

**PS07.00.29 CRYSTAL STRUCTURE AND GUEST MOTIONAL BEHAVIOR OF  $\text{Cd}(\text{CN})_2$  CYCLOHEXANE CLATHRATE. X-RAY DIFFRACTION AND SOLID STATE NMR STUDY.** S. Nishikiori\*, T. Kitazawa†, C. I. Ratcliffe‡, J. A. Ripmeester‡, T. Iwamoto\*, \*Department of Basic Science, Graduate School of Arts and Sciences, The University of Tokyo, †Department of Chemistry, Toho University, ‡Steele Institute for Molecular Sciences, National Research Council of Canada

$\text{Cd}(\text{CN})_2$  has  $\text{Cu}_2\text{O}$ -like structure, where two diamond-like 3D frameworks based on tetrahedral  $\text{Cd}^{2+}$  and bridging  $\text{CN}^-$  are interpenetrated each other.  $\text{Cd}(\text{CN})_2 \cdot \text{G}$  clathrates were prepared on the idea that one framework in  $\text{Cd}(\text{CN})_2$  was replaced with bulky organic guest molecules such as cyclohexane,  $\text{CCl}_4$ , etc. X-ray study on  $\text{Cd}(\text{CN})_2$  cyclohexane clathrate revealed that the host lattice has the diamond-like 3D framework and guest cyclohexane molecule is trapped in empty space of the host lattice. However, two questions remained. One was about ordering of the bridging  $\text{CN}^-$ . X-ray showed orientation of the  $\text{CN}^-$  was in disordered state. However, it has been believed that  $\text{CN}^-$  in  $\text{Cd}(\text{CN})_2$  is ordered.  $^{113}\text{Cd}$  MAS NMR revealed that the  $\text{CN}^-$  was in disordered state in  $\text{Cd}(\text{CN})_2 \cdot \text{G}$  and even in  $\text{Cd}(\text{CN})_2$ . Another question was about structure and motional behavior of the cyclohexane. X-ray showed only diffuse electron density around the center of the cavity.  $^2\text{H}$ -NMR powder patterns indicated that the cyclohexane was in rapid random isotropic motion at room temperature and this isotropic motion and the inversion of the cyclohexane ring began to freeze in lower temperature region.

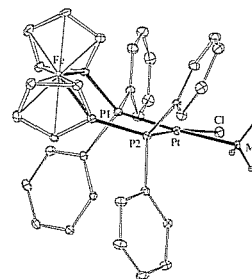
**PS07.00.30 A PROPOSED "NOISE" LEVEL FOR THE DISCRIMINATION BETWEEN INTRA- AND INTERMOLECULAR GEOMETRIC EFFECTS IN  $\text{Pt}(\text{II})$ -COMPLEXES.** Åke Oskarsson, Karin Löqvist, Lars-Ivar Elding, Inorganic Chemistry 1, Chemical Center, University of Lund, P. O. Box 124, S22100 Lund, Sweden

Crystallographic data are often directly used as a basis for conclusions of chemical significance. For example, observed differences in Pt-Cl bond lengths in different structures may be used to evaluate *cis*- and *trans*-influence in square-planar complexes. However, crystallographic bond lengths are not determined by intramolecular effects alone but also packing effects. To establish a reasonable level of significance for an evaluation of an intramolecular "chemical" effect, it is necessary to consider the combined outcome of the experimental errors and packing effects. We have determined each of the crystal structures of  $[\text{PtCl}(\text{dms})_3](\text{PF}_6)$  and  $[\text{PtCl}(\text{dms})_3](\text{CF}_3\text{SO}_3)$  from two independent data sets using different crystals. Comparisons of the two data sets for one compound using half-normal probability plots revealed only small systematic errors and the e.s.d.'s are not under-estimated more than 15-20%. Cross-comparisons of the geometry in the  $\text{Pt}(\text{II})$ -complex in the different compounds gave "noise" levels for differences in Pt-Cl and Pt-S distances of 0.014 and 0.024 Å for 95 and 99% confidence interval, respectively. Therefore we propose that observed differences of Pt-Cl or Pt-S distances should be at least 0.02 Å to be claimed to be the result of intramolecular effects.

