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Influence of Axial Ligation on the Spin State and Exchange Coupling in Heterotrimetallic Bis[iron(III) porphyrin]–Copper(II) Maleonitrile Triple-Decker Complexes

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Magnetic susceptibility studies on the heterotrimetallic triple-decker complex bis[(*meso*-tetraphenylporphyrinato)iron(III)] μ-bis(*cis*-1,2-dicyano-1,2-ethylenedithiolato-*S*,*S*′)cuprate(II), [Fe^{III}TPP][Cu(MNT)$_2$][Fe^{III}TPP] (**1**), and its six-coordinate analogue bis[(*meso*-(*o*-(5-(*N*-imidazolyl)valeramido)phenyl)triphenylporphyrinato)iron(III)] μ-bis(*cis*-1,2-dicyano-1,2-ethylenedithiolato-*S*,*S*′)cuprate(II), [Fe(TPP-T)][Cu(MNT)$_2$][Fe(TPP-T)] (**3**), have revealed exchange coupling between intermediate-spin ($S = {}^3/_2$) iron(III) and copper(II) in **1** and exchange coupling between low-spin ($S = {}^1/_2$) iron(III) and copper(II) in **3**. Effective exchange coupling constants of $J_{\text{Fe–Cu}}$ (−3.8 cm^{-1}) and $J_{\text{Fe–Fe}}$ (−4.5 cm^{-1}) in **1** and −4.5 and −5.9 cm^{-1} in **3** may be understood in terms of the structures of the molecules and the available superexchange coupling pathways.

Introduction

There is strong evidence that the active site of the resting form of cytochrome *c* oxidase (CcO) contains a copper(II) entity and an iron(III) heme.[1] Since there is no observable EPR signal from the ferric heme–copper(II) units, it has been proposed that the iron and copper ions are strongly exchange-coupled antiferromagnetically by superexchange through bridging ligands.[2–6] However, potential model compounds involving imidazolate and oxide bridging ligands have not exhibited magnetic properties similar to those of the enzyme.[7–12]

It has been suggested, on the basis of the results of EXAFS studies, that the iron–copper active site pair may be bridged by thiolate sulfur.[13] With this suggestion in mind, the chemistry of iron porphyrin linked with copper dithiolate complexes was explored. Treatment of (*meso*-tetraphenylporphyrinato)iron(II) with a stoichiometric amount of tetrabutylammonium bis(*cis*-1,2-dicyano-1,2-ethylenedithiolato)copper(III) in dry benzene under nitrogen results in the formation of the heterotrimetallic triple-decker complex bis[(*meso*-tetraphenylporphyrinato)iron(III)] μ-bis(*cis*-1,2-dicyano-1,2-ethylenedithiolato-*S*,*S*′)cuprate(II), [Fe^{III}TPP][Cu(MNT)$_2$][Fe^{III}TPP] (**1**).[14] Although the crystal and molecular structures of **1** are not available, the structure of the heterotetrametallic quadruple-decker complex [Cu^{III}(MNT)$_2$][Fe^{III}TPP][Cu^{II}(MNT)$_2$][Fe^{III}TPP] (**2**) has been determined,[15] and it is reasonable to conclude that the structural features of **1** are similar to those of the corresponding fragment of **2**, with one important difference. In **2**, one iron porphyrin unit is sandwiched between [Cu^{III}(MNT)$_2$]$^-$ and [Cu^{II}(MNT)$_2$]$^{2-}$, and this iron is six-coordinate with axial Fe–S distances of 2.956 Å (to [Cu^{III}(MNT)$_2$]$^-$) and 2.549 Å (to [Cu^{II}(MNT)$_2$]$^{2-}$). The second iron in the tetrametallic complex is five-coordinate. The metrical parameters of this latter, five-coordinate iron are consistent with a predominantly intermediate-spin state,[16] but the spin state of the six-coordinate iron is difficult to deduce from the structural data. Unfortunately, synthetic problems have precluded the preparation of an adequate quantity of **2** for a spin-state determination by magnetic susceptibility measurements.

