Structure and Ferromagnetic Interactions in Open-Shell Supramolecular Assemblies Constructed from Radical Cations and Hexacyanometallate Anions

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Abstract: The goal of our work was to design in a controlled manner open-shell supramolecular assemblies with dominant intermolecular ferromagnetic interactions. Along this line, the compounds of formula $rad_6M(CN)_6I_3\cdot 2H_2O$ with M = Cr, Fe, and Co have been synthesized; rad^+ stands for the 2-(3-*N*-methylpyridinium)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazo-1-oxyl 3-*N*-oxide radical cation. The crystal structures have been solved. The three compounds are isomorphous. They crystallize in the trigonal space group *P*3 ($a = 13.178(3)$ Å, $c = 10.763(6)$ Å for M = Fe). The structure may be viewed as a two-dimensional honeycomb lattice, with three kinds of hexagons and three kinds of rad- - -rad magnetic interactions. In addition, for M = Cr and Fe, there is a fourth kind of magnetic interaction, occurring between the $M(CN)_6^{3-}$ anion and the radical core. The magnetic properties of the three compounds have been investigated. They are characteristic of dominant ferromagnetic interactions to which weak antiferromagnetic interactions are superimposed. A quantitative interpretation of the magnetic data has been developed. In particular, for the chromium derivative, three out of four interactions have been found to be ferromagnetic, including the rad- - -$Cr(CN)_6$ interaction. The spin topologies of our supramolecular assemblies have been discussed in the context of the spin frustration phenomenon. The potentialities of the supramolecular chemistry of open-shell units have been emphasized.

Introduction

Molecular magnetism is a rather new field of research which has emerged for a decade or so.[1] Perhaps, the heart of the discipline concerns the chemistry and the physics of open-shell molecular assemblies. In a certain sense, molecular magnetism may be considered as the facet of supramolecular chemistry dealing with open-shell units. The presence of unpaired electrons leads to a large variety of physical properties such as long-range magnetic ordering[2−13] or molecular bistability with hysteresis effect.[13−17]

The magnetic properties of molecular assemblies constructed from open-shell units depend on the way the local spins interact within the lattice. The interactions may occur either through bonds or through space. In the former case, the spin carriers are linked to each other, either directly or, more frequently, through diamagnetic bridges. The compounds then acquire some polymeric character. In the latter case, on the other hand, the compounds retain a genuine molecular character; the interactions, however, are usually weaker. Until now, we have been essentially interested by through-bond interactions and have described several families of one-, two-, and three-dimensional polymeric species.[12,18] In contrast, in this paper, we are concerned by molecular assemblies in which all the interactions take place through space. Our objective was to synthesize in a controlled manner such molecular assemblies with dominant ferromagnetic interactions. Along this line, we have been inspired by two pieces of information: (i) In a very interesting series of papers, Awaga and co-workers have demonstrated that the 2-(3-*N*-methylpyridinium)-4,4,5,5-tetramethyl-4,5-dihydro-

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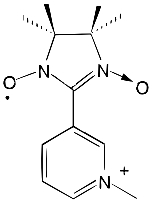
1*H*-imidazo-1-oxyl 3-*N*-oxide radical cation,



hereafter abbreviated as rad$^+$, tends to crystallize in a two-dimensional triangular lattice with unusually large intermolecular ferromagnetic interactions.[19−22] Subsequently, the mechanism of this ferromagnetic interaction was investigated theoretically;[23] (ii) Figgis and co-workers have determined the spin density distribution for the hexacyanochromate(III) trianion from polarized neutron diffraction data and have found that the terminal nitrogen atoms of the cyano groups bore a significant negative spin density, with an axial (or σ) symmetry with respect to the Cr−C−N directions.[24,25] It then occurred to us that the intermolecular interaction between this negative spin density and the positive spin density on the N−O groups of the nitronyl nitroxide function could also give rise to ferromagnetic couplings, according to the McConnell mechanism.[26] It must be recalled here that the hexacyanometallate anions were also utilized as building blocks either to obtain ferro- and ferrimagnetic Prussian blue-like phases[27−30] or to synthesize polymeric bimetallic compounds with a more molecular character,[31] and in radical cation salts combining conducting and magnetic subsystems.[32]

This paper is devoted to the synthesis, crystal structure, and magnetic properties of the compounds $rad_6M(CN)_6I_3{\cdot}2H_2O$ with M = Cr, Fe, and Co. We will show that these compounds possess an elegant two-dimensional structure with dominant ferromagnetic interactions along with quite interesting spin topologies.

Experimental Section

Syntheses. radI. The free radical 2-(3-pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-oxyl 3-*N*-oxide was synthesized using the method described by Ullman.[33,34] The methylpyridinium iodide, radI, was obtained as described by Awaga et al.[19]

$rad_6M(CN)_6I_3{\cdot}2H_2O$ (M = Cr, Fe, and Co). The iron derivative was prepared as follows: 451 mg (1.2 mmol) of radI was added to a suspension of 107 mg (0.2 mmol) of $Ag_3Fe(CN)_6$ in 20 mL of water. The mixture was stirred for 15 min, then filtered to eliminate AgI. The resulting solution was evaporated until dryness at room temperature under vacuum, and the resulting solid was redissolved in methanol. Hexagonal plate-shaped single crystals were obtained by slow evaporation at room temperature. $rad_6Co(CN)_6I_3{\cdot}2H_2O$ was obtained in the same way as $rad_6Fe(CN)_6I_3{\cdot}2H_2O$, using $Ag_3Co(CN)_6$ instead of $Ag_3Fe(CN)_6$. On the other hand, $rad_6Cr(CN)_6I_3{\cdot}2H_2O$ was synthesized by mixing together 65.1 mg (0.2 mmol) of $K_3Cr(CN)_6$ dissolved in 10 mL of water and 451 mg (1.2 mmol) of radI dissolved in 10 mL of water. Hexagonal plate-shaped single crystals of $rad_6Cr(CN)_6I_3{\cdot}2H_2O$ were obtained by slow evaporation at room temperature. These crystals are slightly less soluble as those of KI.

