Naval Research. M.J.W. acknowledges a fellowship from the Alfred P. Sloan Foundation.

Registry No. $Co(NH_3)_5OAc^{2+}$, 16632-78-3; $Co(NH_3)_6$, 14695-95-5; $Ru(NH_3)_6{}^{2+}$, 19052-44-9; $Co(NH_3)_5(HCOO)^{2+}$, 19173-64-9; $Co(NH_3)_5(CCl_3COO)^{2+}$, 19998-53-9; $Co(NH_3)_5(CF_3COO)^{2+}$, 19173-66-1; $Co(NH_3)_5((CH_3)_3CCOO)^{2+}$, 33887-25-1; $Co(NH_3)_5(CH_3C(O)COO)^{2+}$, 19306-91-3; $Co(NH_3)_5(HC(O)COO)^{2+}$, 19306-90-2; $Co(NH_3)_5(CH_2OHCOO)^{2+}$, 31279-86-4; $Co(NH_3)_5(CH_3C(OH)HCOO)^{2+}$, 34464-03-4; $Co(NH_3)_5(CH_2FCOO)^{2+}$, 51965-33-4; $Co(NH_3)_5L^{2+}$ (L = cyclopentylcarboxylato), 51965-54-9; $Co(NH_3)_5L^{2+}$ (L = (cyclopentylmethyl)carboxylato), 96041-24-6; $Co(NH_3)_5L^{2+}$ (L = cyclohexylcarboxylato), 52593-65-4; $Co(NH_3)_5L^{2+}$ (L = (cyclohexylmethyl)carboxylato), 51965-55-0; $Co(NH_3)_5L^{2+}$ (L = (cyclohexylethyl)carboxylato), 96041-25-7; $Co(NH_3)_5L^{2+}$ (L = benzoato), 30931-77-2; $Co(NH_3)_5L^{2+}$ (L = benzeneacetato), 40544-43-2; $Co(NH_3)_5L^{2+}$ (L = benzenepropanato), 96041-26-8; $Co(NH_3)_5L^{2+}$ (L = benzenepropenato), 96148-95-7; $Co(NH_3)_5L^{2+}$ (L = furan-3-carboxylato), 88563-81-9; $Co(NH_3)_5L^{2+}$ (L = furan-2-carboxylato), 51965-57-2; $Co(NH_3)_5L^{2+}$ (L = furan-2-propenato), 52021-51-9; $Co(NH_3)_5L^{2+}$ (L = pyridine-3-carboxylato), 52021-52-0; $Co(NH_3)_5L^{2+}$ (L = pyridine-4-carboxylato), 58846-54-1; $Co(NH_3)_5L^{2+}$ (L = pyridine-2-acetato), 62816-16-4; $Co(NH_3)_5L^{2+}$ (L = pyridine-3-propenato), 46840-94-2; $Co(NH_3)_5L^{2+}$ (L = thiophene-2-carboxylato), 55835-99-9; $Co(NH_3)_5L^{2+}$ (L = thiophene-2-acetato), 88563-74-0; $Co(NH_3)_5L^{2+}$ (L = thiophene-2-propanato), 88563-75-1; $Co(NH_3)_5L^{2+}$ (L = thiophene-2-butanato), 88563-76-2; $Co(NH_3)_5L^{2+}$ (L = thiophene-3-carboxylato), 88563-77-3; $Co(NH_3)_5L^{2+}$ (L = thiophene-3-acetato), 88563-78-4; $Co(NH_3)_5L^{2+}$ (L = thiophene-2-propenato), 88642-97-1; Ag, 7440-22-4; Au, 7440-57-5; Hg, 7439-97-6; Cl^-, 16887-00-6.

