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

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)]$_2$Fe(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$_3$NC → CF$_3$CN Isomerization Energy

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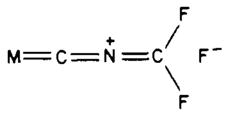
Core binding energy data for CF$_3$NC, Cr(CO)$_5$CNCF$_3$, and W(CO)$_5$CNCF$_3$ indicate that CF$_3$NC is a very strong π-acceptor ligand, practically as strong as CO. The core and fluorine lone-pair valence ionization potentials of CF$_3$NC and CF$_3$CN show that the net interaction of the fluorine lone-pair orbitals with other orbitals in these molecules is zero. The core data for CF$_3$NC and CF$_3$CN, when interpreted with the equivalent cores approximation, lead to a CF$_3$NC → CF$_3$CN isomerization energy of −23 kcal mol^{-1}.

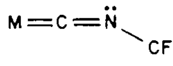
The avilability of a relatively efficient method for preparing trifluoromethyl isocyanide[2] has led to studies of the properties of this molecule,[3,4] including the use of the molecule as a ligand in transition-metal coordination compounds.[5-9] Because alkyl isocyanides are generally considered to 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$_3$NC, Cr(CO)$_5$CNCF$_3$, W(CO)$_5$CNCF$_3$, CF$_3$CN, 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$_3$NC and CF$_3$CN and the CF$_3$NC → CF$_3$CN isomerization energy.

Back-Bonding to the CF$_3$NC Ligand

The binding energies of all the atoms in the ligand CF$_3$NC 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$_3$NC 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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Table I. Core Binding Energies (eV) of CF_3NC, $Cr(CO)_5CNCF_3$, $W(CO)_5CNCF_3$, and Related Compounds

	C 1s													
	CF$_3$ group		CN group		CO group		N 1s		O 1s		F 1s		Cr 2p$_{3/2}$ or W 4f$_{7/2}$	
compd	E_B	fwhm[a]	E_B	fwhm	E_B	fwhm	E_B	fwhm	E_B	fwhm	E_B	fwhm	E_B	fwhm
CF_3NC	301.35 (3)[b]	1.27 (10)	294.28 (4)	1.74 (15)			407.97 (3)	1.26 (7)			695.53 (3)	1.83 (8)		
$Cr(CO)_5CNCF_3$	299.09 (7)	3.30 (46)[c]			292.89 (2)	1.58 (6)	405.73 (4)	1.56 (9)	539.49 (2)	1.57 (5)	694.40 (2)	1.95 (5)	581.74 (2)	1.25 (8)
$W(CO)_5CNCF_3$	299.13 (10)	2.97 (44)[c]			292.95 (3)	1.50 (10)	405.62 (6)	1.50 (16)	539.43 (3)	1.54 (9)	694.49 (2)	2.00 (6)	37.72 (3)	1.23 (6)
$BH_3{\cdot}CNCH_3$[d]							407.13 (2)	1.29 (8)						
$Cr(CO)_5CNCH_3$					292.51 (3)	1.74 (10)	405.68 (5)	1.58 (18)	538.85 (2)	1.59 (7)			581.20 (2)	1.19 (9)
$Cr(CO)_6$[e]					293.2				539.5				581.9	
$W(CO)_6$[e]					293.17				539.5				37.8	
CH_3NC[f]							406.67 (4)	1.40 (9)						
CF_3CN	300.72 (4)	1.37 (15)	293.96 (4)	1.52 (13)			407.42 (3)	1.23 (8)			695.48 (2)	1.79 (6)		

[a] Full width at half-maximum. [b] Uncertainty in last digit indicated parenthetically. [c] Band broadened by CO shake-up contributions. [d] Reference 13. [e] Jolly, W. L.; Bomben, K. D.; Eyermann, C. J. *At. Data Nucl. Data Tables* **1984**, *31*, 433. [f] Reference 19.

It is instructive to compare the differences in the nitrogen binding energies between CF_3NC and the CF_3NC complexes with the corresponding differences between CH_3NC and the complexes $BH_3{\cdot}CNCH_3$ and $Cr(CO)_5CNCH_3$. In a previous study,[17] we have shown that there is little back-bonding in $BH_3{\cdot}CNCH_3$. Hence, the nitrogen binding energy shift of +0.46 eV for this molecule can be ascribed mainly to the withdrawal of electron density from CH_3NC by the BH_3 group. The shift of −0.99 eV in the case of $Cr(CO)_5CNCH_3$ is thus clear evidence for back-bonding to the methyl isocyanide ligand. And the negative shifts of more than 2 eV in the case of the CF_3NC complexes show that CF_3NC is an extremely strong π-acceptor ligand.

