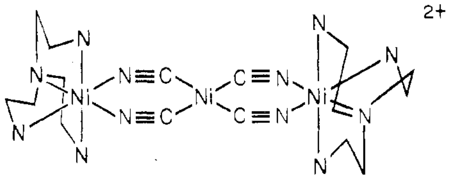
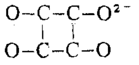
$(tren)_2(CN)_4]X_2$ compounds and for all four compounds a strong $\nu(CN^-)$ band was seen at 2160 ± 2 cm^{-1}. The constancy of position again speaks to having a common $Ni_3(tren)_2(CN)_4^{2+}$ cation. It is interesting that $\nu(CN^-)$[10] for $K_2Ni(CN)_4$ is 2135 cm^{-1}, which is appreciably lower energy than observed for our compounds. If there is a $Ni(CN)_4^{2-}$ moiety in our compounds and if it is bridging between $Ni(tren)^{2+}$ moieties, $\nu(CN^-)$ would be expected to increase in energy over that for "free" $Ni(CN)_4^{2-}$. It is possible to make a compound approximating to $[Ni_3(tren)_2(CN)_4](CN)_2$ and this compound has a second CN^- band at 2140 cm^{-1}. In view of the above structurally characterized systems the probable structure for $Ni_3(tren)_2(CN)_4^{2+}$ is as shown in the following drawing:



The octahedral geometry about the $Ni(tren)^{2+}$ moieties is also supported by the appearance of a series of tren ir bands in the 1100–1400 cm^{-1} region which we have found[11] to be indicative of the effective symmetry of the tren ligand and thereby the metal coordination environment.

The above proposed structure for the $Ni_3(tren)_2(CN)_4^{2+}$ cation leads to two expectations as far as magnetic susceptibility is concerned. First, only two of the three nickel atoms are paramagnetic. Second, from our work[5] on oxalate and squarate



bridged nickel(II) dimers it might be anticipated that the $Ni(CN)_4^{2-}$ bridge would support a weak antiferromagnetic interaction between the $Ni(tren)^{2+}$ centers. Both of these expectations are realized in the variable-temperature magnetic susceptibility data illustrated in Figure 1; see Table II[4] for data and theoretical fitting for $[Ni_3(tren)_2(CN)_4](ClO_4)_2$. The effective magnetic moment μ_{eff} for this compound at 283°K is seen to be 4.49 BM. Assuming that all three nickel atoms contribute equally to the susceptibility gives (division by $3^{1/2}$) a nonsensical 2.59 BM per Ni(II). If one nickel is assumed to be diamagnetic, then the other two nickel(II) centers have μ_{eff} = 3.19 BM, which is very reasonable for a cis-disubstituted $Ni(tren)^{2+}$ moiety.[11] The presence of an antiferromagnetic interaction in the $Ni_3(tren)_2(CN)_4^{2+}$ cation is also evident from the μ_{eff} vs. temperature curve in Figure 1. The μ_{eff} per molecule is relatively constant at 4.49 BM from 283 to ~40°K whereupon it decreases smoothly to 3.62 BM at 4.2°K. From our experience it is clear that this degree of attenuation in susceptibility cannot be attributed only to the effects of single-ion zero-field (*D*) interactions of an Ni(II) complex. This is substantiated, in part, by the μ_{eff} vs. temperature curve illustrated in Figure 1 for the *monomeric* compound $Ni(tren)(SCN)_2$. Least-squares fitting of the susceptibility data for $[Ni_3(tren)_2(CN)_4](ClO_4)_2$ to the theoretical equations[5] for an octahedrally coordinated nickel(II) dimer give $J = -1.0$ cm^{-1} ($-2J\hat{S}_i\cdot\hat{S}_j$ Hamiltonian), $g = 2.22$, $D = 0.001$ cm^{-1}, and an intermolecular interaction of $Z'J' = -0.01$ cm^{-1}. The magnitude of antiferromagnetic interaction in the $[Ni_3(tren)_2(CN)_4](ClO_4)_2$ system is to be compared with that observed for the oxalate-bridged ($J = -17$ cm^{-1}) and squarate-bridged ($J = -0.4$ cm^{-1}) nickel(II) dimers.[5] A more detailed analysis of the exchange mechanism awaits a single-crystal X-ray structure. Variable-temperature (4.2–283°K) data were also collected for $[Ni_3(tren)_2(CN)_4]I_2$ and were found to be very comparable with those for the perchlorate salt.