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Magnetic, EPR, and Mössbauer Properties of an $S = {}^3/_2$ Ground State Heterotrinuclear Cluster Containing One Iron(III) and Two Copper(II) Ions

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Magnetic susceptibility data and EPR and Mössbauer spectra are reported that are attributed to formation of the heterotrinuclear cluster $[[Cu(Mesalen)]_2Fe(acac)](NO_3)_2$ ($MesalenH_2$ = *N,N′*-bis(methylsalicylaldehyde) ethylenediimine; acac = acetylacetonato). The material has not yet been isolated in crystalline form suitable for X-ray structure analysis. The magnetic data have been used to deduce the indicated structure. The Cu(II) ions are equally coupled antiferromagnetically ($J_{Cu-Fe} = -63$ cm^{-1}, $g = 2.08$) to the Fe(III) ion but are only weakly coupled ($J_{Cu-Cu} = 0$) to each other. The resulting $S = {}^3/_2$ coupled ground state is split by crystal field interactions described by a positive D term ($D = 7.2$ cm^{-1}). Only the ground doublet is EPR active, with g factors of 4.68, 3.26, and 1.96. The Mössbauer spectra at all temperatures are relaxation broadened; hence, accurate assignment of hyperfine parameters could not be made. The data for the helium temperature range show spectra consistent with an effective relaxation rate that increases as temperature is lowered. This arises from depopulation of the excited, slowly relaxing Kramers doublet with concomitant population of the more rapidly relaxing, EPR active, ground doublet.

Introduction

The magnetism of transition-metal cluster complexes is often dominated by intracluster exchange interactions that reflect important chemical bonds involving the metal atoms. Many homobinuclear and homopolynuclear metal complexes are known that display interesting magnetic properties dependent upon such exchange interactions. By contrast, the literature regarding heterobinuclear and heteropolynuclear metal clusters is much less extensive. One area of current interest involves Cu(II)–Fe(III) heterodimers, which are potential analogue compounds for a redox center of the cytochrome oxidase molecule.[2–4] These systems also raise important magnetochemical questions in which the focus is more upon the fundamental electronic properties of the compound.[5,6] In this context, we report here evidence for what appears to be the first example of a heterotrinuclear cluster containing two Cu(II) ions and one Fe(III) ion. As shown below these ions are in the present case antiferromagnetically coupled to an $S = {}^3/_2$ ground state. The complex, $[[Cu(Mesalen)]_2Fe(acac)](NO_3)_2$, noted as [2Cu-Fe] ($MesalenH_2$ = *N,N′*-bis(methylsalicylaldehyde) ethylenediimine; acac = acetylacetonato), may be described as a derivative of the $Fe(acac)_3$ complex in which two bidentate acac ligands have been replaced by two Cu(Mesalen) molecules acting as bridging bidentate ligands. Such structures have been described previously by Sinn and co-workers, who reported adducts of Cu(salen) with divalent metal complexes.[7] At present, the [2Cu-Fe] compound has not been obtained in crystalline form suitable for X-ray structure analysis. However, the combination of magnetic susceptibility and EPR and Mössbauer spectroscopy techniques clearly demonstrates the presence of exchange coupling between metal atoms, reveals certain electronic properties of the molecule, and allows predictions of structural features to be made.

Experimental Section

Synthesis. Cu(Mesalen) (0.003 mol) was dissolved in 250 mL of dichloromethane, and the solution was mixed with $Fe(acac)_3$ (0.0005 mol) and $Fe(NO_3)_3 \cdot 9H_2O$ (0.001 mol) dissolved in 50 mL of methanol. A dark purple solution resulted, which was then heated and stirred for 2 h at 40 °C. The solution was allowed to cool at room temperature, and a brown-black precipitate was obtained after 2–3 h. The precipitate was filtered, washed with dichloromethane, and dried under vacuum. Anal. Calcd for $C_{41}H_{43}N_6O_{12}Cu_2Fe \cdot 0.5CH_2Cl_2 \cdot 0.5H_2O$: C, 47.6; H, 4.3; N, 8.03; Cl, 3.39; Cu, 12.15; Fe, 5.34. Found: C, 47.43; H, 4.26; N, 8.16; Cl, 3.56; Cu, 11.96; Fe, 5.34.

Infrared Spectra. The complex was examined by standard IR methods to determine changes in bands of the reactant metal complexes and to determine characteristic bands of the trinuclear cluster; see below.

Magnetism. The magnetic measurements employed polycrystalline samples weighing about 4 mg and yielded the results shown in Figure 1. The experiments utilized a variable-temperature (4.2–300 K) Faraday-type magnetometer equipped with an Oxford Instruments continuous-flow cryostat. A negligible dependence of the susceptibility on magnetic field was observed at room temperature. The susceptibility was corrected for diamagnetism, estimated at -535×10^{-6} cm^3/mol.

