SYNTHESIS AND STRUCTURAL PROPERTIES OF TRIOSIUM CARBONYL CLUSTERS CONTAINING OXIME LIGANDS

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Abstract: The coordination chemistry of oxime has been well documented. Metal clusters containing oximato ligands are also known, however, their chemical properties have not yet been well developed. The reactivity of oximes towards triosmium clusters is one of our current interests. Treatment of a CH₂Cl₂ solution of [Os₃(CO)₁₀(NCMe)₂] with phenyl 2-pyridyl ketoxime at ambient conditions afforded the bridging oximato clusters [Os₃(CO)ₓ(μ-hepto-3-ON=CPh(NCMe)₂)]₁ and [Os₃(μ-H)(CO)ₓ(μ-hepto-3-ON=CPh(NCMe)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-heptao-2 fashion. The molecule of 1 contains two oximato ligands which chelate to the metal core in a μ-heptoo-3 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 n with two right-hexagonal holes [vertex to vertex distance ca. 18.4 Å].

Keywords: TRIOSIUM CLUSTERS, OXIME, N-O CLEAVAGE


SYNTHESIS AND STRUCTURE OF THE DINUCLEAR RHODIUM-BINAP COMPLEX

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Abstract: Although group 9 transition metal complexes of a general formula eM(dpiphosphine) (M = 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 such species in situ. The neutral rhodium complex II was prepared as an air-stable product from [RhCl(dpiphosphine)] (dpiphosphine = BINAP (2,2'-ηηηf-binaphthyl) (Ia), or BPBP (2,2'-ηηηf-biphenyl) (Ib)) as extremely air-sensitive complexes. These complexes Ia and Ib reacted easily with methanol and water to give the oxidative addition products. However, the structure of [RhCl(binap)] has not been determined. We herein report structure determination of [RhCl(S-binap)] (I). The neutral rhodium complex II was prepared as an air-stable product from [RhCl(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 Rh₃ (μ-Cl) - core shows a bent geometry with a hinge angle of 126.08(3)° [cf. [IrCl(RR-binap)] solvated by [IrCl(1)] (Ir₁ 123.9(1)°)]. The whole structure is very similar to that of [IrCl(1)] (Irbinap)]. The ²³⁷Pr NMR shows a doublet signal at δ 49.5 (d, JPr= 196 Hz). Different from complexes Ia and Ibb, complex II does not react with protic molecules (H₂O, MeOH, etc.).

Keywods: RHODIUM IRIDIUM BINAP DINUCLEAR COMPLEX


CHANGE OF THE COORDINATION MODE IN QUINAZOLINE-BRIDGED COPPER COMPLEX

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Abstract: 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 [Cu(fac)(μ₃-O)], where fac=quinazoline and fac=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 2.315 Å and O1-Cu1 1.949 to 1.992 Å. No electronic phase transition was observed from DSC and the lattice constants. The expansion coefficient of the lattice volume, however, changed between 120 K and 200 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.

Keywords: COPPER COMPLEX RIGID BODY ANALYSIS TEMPERATURE DEPENDENT STRUCTURE ANALYSIS