Table 1. Crystal and Refinement Data for $rad_6M(CN)_6I_3{\cdot}2H_2O$ [M = Fe(III), Cr(III), Co(III)]

formula	$FeI_3C_{84}O_{14}N_{24}H_{118}$	$CoI_3C_{84}O_{14}N_{24}H_{118}$	$CrI_3C_{84}O_{14}N_2H_{118}$
form wt	2124.59	2127.67	2120.74
cryst syst		trigonal	
space group		*P*3 (no. 142)	
a, Å	16.203(3)	16.178(3)	16.270(2)
b, Å	16.203(3)	16.178(3)	16.270(2)
c, Å	10.788(6)	10.763(6)	10.860(9)
V, Å^3	2453(3)	2439.7(3)	2489.4
Z	1	1	1
d_{calcd}, g·cm^{-3}	1.438	1.448	1.415
no. of unique reflns	3188	2847	4014
R_{int}	0.043	0.035	0.047
no. of reflns $I \geq 3\sigma(I)$	1743	2102	1884
no. of variables	384	389	380
$R(F)$	0.058	0.049	0.061
$R_w(F)$	0.074	0.067	0.077
GOF	1.660	1.784	1.738

Crystallographic Data Collection and Structure Determination. The X-ray data collection was performed on an Enraf-Nonius CAD4 diffractometer equipped with graphite-monochromated Mo Kα (λ = 0.710 73 Å) radiation. The unit cell parameters were determined and refined from setting angles of 25 accurately centered reflections. Data were collected with the $\theta - 2\theta$ scan method. Three standard reflections were measured every hour and revealed no fluctuation in intensities. Intensities were corrected for Lorentz and polarization effects. The structure was solved by direct methods and successive Fourier difference syntheses. An empirical absorption correction was applied, using the DIFABS procedure.[35] The refinements (on F) were performed by the full-matrix least-squares method (H atoms, both found by Fourier synthesis and placed at computed positions, were not refined). The scattering factors were taken from *International Tables for X-Ray Crystallography* (1974). All the calculations were performed on a microVAX 3100 computer using the Molen programs.[36]

The crystallographic data are presented in Table 1. Tables of atomic coordinates, bond lengths, bond angles, and anisotropic thermal parameters are given as supporting information.

Magnetic Measurements. For the three compounds $rad_6M(CN)_6I_3{\cdot}2H_2O$, with M = Cr, Fe, and Co, measurements were carried out with two apparatuses, namely a Quantum Design SQUID magnetometer and a Faraday-type magnetometer. The measured susceptibilities were corrected of the core diamagnetism estimated as -1050×10^{-6} cm^3 mol^{-1}.

EPR Spectra. The X-band powder EPR spectra were recorded at various temperatures between 4.2 and 300 K with an ER 200D Bruker spectrometer, equipped with a helium continuous-flow cryostat, a Hall probe, and a frequency meter.

Crystal Structure of $rad_6Fe(CN)_6I_3{\cdot}2H_2O$

The three compounds $rad_6M(CN)_6I_3{\cdot}2H_2O$, with M = Cr, Fe, and Co, are isomorphous. We describe here the crystal structure for M = Fe. The compound crystallizes in the trigonal space group *P*3. Let us note that this space group is chiral. The

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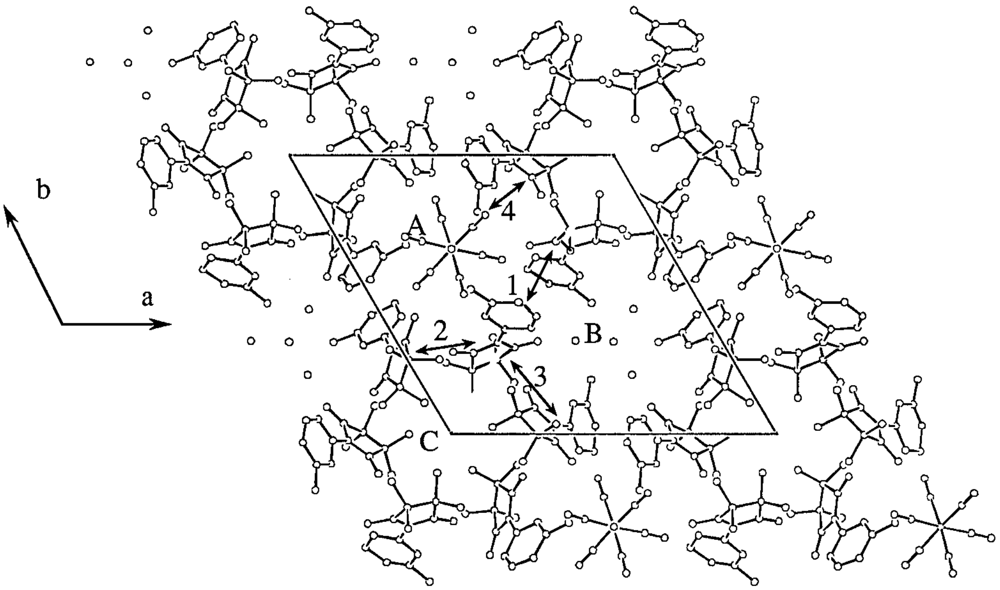


Figure 1. View of the *ab* plane for $rad_6Fe(CN)_6I_3{\cdot}2H_2O$.

