

**PS07.01.08 SYNTHESIS OF  $[\text{IrCl}_6]^{2-}$   $\{[\text{HP-}i\text{-Pr}_3]^+\}_2$ , 1 AND  $[\text{Ir}_2\text{Cl}_8(\text{P-}i\text{-Pr}_3)]^{2-}$   $\{[\text{HP-}i\text{-Pr}_3]^+\}_2$ , 2, TWO POSSIBLE STARTING MATERIALS FOR THE DIRECT SYNTHESIS OF  $\text{Ir}^{\text{V}}(\text{H})_2(\text{Cl})_3(\text{P-}i\text{-Pr}_3)_2$ , 3. CRYSTAL STRUCTURES OF 1, 2 AND 3.** P. Mura, M. Allevi, A. Ettore, Istituto di Strutturistica Chimica "G. Giacomello", CNR, C.P. N° 10, 00016 Monterotondo Stazione - Roma - Italy

Very few iridium(V) ( $d^4$ ) complexes are known<sup>2</sup>. To our knowledge phosphine complex  $\text{Ir}^{\text{V}}(\text{H})_2(\text{Cl})_3(\text{P-}i\text{-Pr}_3)_2$ , 3<sup>1</sup> is the first Ir(V) compound in which hydride and chloride ligands are present. We obtained complex 3 as by-product in the synthesis of the  $\text{Ir}^{\text{III}}(\text{H})(\text{Cl})_2(\text{P-}i\text{-Pr}_3)_2$ , 4<sup>3</sup>. Despite our efforts, the direct synthesis of 3 was unsuccessful. The syntheses of  $[\text{IrCl}_6]^{2-}$   $\{[\text{HP-}i\text{-Pr}_3]^+\}_2$ , 1 and  $[\text{Ir}_2\text{Cl}_8(\text{P-}i\text{-Pr}_3)]^{2-}$   $\{[\text{HP-}i\text{-Pr}_3]^+\}_2$ , 2 may give us two possible starting materials to obtain 3. In fact complexes 1 and 2 are also two transient intermediates in the synthesis of 4 and probably, before, of 3: reductive elimination of a molecule of HCl by 3 may give rise to 4<sup>3</sup>. Crystallographic data: For  $[\text{IrCl}_6]^{2-}$   $\{[\text{HP-}i\text{-Pr}_3]^+\}_2$ , 1 (at 298 K),  $a=9.314(1)$  Å,  $b=15.415(2)$  Å,  $c=10.073(1)$  Å,  $\beta=95.38(1)^\circ$  in space group  $P2_1/n$ . For  $[\text{Ir}_2\text{Cl}_8(\text{P-}i\text{-Pr}_3)]^{2-}$   $\{[\text{HP-}i\text{-Pr}_3]^+\}_2$ , 2 (at 298 K),  $a=16.360(4)$  Å,  $b=13.967(2)$  Å,  $c=18.603(3)$  Å,  $\beta=93.74(2)^\circ$ , in space group  $P2_1/c$ . For  $\text{Ir}^{\text{V}}(\text{H})_2(\text{Cl})_3(\text{P-}i\text{-Pr}_3)_2$ , 3 (at 298 K),  $a=8.761(2)$  Å,  $b=8.823(1)$  Å,  $c=9.808(2)$  Å,  $\alpha=100.66(1)^\circ$ ,  $\beta=91.20(1)^\circ$ ,  $\gamma=119.72(1)^\circ$  in space group  $P1$ .

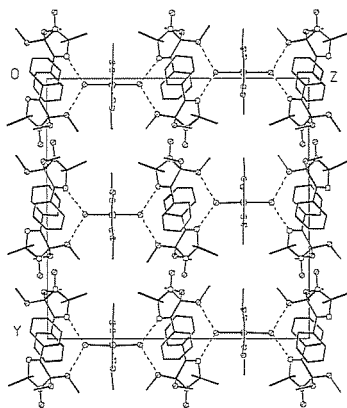
(1) Presented in part to the XVI Congress of IUCr, 1993, Beijing, China, Collect. Abstract p. 240.

(2) M. Loza, J. W. Faller, R. H. Crabtree, *Inorg. Chem.*, 1995, 34, 2937 and reference therein.

(3) D. Capitani, P. Mura submitted to *Inorg. Chem.*

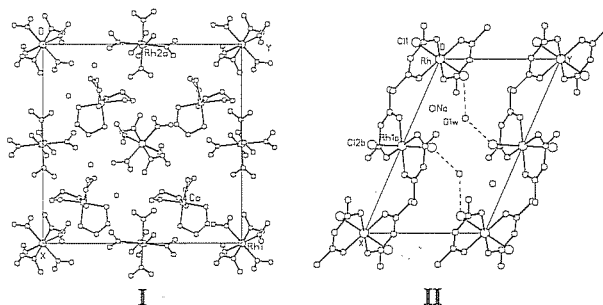
**PS07.01.09 CRYSTAL STRUCTURE OF NICKEL(II) AND COBALT(II) ADDUCTS WITH 3-IMIDAZOLINE NITROXIDE.** N.V. Pervukhina, A.B. Burdukov, V.I. Ovcharenko, Institute of Inorganic Chemistry Sib. Branch RAS, Novosibirsk, Russia, International Tomography Center Sib. Branch RAS, Novosibirsk, Russia