EPR. The polycrystalline powder spectra (Figure 2) were recorded at X-band with use of a Bruker ER-200D spectrometer, also equipped with an Oxford Instruments continuous-flow cryostat (4.2–300 K).

Mössbauer Spectroscopy. The Mössbauer data (Figure 3) were obtained with a constant-acceleration spectrometer and source of ^{57}Co

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(1) (a) Université de Paris-Sud. (b) Oregon State University.

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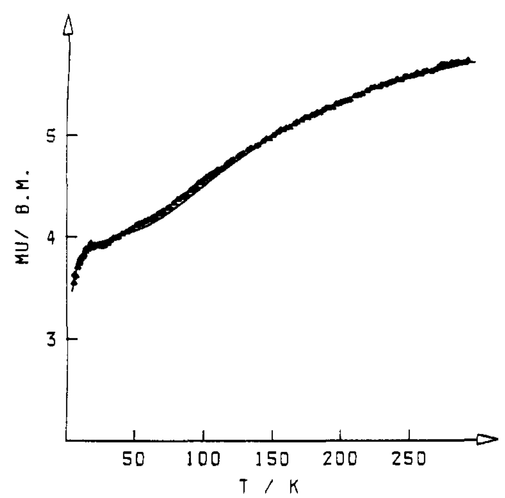

Figure 1. Magnetic moment data for the trinuclear cluster over the temperature interval 4.2–300 K. The solid line plot is the fit to the magnetic data of eq 4 and 5, according to a least-squares minimization procedure.

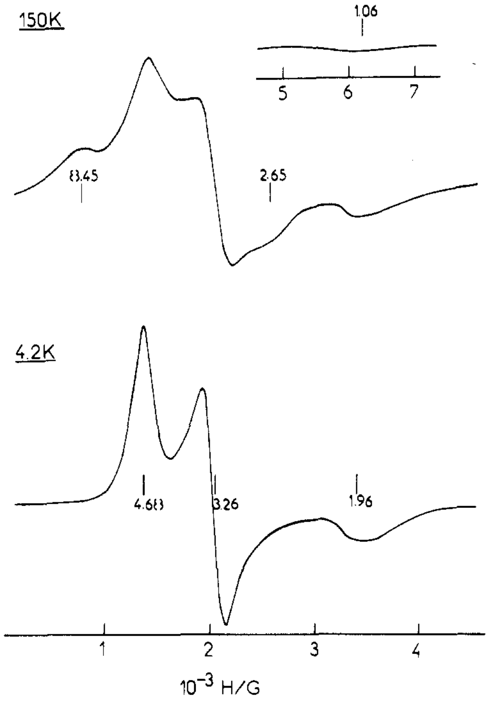

Figure 2. Electron paramagnetic resonance data for the sample temperatures 4.2 and 150 K. Effective g factors, associated with the Kramers doublet ($\pm^1/_2$) of the $S = {}^3/_2$ manifold, are 4.68, 3.26, and 1.96 for 4.2 K experiment.

diffused in rhodium metal. Absorber temperatures were 77, 4.2, and 1.3 K.

Results and Discussion

Although the crystal structure of the [2Cu-Fe] complex is not known, the magnetic and spectroscopic data are sufficient to deduce the occurrence of a magnetically coupled heterotrinuclear unit containing one Fe(III) and two Cu(II) ions. On the basis of the reactant metal complex units and the physical and chemical evidence, the new species can be described as an oxygen-bridged trimer, as shown in Figure 4. Each copper is located in the N_2O_2 site of the salen ligand, and the iron is octahedrally surrounded by four phenolic oxygen atoms from the salen groups and two oxygen atoms from the acac ligand.

Evidence for condensation of the monomeric complexes is provided by IR spectra for the Cu(Mesalen) and Fe(acac) groups in the complex. Two bands located at ν = 1530 cm^{-1} and ν = 1550 cm^{-1} are observed instead of the characteristic ν_{CO} = 1540 cm^{-1} band of the phenolic group of salen, which has been shown to be shifted to higher energy when the oxygen atoms bridge two metal atoms.[8] These two bands also happen to occur at the same positions as the ν_{CO} bands in Fe(acac)$_3$ where, however, they are much broader. An additional, spectral feature of the cluster is a new band, ν = 1480 cm^{-1}, which cannot be assigned to either of the isolated complexes and is apparently a signature of trinuclear cluster formation. Finally, the broad ν_{CO} = 930 cm^{-1} band of Fe(acac)$_3$ is split into two well-defined bands at 940 and 920 cm^{-1}.