**PS07.00.31 X-RAY CRYSTALLOGRAPHIC, NMR AND KINETIC CORRELATION OF SELECTED  $\text{Pt}(\text{II})$  COMPLEXES.** S. Otto; A. Roodt, Department of Chemistry; University of the Orange Free State; Bloemfontein; 9300; South Africa; e-mail: CHJJ@UOVSM1.uovs.ac.za

A variety of related  $\text{Pt}(\text{II})$  compounds were synthesised and characterised with the aid of various physical techniques, such as X-ray crystallography and multi-nuclear NMR spectroscopy. In general the compounds contained one labile group, Cl<sup>-</sup> in this case; one strong  $\sigma$  donating ligand like H<sup>-</sup>,  $\text{CH}_3^-$  or  $\text{C}_6\text{H}_5^-$  and two tertiary phosphine<sup>1</sup> or arsine<sup>2</sup> ligands which could be either *cis* or *trans* to one another. Some lesser known mono- and bidentate ferrocene containing

phosphine ligands were among those used in the study. The aim of the investigation was to manipulate the reactivity of the  $\text{Pt}(\text{II})$  centre and to bring the observed kinetic results in correlation with the obtained physical parameters like bond distances, chemical shifts and coupling constants of the various ligands under investigation. One example of a compound investigated in this study is:



1 Otto, S., Roodt, A., Leipoldt, J.G. (1995). *S. Afr. J. Chem.* **48**, 3/4, 92  
2 Otto, S., Roodt, A. (1995). *Acta Cryst.* **C51**, 1105

**PS07.00.32 STRUCTURES OF RHENIUM COMPLEXES: HOW CRYSTALLOGRAPHY CAN BE AN ESSENTIAL, BUT SOMETIMES MISLEADING, TOOL.** Céline Pearson and André L. Beauchamp, Département de chimie, Université de Montréal, C.P. 6128, Succ. Centre-ville, Montréal, Québec, H3C 3J7.

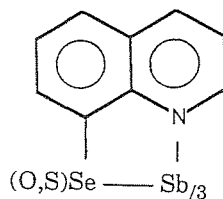
Crystallography is the most powerful identification method for complexes with a paramagnetic metal centre. As part of our project aimed at the synthesis of rhenium(III) dimers containing purine ligands, rhenium(III) and (IV) monomers are being considered as intermediates to these dimers. The paramagnetism of these products makes the use of nmr very difficult as an identification tool. Nevertheless,  $^1\text{H}$  nmr is being used to characterize the products in solution and since the major identification rules applicable to diamagnetic compounds no longer hold for such systems, reliable methods are needed to corroborate the results. Several crystal structures were solved, which generally supported the conclusions based on spectroscopic results. However, in the case of a product whose spectroscopic and other properties corresponded to  $\text{ReCl}_4(\text{MeCN})(\text{Me}_2\text{-adenine})$ , the crystal structure showed that nucleophilic attack had taken place on the ligand during the reaction.

In another reaction, a by-product formed as green crystals insoluble in most solvents. The structure solved easily to a R factor of 2% and the molecules appeared to be the rhenium(VI) monomer *trans*- $\text{ReO}_2\text{Cl}_2(\text{PPh}_3)_2$ . Bond lengths were consistent with this formulation and all thermal ellipsoids looked normal, but the presence of an unusual infrared band remained puzzling. Very careful analysis helped elucidate the identity of this intriguing structure, which turned out to contain a  $\text{Re}(\text{V})$  centre.