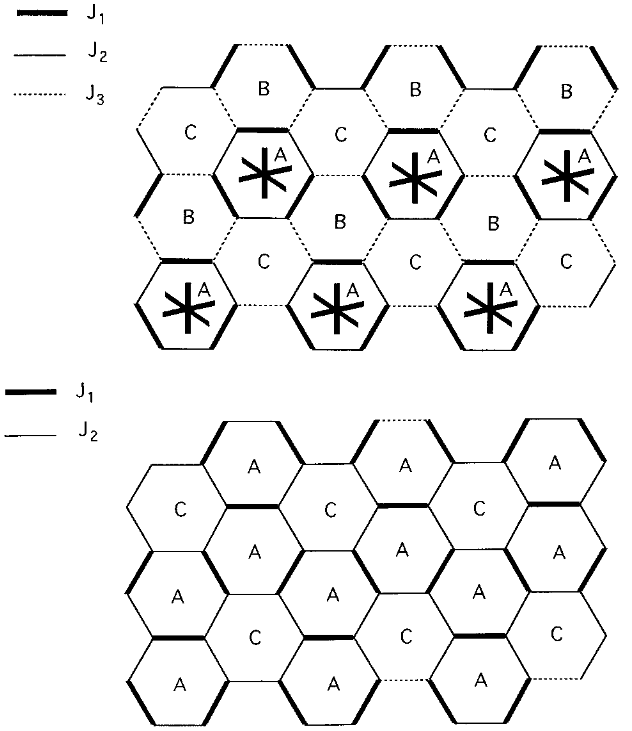


Figure 2. (top) Schematic representation of the three kinds of hexagons together with the different interactions between radical cations in the *ab* plane of $rad_6M(CN)_6I_3{\cdot}2H_2O$. (bottom) Same representation for radX (see text).

structure has a pronounced two-dimensional character. The two crystallographically independent rad^+ units form a sort of honeycomb lattice in the *ab* plane, consisting of three kinds of hexagons, noted A, B, and C, as shown in Figure 1. The iron atom of a $Fe(CN)_6{}^{3-}$ unit projects at the center of hexagon A. A iodide ion, a water molecule, and another iodide ion in a disordered position project at the center of hexagon B. Finally, a iodide ion projects at the center of hexagon C. Each hexagon of one kind is surrounded by three hexagons of a second kind and three hexagons of the third kind, as shown in Figure 2.

The *ab* honeycomb layers stack along the *c* direction with an interlayer separation of 10.763(6) Å, as depicted in Figure 3. This figure shows that the iron atoms of the $Fe(CN)_6{}^{3-}$ anions are not at the centers of hexagons A, but displaced along the *c* direction, with three cyano groups pointing toward the rad^+ units and the other three cyano groups pointing outside the layers. Similarly, the iodide ions and the water molecules are located between rather than within the layers.

The magnetic properties of the $rad_6M(CN)_6I_3{\cdot}2H_2O$ compounds will depend on the way the various spin carriers interact with each other. Therefore, it is crucial to examine the intermolecular interactions in a thorough manner. Actually, the rad- - -rad interactions are of three kinds, noted 1, 2, and 3. In addition, there is the rad- - -$M(CN)_6$ interaction, noted 4, that we already briefly mentioned. These interactions, 1−4, are represented in Figure 4.

Interaction 1 involves two rad^+ units in a head-to-tail position, with the methyl groups oriented outside the pair. The two shortest separations occur between a nitroxide oxygen atom of one unit and the pyridinium ring carbon atom in *para* position with respect to the sp^2 carbon of the other unit, with O2- - -C17 = 2.998 Å and O3- - -C4 = 3.063 Å. These two distances are the shortest rad- - -rad separations of the structure as a whole. Much the same kind of interaction was observed by Awaga and co-workers in the structure of radX, where X is a combined monovalent anion such as $(BF_4)_{0.72}I_{0.28}$.[20]

Interaction 2 involves an oxygen atom of one of the units and a nitroxide nitrogen atom of the other unit, with O4- - -N3 = 3.176 Å. The nearest shortest separation occurs between the O4 oxygen atom and the sp^2 carbon atom, C7, bound to N3, with O4- - -C7 = 3.182 Å. The two rad^+ units are tilted with respect to each other but are not orthogonal.

Interaction 3 involves two rad^+ units which are almost perpendicular to each other. The dihedral angle between the two NOCNO mean planes of the nitronyl nitroxide groups is equal to 92.8°. The shortest intermolecular interaction occurs between a nitroxide oxygen atom of a unit and the sp^2 carbon atom of the other unit, with O1- - -C20 = 3.042 Å. The nearest shortest separation occurs between O1 and the nitroxide nitrogen atom, N5, bound to C2O, with O1- - -N5 = 3.164 Å.

These interactions (1−3) between adjacent rad^+ units within the honeycomb lattice are indicated in Figure 2 where the interaction parameters are noted J_1, J_2, and J_3. Within each hexagon, there is an alternation of two kinds of interaction: 1 and 2 in hexagons A, 1 and 3 in hexagons B, and 2 and 3 in hexagons C. We will come back to this topology in the Discussion.

