

dipolar zwitterionic form. The Cu(II) complexes seem to crystallize as isolated entities since only intramolecular H-bonds are found. However two disordered water positions can be found in a Fourier difference map, and two extra oxygen atoms were included in the refinement so that their occupancy adds to unity.

**Keywords:** X-ray crystallography of coordination compounds, copper coordination compounds, single crystals

#### P.07.01.28

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#### Spectroscopic and Structural Investigation of $ZnI_2(\text{nicotinamide})_2$ , $[Zn(\text{H}_2\text{O})_2(\text{picolinamide})_2]I_2$ and $ZnI_2(\text{isonicotinamide})_2$

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The zinc(II) complexes of nicotinamide, picolinamide and isonicotinamide with iodide were synthesized and characterized by FT-IR and XRD techniques. In both the nicotinamide (na) and isonicotinamide (iso) Zn(II) complexes the Zn(II) ion is coordinated by two iodide ligands and two N atoms either of na or of iso ligands in a distorted tetrahedral coordination environment. The zinc(II) complex with picolinamide (pa) has a different environment having a stable five-membered chelate coordination through the ring N and O atoms of pa ligand and has a slightly distorted octahedral geometry.

The  $ZnI_2(\text{na})_2$ ,  $[Zn(\text{pa})_2(\text{H}_2\text{O})_2]I_2$  and  $Zn(\text{iso})_2I_2$  complexes are all crystallized in monoclinic system with space groups  $C2/c$ ,  $P2_1/n$ ,  $C2/c$ , respectively. All these complexes are stabilized through intermolecular hydrogen bondings together with  $\pi \dots \pi$  interactions.

**Keywords:** IR and XRD, zinc complexes, amides

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#### Green-yellow Thermochromism of (N-methyl-2,6-lutidinium) $_2$ $\text{CuCl}_4$

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The previously reported, green, room temperature phase of (N-methyl-2,6-lutidinium) $_2$   $\text{CuCl}_4$  consists of layers of square-planar  $\text{CuCl}_4^{2-}$  anions interspersed with coplanar organic cations.

The temperature behavior of the compound was studied, and a thermochromic phase transition from green to yellow found at 67 °C. The crystal structure of the high temperature yellow phase of  $(\text{C}_8\text{H}_{12}\text{N})_2\text{CuCl}_4$  was determined at 77(1) °C with unit cell parameters triclinic,  $P\bar{1}$ ,  $a = 7.9350(5)$  Å,  $b = 9.1550(7)$  Å,  $c = 16.144(2)$  Å,  $\alpha = 75.467(4)^\circ$ ,  $\beta = 86.975(4)^\circ$ ,  $\gamma = 64.505(5)^\circ$ ,  $V = 1022.64(15)$  Å<sup>3</sup>,  $Z = 2$ .

The structure of the high temperature phase consists of flattened  $\text{CuCl}_4^{2-}$  tetrahedra with the two unique organic cations now canted relative to one another rather than coplanar. The canting of the organic cations lengthens the short aromatic C-H...Cl contacts in the low temperature phase which appear to stabilize the square planar over the flattened tetrahedral anion geometry.

Previous examples of green-yellow thermochromism in the  $\text{A}_2\text{CuCl}_4$  family have occurred only in the presence of strong N-H...Cl hydrogen bonding, which stabilizes the square planar anion geometry in the low-temperature phase. The title compound is the first known to exhibit this behavior in the absence of strong N-H...Cl hydrogen bonding.

**Keywords:** copper complexes, phase transitions, hydrogen bonding

#### P.07.01.30

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#### Structure of Hydrido(carboxylato)Ir(III) Complexes and Catalytic Symmetric Hydrogenation of Imines

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Recently, we have succeeded in the isolation and characterization of  $[\text{IrCl}(\text{binap})_2]_2$  **1** {binap = 2,2'-bis(di-phenylphosphino)-1,1'-binaphthyl}. [1] Complex **1** reacted easily with methanol and water to give the oxidative addition products. [2] Here we report on the highly diastereoselective oxidative addition of carboxylic acids to  $[\text{IrCl}(\text{binap})_2]_2$ , which gave mononuclear hydrido( $\eta^2$ -carboxylato)Ir(III) complexes.