The crystal and molecular structures of novel compound  $\text{Ni}(\text{hfac})_2(\text{H}_2\text{O})_2\text{L}_2$  (hfac=hexafluoroacetylacetonato-, L=2,2-dimethyl-5,5-dimethoxy-4-phenyl-3-imidazoline-1-oxyl) have been determined by single-crystal X-ray analysis ('SYNTEX P2<sub>1</sub>', MoK, /2-scan). The coordination polyhedron of the nickel atom is formed by four hfac oxygen atoms (Ni-O 2.009(2)-2.036(2) Å) and two water oxygens (Ni-O 2.075(3) and 2.029(3) Å) which comprise almost regular octahedron. The nitroxide moieties L do not participate in coordination but form the H-bonds with coordinated water molecules ( $\text{N}\cdots\text{H}$  2.01, 1.93 Å and  $\text{O}(\text{CH}_3)\cdots\text{H}$  2.00, 1.97 Å), therefore joining  $\text{Ni}(\text{hfac})_2(\text{H}_2\text{O})_2$  fragments in extended structure. The crystals of  $\text{Ni}(\text{hfac})_2(\text{H}_2\text{O})_2\text{L}_2$  are orthorhombic, space group  $P2_12_12_1$ , with 8 molecules on unit cell of dimensions  $a=11.625(3)$  Å,  $b=19.467(7)$  Å,  $c=19.547(8)$  Å,  $V=4423.5(3)$  Å<sup>3</sup>,  $D=1.513$  g·cm<sup>-3</sup>, 1272 unique  $I_{\text{hkl}} > 2\sigma_I$ ,  $R=0.0458$ . The complex  $\text{Co}(\text{hfac})_2(\text{H}_2\text{O})_2\text{L}_2$  is isostructural to  $\text{Ni}(\text{hfac})_2(\text{H}_2\text{O})_2\text{L}_2$  according to powder diffraction data.



**PS07.01.10 'CLOSEST PACKINGS' LAW IN CRYSTAL STRUCTURES OF NEW Rh(III) COMPLEXES.** N.V. Podberzskaya, G.V. Romanenko, Institute of Inorganic Chemistry Sib. Branch RAS, Novosibirsk, Russia

Crystal structures of two novel coordination Rh(III) compounds were determined (SYNTEX P2<sub>1</sub>, MoK, /2-scan, 3°250): cubic  $[\text{Co}(\text{en})_3][\text{Rh}(\text{NO}_2)_6]\cdot 3\text{H}_2\text{O}$ ,  $\text{en}=\text{C}_2\text{H}_8\text{N}_2$  (I) ( $a=16.540(5)$  Å,  $V=4525(2)$  Å<sup>3</sup>,  $\text{Pa}3$ ,  $Z=8$ ,  $D_c=1.974$  g·cm<sup>-3</sup>, 589 unique  $I_{\text{hkl}} > 2\sigma_I$ ,  $R=0.0905$ ) and triclinic  $\text{Na}[\text{Rh}(\text{acac})_2\text{Cl}_2]\cdot \text{H}_2\text{O}$ ,  $\text{acac}=\text{C}_5\text{H}_7\text{O}_2^-$  (II) ( $a=12.616(6)$ ,  $b=8.411(4)$ ,  $c=8.499(4)$  Å,  $\alpha=108.37(4)$ ,  $\beta=95.47(4)$ ,  $\gamma=110.45(4)^\circ$ ,  $V=780.3$  Å<sup>3</sup>,  $P1(-)$ ,  $Z=2$ ,  $D_c=1.758$  g·cm<sup>-3</sup>, 1200 unique  $I_{\text{hkl}} > 2\sigma_I$ ,  $R=0.0463$ ). In I, the joint packing of the complex cations, anions and water molecules presents the stacking after the three-layered closest packing with the combination of NaCl and CaF<sub>2</sub> structure types; in II, the complex anions produce the stacking after the hexagonal closest packing with Na<sup>+</sup> and H<sub>2</sub>O located in its cavities. The presence of organic ligands in the composition of the complexes does not contradict our understanding of packing rules for inorganic coordination compounds in the description of complex cations and anions as the quasi-spheric particles of the  $R_{\text{ef}}$  radius.



**PS07.01.11 BULK HELICIDS IN CRYSTAL STRUCTURES OF RARE-EARTH AND SODIUM TETRAKISPIVALOYLTRIFLUOROACETONATES,  $\text{NaLn}(\text{PTA})_4$ .** T.M. Polyanskaya, G.V. Romanenko, N.V. Podberzskaya, Institute of Inorganic Chemistry Sib. Branch RAS, Novosibirsk, Russia

We have carried out an X-ray study of the volatile  $\text{NaLn}(\text{PTA})_4$  (Gd-Lu) complexes. The parameters for Er are as follows:  $a=13.114$ ,  $c=21.004$  Å, sp. gr.  $P3_1$ ,  $Z=3$ . In the structure, each PTA ligand performs a tridentate function, forming a six-membered chelate cycle with the Er atom, and, besides, coordinates the neighboring Na atom by the additional Na-O bond. The coordination polyhedron of each metal atom includes the O atoms of four PTA ligands. The Na atom bridges two non-equidistant Er atoms (3.833 and 3.893 Å). The M-O bond strengths are much the same (the mean Er-O and Na-O bond values 2.325 and 2.396 Å). Four vertices of the eight-vertex Na polyhedron are occupied by the F atoms (the mean Na-F 2.678 Å) of the same PTA ligands which are shared by Na and Er. The trans-edge-sharing eight-vertex polyhedra about Er and Na form the array with extended structure which runs toward a crystallographic 3<sub>1</sub> axis, but the Er and Na ions are not sited on the axis and the extended array has a 'helical' structure. The independent link of the array is equal to two polyhedra: the Na1 atom, nearest to Er, supposedly converts into a gaseous phase.