The established chemistry of iron porphyrins has permitted the synthesis and characterization of an analogue of **1** that has six-coordinate iron. The new complex is bis[(*meso*-(*o*-(5-(*N*-imidazolyl)valeramido)phenyl)triphenylporphyrinato)iron(III)] μ-bis(*cis*-1,2-dicyano-1,2-ethylenedithiolato-*S*,*S*′)cuprate(II), [Fe(TPP-T)][Cu(MNT)$_2$][Fe(TPP-T)] (**3**). The results of the magnetic susceptibility studies of **1** and its six-coordinate analogue **3** are reported in this article.

Experimental Section

Synthesis. [FeTPP][Cu(MNT)$_2$][FeTPP]. In an inert-atmosphere box Fe^{II}TPP (0.154 g, 2.3 × 10^{-4} mol) and [TBA]$^+$[Cu^{III}(MNT)$_2$]$^-$ (0.136 g, 2.3 × 10^{-4} mol) were stirred together in 150 mL of benzene for 3 h at room temperature. The solution was filtered, the solid [TBA$^+$]$_2$[Cu^{II}(MNT)$_2{}^{2-}$] was washed with 10 mL of benzene, and the wash was added to the filtrate. A 300-mL quantity of heptane was added to the filtrate and the solution allowed to sit for 2 h before being filtered with suction on a medium frit. The brown-purple solid was first washed three times with 2-mL portions of CH_3NO_2 to remove any [TBA$^+$][Cu^{III}(MNT)$_2{}^-$] and [TBA$^+$]$_2$[Cu^{II}(MNT)$_2{}^{2-}$] and then once with 2 mL of benzene. The powder was dried by the suction of N_2 from the inert-atmosphere box through the frit; yield 0.104 g. Anal. Calcd for $Fe_2CuC_{96}H_{56}N_{12}S_4$: C, 68.59; H, 3.36; N, 10.00; Fe, 6.66; Cu, 3.78. Found: C, 68.52; H, 3.33; N, 9.78; Fe, 5.93; Cu, 3.85.

[FeTPP-T][Cu(MNT)$_2$][FeTPP-T]. (*meso*-(*o*-(5-(*N*-imidazolyl)valeramido)phenyl)triphenylporphyrinato)iron(II) (Fe^{II}TPP-T) was prepared by the method of Collman et al.[17] In an inert-atmosphere box Fe^{II}TPP-T (0.214 g, 2.57 × 10^{-4} mol), [TBA$^+$][Cu^{III}(MNT)$_2{}^-$] (0.16 g, 2.76 × 10^{-4} mol), and 200 mL of benzene were stirred for 2 h. The solution was filtered, and the first crop of crude solid product was obtained. Heptane (400 mL) was added to the filtrate, and the solution was allowed to sit for 24 h before a second crop of product was filtered. Each crop of dried product was washed repeatedly with small portions of CH_3NO_2 until a uniform orange-brown color was imparted to the wash (several milliliters). Each sample was dried with suction. The combined

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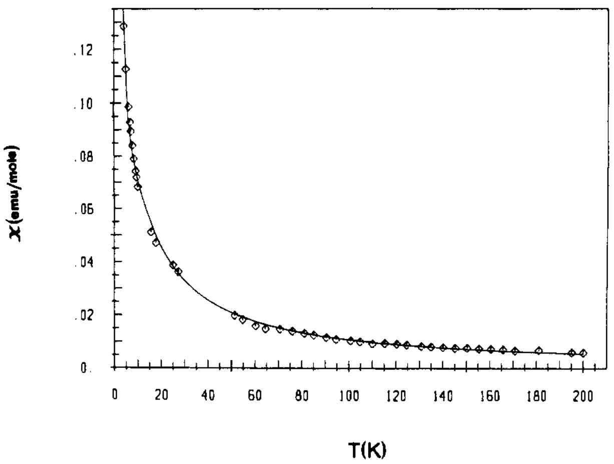

Figure 1. Magnetic susceptibility data for [FeTPP-T][Cu(MNT)$_2$]-[FeTPP-T]. The solid line is the best-fit theoretical calculation as described in the text.

yield was 0.170 g. Anal. Calcd for $Fe_2CuC_{112}H_{78}N_{18}S_4O_2$: C, 66.88; H, 3.91; N, 12.53. Found: C, 66.01; H, 3.98; N, 12.14.

