234 07-Crystallography of Organometallic and Coordination Compounds

PS-07.04.40 CRYSTAL STRUCTURE OF $Ru_3(CO)_9(C_6H_5)_2N_2HCS$

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A new type compound $Ru_3(CO)_9(C_6H_5)_2N_2HCS$ was synthesized by refluxing $Ru_3(CO)_{12}$ and $C_6H_5NHCSNHC_6H_5$ in THF. The cluster was characterized by IR, ^1H NMR, the elementary analysis and melting point and the crystal structure has been determined by crystal diffraction method.

The title compound was synthesized by the reaction of $Ru_3(CO)_{12}$ with $C_6H_5NHCSNHC_6H_5$ in THF solvent. $Ru_3(CO)_{12}$ (0.3003g, 0.43mmol) and $C_6H_5NHCSNHC_6H_5$ (0.2146g, 0.94mmol) were dissolved in THF (25ml). After stirring for 12hr 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 $Ru_3(CO)_9(C_6H_5)_2N_2HCS$. (Yield 41%) with 145°C decomposition point. The crystal structure was determined with a Enraf-Nonius CAD-4 diffractometer, Using MoK$_\alpha$ radition. $\omega/2\theta$ scans, 2600 reflections were collected, in which 2584 are independent reflections, and 2377 are observed reflections with $I>3\sigma(I)$ were used in all calculations.

*This paper is supported by National Natural Science Foundation of China State Key Laboratory of Structural Chemistry. Shanghai Laboratory of Organic Chemistry Academia Sinica, State Key Laboratory for OSSO.

The crystal belongs to monoclinic, space group is P21/m. Cell parameters (given below): a, 9.604(2)Å; b, 14.279(5)Å; c, 9.986(1)Å, β: 103.45(1)°, Crystal dimensions are 0.40x0.35x 0.30mm. V=1331.9Å^3, Z=2 D_x=1.951g/cm^3, 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 abridged 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.

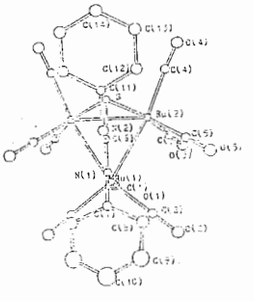

Fig.1 Structure of $Ru_3(CO)_9(C_6H_5)_2N_2HCS$.

Fig.1 shows, there are two characteristics of molecular configuration of this new compound.

1. Molecular geometry is Cs symmetry.
2. Organic ligand coordinate to trinuclear Ru cluster via N and μ_2-S.

PS-07.04.41 THE CRYSTAL STRUCTURE OF TWO COMPLEXES OF COBALT(III) TETRAAZA MACROCYCLIC LIGANDS.

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The structure of two compounds: (A) carbonato(c-rac-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetra-decane)cobalt(III) perchlorate, $[CoCO_3(N_4C_{16}H_{36}).ClO_4]$ and (B) cis-dichloro(c-rac-5,12-dimethyl-1,4,8,11-tetraazacyclotetradecane)cobalt(III) chloride, $[CoCl_2(N_4C_{12}H_{28})Cl]$ have been determined by X-ray diffraction. Their crystal data are: (A) Orthorhombic, $P22_12_1$, 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=16.100(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 chair 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 macrocyclic ligand the Co(III) ion is six coordinated in distorted octahedral geometry with tetraamine 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 macrocyclic ligand. The four Co-N distances are equal to 1.989(3)Å, comparable with the Co-N distances found in the complexes of diazido(c-meso-5,12-dimethyl-1,4,8,11-tetraazacyclotetradecane)cobalt(III) azide (Restivo, Ferquson, Hay & Piplani, J. C. S.Dalton,1978,1131-1134). 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].