**PS07.00.33 STRUCTURE OF ANTIMONY (III) 8-SELENOL-,8-MERCAPTO-AND 8-OXYQUINOLINATE.** L.Pech, Yu..Bankovsky, V.Belsky, A.Stach, J.Ashaks, Institute of Inorganic Chemistry,Latvian Academy of Sciences, Latvia

Investigation structure of 8-oxyquinoline, 8-mercaptoquinoline and 8-selenolquinoline metal complexes is of a great interest because it offers the possibility to elucidate some regulatives of spatial structure of the mentioned compounds depending on the nature of ligand (O,S,Se) atoms. The object of the present work is the study of crystal and molecular structure of  $\text{Sb}(\text{C}_9\text{H}_6\text{NSe})_3(\text{I})$  in comparison with the structures of  $\text{Sb}(\text{C}_9\text{H}_6\text{NS})_3(\text{II})$  and  $\text{Sb}(\text{C}_9\text{H}_6\text{NO})_3(\text{III})$ .

By our offered X-raying method values of dihedral angles between coordination planes restricted by OSbN, SSbN and SeSbN (in Fig.) it is shown, that in molecules of octahedral complexes of transition metals the angles are close to  $90^\circ$ . But these angles diverge considerably more in octahedral complexes of non-transition elements.



The dihedral angles between the coordination planes  $\text{SeSbN}$ ,

SSbN and OSbN (1/2,1/3,2/3) in the complexes I-III are: 84.0, 84.0, 84.0°(I), 78.1, 85.7, 83.9°(II) and 79.4, 84.0, 163.1°(III).

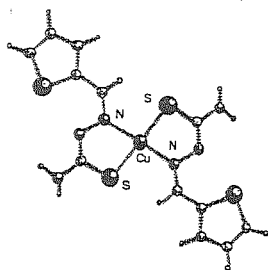
The angles Se-Sb-Se, S-Sb-S and O-Sb-O of chelate metalocycles I-III are 87.1, 87.1, 87.1° (I); 87.3, 84.3 and 87.2° (II) and 86.8, 86.5 and 75.4°(III). The breach of five membered metalocycles trough the lines Se...N, S...N and O...N angles are 20.1, 20.1, 20.1° (I); 29.6, 11.2, 28.2° (II); 0.3, 2.9 and 9.8° (III). Crystal data I - a=b=c=11.2710(10) Å,  $\alpha=\beta=\gamma=99.32(2)^\circ$ , Z=2, sp.gr. R3.

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**PS07.00.34 STRUCTURAL AND SPECTROSCOPIC STUDIES IN THE  $[M(C_6H_6N_3S_2)_2]$  [M= Cu(II), Ni(II)] COMPOUNDS.** J. L. Pizarro, J. GarcíaTojal, L. Lezama, M. I. Arriortua, Depts. de Mineralogía-Petrología y Química Inorgánica. Universidad del País Vasco. Aptdo 644. 48080 Bilbao. Spain.

The  $[M(C_6H_6N_3S_2)_2]$  compounds, where M= Cu(II), Ni(II), crystallize in the P2<sub>1</sub>/c monoclinic space group, with a= 7.541(1), b= 7.243(1), c= 16.179(5) Å,  $\beta= 102.71(2)^\circ$ , Z= 2, R= 0.024, wR= 0.043, for the copper(II) compound, and a= 7.476(1), b= 7.298(1), c= 15.862(5) Å,  $\beta= 101.13(2)^\circ$ , Z= 2, R= 0.032, wR= 0.049, for the nickel(II) complex. The structure

of both compounds consists of discrete monomeric molecules with four coordinate square planar copper(II) and nickel(II) ions (see Figure). The metal ion is joined to two thiophene-2-carbaldehyde thiosemicarbazone ligand by the azomethinic nitrogen and the sulphur atom of the thioamide group.



IR, reflectance and EPR spectra together with the antitumor activity will be discussed.