Magnetic Susceptibility Measurements. Magnetic susceptibilities of finely ground powdered samples contained in Lucite sample holders were measured at 1.0 T by using a Princeton Applied Research Model 155 Foner-type[18] vibrating-sample magnetometer as described previously.[19] The magnetometer was calibrated with $HgCo(NCS)_4$,[20] and the experimental magnetic susceptibility data were corrected for the diamagnetism of constituent atoms by using Pascal's constants[21] and Eaton and Eaton's correction for TPP^{2-}.[22]

Mössbauer Measurements. The Mössbauer spectrometer was of the constant-acceleration type and was operated in connection with a 256-channel analyzer in the time scale mode. The source was ^{57}Co diffused in rhodium and was kept at room temperature at all times. Spectra were recorded in horizontal transmission geometry, and each run lasted 24 h. Calibration employed the known hyperfine splittings in the metallic iron spectrum, and the isomer shifts reported here are relative to iron metal at room temperature. In calibration experiments with thin iron foils, line widths were typically 0.32 mm s^{-1}. An applied field of 0.13 T transverse to the γ beam was achieved with a permanent magnet. Samples were kept either at 4.2 K (by immersion in liquid helium) or at room temperature for the duration of each run.

Results

Magnetic susceptibility data for [FeTPP-T][Cu(MNT)$_2$]-[FeTPP-T] and [FeTPP][Cu(MNT)$_2$][FeTPP] are presented in Figures 1 and 2, respectively. The magnitudes of the magnetic moments at the highest temperatures of the measurements (3.09 μ_B for **3** and 5.98 μ_B for **1**) argue strongly for spin-state assignments of ($^1/_2$, $^1/_2$, $^1/_2$) for [iron(III), copper(II), iron(III)] in [FeTPP-T][Cu(MNT)$_2$][FeTPP-T] and ($^3/_2$, $^1/_2$, $^3/_2$) for [iron(III), copper(II), iron(III)] in [FeTPP][Cu(MNT)$_2$][FeTPP], since three uncoupled $S = {}^1/_2$ spins in a cluster should have a magnetic moment of 3 μ_B while two uncoupled $S = {}^3/_2$ spins plus one $S = {}^1/_2$ spin should have a magnetic moment of 5.7 μ_B. These spin-state assignments are consistent with the six-coordinate structure of iron with the strong axial donor, the imidazole group, in [FeTPP-T][Cu(MNT)$_2$][FeTPP-T] and with the five-coordinate structure of iron in [FeTPP][Cu(MNT)$_2$][FeTPP].

Mössbauer spectral parameters, which are given in Table I, support the spin-state assignments. At both room temperature and 4.2 K, the spectra are consistent with a single type of iron(III) in each complex. At 4.2 K, the spectrum of **1** in an applied field of 0.13 T exhibits well-resolved paramagnetic hyperfine structure. Such structure is absent in the preliminary spectral studies of **3**. An analysis of the Mössbauer spectral data will be presented elsewhere.[23]

Table I. Mössbauer Data (ΔE_Q and δ) for [FeTPP][Cu(MNT)$_2$][FeTPP] (**1**) and [FeTPP-T][Cu(MNT)$_2$][FeTPP-T] (**3**)

compd	temp, K	ΔE_Q, mm/s	δ, mm/s (Fe^0)
1 (TPP)	298	3.13	0.24
1 (TPP)	4.2	3.30	0.36
3 (TPP-T)	4.2	3.04	0.30[a]

[a] No magnetic hyperfine splitting observed in a 1.3-kG field.

The Hamiltonian appropriate for the exchange interaction in these heterotrimetallic compounds is[24]

$$\mathbf{H} = -2J_{12}\mathbf{S}_1\cdot\mathbf{S}_2 - 2J_3\mathbf{S}_{12}\cdot\mathbf{S}_3$$

where the subscripts 1 and 2 label the two iron(III) spins, and S_3 corresponds to the spin of copper(II). Here $\mathbf{S}_{12} = \mathbf{S}_1 + \mathbf{S}_2, ..., |\mathbf{S}_1 - \mathbf{S}_2|$, and the total spin of the system is given by $\mathbf{S} = \mathbf{S}_{12} + \mathbf{S}_3, ..., |\mathbf{S}_{12} - \mathbf{S}_3|$. The energies of the spin states are given by

