07-Crystallography of Organometallic and Coordination Compounds

PS-07.04.40 CRYSTAL STRUCTURE OF Ru₄(CO)₆(µ₃-C₅H₅N)₂H₂NCS
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A new type compound Ru₄(CO)₆(µ₃-C₅H₅N)₂H₂NCS was synthesized by refluxing Ru₄(CO)₁₂ and C₅H₅NHSNC≡CS in THF. The cluster was characterized by IR, ¹H NMR, the elemental analysis and melting point, and the crystal structure has been determined by crystal diffraction method.

The title compound was synthesized by the reaction of Ru₄(CO)₁₂ with C₅H₅NHSNC≡CS in THF solvent. Ru₄(CO)₁₂ (0.398g, 0.43mmol) and C₅H₅NHSNC≡CS (0.216g, 0.94mmol) were dissolved in THF (25mL). After stirring for 12h at 80°C, a brown-red solution was filtered and evaporated under reduced pressure. The residue was extracted with dichloromethane/hexane(5:1). The extraction was separated by fractional crystallization and afforded solid product Ru₄(CO)₆(µ₃-C₅H₅N)₂H₂NCS. (Yield 41%), with 140°C decomposition point. The crystal structure was determined with a Enraf-Nonius CAD-4 diffractometer. Using MoK radiation, 6,200 reflections, 2800 reflections were collected, in which 2840 are independent reflections, and 2371 are observed reflections with I/σ(I) were used in all calculations.

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The crystal belongs to monoclinic, space group is P2₁/n. Cell parameters (given below): a = 9.60(2) Å; b = 14.2795(8) Å; c = 9.886(1) Å. β = 103.45(1)°. Crystal dimensions are 0.45x0.35x0.30mm. V = 1391.9 Å³. Z = 2. Dm = 1.85g/cm³. μ = 17.73cm⁻¹.

The final refinement by full-matrix least-squares method with the coordinates and anisotropic thermal parameters gave final R = 0.038, Rw = 0.048. The structure and the numbering of atoms is depicted in Fig.1. bond distances and angles are abbreviated in present paper. The molecular geometry is consistent with the characteristic structure of the new compound and is confirmed by the good agreement between the observed and the calculated data.

Fig.1 Structure of Ru₄(CO)₆(µ₃-C₅H₅N)₂H₂NCS.

Fig.1 shows, there are two characteristics of molecular configuration of this new compound.
1. Molecular geometry is Cs symmetry.
2. Organic liganding coordinate to tri-nuclear Ru cluster via N and µ=Z.

PS-07.04.41 THE CRYSTAL STRUCTURE OF TWO COMPLEXES OF COBALT(III) TETRAAZA MACROCYCLIC LIGANDS. By Tahir H. Tahirov, Tian-Huey Lu, Department of Physics, Bor-Hsun Chen* and Chung-Sung Chung, Department of Chemistry, National Taiwan University, Taipei, Taiwan 300, China.

The structure of two compounds: (A) cis-dichloro(cocr-5,7,12,14-tetraazacyclotetradecane)cobalt(III) chloride, CoCl₂(N₄C₁₂H₂₈)Cl₂ have been determined by X-ray diffraction. Their crystal data are: (A) Orthorhombic, P2₁2₁2₁, a=7.185(5), b=9.552(3), c=16.742(3) Å , R=0.064 ; (B) Monoclinic, C₂/c , a=9.178(1), b=11.722(2), c=16.1005(5) Å , β = 90.96(2)° , R=0.045. The two compounds have the same structures of two five-membered and two six-membered chelate rings, and five-membered rings are in gauche form and six-membered ring of chain form, and the same configurations of chiral nitrogen centres of 1SR,4SR,8SR,11SR. In compound (A), the O atoms of the carbonate ion are in cis configuration relative to the macroyclic ligand the Co(III) ion is six coordinated in distorted octahedral geometry with tetrasamine N atoms equatorial and two cis O atoms of the carbonate ion axial. The axial Co-O bond distances are shorter than the equatorial Co-N bond distances. In compound (B) there are two Cl atoms cis to the macroyclic ligand. The four Co-N distances are equal to 1.989(3) Å, comparable with the Co-N distances found in the complexes of dioxido(cocr-5,12-dimethyl-1,4,8,11-tetraazacyclotetradecane)cobalt(III) azide (Retivo, Ferguson, Ey & Pipiani, J. C. S. Dalton, 1978, 1311-1134). The two Co-Cl distances are 2.262(1) Å which agrees well with the Co-Cl distances in other cobalt(III) complexes. Work was supported by National Science Council, Taiwan, China.