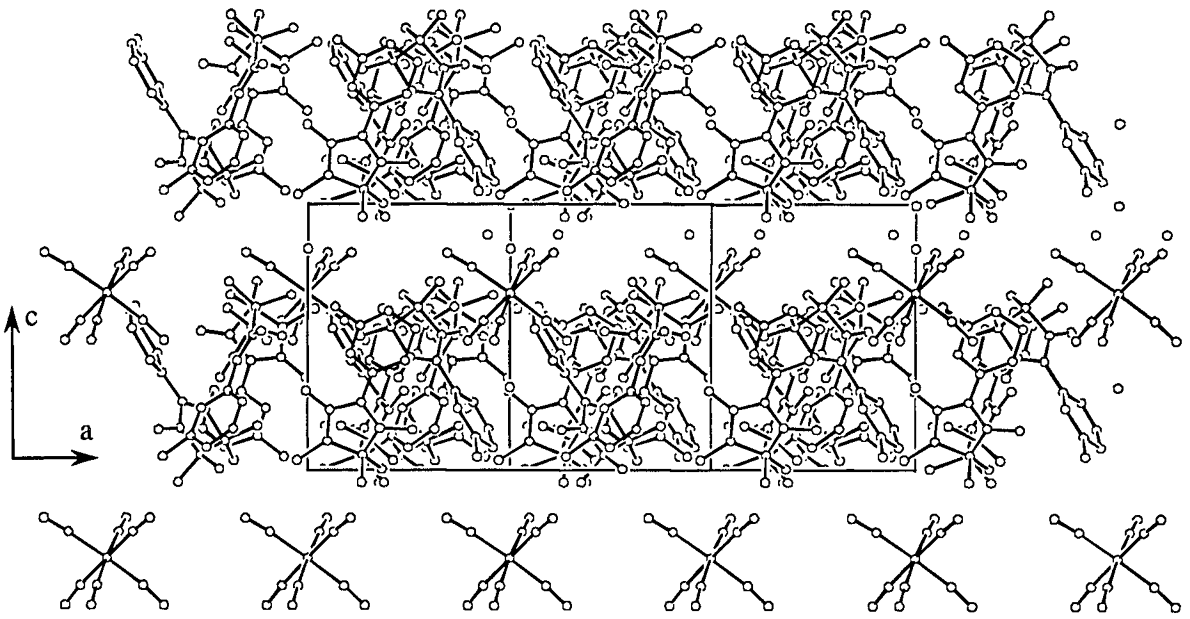
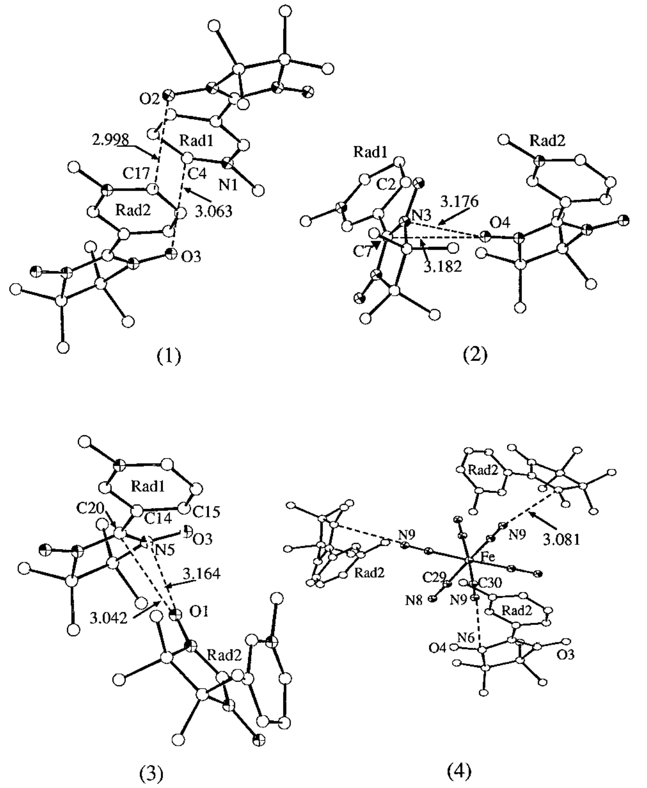


Figure 3. View of the *ac* plane for $rad_6Fe(CN)_6I_3{\cdot}2H_2O$.



(1) (2)

(3) (4)

Figure 4. Details of the four types of magnetic interactions in rad_6-$Fe(CN)_6I_3{\cdot}2H_2O$.

Interaction 4 occurs between the $Fe(CN)_6^{3-}$ anion and three symmetry-related radical cations close to the cyano groups. The shortest separation involves a nitroxide nitrogen atom and a cyano nitrogen atom, with N6- - -N9 = 3.081 Å. The C−N direction of a cyano group is almost perpendicular to the ONCNO mean plane of the nitronyl nitroxide group close to the CN^- ligand.

Magnetic Properties

Experimental Data. The magnetic properties of the three compounds $rad_6M(CN)_6I_3{\cdot}2H_2O$ (M = Cr, Fe, and Co) are represented in the form of the $\chi_M T$ versus T curves in Figure 5, χ_M being the molar magnetic susceptibility and T the temperature. These curves are represented separately as supporting information.

