each basis set description agree to within, at worst, 40 kJ mol⁻¹. Detailed results of this study will be presented.

[1] E.R.T. Tiekink: *Main Group Chemistry News*, **3**, 1995, 12 - 16; *Appl. Organomet. Chem.* **5**, 1991, 1 - 21; *Main Group Met. Chemistry*, **15**, 1992, 161 - 186; E.R.T. Tiekink and G. Winter: *Rev. Inorg. Chem.*, **12**, 1992, 183 - 302.

PS11.07.22 INFLUENCE OF FLUORO SUBSTITUTION ON PACKING OF STYRYLCOUMARINS AND THEIR PHOTOBHAVIOUR IN THE CRYSTALLINE STATE. K.

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The correlation between reactive molecules in crystals and stereochemistry of the photoproducts has been a subject of intensive study(a). Crystals of styryl- coumarins and chloro - substituted derivatives yield centrosymmetric crystals leading to anti-HT photodimers. However, replacement of a hydrogen by fluorine as in 4-(4'-fluoro styryl) coumarin (1) and 4-(2'-fluoro styryl) coumarin (2) produces syn-HH dimers across the styrenic double bond(b). Whereas 4-(3'-fluoro styryl) coumarin (3) and 4-styryl, 6-fluoro coumarin (4) produces anti-HT dimers. The packing modes vary depending upon the position at which fluorine is substituted. In all these structures, there are no significant short intermolecular F...F, F...H, F...C and F...O contacts although in (3) there are a few C-H...F interactions. These observations suggest that long range electrostatic interactions might also play a significant role in these crystals.

(a) V. Ramamurthy and K. Venkatesan; *Chem. Rev.*, 1987, 87, 433.

(b) K. Vishnumurthy, T. N. Guru Row and K. Venkatesan; *J. Chem. Soc., Perkin Trans. 2* (in press).

PS11.07.23 CRYSTAL STRUCTURES OF TEMPO RADICALS SHOWING FERROMAGNETIC INTERACTIONS. H. Yamamoto, H. Yoshikawa, M. Yasui, T. Ishida, T. Nogami and F. Iwasaki, Department of Applied Physics and Chemistry, The University of Electro-Communications, Chofu, Tokyo 182, Japan

Some of the 4-arylmethyleneamino-TEMPO radicals (TEMPO = 2,2,6,6-tetramethyl-piperidin-1-oxyl) were revealed to show inter-molecular ferromagnetic interactions, of which **1** ~ **5** and **13** exhibit a ferromagnetic transition (T_c) at an extremely low temperature [T. Nogami, et al. *Chem. Letters*, 29-32 (1994), T. Ishida et al. *Chem. Letters*, 919-922 (1994)]. **6** ~ **11** showed only a ferromagnetic interaction ($\theta > 0$), while **12** showed an antiferromagnetic interaction ($\theta < 0$). The X-ray structure analyses were performed on these crystals at room temperature to investigate whether any systematic intermolecular interactions were demonstrated among these crystals.

Ar-CH=N-TEMPO• (Ar: **1** Ph; **2** p-Cl-Ph; **3** p-biPh; **4** p-PhO-Ph; **5** p-PhS-Ph; **6** p-Br-Ph; **7** 3,5-diCl-Ph; **8** 2-Py; **9** 3-Py; **10** 4-Py; **11** Naph; **12** p-F-Ph) Ar-CH₂NH-TEMPO• (Ar: **13** Ph)

For all crystals, two-dimensional O...O networks are constructed, although of which forms are various. In **2**, O atoms arrange to form a pleated sheet with the first and the second nearest

O...O distances of 5.91 and 5.96 Å, respectively. Between sheets the aryl groups of each sheet arrange alternately with face-to-face. Crystal structures of **3**, **6** and **10** belong to the same category as **2**. In **1** and **9**, which are isomorphous, top and bottom lines of the pleats are not straight but zigzag. The nearest aryl groups belonging to the neighboring sheets arrange herringbone-like. The networks of **7** and **12** are constructed with zigzag lines, so that the surface of the sheet is rough in all directions. In **4**, there are no intersheet interactions between aryl groups, because the sheet is almost flat perpendicular to the crystallographic polar axis. This arrangement is quite different from the other crystals. In all these crystals sheet-like arrangement of the N-O radicals are considered to be essentially important for the magnetic interactions. Magnetic interactions may be transferred via intermolecular interactions of side chains, since the intra- and intersheet O...O distances are so long for the direct evidence of the systematic interactions which manifests the magnetic character.