$$E(S,S_{12}) = J_{12}[2S_1(S_1 + 1) - S_{12}(S_{12} + 1)] + J_3[S_{12}(S_{12} + 1) + S_3(S_3 + 1) - S(S + 1)]$$

The g values of the exchange-coupled states are given by

$$g = g_1 - (g_3 - g_1)[\sigma(S)]$$

where

$$\sigma(S) = [S_{12}(S_{12} + 1) - S_3(S_3 + 1) - S(S + 1)]/2S(S + 1)$$

The first-order Zeeman coefficient contribution to the Van Vleck equation[25] is given by

$$\sum_M E_1{}^2 = {}^1\!/_3 S(S + 1)(2S + 1)[g_1 - (g_3 - g_1)(\sigma(S))]^2\mu_B{}^2$$

and the second-order contribution is

$$-2\sum_M E_2 = -2({}^1\!/_3)(g_3 - g_1)^2\mu_B{}^2\sum S'\,\tau(S,S')/E(S,S')$$

where

$$\tau(S,S') = (S_{12} + S_3 + 1 + \bar{S})(S_{12} + S_3 + 1 - \bar{S}) \times (\bar{S} + S_{12} - S_3)(\bar{S} + S_{12} - S_3)/4\bar{S}^2$$

$\bar{S}$ is the larger of S and S', and

$$E(S,S') = E_0(S,S_{12}) - E_0(S',S_{12})$$

Off-diagonal matrix elements

$$\langle SS_{12}M|\mathbf{S}_{3z}|S'S'_{12}M'\rangle$$

have $S' = S \pm 1$, $S_{12} = S'_{12}$, and $M = M'$.

It was anticipated that the g values for the iron(III) entities and $[Cu(MNT)_2]^{2-}$ would differ, and Van Vleck equations including second-order terms were derived for the two cases, those being ($^1/_2$, $^1/_2$, $^1/_2$) and ($^3/_2$, $^1/_2$, $^3/_2$). The Van Vleck equations were modified to account for a mean-field correction arising from intercluster interactions. The corrected magnetic susceptibility expression was of the form

$$\chi_M{}^{cor} = \chi_M{}^{cluster}/(1 - 2zJ'\chi_M{}^{cluster}/N\mu_B{}^2g^2)$$

Finally, an allowance for the presence of paramagnetic impurities, assumed to be monomeric iron(III) species, was made by using the expression

$$\chi_M = \chi_M{}^{cor}(1 - P) + P\chi_M{}^{monomer}$$

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Table II. Magnetic Parameters for [FeTPP-T][Cu(MNT)$_2$][FeTPP-T] and [FeTPP][Cu(MNT)$_2$][FeTPP]

compd	$J_{\text{Fe-Fe}}$, cm^{-1}	$J_{\text{Fe-Cu}}$, cm^{-1}	g(Fe)	zJ', cm^{-1}	$J^{\text{eff}}_{\text{Fe-Fe}}$, cm^{-1}	$J^{\text{eff}}_{\text{Fe-Cu}}$, cm^{-1}
[FeTPP-T][Cu(MNT)$_2$][FeTPP-T]	−4.5	−3.8	1.97	1.4	−4.5	−3.8
[FeTPP][Cu(MNT)$_2$][FeTPP]	−0.66	−1.1	2.16	0.15	−5.9	−3.3

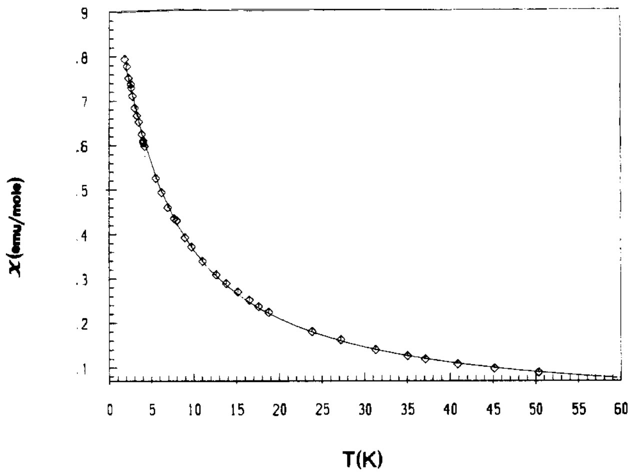

Figure 2. Magnetic susceptibility data for [FeTPP][Cu(MNT)$_2$]-[FeTPP]. The solid line is the result of the best-fit theoretical calculation as described in the text.

where P is the fraction of monomeric impurity.