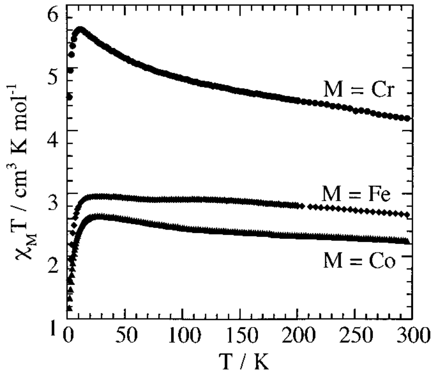


Figure 5. $\chi_M T$ versus T curves for the three compounds $rad_6M(CN)_6I_3{\cdot}2H_2O$, with M = Cr, Fe, and Co.

Let us start by $rad_6Co(CN)_6I_3{\cdot}2H_2O$, where the only spin carriers are the radical cations. At room temperature, $\chi_M T$ is equal to 2.24 cm^3 K mol^{-1}, which exactly corresponds to what is expected for six isolated radical spins. As the temperature is lowered, $\chi_M T$ increases, reaches a maximum around 20 K with $\chi_M T = 2.64$ cm^3 K mol^{-1}, then decreases as T is lowered further. At 2 K, $\chi_M T$ is equal to 1.18 cm^3 K mol^{-1}. Such a behavior is characteristic of dominant ferromagnetic interactions to which weak antiferromagnetic interactions are superimposed. It is worth noticing that even in the high-temperature range, say above 100 K, $\chi_M T$ increases upon cooling, which indicates that some ferromagnetic interactions are unusually large for nitronyl nitroxide radicals.

For $rad_6Fe(CN)_6I_3{\cdot}2H_2O$, $\chi_M T$ is equal to 2.65 cm^3 K mol^{-1} at room temperature, a value which closely corresponds to what is expected for six radical and one low-spin iron(III) spins. As T is lowered, $\chi_M T$ smoothly increases and shows a maximum around 20 K, with $\chi_M T = 2.96$ cm^3 K mol^{-1}, then falls rapidly. At 2 K, $\chi_M T$ is equal to 1.60 cm^3 K mol^{-1}. The profile of the $\chi_M T$ versus T plot is not regular but shows a sort of rounded secondary maximum around 120 K. We carefully checked that this profile is intrinsic; it was observed for several samples coming from different preparations and with both SQUID and Faraday-type magnetometers.

The $\chi_M T$ versus T curve for $rad_6Cr(CN)_6I_3{\cdot}2H_2O$ also reveals dominant ferromagnetic interactions. At room temperature, $\chi_M T$

is equal to 4.12 cm^3 K mol^{-1}, which is slightly higher than the value expected for six radical spins and a $S_{\mathrm{Cr}} = {}^3/_2$ spin for the Cr(III) ion. As T is lowered, $\chi_M T$ increases up to a maximum value of 5.64 cm^3 K mol^{-1} reached around 12 K. Below 12 K, $\chi_M T$ rapidly falls down; the $\chi_M T$ value at 2 K is 4.53 cm^3 K mol^{-1}.

A Priori Discussion on the Nature of the Interactions. In this section, we would like to estimate the nature and the order of magnitude of the interactions between spin carriers from both the structural information and previously reported results.

Interaction 1 between head-to-tail radical cations has been found to be strongly ferromagnetic in rad$(BF_4)_{0.72}I_{0.28}$.[20] The mechanism of this interaction might be the coupling between the ground configuration and some excited configurations arising from the transfer of an electron from the π* singly occupied molecular orbital (SOMO) of a unit localized on the nitronyl nitroxide group toward an empty orbital localized on the pyridinium ring of the other unit (or from a doubly occupied orbital localized on the pyridinium ring of a unit toward the SOMO of the other unit).[23,37,38] For rad$(BF_4)_{0.72}I1_{0.28}$, the parameter associated with this interaction has been found as $J = 17$ cm^{-1}, with a spin Hamiltonian of the form $-J\mathbf{S}_{\mathrm{rad1}}\cdot\mathrm{S}_{\mathrm{rad2}}$.

The rather short O4- - -N3 separation in interaction 2 is expected to give rise to an antiferromagnetic coupling, owing to the overlap between the two π* SOMOs.[20,37,38] Such an antiferromagnetic interaction has been also observed in rad$(BF_4)_{0.72}I_{0.28}$. Its magnitude strongly depends on the separation between the nitroxide groups[22] but in any case remains weak, on the order of the wavenumber.

Interaction 3 may be expected to be ferromagnetic. The orthogonality of the nitronyl nitroxide groups leads to the orthogonality of the π* SOMOs.[37,38] Furthermore, the short distance between a N$-$O group and a sp^2 carbon atom may also favor a parallel spin alignment, according to the McConnell mechanism.[22]

The nature of the interaction 4 evidently depends on the spin distribution on the $M(CN)_6{}^{3-}$ anion. This spin distribution, deduced from polarized neutron diffraction, is known for both the hexacyanochromate[24,25] and the hexacyanoferrate;[39] the data seem to be more accurate in the former case. Around each nitrogen atom of a cyano group, there is a π positive and a σ negative spin density (see Figure 6). The overlap between the positive spin density on the nitroxide groups and the σ negative spin density on the cyano groups might favor a ferromagnetic interaction, as schematized in Figure 6.

Attempt of a Quantitative Approach. Let us first focus on $rad_6Co(CN)_6I_3{\cdot}2H_2O$, where the only spin carriers are the rad$^+$ cations. We have seen that there are three kinds of interactions, noted 1$-$3, with the interaction parameters $J_1$$-$$J_3$. Interactions 1 and 3 are expected to be ferromagnetic, while interaction 2 is expected to be weakly antiferromagnetic. To the best of our knowledge, there is no available model to determine the magnetic susceptibility of such a honeycomb lattice with three different interaction parameters. Furthermore, even if such a model could be built, it would be overparametrized, and trying to determine three interaction parameters from the χ_M versus T curve would be almost meaningless. That is why we decided to explore successively two borderline models, namely $J_3 = 0$, then $J_1 = J_3$.