Reaction of (*S*)-**1** with several carboxylic acids proceeded smoothly at r.t. to give  $[\text{IrCl}(\text{H})(\text{O}_2\text{CR})\{(S)\text{-binap}\}]$  (*S*)-**2** (R = CH<sub>3</sub>, *p*-tolyl, etc.) as air-stable almost colorless solids in good yields. The absolute configuration of  $[\text{IrCl}(\text{H})(\text{O}_2\text{CC}_6\text{H}_4\text{CH}_3\text{-4})\{(S)\text{-binap}\}]$  was elucidated to be (*S*)-OC-6-23-A. Catalytic activity for these complexes for asymmetric hydrogenation of prochiral imines will also be discussed.

[1] Yamagata T., Iseki A., Tani K., *Chem. Lett.*, 1997, 1215-1216. [2] Yamagata T., Iseki A., Tani K., *Angew. Chem. Int. Ed.*, 1998, **37**, 3381-3383.

**Keywords:** absolute configuration, asymmetric catalysis, carboxylate complexes

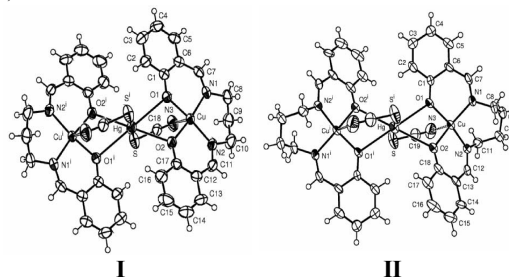
#### P.07.01.31

*Acta Cryst.* (2005). A61, C301

#### Synthesis, Characterization and Crystal Structure of new Transition Metal Compounds of Thiocyanate

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Two similar hetero-trinuclear centrosymmetric Cu-Hg-Cu Schiff base complexes were prepared and characterized by elemental analysis, NMR, IR and UV-Vis spectroscopy. The crystal structures of the title compounds reveal that  $\text{Hg}[\text{Cu}(\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_2)\text{SCN}]_2$  (I) crystallizes in the triclinic  $P\bar{1}$  space group and  $\text{Hg}[\text{Cu}(\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_2)\text{SCN}]_2$  (II) crystallizes in the monoclinic  $P2_1/c$  space group. The central Hg atom of the compounds, which is located on an inversion centre, has a distorted octahedral coordination geometry. In both compounds, there are long range interactions between Cu and N atoms of the bridging SCN group at the axial position. The coordination geometry of the inversion-related terminal Cu atoms of the compounds is square-pyramidal. The Cu-Hg pairs are triple bridged by the O atoms of the Schiff base ligands and by the SCN groups. The Cu...Hg distance is 3.7623(9) Å (I) and 3.7778(17) Å (II).



**Keywords:** crystal structure, thiocyanate complexes, copper(II) and mercury(II) complexes

#### P.07.01.32

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#### Crystal Structure of Trimethyltin hydroxide, $(\text{CH}_3)_3\text{SnOH}$

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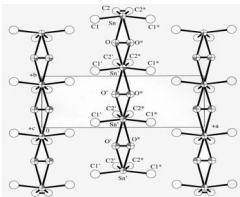
It has been reported that  $(\text{CH}_3)_3\text{SnOH}$  has many incommensurate structures in crystalline state. So far, the precise structure analysis has not been reported. Only one X-ray crystal structure analysis without three dimensional coordinates available has been reported. [1]

We took a X-ray structure analysis of title compound to get a information of incommensurateness using a Rigaku RAXIS-RAPID Imaging Plate diffractometer with graphite Mo-K $\alpha$  radiation.

As this compound is very unstable in air, crystal was sealed in a capillary under nitrogen atmosphere in a glove box.

Crystal data of (CH<sub>3</sub>)<sub>3</sub>SnOH: Orthorhombic, *Pmm*2<sub>1</sub>, *a* = 11,207(1) Å, *b* = 4.171(1) Å, *c* = 6.652(1) Å, *V* = 310.9(1) Å<sup>3</sup>, *Z* = 2, *R* = 0.140.

