

CRYSTAL STRUCTURE OF THE PMBP-M-Cl-ANILINE WITH ITS Co (II) COMPLEXJ.L. Wang¹ Y. Yang¹ M. Yu² F.M. Miao¹¹Tianjin Normal University Institute of Chemical And Crystallography HeXi Disinct WeiJing Road No.241 TIANJIN 300074 CHINA ² The University of Tianjin Scientific and Technology

The crystal data of the PMBP-m-Cl-aniline (I) and its Co (II) complex are as follows: (I): $a = 9.678(3)$, $b = 9.999(3)$, $c = 10.867(3)$ Å, $\alpha = 92.764(6)$, $\beta = 73.792(6)$, $\gamma = 102.593(6)^\circ$, triclinic, space group $P-1$. The final refinement $R = 0.0476$, $S = 0.921$. (II): $a = 19.294(10)$, $b = 10.157(5)$, $c = 21.995(12)$ Å, $\beta = 98.997(12)^\circ$, monoclinic, space group $P-1$. The final refinement $R = 0.0759$, $S = 0.856$. In the compound (I), the O(1), C(1), C(2), C(5) and N(3) atoms form a plane, the largest deviation nearing 0.0018 Å. The bond lengths of the pyrazolone ring is between the single and double bonds, the dihedral angle between the pyrazolone ring and the O(1)-C(1)-C(2)-C(5)-N(3) plane is 4.42° , which indicate they are form a big conjugate system. The intra-molecular hydrogen bond is found, the bond length and angle of N(3)-H(3) ... O(1) are 2.669 Å and 143.56° . These cases indicate that the title molecules in the crystal packing are hold together not only by electrostatic attraction but also by intra-molecular hydrogen bonds.

Fig 1 The structure of the Compound(I) Fig 2. The structure of the Co Complex (II) In the Co complex (II), the Co(II) ion is coordinated by O(1), O(2) atoms of two pyrazolone rings and N(1), N(2) atoms to form a light distorted tetrahedral configuration. The four coordinated bond lengths of Co (1)-O(1), Co (1)-O(2), (4), Co (1)-N (1) and Co (1)-N (2) are 1.932(7), 1.944(7), 1.994(8) and 1.965(9) Å, respectively.

Keywords: CRYSTAL STRUCTURE PMBP M CHLORO ANILINE Co (II) COMPLEX

SYNTHESIS AND STRUCTURE OF THE DINUCLEAR RHODIUM-BINAP COMPLEX

T. Yamagata K. Hoshida K. Tani

Graduate School of Engineering Science, Osaka University Department of Chemistry Machikaneyama-Cho 1-3 TOYONAKA OSAKA 560-6248 JAPAN

Although group 9 transition metal complexes of a general formula $eM(\text{diphosphine})_f$ ($M = \text{Rh, Ir}$) generated *in situ* have often been proposed as versatile catalyst precursors for general catalytic reactions like hydrogenation of olefin, imine, etc, examples of isolation and characterization of such species are rare. Recently we have succeeded in isolation and characterization of $[\text{IrCl}(\text{diphosphine})]$ (I) {diphosphine = BINAP (2,2-η-f-bis(diphenylphosphino)-1,1-η-f-binaphthyl) (Ia), or BPBP (2,2-η-f-bis(diphenylphosphino)-1,1-η-f-biphenyl) (Ib)} as extremely air-sensitive complexes.

These complexes Ia and Ib reacted easily with methanol and water to give the oxidative addition products.¹ However, the structure of $[\text{RhCl}(\text{binap})]$ has not been determined. We herein report characterization and structure of $[\text{RhCl}(\text{S-binap})_2]$ (II). The neutral rhodium complex II was prepared as an air-stable product from $[\text{RhCl}(\text{cod})]$ and (S)-BINAP in dry toluene. Complex II has a dinuclear structure having bridging chloride ligands and each rhodium atom has a square planar coordination geometry. The $\text{Rh}_2(\mu\text{-Cl})$ core shows a bent geometry with a hinge angle of $126.08(3)^\circ$ [cf. $[\text{IrCl}(\text{R-binap})_2]$ II: $123.9(1)^\circ$]. The whole structural feature is very similar to that of $[\text{IrCl}(\text{R-binap})_2]$.¹ The ³¹P NMR shows a doublet signal at δ 49.5 {d, $J_{\text{P-Rh}} = 196$ Hz}. Different from complexes Ia and Ib, complex II does not react with protic molecules (H₂O, MeOH, etc.).

Crystal data of II.2THF: monoclinic, $P2_1$, $a = 19.0678(3)$, $b = 13.6737(2)$, $c = 18.9170(3)$ Å, $\beta = 127.3310(3)^\circ$, $V = 3921.8(1)$ Å³, $T = 223$ K, $R_1 = 0.0502$, $wR_2 = 0.0900$ for 21563 [I>2σ(I)], $R_1 = 0.0671$, $wR_2 = 0.0949$ for 25877(all data).