The Van Vleck equations were fitted to the experimental magnetic susceptibility data by using a Simplex nonlinear least-squares fitting program[26] with the criterion of best fit being the minimum value of the function

$$F = \sum_i [\chi_M^{\text{obsd}} - \chi_M^{\text{calcd}}]^2 / [\chi_M^{\text{obsd}}]^2$$

In order to obtain fits of the theoretical expression to the experimental data, it was necessary to establish certain constraints. First, the g value of the [Cu(MNT)$_2$]$^{2-}$ entity was set equal to 2.046, the value found in several salts of [Cu(MNT)$_2$]$^{2-}$,[27] and this parameter was held constant during the calculations. It was anticipated that $J_{\text{Fe-Fe}}$ would be vanishingly small, and this parameter was set to zero in the initial calculations. However, it was impossible to fit the experimental data with $J_{\text{Fe-Fe}}$ held equal to zero. In the final calculations $J_{\text{Fe-Fe}}$ was set equal to zero, but it was allowed to vary. The best-fit parameters are listed in Table II, and the solid lines shown in Figures 1 and 2 were generated with these parameters and the modified Van Vleck equations described above. It was not necessary to include monomeric impurities in the fitting processes.

Discussion

Exchange Coupling Model. The model adopted for the analysis of the magnetic susceptibility data has some limitations. First, Heisenberg exchange was assumed. The assumption is generally valid for copper(II) exchange-coupled systems,[28] but the applicability of Heisenberg exchange for low-spin $S = {}^1/_2$ iron(III) and intermediate-spin $S = {}^3/_2$ iron(III) must be considered on a case by case basis.[29] One of the major complications arises from the possible quantum mechanically spin-mixed nature of these nominal spin states, with a criterion for the description of the single-ion electronic state being the magnitude of the magnetic moment. As pointed out above, the magnitudes of the magnetic moments of the cluster argue strongly for a spin-state assignment of $S = {}^1/_2$ for iron(III) in [FeTPP-T]$^+$ and $S = {}^3/_2$ in [FeTPP]$^+$. The success of fitting the data with g values for these entities that are near 2.0 provides support for the correctness of the spin-state assignments and the applicability of Heisenberg exchange theory for these heterometallic clusters.

The second limitation involves the neglect of zero-field splitting effects. The ground state in [FeTPP-T][Cu(MNT)$_2$][FeTPP-T] is a doublet with the quartet state lying at 11.4 cm^{-1} above the ground state. A small zero-field splitting in a state lying that far above the ground state would have little effect on the parameters from best-fit calculations.

Single-ion zero-field splitting in the $S = {}^3/_2$ [FeTPP]$^+$ entities could introduce some anisotropy in the exchange. However, such effects are difficult to detect in magnetic susceptibility studies on powders, and none were apparent in this study.

Net Effective Exchange. It is possible to make comparisons involving different spin configurations by accounting for the numbers of electrons and orbitals that are involved in the exchange processes. The observed exchange coupling constants are given by the expression[24,30]

$$J_{\text{ij}} = (n_{\text{i}} n_{\text{j}})^{-1} \sum_{\text{a,b}} J(a_{\text{i}}, b_{\text{j}})$$

where $J(\text{a}_\text{i},\text{b}_\text{j})$ values are the individual orbital contributions to the exchange parameter and n_i and n_j are the numbers of the unpaired electrons in orbitals a and b on spin centers i and j. The net effective exchange parameter becomes

$$J^{\text{eff}}_{\text{ij}} = n_{\text{i}} n_{\text{j}} J_{\text{ij}}$$

These parameters are listed in Table II.

