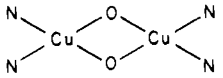
the angle Cu–O–Cu is 102.50 (8)°. These values suggest the possibility that a relatively strong antiferromagnetic interaction operates between the Cu(II) ions.[12] In fact, the magnetic moments were 0.87 μ_B at 299 K and 0.19 μ_B at 81 K.[13] No ESR signal was observed in DMF solution at liquid nitrogen temperature.

A DMF solution of the complex shows three electronic absorption bands at 13.7×10^3 ($\epsilon = 340$), 16.6×10^3 ($\epsilon = 320$), and 25.4×10^3 cm^{-1} ($\epsilon = 2200$). The spectrum was essentially the same as a solid-state absorption spectrum in Nujol mull, indicating that the coordination geometry remains unchanged in solution. Two bands at lower energy are assigned to d–d transitions. It has been reported that binuclear copper(II) complexes having the



chromophore show a characteristic band at (24–29) $\times 10^3$ cm^{-1} associated with a $p\pi(O) \rightarrow d_{x^2-y^2}(Cu)$ transition.[14] This binuclear band corresponds to the absorption at 25.4×10^3 cm^{-1}.

Further characterization and study on the related chemistry are in progress.

Acknowledgment. The authors thank Professors S. Kida and H. Okawa for magnetic susceptibility measurements.

Registry No. Me_6[22]dieneN_4·$2HClO_4$, 86012-79-5; *meso*-Me_6-[22]aneN_4, 86012-80-8; *rac*-Me_6[22]aneN_4, 86087-12-9; [Cu_2-(Me_6[22]aneN_4)$(OCH_3)_2$]$(ClO_4)_2$, 85995-18-2; Me_6[20]dieneN_4·$2HClO_4$, 85995-23-9; Me_6[26]dieneN_4·$2HClO_4$, 85995-25-1; Me_6-[34]dieneN_4·$2HClO_4$, 85995-27-3; Me_6[20]aneN_4, 85995-28-4; Me_6[26]aneN_4, 85995-29-5; Me_6[34]aneN_4, 86012-81-9; hexamethylenediamine dihydroperchlorate, 41195-09-9; hexamethylenediamine, 124-09-4; acetone, 67-64-1; pentamethylenediamine hydroperchlorate, 85995-19-3; octamethylenediamine hydroperchlorate, 85995-20-6; dodecamethylenediamine hydroperchlorate, 85995-21-7.

Supplementary Material Available: Tables of atomic coordinates of non-hydrogen atoms and bond lengths and angles and a stereoview of the molecular structure (3 pages). Ordering information is given on any current masthead page.

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Localized Ion States in the Valence Photoelectron Spectra of Mixed-Metal Carbonyl Sulfide Clusters

Sir:

Advances in the field of cluster chemistry in the past decade have been substantial, and numerous reviews have appeared discussing their unique chemical and structural properties.[1] These compounds are of additional interest because of the possible similarities between chemisorption on transition-metal surfaces and the chemistry of transition-metal clusters.[2] Two important catalytic aspects of the interaction between metals and sulfur are the effectiveness of sulfur as a catalyst poison and the importance of metal sulfides for hydrodesulfurization.[3] In our previous work we have found that the combination of photoelectron (PE) spectroscopy has proven useful in elucidating the electronic structure of cluster systems.[4]

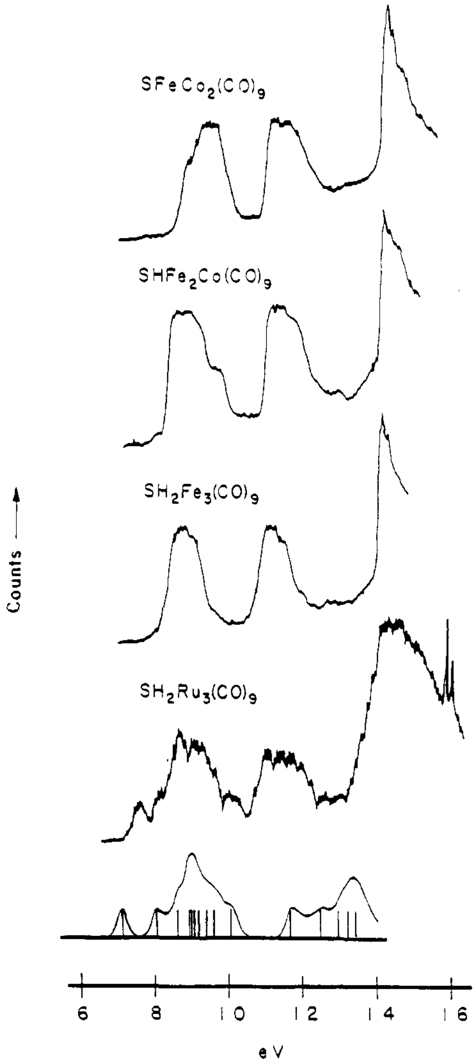

Figure 1. Partial photoelectron spectra for $SFeCo_2(CO)_9$, $SHFe_2Co(CO)_9$, $SH_2Fe_3(CO)_9$, and $SH_2Ru_3(CO)_9$. The theoretical spectrum of $SH_2Fe_3(CO)_9$ derived from Fenske–Hall molecular orbital calculations is shown under the experimental PE spectra.

