PS07.01.08 SYNTHESSES OF [IrCl4]+·[(HP-i-Pr3)2]+ 1 AND [Ir2Cl6(P2P)]2·[(HP-i-Pr3)2]+ 2, TWO POSSIBLE STARTING MATERIALS FOR THE DIRECT SYNTHESIS OF Ir(H)3Cl)3(P2P)2·31. CRYSTAL STRUCTURES OF 1, 2 AND 3. P. Mura, M. Allevi, A. Eitore, Istituto di Sistematica Chimica "G. Giaquinto", CNR, C.P. N. 10, 00016 Monterotondo Stazione – Roma - Italy

Very few iridium(V) (d6) complexes are known. To our knowledge, the first phosphine complex Ir(H)(Cl)3(P2P)2·31 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 Ir(H)(Cl)3(P2P)2·4. Despite our efforts, the direct synthesis of 3 was unsuccessful. The syntheses of [IrCl4]+·[(HP-i-Pr3)2]+ 1 and [Ir2Cl6(P2P)]2·[(HP-i-Pr3)2]+ 2 may give 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 cleavage of HCl by 3 might give rise to 4. Crystallographic data: For [IrCl4]+·[(HP-i-Pr3)2]+ 1 (at 298 K), a= 9.314(1) Å, b= 15.415(2) Å, c= 10.703(1) Å, β= 95.38(1)° in space group P21/k/n. For [Ir2Cl6(P2P)]2·[(HP-i-Pr3)2]+ 2 (at 298 K), a= 16.360(4) Å, b= 15.967(2) Å, c= 18.603(3) Å, β= 93.74(2)°, in space group P21/c. For Ir(H)(Cl)3(P2P)2·31 (at 298 K), a= 8.761(2) Å, b= 8.823(1) Å, c= 9.808(2) Å, α= 100.66(1)°, β= 91.20(1)°, γ= 119.72(1)° in space group P1. 1 (1) Presented in part to the XVI Congress of IUCr, 1993, Beijing, China, Collectif Abstract p. 290. (2) M. Loca, J. W. Fuller, R. H. Crabtree, Inorg. Chem., 1995, 34, 2957 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 compounds Ni(hfac)(H2O)2L2 (hfac=hexafluoracetetylacetonato, L=2-dimethyl-5,5-dimethoxy-4-phenyl-3-imidazolin-1-oxyl) have been determined by single-crystal X-ray analysis (SYNTAX P21. MoKα, 293K). The coordination polyhedron of the nickel atom is formed by four hfac oxygen atoms (Ni-O 2.099(2) Å and water oxygen (Ni-O 2.075(3) Å and 2.029(3) Å) which comprise almost regular octahedron. The nitrooxide ligands do not participate in coordination but form the H-bonds with coordinated water molecules (N•••O=2.01, 1.93 Å and O(CCH3)•••H=2.00, 1.97 Å), therefore joining Ni(hfac)(H2O)2 fragments in extended structure. The crystals of Ni(hfac)(H2O)2L2 are orthorhombic, space group P212121, with 8 molecules on unit cell of dimensions a=11.625(3) Å, b=19.467(7), c=19.547(8) Å, V=4423.5(3) Å3, D = 1.513 g cm-3, 1272 unique I(0) = 2em, R=0.0458. The complex Cu(hfac)(H2O)2L2 is isostructural to Ni(hfac)(H2O)2L2 according to powder diffraction data.

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

Crystal structures of two novel coordination Rh(III) compounds were determined (SYNTAX P21. MoKα, 293K): cubic [Co(en)3]3[Rh(ONO2)3]·3H2O, en=C2H2N2 (I) (a=16.540(5) Å, V=5252(2) Å3, P33, Z=8, D0=1.974 g cm-3, 589 unique I(0) = 2em, R=0.0905) and triclinic Na[Rh(acac)2Cl]·H2O, acac=C2H2O2- (II) (a= 12.616(6), b = 8.411(4), c = 8.499(4) Å, a=90.97(4), b= 95.47(4), γ= 110.45(4)°, V = 780.3 Å3, P1c1, Z = 2, D0=1.758 g cm-3, 1200 unique I(0) = 2em, 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 NaF structure types; in II, the complex anions produce the stacking after the hexagonal closest packing with Na+ and H2O 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-spherical particles of the Rcr radius.

PS07.01.11 BULK HELICOIDAL IN CRYSTAL STRUCTURES OF RARE-EARTH AND SODIUM TETRASPIIVALOYLPHTHALACETONATES, NaLn(PTA)4. T.M. Polyanitskaya, G.V. Romanenko, N.V. Podberenzayska, Institute of Inorganic Chemistry Sib. Branch RAS, Novosibirsk, Russia

We have carried out an X-ray study of the volatile NaLn(PTA)4 (Gd-La) complexes. The parameters for Er are as follows: a=13.114, c=21.004 Å, sp. gr. P21, 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-equivalent Er atoms (3.833 and 3.893 Å). The M-O bond strengths are much the same (the mean Eu-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). The combination of the PTA ligands which are shared by Na and Er. The trans-edge-sharing eight-vertex polyhedron about Er and Na form the array with extended structure which runs toward a crystallographic 3 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 NaI atom, nearest to Er, supposedly converts into a gaseous phase.