References

1) Yamagata, T. et al., (1997) Chem. Lett., 1215-1216.

2) Tani, K. et al., (1998) Angew. Chem. Int. Ed., 37, 3381-3383

Keywords: RHODIUM IRIIDIUM BINAP DINUCLEAR COMPLEX

SYNTHESIS AND STRUCTURAL PROPERTIES OF TRIOSMIUM CARBONYL CLUSTERS CONTAINING OXIME LIGANDS

J. S.-Y Wong W.-T. Wong

The University of Hong Kong Department of Chemistry Rm 508, Department of Chemistry, The University of Hong Kong Pokfulam Road HONG KONG NIL HONG KONG

The coordination chemistry of oxime has been well documented. Metal clusters containing oximato ligands are also known, however, their chemical properties have not been well developed. The reactivity of oximes towards triosmium clusters is one of our current interests. Treatment of a CH₂Cl₂ solution of $[\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2]$ with phenyl 2-pyridyl ketoxime at ambient conditions afforded the bridging oximato clusters $[\text{Os}_3(\text{CO})_8\{\mu\text{-hepto3-ON}=\text{CPh}(\text{NC}_5\text{H}_4)\}_2]$ 1 and $[\text{Os}_3(\mu\text{-H})(\text{CO})_6\{\mu\text{-hepto3-ON}=\text{CPh}(\text{NC}_5\text{H}_4)\}_2]$ 2 in moderate yields. Red rod-shaped crystals of 1 suitable for X-ray analysis were obtained by slow evaporation from a n-hexane-CH₂Cl₂ solution. Cluster 1 consists of an open triosmium triangle with two oximato ligands spanning the open Os-Os edge [3.59 Å] via the N-O group in a μ-hepto2 fashion. The molecule of 1 contains two oximato ligands which chelate to the metal core in a μ-hepto3 manner. The ligand is bound to the cluster by coordination of the nitrogen lone pair and the oximato oxygen and nitrogen atoms. The oximato oxygen atoms span to the neighboring metal centre over the open metal-metal edge. An interesting aspect of the structure of 1 is its molecular packing. The molecules are spatially arranged in a rarely observed manner and are packed together to form a shape of Arabic number 8 with two right-hexagonal holes [vertex to vertex distance ca. 18.4 Å].

Keywords: TRIOSMIUM CLUSTERS, OXIME, N-O CLEAVAGE

CHANGE OF THE COORDINATION MODE IN QUINAZOLINE-BRIDGED COPPER COMPLEX

M. Yasui M. Iegaki D. Hashizume F. Iwasaki

The Univ. of Electro-Communications Dept. of Applied Physics and Chemistry 1-5-1 Chofugaoka CHOFU-CITY TOKYO 182-8585 JAPAN

Some Cu(II) transition complexes, coordinated by pyrimidines or related compounds which have meta-coordination positions, showed magnetic interactions (Ishida and Nogami 1997). Crystal structure analyses revealed that the one-dimensional polymer structures bridged via meta-N ligands on the axial-equatorial position are essential for the ferromagnetic properties (M. Yasui et al., 2001). In the case of $[\text{Cu}(\text{hfac})_{(\text{qz})}]$, where qz=quinazoline and hfac=1,1,1,5,5,5-hexafluoropentane-2,4-dionate, the coordination mode of the meta-N atoms is an axial-axial at room temperature. The bond lengths around the Cu1 atom are significantly changed at 120 K, that is, N1-Cu1 2.182 to 2.043 and O1-Cu1 2.070 to 2.189 Å, while N2-Cu2 and O2-Cu2 remain unchanged. Thus the coordination mode is an axial-equatorial at 120 K. No evidence of the first-order transitions was observed from DSC and the lattice constants. The expansion coefficient of the lattice volume, however, changed at about 210 K. This corresponds that the structural transition is a second-order. The detailed temperature-dependent structure analyses showed that Cu1-O1 and Cu1-N1 lengths changed gradually and the coordination modes were changed at 255 K. The analysis of the rigid-molecular vibration of the quinazoline moiety revealed that these gradual changes ascribed to the molecular rotation of the quinazoline ring.

References

Ishida, T. and Nogami, T. (1997). Recent Res. Dev. Pure Appl. Chem. 1, 1-15.

Yasui, M., Ishikawa, Y., Ishida, T., Nogami, T. and Iwasaki, F. (2001). Acta Cryst. B57, 772-779.

Keywords: COPPER COMPLEX RIGID BODY ANALYSIS TEMPERATURE DEPENDENT STRUCTURE ANALYSIS