found previously for the cis isomer. In general the trans isomer hydrolyzes somewhat more slowly than the cis counterpart but the differences are not significant. In 0.1 *M* chloride ion the hydrolysis product is converted completely back into the *trans*-dichlorobis(ethylenediamine)ruthenium(III) species which is identified by its spectrum. Unlike the corresponding acid hydrolysis of *trans*-$CoCl_2en_2^+$ which is accompanied by some 35% isomerization to the cis form,[6] the trans ruthenium(III) system shows complete retention of geometry. Retention of configuration during both acid and base hydrolysis of *cis*-$RuCl_2en_2^+$ has previously been found.[3]

Registry No. *cis*-$[RuCl_2en_2]Cl$, 22294-93-5; *cis*-$[RuBr_2en_2]Br$, 55822-57-6; *trans*-$[RuCl_2en_2]Cl$, 55822-58-7; *trans*-$[RuCl_2en_2]I$, 55822-59-8; *trans*-$[RuBr_2en_2]Br$, 55870-35-4; *trans*-$[Ru(H_2O)_2en_2]^{3+}$, 55870-36-5; *trans*-$[RuClH_2Oen_2]^{2+}$, 55870-37-6.

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Magnetic Exchange Interactions in Transition Metal Dimers. VI. The Tetracyanonickelate(II) Ion as a Bridging Group

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Very recently we reported[3] the results of a single-crystal X-ray, infrared, and ESR study of $[Cu_2(tren)_2(CN)_2](BPh_4)_2$, where tren = 2,2',2''-triaminotriethylamine. It was found that the copper atom environment is trigonal bipyramidal and that the complex is dimeric by virtue of the coordinated cyanide on each copper atom hydrogen bonding through its nitrogen to a primary amine of the tren ligand coordinated to the second copper. Attempts to prepare the analogous nickel(II) complex have given complexes with the composition $Ni_3(tren)_2(CN)_4X_2$, where $X^- = ClO_4^-$, I^-, and PF_6^-. Data will be presented in this note to show the presence of an $Ni(CN)_4^{2-}$ bridging group in $Ni_3(tren)_2(CN)_4X_2$.

Experimental Section

Samples of $Ni_3(tren)_2(CN)_4X_2$ were prepared by dissolving $NiSO_4 \cdot 6H_2O$, NaCN, and tren in boiling 50% H_2O/ethanol in a 3:4:2 ratio, and then adding a boiling 50% H_2O/ethanol solution containing an excess of NaX. Cooling the resulting solution in an ice bath gave bluish purple, crystalline products. Analytical data for all compounds are given in Table I.[4]

Variable-temperature (4.2–283°K) magnetic susceptibility measurements were made with a PAR Model 150A magnetometer as described in a previous paper.[5] Infrared spectra were run with a Perkin-Elmer Model 457 spectrometer using 13 mm KBr pellets. Electronic absorption data were measured using a Cary 14 spectrophotometer; KBr pelleted samples were run and pellet dispersion was compensated by employing a pellet of ~1% $Na(BPh_4)$ in KBr in the reference beam.

Results and Discussion

Cooling a 50% H_2O/ethanol solution of Ni^{2+}, tren, CN^-, and X^- (PF_6^-, I^-, and ClO_4^-) gives a compound that analyzes as $Ni_3(tren)_2(CN)_4X_2$ as indicated by the analytical data given in Table I.[4] The fact that the $Ni_3(tren)_2(CN)_4^{2+}$ cation can be precipitated by a variety of anions, differing greatly in size, suggests that the trinickel(II) cation is a molecular species. The $[Ni_2(tren)_2(CN)_4]X_2$ compounds are not sufficiently soluble for effective molecular weight determination by vapor-pressure osmometry; however, their insolubility does support the proposal for the presence of the $Ni_3(tren)_2(CN)_4^{2+}$ cation. It seems unlikely that for the series of X^- anions used that one would isolate in each case the same collection of Ni(II) monomers.

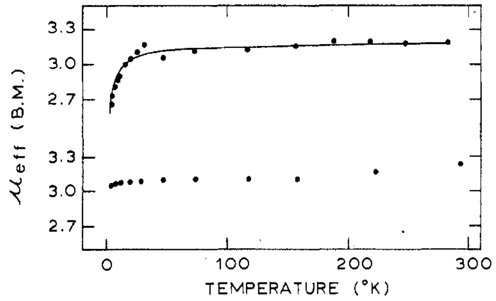
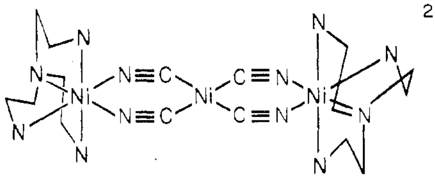


Figure 1. Magnetic susceptibility data for $[Ni_3(tren)_2(CN)_4](ClO_4)_2$ (top) and $Ni(tren)(SCN)_2$ (bottom) as a function of temperature. The data for the former are plotted as μ_{eff} per paramagnetic nickel ion and the solid line is a least-squares theoretical fit line.