From the data in Table I, it can be seen that the binding energies of the chromium atom and the carbonyl carbon and oxygen atoms of $Cr(CO)_5CNCF_3$ are markedly higher than those of $Cr(CO)_5CNCH_3$ and very similar to those of $Cr(CO)_6$. Similarly, the tungsten and carbonyl carbon and oxygen binding energies of $W(CO)_5CNCF_3$ are close to those of $W(CO)_6$. These data confirm the fact that CF_3NC is a much stronger π acceptor than CH_3NC and show that CF_3NC is practically as good a π acceptor as carbon monoxide.

Prediction of Fluorine Nonbonding Lone-Pair Ionization Potentials

By using the fluorine core binding energies of HF, CF_3NC, and CF_3CN and the fluorine lone-pair ionization potential of HF, we calculate that the fluorine lone pairs of CF_3NC and CF_3CN would have ionization potentials of 17.04 and 17.00 eV, respectively, if they were strictly nonbonding in character.[18] In fact, the four symmetry sets of the fluorine lone pairs in these molecules have varying degrees of bonding or antibonding character due to interactions of the fluorine atomic orbitals with themselves. However, the degeneracy-weighted averages of the ionization potentials of each set (17.03 and 16.91 eV, respectively[19]) are remarkably close to the values predicted for the strictly nonbonding orbitals and indicate that the net interaction of the lone pairs with other orbitals in the molecules (such as the C≡N π and π^* orbitals) is zero. We believe that this result is not a consequence of cancellation of antibonding and bonding interactions with other orbitals in the molecule, but simply a consequence of negligible overlap of the fluorine lone pairs with other molecular orbitals. The close agreement of the predicted ionization potentials and the centers of gravity suggests that the UPS assignments[4] of CF_3NC and CF_3CN are probably correct.

$CF_3NC \rightarrow CF_3CN$ Isomerization Energy

According to the equivalent cores approximation,[20] the valence electrons of a molecule are essentially equally affected by the removal of a core electron from an atom in the molecule and by the addition of a proton to the nucleus of that atom. By applying this approximation, it is possible to obtain the heats of ordinary chemical reactions from core binding energy data.[21] For example, from the carbon binding energies of CH_3NC and CH_3CN, the $CH_3NC \rightarrow CH_3CN$ isomerization energy has been estimated[22] as −30 kcal mol^{-1}, a value to be compared with the calorimet-

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(13) Back-bonding into σ^* C–F ligand orbitals is known to weaken and lengthen the C–F bonds.[14] For example, in $CF_3Mn(CO)_5$, the C–F bond length is 1.370 Å,[15] whereas in CF_3I and CF_3H it is 1.33 Å.[16]

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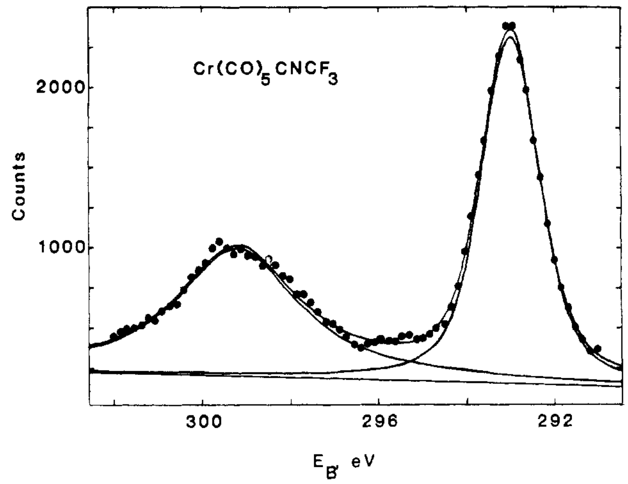

Figure 1. Carbon 1s spectrum of Cr(CO)$_5$CNCF$_3$. The primary, low binding energy peak is due to the CO groups and the isocyano carbon atom; the broad high binding energy peak is due to shake-up and the CF$_3$ carbon atom.