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Registry No. $[Ni_3(tren)_2(CN)_4](ClO_4)_2$, 55822-71-4; $[Ni_3(tren)_2(CN)_4]I_2$, 55822-72-5; $[Ni_3(tren)_2(CN)_4](PF_6)_2$, 55822-73-6; $[Ni_3(tren)_2(CN)_4](CN)_2$, 55822-74-7; $Ni(tren)(SCN)_2$, 55822-75-8.

Supplementary Material Available. Tables I and II (analytical and magnetic susceptibility data, respectively) will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number AIC50212Z-10-75.

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Photoelectron Spectra of $Fe(CO)_4X_2$ (X = Br, I). Transition Metal Analogs of the Methylene Halides

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The photoelectron spectra of the pentacarbonyl halides of manganese, $Mn(CO)_5X$, clearly indicate that the highest occupied molecular orbital is primarily halogen π in character.[2,3] The relative amounts of d_π and X_π character for this level have been suggested by McLean to vary with halogen, with the chloro complex presumably having more d_π than X_π character;[4] other workers have suggested a considerably smaller admixture of the d_π orbitals.[5,6] A study of the rhenium analogs, in which the variation in energy of levels described as d_π and X_π was examined and contrasted with the $Mn(CO)_5X$ results, shows that the highest filled level is indeed mainly X_π in character.[7] Hall has also offered a somewhat different interpretation of the rhenium results.[8]

We here report the photoelectron spectra of $Fe(CO)_4Br_2$ and $Fe(CO)_4I_2$ and demonstrate that the several highest filled levels are predominantly derived from X_π orbitals.

Experimental Section

$Fe(CO)_4Br_2$ and $Fe(CO)_4I_2$ were prepared according to literature methods.[9] He(I) (21.22 eV) spectra were recorded on a Vacuum Generators ESCA-2 photoelectron spectrometer operating at 40-meV resolution. The ionization chamber was maintained at room temperature. The argon line at 15.76 eV was used as a single internal standard. Samples were directly volatized in the sample chamber. Spectra were repeated several times to verify accuracy.

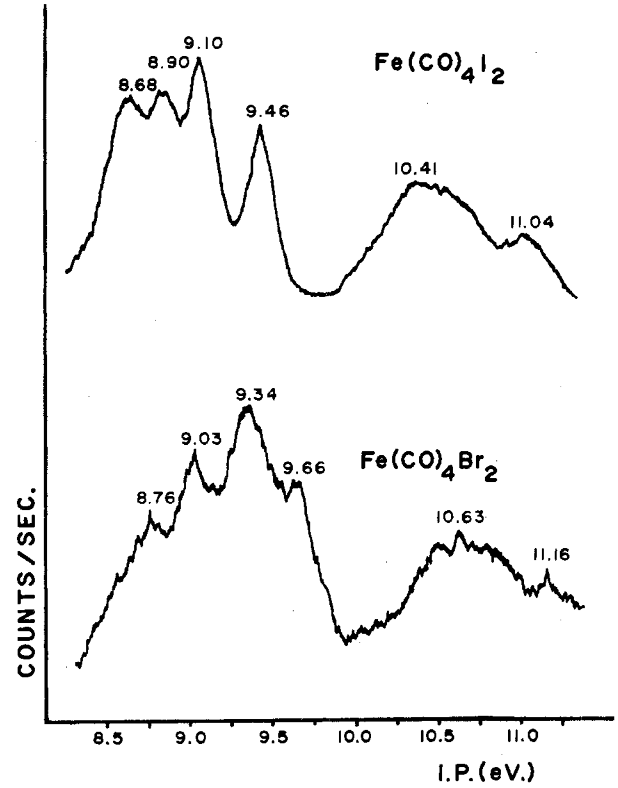

Figure 1. Ultraviolet photoelectron spectra of $Fe(CO)_4Br_2$ and $Fe(CO)_4I_2$.