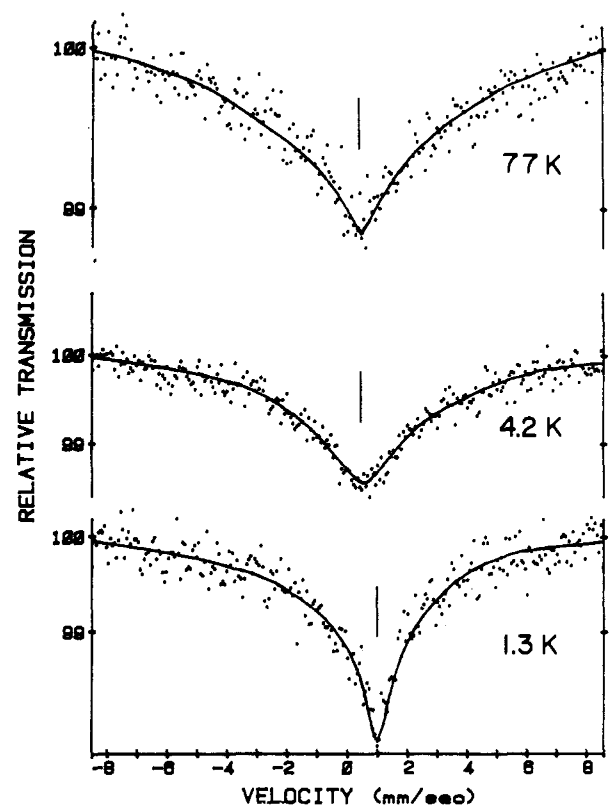

Figure 3. Mössbauer spectra for samples at 77, 4.2, and 1.3 K. Solid lines are guides to the eye: they are drawn by hand through data.

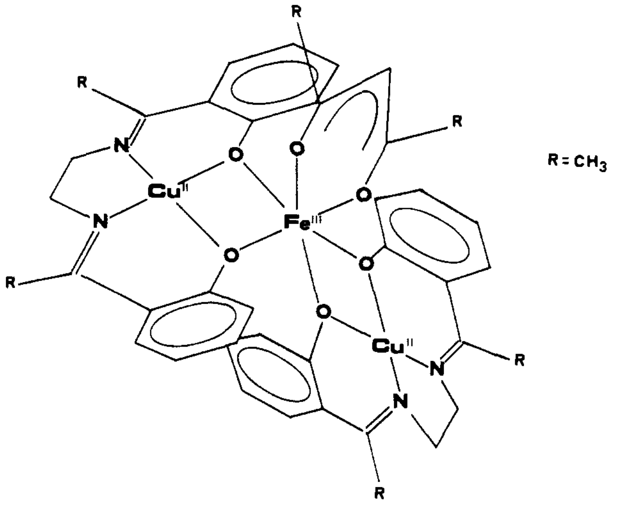

Figure 4. Assumed structure for the heterotrinuclear complex. The nitrate anions NO_3^- are omitted.

The magnetic properties of the cluster must be consistent with the presence of the constituent metal atoms: two Cu(II), each with spin $^1/_2$, and one Fe(III), with spin $^5/_2$. The possibility of magnetically independent metal ions, or ferromagnetically coupled atoms, is ruled out by the magnetic susceptibility data of Figure 1. The observed moment is much lower than one expected for either of those possibilities. Indeed, the moment of the sample

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decreases with decreasing temperature from 300 to 30 K, at which point a plateau is reached, which continues to 15 K, where a further decrease continues to the lowest temperature of the measurement, 4.2 K. Thus, below about 30 K, a Curie law is observed with an effective moment of 3.92 μ_B, which is close to the predicted value of 3.88 μ_B expected for an $S = {}^3/_2$ multiplet with $g = 2$. This magnetic behavior is easily explained as an intramolecular, antiferromagnetic coupling of the two spin ${}^1/_2$ Cu(II) ions with the spin ${}^5/_2$ Fe(III) ion to yield a minimum total spin ${}^3/_2$ ground state for the cluster. At higher temperatures, a larger effective moment is found owing to population of excited multiplets of higher spin multiplicity and larger magnetic moment. At lower temperatures, near 15 K, the moment decreases because the thermal energy kT is of the order of the zero-field splitting. The upper of the two Kramers doublets is depopulated, leaving a single Kramers level to contribute to the moment.