PS11.07.24 CRYSTAL STRUCTURES OF COPPER COMPLEXES SHOWING FERROMAGNETIC INTERACTION. M. Yasui, Y. Ishikawa, T. Nogami, T. Ishida and F. Iwasaki, Dept. of Applied Physics and Chemistry, The Univ. of Electro-Communications, Chofu, Tokyo 182, Japan

We have determined the crystal structures of copper(II) complexes coordinated with pyrimidine derivatives showing ferromagnetic interactions. [Cu(hfac)₂(quinazoline)] (**I**), [Cu(hfac)₂(pyrimidine)] (**II**), [Cu(hfac)₂(4-methylpyrimidine)] (**III**), where hfac is 1,1,1,5,5,5-hexafluoropentane-2,4-dionate, [Cu(NO₃)₂(pyrimidine)₂] (**IV**), and [Cu(NO₃)₂(pyrimidine)(H₂O)₂] (**V**). For **I**, the ferromagnetic transition was observed at about 0.12K [Ishida *et al.*, *Synthetic Metals*, **71**, 1791 (1995)]. The ferromagnetic interaction was observed for **II**, **III**, and **IV**.

X-ray analysis revealed that the crystals of **III** have two modifications, a polymer structure [Cu(hfac)₂(4-methylpyrimidine)]_n (**IIIa**), and a trinuclear complex [Cu(hfac)₂]₃(4-methylpyrimidine)₂ (**IIIb**).

All complexes, except for **IIIb**, form one-dimensional polymer structures in which the quinazoline or pyrimidine derivatives play a role of a bridging ligand. For **I**, two bridging ligands coordinate a Cu atom on both axial positions. The hfac ligands coordinate in an equatorial plane. Thus the Cu atom has a distorted octahedral structure. The complex **V** has a similar polymeric structure with two nitrates and two water molecules. In **II** and **IIIa**, which have also one-dimensional polymer structures with a distorted octahedral Cu, two bridging pyrimidine moieties are cis to one another. A Cu atom of **IV** is penta-coordinated with two bridging pyrimidines, one non-bridging pyrimidine and two nitrates. One nitrogen atom of non-bridging pyrimidine is free. The complex **IIIb** has a trinuclear structure. The central Cu atom has an octahedral structure while the terminal Cu atoms have a penta-coordinated square-pyramidal structure. The one-dimensional structure may be related to the ferromagnetic interaction except for **V**.

PS11.07.25 ABILITY OF SOME SPECIFIC NATURAL STRUCTURES TO INTERACT CONCURRENTLY CONTRARY TO DIOXIN. ESR STUDY. Pham The Vung, Nguyen Van Tri, Dinh Pham Thai, Hanoi University of Technology, Ha Van Mao, Dinh Ngoc Lam, Cancer Research Center, Hanoi, Vietnam

On the basis of the ESR experimental results, some new active natural complexes (symbolized XD*) present in special vegetable produces have been revealed. The nucleus structure of these complexes can show an electron Spin combination almost similar to the one of Dioxin (2,3,7,8- TCDD). However, it is especially remarkable that the Spin combination of XD* occupies a quintuplet ground state (S = 4/2) with a deeply negative exchange ener-

gy ($J < 0$). This behaviour opposes entirely to the one of Dioxin possessing a combination of four π electron Spins with a singlet ground state ($S=0$) and a positive exchange energy ($J > 0$). Special binding complexes of Dioxin to XD* structures have been also observed with a negative exchange energy ($J < 0$). These [XD*- Dioxin] complexes appear with a very high probability, about 10^5 times of the one of the [Hemoglobin - Dioxin] complex in human blood and of the [Mn- Porphyrinoprotein - Dioxin] complex in human liver. The properties of these interaction complexes corresponding with the results achieved in some respective experimental clinical studies over a long period of time suggest that the specific natural XD* structures are able to conquer and arrest potently Dioxin molecules, i.e. to interact concurrently contrary to the toxicity of Dioxin, namely to its carcinogenous activity. This activity depends on many factors such as the concentration and the lifetime of the XD* state, the kinetic conditions of the surrounding and the interaction.

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PS11.07.26 INTERRELATING MELTING POINT, DENSITY, HYDROGEN BONDING, MOLECULAR CONFORMATION AND SOLUBILITY IN A PAIR OF ORGANIC SALTS. Li, N.1, Luft, J.1, Pangborn, W.1, Duax, W.L.1, and Perlman, M.2. ¹Hauptman-Woodward Medical Research Inst., Inc., Buffalo, N.Y. 14203 and ²Cambridge NeuroScience, Cambridge, MA 02139.