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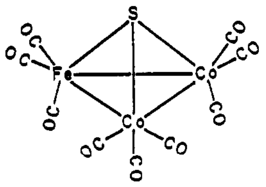
The synthesis of the first mixed-metal carbonyl sulfide cluster, $SFeCo_2(CO)_9$, was reported in 1964.[5] The X-ray crystal structure of this compound (1) confirmed that the



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geometry consists of a triangle of metal tricarbonyl fragments capped by the sulfur atom.[6] The structure of the remaining clusters in the isoelectronic series can be generated from $SFeCo_2(CO)_9$ by substituting a cobalt atom with an iron-hydrogen group. The compounds were prepared as described in the literature: $SFeCo_2(CO)_9$,[5] $SHFe_2Co(CO)_9$,[7] $SH_2Fe_3(CO)_9$,[8] and $SH_2Ru_3(CO)_9$.[9] The spectra were recorded on a Perkin-Elmer PS-18, and the MO calculations were done with use of the Fenske–Hall approach.[10]

The PE spectra of these clusters, $SH_{n-1}Co_{3-n}Fe_n(CO)_9$ ($n = 1$–3) and $SH_2Ru_3(CO)_9$, are shown in Figure 1. The ionization energy (IE) range of interest spans 8–14 eV. The IE region above 14 eV will not be discussed because of the normally broad and poorly resolved bands due to the carbonyls' 5σ and 1π ionizations. Each spectrum shows two predominant bands occurring below 14 eV. The band at lower IE can be reasonably assigned to ionizations that represent metal–metal bonds and metal–carbonyl π bonds, the t_{2g}^6-like electrons of each $M(CO)_3$ fragment. The second band consists of sulfur 3p lone pairs and the mixture of energy-equivalent M–H–M and M–S interactions.[11] Our calculations show that the introduction of M–H–M interactions corresponds to a proportional decrease in M–M bonds. These results are identical with those of the work on isoelectronic pure metal–carbonyl and hydrido–metal–carbonyl clusters.[12]

There is an interesting change in the shape of the lower energy band with the Fe/Co ratio. As the Fe character increases, the lower energy side of the first band increases in peak intensity. Conversely, the higher energy portion of the first band decreases in peak intensity and completely disappears in $SH_2Fe_3(CO)_9$. Unlike the first-row transition-metal sulfides, the first and second IE bands for the Ru analogue are much broader and consist of a number of distinguishable peaks.

The theoretical spectrum of $SH_2Fe_3(CO)_9$ derived from MO calculations and Koopmans' theorem[13] is plotted at the bottom of Figure 1. The theoretical spectrum is very similar to the spectrum of the $SH_2Ru_3(CO)_9$ cluster but dissimilar to the spectrum of the $SH_2Fe_3(CO)_9$ cluster. The IE's predicted by using Koopmans' theorem and calculations for the first-row transition-metal clusters, which are spread over a large energy range, do not match the experimental IE's. Even the experimental spectra of $SH_2Fe_3(CO)_9$ and $SH_2Ru_3(CO)_9$ are surprisingly different. Some of this difference is expected since second-row transition metals have larger ligand field splittings because of the large spatial extent of the 4d orbitals.

Calculations on the neutral Fe–Co clusters suggest delocalized bonding with mixing between the Fe and Co orbitals. However, the spectra appear to consist of discrete regions. Furthermore, the magnitude of the IE gap between the peak maxima of Co (9.4 eV) and Fe (8.5 eV) suggests little mixing between Fe and Co in the ionic states. The shape and splitting of the first band is most easily explained by assuming both Fe and Co valence electrons are localized upon ionization. Thus, the $FeCo_2$ cluster has an Fe peak followed by a Co peak of twice the intensity. The Fe_2Co cluster then has a strong Fe peak followed by a Co peak of half the intensity. Finally, the Fe_3 cluster has a narrow band consisting of only Fe-localized ionizations.

The metal–metal interactions for first-row transition metals are weaker and less diffuse than for Ru; therefore, the Co and Fe valence electrons are more likely to localize upon ionization than are those of Ru. If the first-row transition metal's valence electrons do localize upon cluster ionization, then one can explain why the Ru spectrum corresponds more closely to the theoretical spectrum than the Fe analogue. The observed differences between Fe and Ru spectra cannot be explained as spin–orbit or simple (delocalized) relaxation energy effects. The intraatomic relaxation, as opposed to the delocalized extraatomic relaxation, is expected to be the largest for the removal of an electron from a localized orbital because the remaining electron density flows toward the localized hole.[14] Furthermore, this relaxation energy should be larger for the compact 3d subshell in first-row transition metals than for the more diffuse 4d subshell in second-row transition metals.