**PS07.00.35 A LONG C-C BOND IN A TROUBLESOME STRUCTURE.** Douglas R. Powell, Department of Chemistry, University of Wisconsin, 1101 University Ave. Madison, WI 53706 USA; Xiang Ouyang, Zhao Hanhua, and Kim R. Dunbar, Department of Chemistry, Michigan State University, East Lansing, MI 48824 USA

The synthesis of Mn(TCNQ)<sub>2</sub> was undertaken as part of a study of the electronic and magnetic properties of compounds with metal-based radicals bonded to organic ligand radicals. In the crystal structure there are two independent Mn sites each on crystallographic 2-fold axes. Both Mn sites are bonded in an octahedral arrangement to two TCNQ<sup>-</sup> groups, two CH<sub>3</sub>OH groups, and two 1/2[TCNQ]<sub>2</sub><sup>2-</sup> groups. The [TCNQ]<sub>2</sub><sup>2-</sup> moieties are dimers of TCNQ<sup>-</sup> anions joined by a long (1.654(5) Å)  $\sigma$  bond. This type of dimer formation has been seen in other structures.<sup>1-4</sup> The carbons involved in this long bond acquire a tetrahedral geometry blocking a pathway for electron transfer through this group.

This structure was troublesome to solve and refine due to an ambiguity of the Laue symmetry. The cell parameters suggested orthorhombic symmetry [*a* = 14.4910(6) Å, *b* = 27.4207(10), *c* = 13.1146(5),  $\beta=90.0049(8)^\circ$ ]. The preliminary merging R values, however, indicated a much better fit for monoclinic symmetry [*R*<sub>int</sub> = 0.127 mmm, 0.125 2/m(*a*), 0.037 2/m(*b*), 0.125 2/m(*c*)]. Solution in the space group C2/c proceeded with only minor difficulties. The refinement showed that the sample was twinned so as to appear pseudo orthorhombic.

1. *Acta Cryst.* **B33**, 2428 (1977).
2. *Acta Cryst.* **B34**, 540 (1978).
3. *J. Am. Chem. Soc.* **105**, 4608 (1983).
4. *Mol. Crystals & Liquid Crystals* **150**, 473 (1987).

**PS07.00.36 STRUCTURES OF  $[trans-M(H)(H_2)(dppe)_2]^+$ , M=Fe,Ru,Os, BY SINGLE-CRYSTAL NEUTRON DIFFRACTION.** \* J. Ricci<sup>1,2</sup>, A. Albinati<sup>3</sup>, J. Fortin<sup>1,2</sup>, W. Klooster<sup>1</sup>, T. Koetzle<sup>1</sup>, P. Maltby<sup>4</sup>, R. Morris<sup>4</sup>, A. Petroff<sup>4</sup>, Depts. of Chem., Brookhaven Nat. Lab., Upton, NY 11973 USA, Univ. S. Maine, Portland, ME 04103 USA, and Univ. Toronto, Toronto, Ontario M5S 1A1 Canada; and Inst. of Pharm. Chem., Univ. Milan, I-20131 Milan, Italy

Activation of the H<sub>2</sub> ligands in the d<sub>6</sub>-octahedral series  $[trans-M(H)(H_2)-(dppe)_2]^+$ , M= Fe(1), Ru(2), Os(3), is shown to increase in the order Fe~Ru<Os, based on neutron diffraction and NMR. The H<sub>2</sub> activation step, which results from M( $\pi$ )-H<sub>2</sub>( $\sigma^*$ ) backbonding with concomitant lengthening of the H-H bond, is of central importance in a number of catalytic processes. H<sub>2</sub> complexes have been the subject of intense interest ever since their discovery over 10 years ago by Kubas<sup>5</sup> because of their relevance as models for H<sub>2</sub> activation, and their many novel properties including quantum exchange. Essential results from our neutron diffraction studies of **1** BPh<sub>4</sub>, **2** BPh<sub>4</sub>, and **3** BF<sub>4</sub> are now given in the Table together with some NMR information on the complexes in solution. It is apparent that the neutron bond distances, d(H-H), are systematically foreshortened relative to the NMR-derived values which are discussed elsewhere<sup>6</sup>. Therefore it is essential that the neutron distances be corrected for librational motion, and we have attempted to do this based on rigid-body models. The corrections result in much improved agreement for all three complexes.

