Preparation of a New Ruthenium Formato Complex

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Several ruthenium acetato complexes have been prepared by various methods.[1-3] Recently, T. A. Stephenson and G. Wilkinson prepared crystalline complexes with the formula $Ru_2(OCOR)_4Cl$, (R = Me, Et, *n*-Pr); those complexes contain two ruthenium atoms of the formal oxidation state of II and III.[3] These complexes have high magnetic moments over the temperature range of 300—100°K and appear to be the first spin-free complexes of ruthenium.

We have prepared independently the formato and acetato complexes of ruthenium, $Ru_2(HOCO)_4Cl$ and $Ru_2(CH_3OCO)_4X$ (X=Cl, Br, I),[4] by the reaction in a sealed tube of ruthenium (III and IV) chloride with formic and acetic acid solutions respectively.

The formato complex prepared is a black-brown crystal and is not dissolved in any common organic solvents except the alcohols. The infrared spectra of this complex are similar to those of hydrous Cu(II) formate.[5] However, the absorptions of the carboxyl-stretching vibrations of the ruthenium formato complex shift to a lower wave number region compared with those of Cu(II) formate. The degree of the separation of antisymmetric (ω_2) and symmetric (ω_1) carboxyl stretching frequencies in an acetato complex where acetate functions as a bidentate-bridging group may be expected not to be greatly different from that in a free acetate ion.[6] Consequently, the separation between ω_2 and ω_1 in the ruthenium formato complex (about 150 cm^{-1}) suggests that the complex has four bidentate formates. No absorptions due to the OH or the OH_2 group were found in the infrared spectra. The magnetic moment of this complex is 2.92 B.M. per ruthenium atom. This value is similar to those for $Ru_2(CH_3OCO)_4X$[4] and $Ru_2(OCOR)_4Cl$[3] at room temperature and is higher than the magnetic moments of ruthenium d^5 spin-paired complexes.[7]

These findings, along with the molecular weight, suggest a dimer structure, $Ru_2(HOCO)_4Cl$, for the formato complex prepared; the complex is considered to be of a type similar to the acetato complex previously reported.[3]

Experimental. Ruthenium trichloride trihydrate (300 mg) was dissolved in 3 M formic acid (5 m*l*) and was gently heated for about 60 min in a sealed tube. The solution thus obtained was transferred to a porcelain dish and concentrated on a water bath to produce crystals. The crude product was dissolved in a 3 M formic acid solution; this solution was evaporated at room temperature for several days to obtain the crystalline product. The crystals were washed with water and ethanol in turn, and dried *in vacuo*.

Found: Ru, 48.47; Cl, 8.09; C, 11.7%; mol wt, 423. Calcd for $Ru_2(HOCO)_4Cl$: Ru, 48.38; Cl, 8.50; C, 11.50%; mol wt, 417.5.

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