Exchange Coupling in [FeTPP-T][Cu(MNT)$_2$][FeTPP-T]. The electronic configuration of low-spin iron(III) is dependent on the details of the coordination of the iron, including the nature of the ligands and their relative orientations.[31] Generally, the tetragonal or "4 + 1 + 1" coordination results in the electronic configuration $(d_{xz},d_{yz})^4(d_{xy})^1$, although commonly observed deviations from a spin-only magnetic moment suggest quantum-mechanical spin mixing. To a first approximation the unpaired spin may be characterized as residing in d_{xy}. There is general agreement that the unpaired electron on copper(II) in its square-planar complexes resides in $d_{x^2-y^2}$. Therefore, the mechanism of exchange involves three parallel planar spin systems, with iron(III)–copper(II) pairs being ligand-bridged by a thiolato donor that is in the equatorial plane of the copper(II) and in an apical position of the iron(III). Typically, exchange coupling constants that characterize such superexchange interactions are small in magnitude with their signs being determined by structural details such as the M–B–M′ angle and the chemical nature and identity of the bridging ligands. In this particular case, $J_{\text{Fe-Cu}} = -3.8$ cm^{-1}, a quantity whose sign and magnitude are consistent with the low symmetry and rather large

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distances in the bridging network.

The exchange coupling constant of –4.5 cm^{-1} that characterizes the superexchange interaction between the two terminal iron(III) ions is of special interest. As discussed above, attempts to fit the magnetic susceptibility data with this interaction being set to zero yielded unacceptable fits while those fits in which the exchange coupling constant was allowed to vary freely yielded results that matched the data very well. The filled out-of-plane copper(II) (d_{xz},d_{yz}) orbitals provide an effective superexchange pathway for the resultant antiferromagnetic interaction.

Exchange Coupling in [FeTPP][Cu(MNT)$_2$][FeTPP]. The electronic configuration of intermediate-spin $S = {}^3/_2$ iron(III) depends on the details of the coordination sphere of the iron. An electronic configuration of $(d_{xz,yz})^3(d_{xy})^1(d_{z^2})^1$ is frequently found, although the exact mutual placement of the one-electron energy levels depends on the ligand field strengths of the ligands and the details of the structure of the complex. In any event there are two unpaired electrons in out-of-plane orbitals and one unpaired spin in d_{xy}. There are several opportunities for superexchange interactions between the iron electrons and the unpaired electron in $d_{x^2-y^2}$ in $[Cu(MNT)_2]^{2-}$, and the sum of these interactions will determine the sign and magnitude of the iron–copper exchange coupling constant.

The pairwise interactions that contribute to $J^{\mathrm{eff}}{}_{\mathrm{Fe-Cu}}$ are d_{z^2}(Fe)–$d_{x^2-y^2}$(Cu), d_{xz}(Fe)–$d_{x^2-y^2}$(Cu), and d_{xy}(Fe)–$d_{x^2-y^2}$(Cu). Of these, on the basis of the structural results for **2**, the interaction d_{z^2}(Fe)–$d_{x^2-y^2}$(Cu) is expected to be ferromagnetic while the other two pairwise orbital interactions are expected to be antiferromagnetic. Since $J^{\mathrm{eff}}{}_{\mathrm{Fe-Cu}}({}^3/_2,{}^1/_2)$ is nearly the same as $J^{\mathrm{eff}}{}_{\mathrm{Fe-Cu}}({}^1/_2,{}^1/_2)$, and since only the d_{xy}(Fe)–$d_{x^2-y^2}$(Cu) interaction is possible in the low-spin tail porphyrin (TPP-T) trimer, it may be concluded that the ferromagnetic d_{z^2}(Fe)–$d_{x^2-y^2}$(Cu) term and the antiferromagnetic d_{xz}(Fe)–$d_{x^2-y^2}$(Cu) term effectively cancel each other in [FeTPP][Cu(MNT)$_2$][FeTPP].

There are nine pairwise exchange interactions between the two terminal $S = {}^3/_2$ iron(III) ions, and on the basis of the mutual orientation of the magnetic orbitals, some of these are expected to be ferromagnetic in nature while others are expected to be antiferromagnetic. Perhaps the most important of the latter is d_{xz}(Fe)–$d_{\pm1}$(Cu)–d_{xz}(Fe), the superexchange pathway identified above for [FeTPP-T][Cu(MNT)$_2$][FeTPP-T]. Since $|J^{\mathrm{eff}}{}_{\mathrm{Fe-Fe}}({}^3/_2,{}^3/_2)|$ is 30% greater than $|J^{\mathrm{eff}}{}_{\mathrm{Fe-Fe}}({}^1/_2,{}^1/_2)|$, it is clear that the sum of the other antiferromagnetic interactions dominates the sum of the ferromagnetic contributions. Although it is not possible to identify the individual orbital contributions that determine the effective exchange coupling constants, the comparison of these coupling constants for two complexes with similar structures but different spin states has permitted the selection of the predominant superexchange interactions.