Table of Neutron Results, and NMR data for **1** BPh<sub>4</sub>, **2** BPh<sub>4</sub> and **3** PF<sub>6</sub><sup>-</sup>

Complex	Temp.,K	Neutron Diffraction				NMR	
		d(M-H)	d(M-H <sub>2</sub> ) <sup>†</sup>	d(H-H)	d <sub>corr</sub> (H-H)	J(H,D),Hz	d(H-H)
1	20	1.54(1)	1.62(1)	0.82(2)	0.85	30.8	0.87
2	12	1.64(2)	1.81(2)	0.82(3)	0.94	32.4	0.90
3	13	1.62(1)	1.75(2)	0.79(1)	0.96	25.5	1.02
	57	1.60(2)	1.78(4)	0.78(2)			
	100	1.62(2)	1.75(4)	0.72(4)			

<sup>†</sup>Distances in Ångstroms with esd's in parentheses. \*Mean value.

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<sup>1</sup>Brookhaven. <sup>2</sup>S. Maine. <sup>3</sup>Milan. <sup>4</sup>Toronto.

<sup>5</sup>Kubas, G. *J. Acc. Chem. Res.* **1988**, *21*, 120.

<sup>6</sup>Bautista, M. T.; Cappellani, E. P.; Drouin, S. D.; Morris, R. H.; Schweitzer, C. T.; Sella, A.; Zubkowski, J. *J. Am. Chem. Soc.* **1991**, *113*, 4876.

**PS07.00.37 A PACKING OF MONOMERIC AND DIMERIC Rh(III) COMPLEXES IN THE CRYSTAL STRUCTURES OF  $[Rh(H_2O)_6]F_3 \cdot 4H_2O$  &  $[N(CH_3)_4][Rh_2Cl_9]$**  G.V.Romanenko, N.V.Podberzskaya Institute of Inorganic Chemistry, Sib. Branch, Novosibirsk, Russia

The crystal structures of two novel Rh(III) compounds -  $[Rh(H_2O)_6]F_3 \cdot 4H_2O$  (**I**) &  $[N(CH_3)_4][Rh_2Cl_9]$  (**II**), containing halogen ions, have been determined. In these compounds, a radically different functional role of the F<sup>-</sup> and Cl<sup>-</sup> ions is due to their size and a composition of outer-sphere components. The octahedral environment of Rh in **I** is provided by six H<sub>2</sub>O molecules which have displaced the F<sup>-</sup> ions into the outer sphere involving the additional four H<sub>2</sub>O. In **II**, the Rh-octahedra, formed by the Cl<sup>-</sup> ions, are combined into dimers via a common face. The packing of the  $[Rh(H_2O)_6]^{3+}$  ions formed pseudohexagonal layers with Rh-Rh distances equal to [010], 1/2[110] & 1/2[1 -1 0] in the trigon loops of the layer in structure **I**. The one-layer stacking explains a strong quasiperiodicity (*c*/2) in this structure. In vacancies of the trigon loops there are F<sup>-</sup> ions; the common faces of triangular prisms, formed by complex cations, are occupied by F<sup>-</sup> ions and outer-sphere H<sub>2</sub>O molecules.

In **II**, Rh atoms of dimeric anions (on the *z*≡0, 0.35, 0.5 and 0.85 levels) in combination with C atoms of the cations (situated on the axes 3) form regular hexagonal nets of the 1/3a√3 dimension. The one-layer packing (with a pseudoperiod *c*/4) is formed without regard for atomic sorts.

Crystal data (SYNTEX P2<sub>1</sub>, λMoK $\alpha$ ,  $\theta/2\theta$ -scan) for **I**: a=11.910(2), b=6.877(1), c=13.590(3) Å,  $\beta=90.00(3)^\circ$ , V=1113.1(3) Å<sup>3</sup>, space group C2/c, Z=4, d<sub>calc</sub>=2.029 g·cm<sup>-3</sup>, R=0.0257, 919 F<sub>hkl</sub>; for **II**: a=9.083(1), c=20.705(4), V=1479.3(4) Å<sup>3</sup>, space group P31c, Z=2, d<sub>calc</sub>=1.714 g·cm<sup>-3</sup>, R=0.0737, 612 F<sub>hkl</sub>.