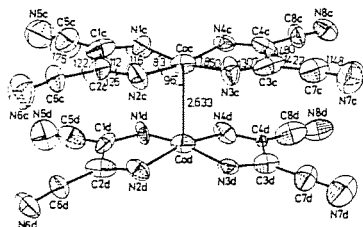


09.5-10 METAL-METAL BONDING OF THE LATER TRANSITION METAL IONS IN HIGH OXIDATION STATES. By D. Liaw, M. Tang, Y. Su, and S. Peng, Dept. of Chemistry, National Taiwan University, and Institute of Chemistry, Academia Sinica, Taipei, Taiwan, Republic of China.

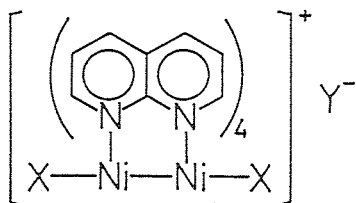
Two unique examples of this type of complexes will be studied. (1) The blue binuclear complex, 1, which can be obtained from diaminomaleonitrile with $\text{Co}(\text{OAc})_2$, followed by oxidation with O_2 , exhibits a strong Co-Co σ -bond and a δ -bond between the two parallel semidiiminosuccinonitrile ligands, (S. Peng, D. Liaw, Y. Wang, A. Simon, *Angew. Chem., Int. Ed.*, 24(1985), 210.)



1

The results of molecular orbital calculations by X_α and Extended Huckel methods will be presented. The electrochemical property of 1 will be discussed.

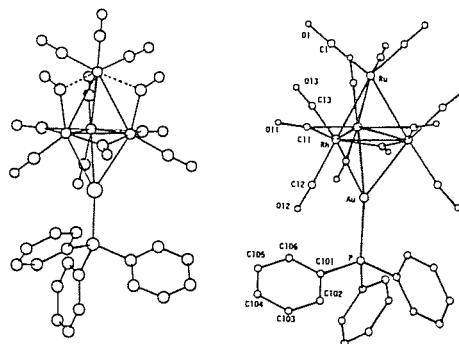
An interesting series of dimeric complexes of the general formula $[\text{Ni}_2(\text{napy})_4\text{X}_2]\text{Y}$ ($\text{X} = \text{halide}, \text{NCS}^-, \text{NO}_3^-$, $\text{Y} = \text{PF}_6^-, \text{B}(\text{C}_6\text{H}_5)_4^-$) has been isolated in which the nickel has the oxidation state of +3/2. (L. Sacconi, C. Mealli, D. Gatteschi, *Inorg. Chem.*, 13(1974), 1985.) A series of structure with different X will be presented. The axial ligand effect on the metal-metal bonding and electrochemical property will be discussed.



09.5-11 STRUCTURAL CHARACTERIZATION OF THE MONOCLINIC FORM OF $\text{Ph}_3\text{PAuRh}_3\text{Ru}(\text{CO})_{12}$ AND ITS CUBIC FORM WITH $\text{Ru}_3(\text{CO})_{12}$

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As a part of the study of structures and properties of the mixed-metal clusters of the iron and cobalt groups containing the triphenylphosphinegold(I) moiety, the X-ray crystal structure analyses of $\text{Ph}_3\text{PAuRh}_3\text{Ru}(\text{CO})_{12}$ (I) and $\text{Ph}_3\text{PAuRh}_3\text{Ru}(\text{CO})_{12} \cdot 1/2\text{Ru}_3(\text{CO})_{12}$ (II) have been performed. The compound was prepared in 30% yield from $\text{HRuRh}_3(\text{CO})_{12}$, where the hydride ligand was removed by KH before the addition of Ph_3PAuCl . The products were separated chromatographically before crystallization, which led to two different crystal forms of the derivative. The form I crystallizes in space group $P2_1/c$ with $a=8.971(1)$, $b=22.501(3)$, $c=17.191(3)$ Å, $\beta=102.97(1)^\circ$, $V=3381.6$ Å³, $D_x=2.37$ gcm⁻³ and $Z=4$. The final $R=0.027$ for 2667 reflections. The form II crystallizes in cubic space group $\text{Pa}3$ with $a=20.647(3)$ Å, $V=8801.3$ Å³, $D_x=2.30$ gcm⁻³ and $Z=8$. The final $R=0.033$ for 1119 reflections. The both crystals were measured on a Enraf-Nonius CAD4 diffractometer using graphite monochromatized MoK α radiation. In the two crystals $\text{Ph}_3\text{PAuRh}_3\text{Ru}(\text{CO})_{12}$ molecules are basically similar the metal atoms forming a trigonal bipyramidal core. According to ³¹P NMR studies the Rh atoms are in the equatorial positions. In the both structures the axial Ru atom contains three terminal carbonyl ligands and the equatorial Rh atoms are bridged by three carbonyls. The molecular symmetry of the form I is lowered to C_1 (C_3 for the form II) by two $\text{Ru}(\mu\text{-CO})\text{-Rh}$ semibridges. There are also significant differences in the metal-metal bond lengths between the two forms. Moreover the crystals of II contain $\text{Ru}_3(\text{CO})_{12}$ molecules, which are disordered over the centre of symmetry.



Molecular structures of $\text{Ph}_3\text{PAuRh}_3\text{Ru}(\text{CO})_{12}$ in I and II.