(i) Model $J_3 = 0$. If one of the two ferromagnetic interactions, 1 or 3, is neglected, the problem is very simplified. It reduces to that of isolated hexagons, as emphasized in Figure 2. These hexagons are the A's if interaction 3 is neglected, or the B's if interaction 2 is neglected. Since it is known that J_1 is large, we assume that J_3 is negligibly small. The zero-field spin Hamiltonian for $rad_6Co(CN)_6I_3{\cdot}2H_2O$ may then be written as

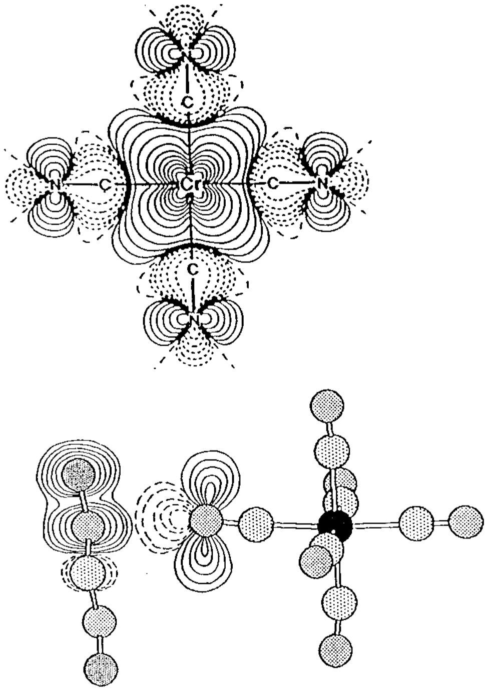


Figure 6. (top) Spin density map for $Cr(CN)_6{}^{3-}$; the positive spin density is in full lines, and the negative spin density is in dotted lines (from refs 24 and 25). (bottom) Interaction between the positive spin density on the nitronyl nitroxide group and the negative spin density on a cyano group of $Cr(CN)_6{}^{3-}$.

$$H_{\mathrm{Co}} = -J_1(\mathbf{S}_1\cdot\mathbf{S}_2 + \mathbf{S}_3\cdot\mathbf{S}_4 + \mathbf{S}_5\cdot\mathbf{S}_6) - J_2(\mathbf{S}_2\cdot\mathbf{S}_3 + \mathbf{S}_4\cdot\mathbf{S}_5 + \mathbf{S}_6\cdot\mathbf{S}_1)$$

and the Zeeman operator in the presence of a magnetic field **H** as

$$H_{\mathrm{Co,ZE}} = (\mathbf{S}_1 + \mathbf{S}_2 + \mathbf{S}_3 + \mathbf{S}_4 + \mathbf{S}_5 + \mathbf{S}_6)g_{\mathrm{rad}}\beta\mathbf{H}$$

where $\mathbf{S}_i$ is the spin operator associated with the local spin $^1/_2$ at the site i, and g_{rad} the Zeeman factor of the radical cation. There is no analytical expression for the magnetic susceptibility of such an hexamer, but the problem may be easily solved by full diagonalization of H_{Co}, using the $|M_{S_1}\cdots M_{S_6}\rangle$ kets as a basis set and then application of the Zeeman perturbation $H_{\mathrm{Co,ZE}}$ using the eigenstates of H_{Co} as a new basis set. A least-squares fitting procedure led to $J_1 = 40$ cm^{-1} and $J_2 = -2.0$ cm^{-1}, the Zeeman factor g_{rad} being equal to 1.98. The agreement factor defined as $\sum[(\chi_M T)^{\mathrm{cal}} - (\chi_M T)^{\mathrm{obsd}}]^2/\sum[(\chi_M T)^{\mathrm{obsd}}]^2$ is then equal to 1.2×10^{-4} (for 136 experimental points).

(ii) Model $J_1 = J_3$. In this model, the magnetic properties can again be quantitatively interpreted. Each hexagon B may be viewed as a ring chain of six equally spaced and ferromagnetically coupled sites. The weak antiferromagnetic interaction, J_2, connecting each site of an hexagon B to a site of another hexagon B (see Figure 2) is described in the mean-field approximation. Such a model led to $J_1 = J_3 = 9.2$ cm^{-1} and $J_2 = -2.0$ cm^{-1}, with $g_{\mathrm{rad}} = 1.99$. The agreement factor, R, has much the same value as in the former model, so that it is not possible at this stage to say which model is the best.

Let us now examine the case of $rad_6Cr(CN)_6I_3{\cdot}2H_2O$ and $rad_6Fe(CN)_6I_3{\cdot}2H_2O$. The complexity of the magnetic problem is even enhanced. What we can do is to consider each of these two compounds as consisting of a honeycomb skeleton of radical cations whose magnetic properties are those of $rad_6Co(CN)_6I_3{\cdot}$

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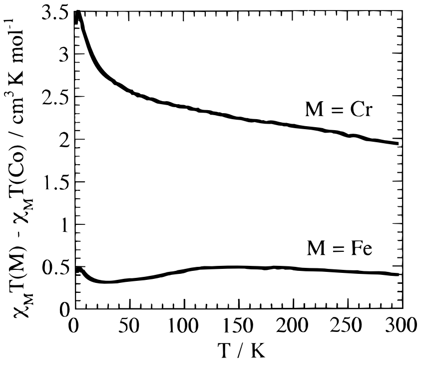
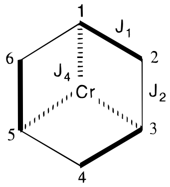


Figure 7. Temperature dependences of $\chi_M T$(Cr) − $\chi_M T$(Co) and $\chi_M T$(Fe) − $\chi_M T$(Co) (see text).

