

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).

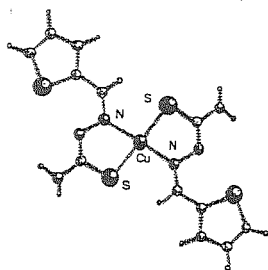
The angles Se-Sb-Se, S-Sb-S and O-Sb-O of chelate metalocycles I-III are 87.1, 87.1, 87.1° (I); 87.3, 84.3 and 87.2° (II) and 86.8, 86.5 and 75.4°(III). The breach of five membered metalocycles through the lines Se...N, S...N and O...N angles are 20.1, 20.1, 20.1° (I); 29.6, 11.2, 28.2° (II); 0.3, 2.9 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 P2₁/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)₂ 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⁻ groups, two CH₃OH groups, and two 1/2[TCNQ]₂²⁻ groups. The [TCNQ]₂²⁻ moieties are dimers of TCNQ⁻ anions joined by a long (1.654(5) Å) σ bond. This type of dimer formation has been seen in other structures.¹⁻⁴ 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*_{int} = 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^{1,2}, A. Albinati³, J. Fortin^{1,2}, W. Klooster¹, T. Koetzle¹, P. Maltby⁴, R. Morris⁴, A. Petroff⁴, 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 H₂ ligands in the d⁶-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 H₂ activation step, which results from M(π)-H₂(σ^*) backbonding with concomitant lengthening of the H-H bond, is of central importance in a number of catalytic processes. H₂ complexes have been the subject of intense interest ever since their discovery over 10 years ago by Kubas⁵ because of their relevance as models for H₂ activation, and their many novel properties including quantum exchange. Essential results from our neutron diffraction studies of **1** BPh₄, **2** BPh₄, and **3** BF₄ 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 elsewhere⁶. 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** BPh₄, **2** BPh₄ and **3** PF₆⁻

Complex	Neutron Diffraction					NMR	
	Temp.,K	d(M-H)	d(M-H ₂) [†]	d(H-H)	d _{corr} (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)			

[†]Distances in Ångstroms with esd's in parentheses. *Mean value.

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⁵Kubas, G. *J. Acc. Chem. Res.* **1988**, *21*, 120.

⁶Bautista, 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⁻ and Cl⁻ ions is due to their size and a composition of outer-sphere components. The octahedral environment of Rh in **I** is provided by six H₂O molecules which have displaced the F⁻ ions into the outer sphere involving the additional four H₂O. In **II**, the Rh-octahedra, formed by the Cl⁻ 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⁻ ions; the common faces of triangular prisms, formed by complex cations, are occupied by F⁻ ions and outer-sphere H₂O 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 P2₁, λMoK α , $\theta/2\theta$ -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) Å³, space group C2/c, Z=4, d_{calc}=2.029 g·cm⁻³, R=0.0257, 919 F_{hkl}; for **II**: a=9.083(1), c=20.705(4), V=1479.3(4) Å³, space group P31c, Z=2, d_{calc}=1.714 g·cm⁻³, R=0.0737, 612 F_{hkl}.