Results and Discussion

Figure 1 shows the photoelectron spectra of $Fe(CO)_4Br_2$ and $Fe(CO)_4I_2$ in the range of ca. 8–11 eV. The quality of the spectrum of the bromo derivative is somewhat less than that for the iodo analog because of the lower volatility of the former. No other bands attributable to these species occur below 14 eV; these higher energy and more poorly resolved bands are assigned as ionizations from Fe–C σ levels and molecular orbitals primarily localized on the CO ligands. The first broad band and most intense band at ca. 8.5–9.5 eV in both complexes are split into four components which are assigned as ionizations from the four X_π levels (a_1, a_2, b_1, and b_2 in C_{2v}). These bands are very similar in appearance to those in the methylene halides, CH_2Br_2 and CH_2I_2,[10] with respect to band shapes and relative intensities; the broadening in the iron carbonyl derivatives relative to the methylene halide spectra is attributed to the greater number of molecular vibrations associated with the transition metal complexes. These bands are at approximately the same energy as are those associated with the X_π levels in the pentacarbonyl halides of manganese and rhenium.[7] They are also similar in appearance to the low-energy bands in the dihalosilanes and -germanes.[11]

The next two highest energy bands are assigned to an overlapping combination of the metal d orbitals (d_{xy}, d_{xz}, and d_{yz} which have symmetries a_2, b_1, and b_2, respectively) and X_σ orbitals (a_1 and b_2 for halogens in the *yz* plane). A band at ca. 10 eV observed in the pentacarbonyl halides of manganese and rhenium is absent in these iron derivatives; this is further evidence for its assignment as the metal b_2 level[7] and not the X_σ level.[3] Unfortunately, it is not presently possible to make more definitive assignments. Still, there is no question that the ionizations arising from the d orbitals are at higher energy than those in the $Mn(CO)_5X$ complexes, which is what one would predict on the basis of increased metal charge and increased atomic number.

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Registry No. $Fe(CO)_4Br_2$, 18475-84-8; $Fe(CO)_4I_2$, 14911-55-8.

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Convenient Synthesis of *trans*-Dichlorotetraamineruthenium(III) Cations

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Considerable effort has recently been devoted toward the discovery of synthetic methods for ruthenium(III) amine complexes.[1-5] The recently reported methods for diacidobis(ethylenediamine)ruthenium(III) complexes have unequivocally yielded cis compounds.[1-4] Our desire to study the photochemical and thermal substitution kinetics of *trans*-tetraamineruthenium(III) complexes has prompted us to examine a new synthetic route which we wish to report.

Although a previous attempt to prepare bis(ethylenediamine)ruthenium(III) complexes by the direct reaction of potassium aquopentachlororuthenate(III) with ethylenediamine was reported unsuccessful,[2] we repeated the method under various reaction conditions and have been successful in preparing *trans*-$[Ru(en)_2Cl_2]^+$. *trans*-$[Ru(cyclam)Cl_2]^+$ was similarly prepared by the direct reaction of $K_2[RuCl_5OH_2]$ with 1,4,8,11-tetraazacyclotetradecane (cyclam).

Experimental Section

***trans*-Dichlorobis(ethylenediamine)ruthenium(III) perchlorate (*trans*-$[Ru(en)_2Cl_2]ClO_4$)** was prepared by refluxing a mixture of $K_2[RuCl_5(OH_2)]$ (Johnson Mathey and Co., 3.8 g, 0.01 mol) and ethylenediamine (1.3 g, 0.02 mol) in methanol (300 ml) for 4 days. The reddish brown solution was then evaporated down to ca. 100 ml in a rotary evaporator and was cooled. The bright red solid which separated out was collected and washed with ethanol and ether. The perchlorate salt was prepared by dropwise addition of perchloric acid to a saturated solution of the solid, which was recrystallized from hot water. The pale orange crystals were collected and washed with ethanol and ether. They were dried under vacuum at 90°; yield 2.94 g (75%). Anal. Calcd for $C_4H_{16}N_4O_4Cl_3Ru$: C, 12.3; H, 4.0; N, 14.3; Cl, 27.3. Found: C, 12.5; H, 4.0; N, 14.6; Cl, 27.5.

***trans*-Dichloro(1,4,8,11-tetraazacyclotetradecane)ruthenium(III) chloride (*trans*-$[Ru(cyclam)Cl_2]Cl$)** was similarly prepared by refluxing a mixture of $K_2[RuCl_5(OH_2)]$ (3.8 g, 0.01 mol) and cyclam (2 g, 0.01 mol) in methanol (300 ml) for 3 days. The compound was recrystallized from 0.1 *M* hydrochloric acid (50 ml). The brown crystals were collected, washed with acetone and ether, and dried under vacuum at 100°; yield 3.0 g (75%). Anal. Calcd for $C_{10}H_{24}N_4Cl_3Ru$: C, 29.5; H, 5.9; N, 13.7; Cl, 26.1. Found: C, 29.8; H, 5.9; N, 13.7; Cl, 26.0.

Physical Measurements. Visible and ultraviolet absorption spectra