Electronic absorption spectroscopy is very sensitive to the nickel(II) coordination geometry.[6] Three peaks are seen in the spectra (KBr pellets) of the $[Ni_3(tren)_2(CN)_4]X_2$ compounds in the region of ~400 to 1200 nm; the spectra show little sensitivity to the X^- counterion. The presence and appearance of the three bands are very characteristic of an octahedral nickel(II) environment. The three bands can be assigned as follows: 11,060 cm^{-1} $[^3T_{2g}(F) \leftarrow {}^3A_{2g}(F)]$, 12,580 cm^{-1} $[^1E_g(P) \leftarrow {}^3A_{2g}(F)]$, and 17,860 cm^{-1} $[^3T_{1g}(F) \leftarrow {}^3A_{2g}(F)]$, which when least-squares fit to the theoretical equations for octahedral Ni(II) give the parameters $Dq = 1106$ cm^{-1}, $B = 940$ cm^{-1}, and $C = 2750$ cm^{-1}. Thus, electronic spectroscopy implies either that all *three* nickel atoms in $Ni_3(tren)_2(CN)_4^{2+}$ have the same environment or more probably that absorptions are to be seen for only one of the nickel atom environments. From what is known about the $Ni(CN)_4^{2-}$ ion, it is reasonable at this point to speculate that one of the nickel atom environments in $Ni_3(tren)_2(CN)_4^{2+}$ approximates that in the tetracyanonickelate ion, which is known[7] to have two low intensity bands at 22,500 cm^{-1} (ϵ 2) and 30,500 cm^{-1} (ϵ 250). Both of these bands would be difficult to see because of dispersion effects associated with KBr pellets in the near-uv and uv regions. The $Ni_3(tren)_2(CN)_4^{2+}$ cation could be viewed then as two $Ni(tren)^{2+}$ moieties *bridged* by $Ni(CN)_4^{2-}$; bis-bidentate bridging would be required to secure an octahedral environment for the two $Ni(tren)^{2+}$ centers. The electronic spectrum of the μ-oxalato $[Ni_2(tren)_2(C_2O_4)](ClO_4)_2$ compound is, in fact, very similar to those for the $[Ni_3(tren)_2(CN)_4]X_2$ compounds. It is our proposal, thus, that the bridging function of the $C_2O_4^{2-}$ anion is fulfilled by the $Ni(CN)_4^{2-}$ anion. Feller and Robson[8] have reported a compound $[Ni(DPK)_2^{2+}][Ni(CN)_4^{2-}]$, where DPK = di-2-pyridyl ketone. The nickel center in the cation was shown to be octahedrally coordinated by virtue of the $Ni(CN)_4^{2-}$ acting as a bidentate ligand; there are two bridging cyanide groups. Also, very recently the single-crystal X-ray structures of a series of Hofmann-type clathrates of the composition $M(NH_3)_2Ni(CN)_4 \cdot 2C_6H_6$, where M = Ni, Cd, Cu, and Mn, have been reported.[9] In these solids there are two-dimensional networks of $[M(NH_3)_2Ni(CN)_4]_\infty$ wherein $Ni(CN)_4^{2-}$ units are bridging between $M(NH_3)_2^{2+}$ moieties with end-to-end CN^- bridging.

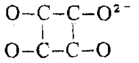
Infrared spectra (KBr pellets) were run for the [Ni3-

(tren)$_2$(CN)$_4$]X$_2$ compounds and for all four compounds a strong ν(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$$^{2+}$ cation. It is interesting that ν(CN$^-$)[10] for K$_2$Ni(CN)$_4$ is 2135 cm^{-1}, which is appreciably lower energy than observed for our compounds. If there is a Ni(CN)$_4$$^{2-}$ moiety in our compounds and if it is bridging between Ni(tren)$^{2+}$ moieties, ν(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)$_4$X$_2$ (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)$_5$X, clearly indicate that the highest occupied molecular orbital is primarily halogen π in character.[2,3] The relative amounts of d$_\pi$ and X$_\pi$ character for this level have been suggested by McLean to vary with halogen, with the chloro complex presumably having more d$_\pi$ than X$_\pi$ character;[4] other workers have suggested a considerably smaller admixture of the d$_\pi$ orbitals.[5,6] A study of the rhenium analogs, in which the variation in energy of levels described as d$_\pi$ and X$_\pi$ was examined and contrasted with the Mn(CO)$_5$X results, shows that the highest filled level is indeed mainly X$_\pi$ 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)$_4$Br$_2$ and Fe(CO)$_4$I$_2$ and demonstrate that the several highest filled levels are predominantly derived from X$_\pi$ orbitals.

Experimental Section

Fe(CO)$_4$Br$_2$ and Fe(CO)$_4$I$_2$ 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.