

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<sup>-1</sup>, depending on the system under study. More significantly, predicted stabilisation energies from each basis set description agree to within, at worst, 40 kJ mol<sup>-1</sup>. 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<sub>c</sub>) 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-CH<sub>2</sub>NH-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)<sub>2</sub>(quinazoline)] (**I**), [Cu(hfac)<sub>2</sub>(pyrimidine)] (**II**), [Cu(hfac)<sub>2</sub>(4-methylpyrimidine)] (**III**), where hfac is 1,1,1,5,5,5-hexafluoropentane-2,4-dionate, [Cu(NO<sub>3</sub>)<sub>2</sub>(pyrimidine)<sub>2</sub>] (**IV**), and [Cu(NO<sub>3</sub>)<sub>2</sub>(pyrimidine)(H<sub>2</sub>O)<sub>2</sub>] (**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)<sub>2</sub>(4-methylpyrimidine)]<sub>n</sub> (**IIIa**), and a trinuclear complex [Cu(hfac)<sub>2</sub>]<sub>3</sub>(4-methylpyrimidine)<sub>2</sub> (**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-