$2H_2O$, in which a $M(CN)_6{}^{3-}$ paramagnetic anion is embedded. The question we are then faced with is the following: is there any interaction between radical skeleton and hexacyanometallate ion, and if it is so, what is its nature? A qualitative answer may be obtained by plotting the temperature dependence of $\chi_M T$(M) − $\chi_M T$(Co), where $\chi_M T$(M) stands for the $\chi_M T$ value of $rad_6M(CN)_6I_3{\cdot}2H_2O$. $\chi_M T$(Cr) − $\chi_M T$(Co) shown in Figure 7 is equal to 1.93 cm^3 K mol^{-1} at 290 K and increases more and more rapidly as T is lowered. This variation does not correspond at all to the Curie law expected for isolated $Cr(CN)_6{}^{3-}$ anions. In the supramolecular assembly, the $Cr(CN)_6{}^{3-}$ unit couples ferromagnetically with the organic skeleton.

In contrast, $\chi_M T$(Fe) − $\chi_M T$(Co) is equal to 0.41 cm^3 K mol^{-1} at 290 K, and does not vary significantly versus temperature. In this case, the magnetic susceptibility data detect no interaction between the $Fe(CN)_6{}^{3-}$ unit and the organic skeleton.

Only in the model (i) where J_3 is assumed to be zero can the parameter J_4 characterizing the interaction between $Cr(CN)_6{}^{3-}$ and rad$^+$ be determined quantitatively. The spin topology is



and the zero-field Hamiltonian for $rad_6Cr(CN)_6I_3{\cdot}2H_2O$ may be written as

$$H_{Cr} = H_{Co} - J_4(\mathbf{S}_1 + \mathbf{S}_3 + \mathbf{S}_5)\cdot\mathbf{S}_{Cr}$$

and the Zeeman perturbation as

$$H_{ZE,Cr} = H_{ZE,Co} + \mathbf{S}_{Cr}\cdot g_{Cr}\,\beta\mathbf{H}$$

where g_{Cr} is the Zeeman factor for the Cr(III) ion. The size of the matrix associated with H_{Cr} is equal to 256 × 256 if the 3-fold symmetry of the problem is not explicitely taken into account. An important simplification in the calculation of the magnetic susceptibility consists to put $g_{Cr} = g_{rad}$; if we do so, the Zeeman matrix on the basis of the eigenstates of H_{Cr} is diagonal. The J_1 and J_2 values were assumed to be transferable from the cobalt to the chromium derivative. The only parameter to be determined is then J_4. Least-squares fitting led to $J_4 = 5$ cm^{-1}. The agreement factor R is then equal to 7.3×10^{-4}; the agreement between measured and calculated magnetic data is far from being excellent. Owing to the complexity of the problem, however, we decided not to try going further. What is unambiguous it is that the rad$^+$- - -$Cr(CN)_6{}^{3-}$ interaction is ferromagnetic.

EPR Properties

The X-band powder EPR spectrum of $rad_6Co(CN)_6I_3{\cdot}2H_2O$ consists of a single narrow line centered at $g = 2.00$. The line width slightly increases as T is lowered, from 3.5 G at room temperature up to 5.6 G at 17 K. Such a behavior is quite classical for radical compounds in the solid state. It is due to spin exchange which averages the dipole interactions and narrows the spectrum. This exchange is the faster as the temperature is the higher.[40,41]

The EPR spectrum of $rad_6Cr(CN)_6I_3{\cdot}2H_2O$ also consists of a single line, centered at $g = 1.995$. The line width, however, is much larger than for the cobalt derivative. It is equal to 75 G at room temperature and reaches 100 G at 10 K.

The spectrum of $rad_6Fe(CN)_6I_3{\cdot}2H_2O$ at the first view is more complicated. It is the superposition of a single line centered at $g = 1.97$ and a very weakly intense five-line spectrum. The relative intensities and the linewidths of the latter spectrum do not change significantly versus temperature. This latter spectrum is very similar to that of the radical cation in solution, or diluted in a diamagnetic host lattice, and most likely arises from impurities or defects in the solid. The line width of the intrinsic signal increases tremendously as T decreases. It is equal to 213 G at 300 K, 300 G at 140 K, and 580 G at 61 K and is not measurable anymore at liquid helium temperature. The same huge temperature dependence of the line width was observed for other $Fe(CN)_6{}^{3-}$−radical cation compounds.[42] We intend to come back to this problem in a subsequent paper. Here, we restrict ourselves to mention that the orbital momentum of the low-spin Fe(III) ion in the $^2T_{2g}$ ground state might be responsable for this behavior.

Discussion

In this section, we would like to discuss successively about the crystal structure, the magnetic properties, and the spin topologies of the compounds $rad_6M(CN)_6I_3{\cdot}2H_2O$.