The obtained crystal structure is shown in figure. This complex has an infinite chain structure through the bridging trimethyltin groups by hydroxide groups along the *b* axis. The co-ordination of each tin atom is approximate trigonal bipyramidal with two hydroxide groups and three methyl groups essentially. Due to the mirror symmetry perpendicular to the *a* axis passing through the tin atom, this complex takes the disordered structure consequently.



[1] Kasai N., et al., *J. Organometal. Chem.*, 1965, **3**, 172.

**Keywords:** tin, hydroxide, disorder

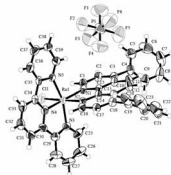
#### P.07.01.33

*Acta Cryst.* (2005). **A61**, C302

#### Crystal Structure of [RuCl(dpphen)(terpy)]PF<sub>6</sub> and [Ru(CH<sub>3</sub>CN)(phen)(terpy)](PF<sub>6</sub>)<sub>2</sub>

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The desired complex was prepared by a sequential procedure with ligand replacement. [RuCl<sub>3</sub>]·H<sub>2</sub>O and 2,2':6',2''-terpyridine (terpy) were mixed in ethyleneglycol (15 ml). The suspended mixture was refluxed for 5 min. in a microwave oven under a purging nitrogen atmosphere. 4,7-Diphenyl-1,10-phenanthroline (dpphen) was added to the refluxing red solution for 10 min. A saturated aqueous solution of KPF<sub>6</sub> (20 ml) was added, and a black-red product began to precipitate. We examined complexes **1** and **2** using X-ray analysis, CV, and UV.



Crystal data of [RuCl(dpphen)(terpy)]PF<sub>6</sub> (**1**) [1] Monoclinic, *C2/c*, *a* = 42.071(1) Å, *b* = 8.6042(1) Å, *c* = 19.9088(1) Å,  $\beta$  = 96.096(2)°, *V* = 7165.9(2) Å<sup>3</sup>, *Z* = 8, *R*(F<sub>2</sub>) = 0.083, *wR*(F<sub>2</sub>) = 0.201 for 28548 measured reflections.

Crystal data of [Ru(CH<sub>3</sub>CN)(phen)(terpy)](PF<sub>6</sub>)<sub>2</sub> (**2**) [2] Triclinic, *P*  $\bar{1}$ , *a* = 8.7861(3) Å, *b* = 10.3590(9) Å, *c* = 17.9636(7) Å,  $\alpha$  = 99.192(7)°,  $\beta$  = 90.389(2)°,  $\gamma$  = 105.774(3)°, *V* = 1551.0 (2) Å<sup>3</sup>, *Z* = 2, *R*(F<sub>2</sub>) = 0.089, *wR*(F<sub>2</sub>) = 0.172 for 14369 measured reflections.

[1] Yoshikawa N., et al., *Acta Cryst.*, 2005, **E61**, m545-m547. [2] Yoshikawa N., et al., *Acta Cryst.*, 2005, **E61**, m55-m56.

**Keywords:** microwave, terpyridine, ruthenium compounds

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#### Structural Studies on Copper(II) Carboxylate Complexes containing Pyrazole

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Polynuclear copper derivatives are the subject of an increasing number of studies [1, 2]. Trinuclear copper derivatives characterized by the presence of the triangular core [Cu<sub>3</sub>( $\mu_3$ -OH)( $\mu$ -pz)<sub>3</sub>(RCOO)<sub>2</sub> (*R* = H, C<sub>2</sub>H<sub>5</sub>, C<sub>3</sub>H<sub>7</sub>)] have been prepared and characterized by X-ray studies. Copper(II) formate gives [Cu<sub>3</sub>( $\mu_3$ -OH)( $\mu$ -pz)<sub>3</sub>(HCOO)<sub>2</sub>-(Hpz)<sub>2</sub>], **1**, whereas copper propionate and butyrate afford [Cu<sub>3</sub>( $\mu_3$ -

OH)( $\mu$ -pz)<sub>3</sub>(C<sub>2</sub>H<sub>5</sub>COO)<sub>2</sub>-(EtOH)], **2**, and [Cu<sub>3</sub>( $\mu_3$ -OH)( $\mu$ -pz)<sub>3</sub>-(C<sub>3</sub>H<sub>7</sub>COO)<sub>2</sub>(MeOH)(H<sub>2</sub>O)], **3**, respectively, both containing solvent molecules coordinated to the copper atoms.