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Registry No. **1**, 81534-76-1; **3**, 107985-43-3; Fe^{II}TPP, 16591-56-3; [TBA$^+$][Cu^{III}(MNT)$_2^-$], 19453-80-6; Fe^{II}TPP-T, 75529-04-3.

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Two Scandium Iodide Carbides Containing Dicarbon Units within Scandium Clusters: $Sc_6I_{11}C_2$ and $Sc_4I_6C_2$. Synthesis, Structure, and the Bonding of Dicarbon

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The title compounds were synthesized from ScI_3, metal, and graphite at 850 °C in sealed niobium containers. Their structures were each refined in space group $P\bar{1}$ (for the two compounds, respectively: $Z = 2, 4$; $a = 10.046$ (3), 10.803 (3) Å; $b = 14.152$ (4), 13.959 (3) Å; $c = 9.030$ (3), 10.793 (4) Å; $\alpha = 104.36$ (3), 106.96°; $\beta = 110.45$ (2), 119.20 (3)°; $\gamma = 89.27$ (2), 87.80 (3)°; $R = 0.040, 0.085$; $R_w = 0.050, 0.111$). $Sc_6I_{11}C_2$ contains discrete M_6X_{12}-type clusters elongated along a pseudo-4-fold axis to accommodate the C_2 unit (d(C–C) = 1.39 (2) Å). The stoichiometry is achieved by bonding of clusters into pairs via four-coordinated I^{i-i} atoms. The phase $Sc_4I_6C_2$, which is of marginal stability, consists of infinite chains of condensed clusters each containing a C_2 unit, namely pairs of centric clusters of $\sim D_{2h}$ symmetry that are connected via shared metal edges by a distorted-trigonal-prismatic cluster. Extended Hückel calculations on $Sc_6I_{11}C_2$ indicate the principal bonding arises between cluster orbitals and π (e_u), π^* (e_g), and $\sigma_s{}^*$ (a_{2u}) orbitals of C_2, with particularly strong bonding to the two metal atoms collinear with C_2 via the last two listed plus σ_p (a_{1g}). The HOMO in $Sc_6I_{11}C_2$ is the cluster-bonding $b_{2g}{}^1$ orbital, consistent with the measured magnetic susceptibility. Comparisons are made with the bonding in $Sc(Sc_6I_{12}C)$ and in other centered clusters.

Introduction

High-temperature studies of the metal-rich halides of scandium, yttrium, zirconium, and the lanthanide elements have revealed an extensive cluster chemistry exists in these systems. In addition, many of these compounds have been found to contain an "interstitial" element centered within each metal octahedron, and extended Hückel calculations have made it clear that this interstitial plays a major role in binding the cluster together. Scandium examples include $Sc(Sc_6Cl_{12}Z)$ and Sc_4Cl_6Z, Z = B, N,[1] and Sc_5Cl_8Z, Z = C, N.[2]

Recently, we reported[3] the first example of this type of chemistry for rare-earth-metal iodides with the synthesis and characterization of $Sc_7I_{12}C$, a compound that contains discrete but distorted $Sc_6I_{12}C$ clusters with a single carbon at each cluster center. It was noted at that time that $Sc_7I_{12}C$ is the most carbon-poor of such ternary iodides and that other, more carbon-rich, phases had been found. Herein we report the syntheses and characterization of two more, $Sc_6I_{11}C_2$ and $Sc_4I_6C_2$, both of which exhibit previously unknown compositions and structures. Interestingly, neither of these compositions has been recognized in extensive studies of the scandium–chlorine–carbon system.[1,2,4]

Both of the new compounds contain dicarbon units within scandium octahedra and thus represent a homologation from the single carbon in $Sc_7I_{12}C$. This interstitial moiety has already been found in gadolinium compounds such as $Gd_2Br_2C_2$,[5] $Gd_{10}Cl_{18}C_4$,[6]

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