rically[23] measured value of -23.7 kcal mol^{-1}. In a completely analogous way, we use the carbon binding energies of CF$_3$NC and CF$_3$CN to calculate the value -23 kcal mol^{-1} for the CF$_3$NC → CF$_3$CN isomerization energy. This value is in remarkably good agreement with the value -22.8 kcal mol^{-1} calculated by the MNDO method.[4]

Experimental Section

Trifluoromethyl isocyanide was prepared by the reduction of CF$_3$NCCl$_2$ over Mg.[2] The vapor pressure at -126 °C (methyl cyclohexane slush) was 66.1 mm and did not vary with the quantity of sample vaporized. The infrared spectrum agreed with that in the literature.[2]

Pentacarbonyl(methyl isocyanide)chromium was prepared by the reaction of [N(CH$_3$CH$_2$)$_4$][Cr(CO)$_5$I] with [(CH$_3$CH$_2$)$_3$O][BF$_4$] in the presence of CH$_3$NC.[24] The compound was purified by sublimation, and its melting point, 68 °C, agreed with the literature value.[25]

The chromium and tungsten pentacarbonyl complexes of trifluoromethyl isocyanide were prepared by a literature procedure.[5] Trifluoroacetonitrile was a gift from Prof. J. Shreeve, University of Idaho.

Vapor-phase X-ray photoelectron spectra were obtained on a GCA/McPherson ESCA 36 spectrometer with a Mg anode. The method used for obtaining the calibrating spectra has been described previously.[26]

The flow of trifluoromethyl isocyanide and trifluoroacetonitrile into the spectrometer was regulated with a needle valve. The trifluoromethyl isocyanide was held at -126 °C during data collection to prevent polymerization. The organometallic compounds were sublimed directly into the spectrometer from a sample reservior held at 10 °C through a large-diameter (1.5 cm) inlet system.

The C 1s spectrum of both the chromium and tungsten pentacarbonyl complexes of trifluoromethyl isocyanide showed two well-separated peaks (Figure 1). We have assigned the narrower peak (fwhm $\approx$ 1.5 eV) at lower binding energy to the CO carbon atoms and the isocyano carbon atom of CNCF$_3$. The broad peak (fwhm > 3 eV) at higher binding energy is a composite of the peak due to the CF$_3$ carbon atom and CO shake-up. The shake-up peak/primary peak intensity ratios, after correction for the contributions to the shake-up peaks of the CF$_3$ carbon atoms, were 0.63 and 0.38 for Cr(CO)$_5$CNCF$_3$ and W(CO)$_5$CNCF$_3$, respectively. These intensity ratios may be compared with the values 0.38 and 0.27 for the comparable bands of Cr(CO)$_6$ and W(CO)$_6$, respectively.[27]

Acknowledgment. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division, U.S. Department of Energy, under Contract No. DE-A003-76SF00098. We thank Professor J. Shreeve for the sample of CF$_3$CN.

Registry No. CF$_3$NC, 19480-01-4; Cr(CO)$_5$(CNCF$_3$), 88902-50-5; W(CO)$_5$(CNCF$_3$), 88902-51-6; Cr(CO)$_5$CNCH$_3$, 33726-04-4; CF$_3$CN, 353-85-5.

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Electronic Spectra of Phthalocyanine Radical Anions and Cations

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The oxidation and reduction of metal phthalocyanines give rise to at least six oxidation states whose electronic spectra are rationalized in some depth in terms of SCF energies and Coulomb and exchange integrals. It is shown that a single set of parameters can reproduce the Q-band energies moderately well. Further, this same set of energies can reproduce differences in electrochemical potentials observed within this redox set. The pattern of variation in the Q-band energies (and in their number) now provides a means for identifying whether it is the metal or the phthalocyanine ligand that is reduced upon addition of an electron to the system.

Introduction

During the past few years, there has been considerable resurgence in interest in the chemistry of the phthalocyanines (Pc). Their high thermal and chemical stability, coupled with their extensive redox chemistry, makes them excellent candidates for electrocatalytic and photocatalytic processes.[2-5]

Our ultimate goal must be to possess sufficient understanding of the electronic structure of these molecules to be able to design catalysts to function in a specified fashion.

Recently our understanding of the electronic spectra of typical MPc complexes (containing the stable ligand oxidation state Pc^{2-}) has been extended to include charge-transfer transitions.[6] We

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