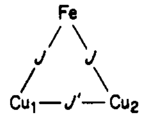
The EPR spectra are consistent with the magnetic susceptibility data. The spectra for 4.2 K show effective g factors, $g_1 = 4.68$, $g_2 = 3.26$, and $g_3 = 1.96$, very similar to those expected for a simple, single-ion level with $S = {}^3/_2$ and subject to zero-field splitting (zfs) of rhombic symmetry, such that the lower Kramers doublet ($\pm{}^1/_2$) only is resonant. This doublet yields an effective moment of 3.02 μ_B, which is just the value obtained by extrapolation of the magnetic moment data to 0 K. The anisotropy of the ground level, as reflected in the EPR data, also shows that the zfs D parameter must be positive. With increasing temperature, additional features appear in the pattern while the contribution from the ground doublet decreases in intensity. The new resonances are most pronounced at g values near 8.45, 2.65, and 1.06. The monotonic temperature dependence of these absorption regions shows that they do not originate from the upper Kramers level of the ground $S = {}^3/_2$ manifold; they are presumably associated with excited multiplets. This in turn means that the upper Kramers level is effectively nonresonant and is highly anisotropic, $g_1 >> g_2 \sim g_3 \sim 0$.

The Mössbauer spectra are consistent with the hyperfine interaction expected from levels derived from the EPR and susceptibility data. The Mössbauer spectra at 77 and 4.2 K show broad patterns characteristic of unresolved paramagnetic hyperfine structure. The maximum absorption occurs near 0 cm/s. Between 4.2 and 1.3 K, the pattern changes. At the lowest temperature there is a poorly resolved quadrupole doublet and the maximum absorption is now noticeably shifted to higher velocities. Because of the width and asymmetry of the patterns, it is difficult to determine accurately the isomer shift and quadrupole splitting. Very rough estimates of the parameters from the 1.3 K data are $\delta E = 0.5$ mm/s and $\Delta E_Q = 0.9$ mm/s (isomer shift relative to natural iron at 300 K). The main feature of these data is a sharpening of the pattern and a shift of the apparent centroid as the temperature is lowered below 4 K. This corresponds to an effective increase in electronic relaxation rate causing a partial motional narrowing of the paramagnetic hyperfine interaction. This increase of effective relaxation rate with decreasing temperature is connected with changes in population of the two Kramers levels, having markedly different magnetic anisotropies, from the $S = {}^3/_2$ ground manifold. Recall that the excited level is highly anisotropic and hence possesses rather slow electronic relaxation compared to the ground doublet, which is much less anisotropic. It is this feature that leads to a slowing down of the fluctuations of the hyperfine magnetic interactions when the excited Kramers level is substantially populated. The effect has been observed previously in hemin.[9] In that case, the $S = {}^5/_2$ manifold of Fe(III) is split into three Kramers doublets, the highest two being highly anisotropic in comparison to the ground doublet. We are not aware of a previous example of this effect being observed in a two-Kramers-level case. The present situation is complicated because the character of the levels is determined by coupled spin states. Some information about these levels is required to model transition rates for input to a relaxation calculation of spectra to compare with the data. Such calculations are in progress and will be reported separately.