Hydrochloride salts of N-(1-Naphthyl)-N'-(3-ethylphenyl) guanidine (NEGH) and an N'-methyl analog aptiganel (CERESTAT^{®1}), which are N-methyl-D-aspartate ion channel blockers, have anomalous physical properties. The melting point of crystals of the salts differ by 70°, their densities differ by 0.12g/cm³, and they exhibit significant differences in solubility. In general, high melting points suggest greater stability. Higher melting compounds of analogous composition might be expected to have higher density and lower solubility than the lower melting compounds. In this case the opposite relationships are observed. The higher melting salt is more soluble and less dense than the lower melting salt. Due to the addition of a methyl group in aptiganel there is a larger volume per molecule. However, the increased volume per molecule (66Å³) is greater than might be expected. In the solid state NEGH has an extended conformation with the planar groups well away from each other. The methyl substitution in aptiganel appears to induce or stabilize a conformation in which the rings are oriented toward one another. Due to its extended conformation planar rings of NEGH are sufficiently exposed to permit stacking that contributes to closer packing of the molecules and higher density but not to a higher melting point. Although there were three NH...Cl hydrogen bonds in each structure, those in NEGH are engaged in forming dimers whereas in aptiganel one of the hydrogen bonds links the molecules into infinite chains. This difference in hydrogen bonding provides the explanation for the anomalous relationship between melting points and density and solubility. Upon initial melting only van der Waals forces must be overcome to melt NEGH crystals, while in aptiganel the crystals do not begin to melt until hydrogen bonds between adjacent molecules are broken. The broader melting point observed for NEGH crystals is due to the fact that initial melting involves breaking van der Waals contacts followed by the disruption of hydrogen bonds as dimers disassociate to form monomers.

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Chiral Compounds of Industrial Interest

MS11.08.01 CONFORMATIONAL STUDIES OF VITAMINS D DERIVATIVES. Kinga Suwinska and Andrzej Kutner, Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland Pharmaceutical Research Institute, Warsaw, Poland

The fat-soluble vitamins D play essential role in stimulation of intestinal calcium transport, bone calcification, bone calcium mobilization, and phosphate transport as well as stimulation of cell differentiation and inhibition of cell proliferation. Vitamins D2 and D3 were found to exist in two almost equimolar equilibrium conformations in both liquid and solid states. The biologically active form of vitamin D3 1,25-hydroxylated derivative was found to exist in solid state as the beta conformer only [1]. To explain the influence of 1-hydroxy substituent on the conformation of the vitamins D the 1-hydroxy vitamin D2 and 1-hydroxy vitamin D3 was crystallized and the structures of those two compounds were solved. For both compounds only one conformer was found in the solid state. The results of crystal structure determinations were compared with the semi-empirical calculations and will be discussed.

1. Suwinska K., Kutner A. (1996). Acta Cryst. B. in press.

MS11.08.02 STRUCTURAL ASPECTS OF DIASTEREOMERIC DISCRIMINATION. Edward J. Valente, Christopher Miller, Gerard Ruggiero, Department of Chemistry, Mississippi College, Clinton, MS 39058, and Drake S. Eggleston, Department of Physical and Structural Chemistry, SmithKline Beecham, Co., King of Prussia, PA, 19401

Systems showing two kinds of diastereoselective solubility disparities are described. In the system of warfarin and its derivatives and (+)-quinidine, a pattern in resolution success (= formation of a separable salt) as a function of warfarin substituent position has been found. Warfarin with a single phenyl substituent in the 3'- or 4'-positions and 2',3', 3',4'- disubstituted warfarins usually form less-soluble salts between their (-)(S)-isomers and (+)-quinidine; their diastereomers are oils. The solid state structures of the less-soluble salts show that a single, strong N-H...O interaction linking warfarin enolate anions with protonated quinuclidine of quinidine. Packing motifs are remarkably similar over the range of substituents demonstrating that how a dominant interior interaction may serve as the basis for successful resolutions within a series of related substances. In the system of mandelic acid and its phenyl substituted derivatives and (-)-ephedrine, both less-soluble and more-soluble salts can be isolated from 95% ethanol. The uniformly unsolvated salts vary from little to strong solubility disparities in aqueous ethanol, properties which correlate with their temperatures and heats of fusion. Six kinds of packing motifs have been found. These demonstrate a considerable range in packing efficiency while retaining correlations with configuration of the mandelate anion. Interior H-bonding type is one of the important organizing principles. Links between some of the packing groups have been found in the form of polymorphs and solid-solid phase transitions in some of the salt phases.