The idea that the remaining electrons localize upon ionization of one of them is not new. In core ionizations it is common to view this as localization of a "hole" caused by removal of one electron.[15,16] An excellent discussion of the localization of the 1s core holes in O_2^+ has recently been presented.[16] Localized holes have also been postulated for the N lone-pair ionizations of $Se(CN)_2$.[17] Similar situations have been found for ionization and other excitation phenomena occurring in the valence shells.[17] Analogous results have also been found for valence ionization in Ni and Cu clusters.[18] Recent ab initio SCF calculations indicate that the 3d hole, but not the 4s hole, in Cu_2^+ is localized with the localized state having lower energy than the delocalized state.[19] Localized metal orbitals were also invoked to obtain an agreement between PE spectra and ab initio calculations on ions of some dinuclear transition-metal complexes.[20] Hence, it is not surprising that the localization of metal electrons upon ionization should occur even in larger transition-metal carbonyl clusters. Although localization of the hole, valence or core, often appears to break the symmetry of the molecule, the symmetry can be recovered by taking appropriate linear combinations of resonance structures or by using a multi-

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configuration self-consistent-field wave function.[16]

The failure of Koopmans' theorem for molecules with first-row transition-metal atoms is well documented.[14] It remains to be seen if this failure also includes the localization of the 3d hole in multinuclear compounds. This work presents the first direct experimental evidence, from the band shapes of the mixed-metal clusters, that this does occur. Although the concept of localization upon ionization provides a simple and unified explanation of several experimental and theoretical observations, it remains to be seen if this is the only explanation.

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Registry No. $SFeCo_2(CO)_9$, 22364-22-3; $SHFe_2Co(CO)_9$, 78547-58-7; $SH_2Fe_3(CO)_9$, 78547-62-3; $SH_2Ru_3(CO)_9$, 32574-35-9.

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Articles

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Polymorphism in Low-Dimensional Materials: X-ray Diffraction Studies on the Temperature Dependence of the Structure of α-Bis(1,2-benzoquinone dioximato)palladium(II)[1]

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X-ray diffraction studies on the structure of the α-form of bis(1,2-benzoquinone dioximato)palladium(II), α-$Pd(bqd)_2$, are reported. Detailed analyses of the structure at 295 and 122 K are presented. At 110 K a second-order phase transformation is observed and results in a commensurate supercell structure ($a' = a$, $b' = 4b$, $c' = c$) below the phase transition. Analysis of diffraction data collected at 76 and 19.5 K indicates that the superstructure results from both translation and rotation of the molecules and can be described in terms of a transverse modulation wave with a maximum displacement of 0.84 Å at 19.5 K. A model for the full supercell structure at 19.5 K has been developed and refined on the basis of superlattice intensity measurements.

Introduction

Structural phase transitions in quasi-one-dimensional inorganic and organic materials have been the subject of numerous physical, theoretical, and structural investigations.[2] As a phase transformation at a finite temperature reflects three-dimensional ordering, the evolution of a phase transition in these systems is sensitive to interchain coupling. In this respect, the phase transition in the prototypical inorganic compound $K_2Pt(CN)_4Br_{0.3}\cdot 3H_2O$ (KCP) is incomplete, with longitudinal and transverse correlation lengths of ~300 Å (about 100 Pt–Pt distances) and ~80 Å (about 9 interchain separations), respectively.[3] The absence of long-range transverse order in the longitudinally modulated low-temperture phase of KCP results from severe disorder in the charge-compensating halide anions and the solvent water molecules.[3]

The range of inorganic solids with quasi-unidimensional structural and electrical properties has been extended recently through the synthesis of the bis(1,2-dione dioximato)metal complexes of Ni(II), Pd(II), and Pt(II).[4] One interesting case arises with the complex $Pd(bqd)_2$ (Figure 1), where bqd is the chelating ligand 1,2-benzoquinone dioximate. Upon addition of a halogen such as I_2, this compound is partially oxidized to form a charge-transfer system[4f,i] with physical properties reminiscent of those displayed by KCP.[3]

The unoxidized $Pd(bqd)_2$ complex crystallizes in two polymorphic modifications at room temperature. In the α-form (orthohombic), the planar coordination complexes are stacked directly upon one another with their molecular planes rigorously perpendicular to the chain propagation direction.[5] In the β-form (monoclinic), the normals to the molecular planes

Table I. Crystallographic Data for α-$Pd(bqd)_2$ Prior to the Phase Transition

$Pd(C_6H_5N_2O_2)_2$, fw 380.63 $Z = 4$
orthorhombic, space group *Ibam* (D_{2h}^{26}) μ(Mo Kα) = 14.42 cm^{-1}

	295 (1) K	122 (1) K
a, Å	20.670 (3)	20.652 (3)
b, Å	9.737 (2)	9.709 (2)
c, Å	6.395 (1)	6.306 (1)
V, Å^3	1287.1	1264.4
density (X-ray), g cm^{-3}	1.964	2.000

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