The analysis may be made more quantitative by introduction of the cluster spin Hamiltonian. The necessary theory has been discussed by Kambe[10] and reviewed by Sinn.[11] Since the copper ions and especially the iron ion display spin-only paramagnetism in their ground states, we assume the intramolecular exchange coupling to be approximated by a Hamiltonian containing isotropic Heisenberg interactions: $\mathcal{H} = -\sum J_{ij}\hat{S}_i\cdot\hat{S}_j$, where J_{ij} are the effective exchange interactions for a pair of atomic spins $\hat{S}_i$ and $\hat{S}_j$. In the case of a trimer with two equivalent Cu(II) ions and one Fe(III) ion, we have

$$\mathcal{H} = -J(\hat{S}_{Cu_1}\cdot\hat{S}_{Fe} + \hat{S}_{Cu_2}\cdot\hat{S}_{Fe}) - J'\hat{S}_{Cu_1}\cdot\hat{S}_{Cu_2} \qquad (1)$$

The meaning of J and J' is indicated by the following diagram, which represents the simplest scheme consistent with the available data:

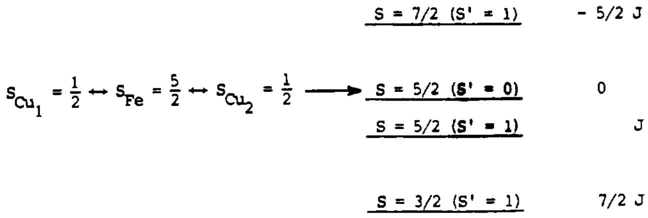


I

We will further assume that the Cu(II) ions have negligible interactions between themselves ($J' << J$). In this case, the eigenvalues of the Hamiltonian

$$\mathcal{H}_{exch} = -J(\hat{S}_{Cu_1}\cdot\hat{S}_{Fe} + \hat{S}_{Cu_2}\cdot\hat{S}_{Fe}) \qquad (2)$$

are easily calculated by using standard angular momentum theory. The procedure is to couple the equivalent copper spins $\hat{S}_{Cu_1}$ and $\hat{S}_{Cu_2}$ to a resultant spin $\hat{S}'$. $\hat{S}'$ is in turn coupled with the iron spin to yield the total spin $\hat{S} = \hat{S}' + \hat{S}_{Fe}$. The Hamiltonian of eq 2 commutes with $\hat{S}$ and $\hat{S}'$, and hence quantum numbers of these operators serve to label the eigenvalues of $\mathcal{H}_{exch}$. This is shown schematically in diagram II.



II

To complete a specification of the cluster, two additional terms are required. One is the Zeeman effect describing the interaction with the external magnetic field; the other describes interactions leading to the zfs of the total-spin multiplets. For a given spin manifold S, we have

$$\mathcal{H}_{cf} + \mathcal{H}_{Zeeman} = \hat{S}\cdot\mathbf{D}\cdot\hat{S} + \mu_B H\cdot\mathbf{g}_S\cdot\hat{S} \qquad (3)$$

with the molecular $\mathbf{g}_S$ and $\mathbf{D}$ tensors related to ionic properties of the copper and iron ions. We suppose the relative orders of the interactions to be $\mathcal{H}_{exch} >> \mathcal{H}_{cf} >> \mathcal{H}_{Zeeman}$ and in this fashion arrive at perturbation theory expressions for the magnetic susceptibility of the molecule. If the ionic g factors for both types of ions are equal and isotropic and if the temperature is large compared to the zfs, the result is

$$\chi_M = \frac{N\mu_B^2}{kT}\left(\frac{g^2}{4}\right)\frac{35 + 35e^{-J/kT} + 10e^{-7J/2kT} + 84e^{5J/2kT}}{3 + 3e^{-J/kT} + 2e^{-7J/2kT} + 4e^{5J/2kT}} \qquad (4)$$

A fit of the high temperature susceptibility data to this equation provides an estimate of the parameters J and g. This procedure subject to a least-squares minimization gave $J = -63$ cm^{-1} and $g = 2.08$ ($R = \sum(\chi_{obsd} - \chi_{calcd})^2/\sum(\chi_{obsd})^2 = 8 \times 10^{-5}$).

In the lowest temperature range (4.2–30 K), the analysis may be restricted to the ground spin multiplet. A similar calculation, now including the axial zfs parameter, leads to the expression

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$$\chi_M = \frac{N\mu_B{}^2}{3kT}\left(\frac{g^2}{4}\right)\left[9 + 12\left(\frac{kT}{2D}\right)\frac{1 - e^{-2D/kT}}{1 + e^{-2D/kT}}\right] \quad (5)$$

Again, a least-squares fit of the data yields $g = 2.05$ and $D = 7.2$ cm^{-1} ($R = 10^{-4}$).