Here we report a comparison of their geometries and their supramolecular architectures which show the formation of interesting 1D coordination polymers.

[1] Solomon E.I., Sundaram U.M., Machonin T.E., *Chem. Rev.*, 1996, **96**, 2563. [2] La Monica G., Ardizzoia G.A., *Progr. Inorg. Chem.*, 1997, **46**, 151.

**Keywords:** copper complexes, X-ray crystal structure, carboxylates

#### P.07.01.35

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#### Crystal Packing of Three-Aqua Sodium Maleate

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Three-Aqua Sodium Maleate was crystallized as a side product in the process of the synthesis of the manganese complexes with mixed ligands [1]. The crystal of NaC<sub>4</sub>H<sub>5</sub>O<sub>7</sub> belongs to the space group *P*-1 with unit cell parameters *a* = 5.9609(14) Å, *b* = 6.3907(16) Å, *c* = 11.2308(27) Å,  $\alpha$  = 104.178(4)°,  $\beta$  = 91.574(4)°,  $\gamma$  = 100.241(4)° and *D*<sub>x</sub> = 1.567 Mg m<sup>-3</sup> for *Z* = 2. The maleate monoanion is the ligand bonded through an oxygen atom to the Na<sup>+</sup> ion. The intramolecular O-H...O hydrogen bond in the maleate monoanion was analysed and compared with literature data [2,3]. The central Na atom is surrounded by six oxygen atoms and forms an octahedral polyhedron with the shape of a deformed quadratic bipyramid. Molecules built in this manner form a polymerized infinite chain along the *a* crystallographic axis. Maleate monoanions alternate with Na ion chains and form a layer in the *ac* crystallographic plane. Viewed along the *a* axis, the packing shows that two chains are related by the inversion center, so that they form a channel along the crystallographic *a* axis.

[1] Stamenković J., Cakić S., Nikolić G., *Chemical Industry*, 2003, **57**, 559. [2] James M.N.G., Williams G.J.B., *Acta Crystallogr.*, 1974, **B30**, 1249. [3] James M.N.G., Williams G.J.B., *Acta Cryst.*, 1974, **B30**, 1257.

**Keywords:** coordination geometry, hydrogen bonds, crystal packing

#### P.07.01.36

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#### Structural Parameters of Several Lanthanide Clusters

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This work presents key structural parameters for a series of amino acid-chelated  $\mu_3$ -hydroxide-containing polygadolinium (and lanthanide analog) complexes with potential as high relaxivity MRI contrast agents. The structures of perchlorate salts of *D*<sub>4h</sub>-symmetry Ln<sub>4</sub>( $\mu_4$ -OH)<sub>2</sub>( $\mu_3$ -OH)<sub>16</sub>(OH<sub>2</sub>)<sub>8</sub>(serine)<sub>20</sub><sup>3+</sup>, *D*<sub>3h</sub>-symmetry Ln<sub>15</sub>( $\mu_5$ -Br)( $\mu_3$ -OH)<sub>20</sub>( $\mu_3$ -histidinate)<sub>15</sub>( $\mu$ -OH<sub>2</sub>)<sub>8</sub>(OH<sub>2</sub>)<sub>20</sub><sup>9+</sup>, *T*<sub>d</sub>-symmetry Ln<sub>4</sub>( $\mu_3$ -OH)<sub>4</sub>(valine)<sub>4</sub>(OH<sub>2</sub>)<sub>8</sub><sup>8+</sup> and Ln<sub>2</sub>(alanine)<sub>4</sub>(OH<sub>2</sub>)<sub>8</sub><sup>6+</sup> complexes will be presented.

Structural parameters (Gd-O and Gd...H distances, Gd-water tilt angles, and H-bonding) that may play a significant role in MRI relaxation mechanisms for these novel complexes will be presented. We will collect neutron diffraction data on the dysprosium analog of one of the complexes at the Intense Pulsed Neutron Source (IPNS) at Argonne National Laboratory in April and hope to include these results.

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**Keywords:** clusters, lanthanides, materials magnetic resonance imaging