Conclusions

The heterotrinuclear cluster described above has been shown to contain antiferromagnetically coupled Cu(II) and Fe(III) ions. The lowest multiplet has total spin $S = {}^3/_2$ and is consistent with the expected ionic spins of ${}^1/_2$ for Cu(II) and ${}^5/_2$ for Fe(III). The magnetic data can be understood in terms of a weak coupling between the copper atoms and a much stronger coupling between iron and copper atoms. This is consistent with the structure shown in Figure 4, where the copper atoms are not bridged directly but where iron and copper atoms are directly connected by bridges.

While satisfactory fits to the susceptibility data were obtained in the high- and low-temperature ranges, it is likely that improved values for the exchange and zfs parameters will be obtained by a self-consistent analysis over the entire temperature range. Likewise, the Mössbauer data require a quantitative discussion including the spin-coupled levels for the various multiplets, especially the ground manifold. These descriptions are currently being sought in order to arrive at a more detailed understanding of the magnetism of this interesting complex.

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Registry No. $[Cu(Mesalen)]_2Fe(acac)(NO_3)_2$, 96129-08-7; Cu(Mesalen), 21350-69-6; $Fe(acac)_3$, 14024-18-1.

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X-ray Photoelectron Spectroscopic Study of Trifluoromethyl Isocyanide. Back-Bonding, Fluorine Lone-Pair Ionization Potentials, and the $CF_3NC \rightarrow CF_3CN$ Isomerization Energy

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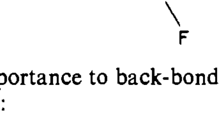
Core binding energy data for CF_3NC, $Cr(CO)_5CNCF_3$, and $W(CO)_5CNCF_3$ indicate that CF_3NC is a very strong π-acceptor ligand, practically as strong as CO. The core and fluorine lone-pair valence ionization potentials of CF_3NC and CF_3CN show that the net interaction of the fluorine lone-pair orbitals with other orbitals in these molecules is zero. The core data for CF_3NC and CF_3CN, when interpreted with the equivalent cores approximation, lead to a $CF_3NC \rightarrow CF_3CN$ isomerization energy of −23 kcal mol^{-1}.

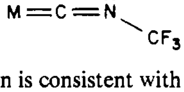
The avilability of a relatively efficient method for preparing trifluoromethyl isocyanide[2] has led to studies of the properties of this molecule,[3,4] including the use of the molecule as a ligand in transition-metal coordination compounds.[5–9] Because alkyl isocyanides are generally considered to be good π-acceptor ligands, one would expect that replacement of the alkyl group by the highly electron-withdrawing CF_3 group would produce an extremely strong π-acceptor ligand. X-ray photoelectron spectroscopy has been shown to be useful for studying the relative π-acceptor character of ligands.[10–12] With this in mind, we have obtained the gas-phase XPS spectra of CF_3NC, $Cr(CO)_5CNCF_3$, $W(CO)_5CNCF_3$, CF_3CN, and related compounds. The core binding energies are presented in Table I. The data not only give information about back-bonding in the transition-metal complexes but also allow us to predict the fluorine nonbonding lone-pair ionization potentials in CF_3NC and CF_3CN and the $CF_3NC \rightarrow CF_3CN$ isomerization energy.

Back-Bonding to the CF_3NC Ligand

The binding energies of all the atoms in the ligand CF_3NC are lower in the chromium and tungsten complexes than in the free ligand. In the case of the carbon atom of the isocyanide group this decrease upon coordination might have been expected, even if CF_3NC were not a good π-acceptor group, because of the increase in relaxation energy associated with the increased coordination number of that atom. However, the marked decreases observed for the other atoms of CF_3 constitute clear evidence for strong back-bonding. The decrease of more than 1 eV in the fluorine binding energies is particularly striking and suggests that back-bonding combined with hyperconjugation as represented by the structure



is comparable in importance to back-bonding with formation of a nitrogen lone pair:



Although this conclusion is consistent with the C–N–C bond angle of 142 (4)°, the C–F bond distance in the chromium complex is not significantly longer than that in the free ligand.[6,13–16]

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