Crystal Structure. To start this discussion, it is probably worthwhile to compare our compounds with the compounds radX described by Awaga and co-workers, where rad$^+$ stands for the same radical cation and X$^-$ for a mixed monovalent anion such as $(BF_4)_{0.72}I_{0.28}$. Awaga's compounds are also two-dimensional but contain only two kinds of hexagons instead of three, as schematized in Figure 2. In these radX compounds, there are also two types of interaction between rad$^+$ units. Their interaction 1 (parameter J_1) is essentially identical to interaction 1 in our compounds; it occurs between two head-to-tail units. The interaction 2 (parameter J_2) is also similar to interaction 2 in our compounds. It may be noticed that Awaga succeeded in varying the intermolecular separations involved in interaction 2 by modifying the size of the combined anion X$^-$. We can say that the $rad_6M(CN)_6I_3{\cdot}2H_2O$ structure is in the meantime reminiscent of and more elaborated than the radX structure. It is remarkable that both structures show a similar dimeric arrangement of head-to-tail rad$^+$ units. The driving force for such an arrangement seems to be the Coulombic attraction between the positive charge on the pyridinium nitrogen atom and the negative charge polarized on the nitroxide oxygen atoms.[20]

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Magnetic Properties. The interpretation of the magnetic properties is obviously more complex for $rad_6M(CN)_6I_3{\cdot}2H_2O$ than for radX, even for M = Co. Let us first focus on this case where the hexacyanometallate anion is diamagnetic. The magnetic properties then depend on three interaction parameters, J_1, J_2, and J_3. J_1 may be expected to have much the same value as in radX, and J_2, to be weakly negative. On the other hand, interaction 3 does not exist in radX and J_3 is unknown, even if its sign may be anticipated to be positive (ferromagnetic interaction) from symmetry considerations (see above). Our approach has allowed successive development of two borderline models. First, J_3 was assumed to be negligibly small. The magnetic problem is then rigorously tractable by diagonalization of $2^6 \times 2^6$ matrices. As expected, J_1 is found to be positive; its value, however, is found to be larger than in radX (40 cm^{-1} as compared to 17 cm^{-1}), which suggests that this model ($J_3 = 0$) is not quite valid; the ferromagnetic correlations in $rad_6Co(CN)_6I_3{\cdot}2H_2O$ seem to be more pronounced than they would be for $J_1 = 17$ cm^{-1} and $J_3 = 0$. Most likely, J_3 is positive as well. The $J_1 = 40$ cm^{-1} value may be considered as an effective value describing all the ferromagnetic interactions. In the alternative model, J_1 and J_3 were supposed to be equal. The magnetic problem is then again tractable, provided that J_2 is assumed to be weak enough with respect to J_1 and J_3 to be treated in the mean-field approximation. In this model, J_1 ($= J_3$) is found as 9.2 cm^{-1}, hence smaller than in radX. $J_1 = J_3 = 9.2$ cm^{-1} may again be considered as an effective value. Probably J_1 is actually larger than this mean value and J_3 weaker. To sum up this discussion, we can say that neglecting J_3 results in a too large J_1 value and assuming $J_1 = J_3$ results in a too weak J_1 value. It is then possible to state that, in $rad_6Co(CN)_6I_3{\cdot}2H_2O$, both J_1 and J_3 are positive, J_1 being dominant.

Replacing Co by Fe, then Cr, in $rad_6M(CN)_6I_3{\cdot}2H_2O$ allows us to add another spin carrier to the system, and the question we are faced with concerns the nature of the interaction, if any, between the magnetic hexacyanometallate and the radical core. To answer this question, we compared the magnetic susceptibility of $rad_6M(CN)_6I_3{\cdot}2H_2O$ to the sum of the magnetic susceptibilities of the $M(CN)_6^{3-}$ anion and the radical core. For M = Fe, we did not detect any interaction between those two fragments. On the other hand, for M = Cr, the two fragments are clearly ferromagnetically coupled, and an estimation of the rad- - -$Cr(CN)_6$ interaction parameter, J_4, was obtained. This ferromagnetic interaction probably arises from the overlap between the axial negative spin density on the cyano nitrogen atoms and the nitroxide positive spin density. The spin density distribution deduced from polarized neutron diffraction for $Fe(CN)_6^{3-}$ also reveals a spin polarization effect resulting in negative spin populations on the carbon atoms.[39] According to the available data, however, the negative spin densities on the nitrogen atoms are less pronounced in $Fe(CN)_6^{3-}$ than in $Cr(CN)_6^{3-}$.

Spin Topologies. The three compounds $rad_6M(CN)_6I_3{\cdot}2H_2O$ offer quite interesting cases of competing magnetic interactions leading to spin frustrated two-dimensional networks. Spin frustration was also realized in the radX compounds studied by Awaga and co-workers. These authors suggested to assimilate the dimeric arrangements of head-to-tail units to spin triplet species, which is valid in the temperature range $T \ll J_1/k$. These triplet species are then antiferromagnetically coupled through J_2, which gives rise to spin frustration on each side of the two-dimensional triangular lattice. In this respect, as pointed by Awaga, the system is reminiscent of a spin − 1 Kagomé antiferromagnet.[22] Let us also assimilate the radical pairs coupled through J_1 to local triplet states. Whatever the sign of J_3 may be, the two-dimensional radical core is frustrated. This frustration is even enhanced when the $M(CN)_6^{3-}$ anion in the hexagon A couples ferromagnetically with three out of six rad^+ units.

The $J_3 = 0$ model considered in our quantitative approach deserves to be discussed further. In this case, as already mentioned, the hexagons A are magnetically isolated, and the concept of spin frustration becomes questionable. This concept has been introduced by solid state physicists for extended networks,[43,44] and its extension to isolated molecular species is not obvious. In extended networks, competing interactions lead to highly degenerate ground states; the spins are unable to decide which state to be. Our opinion is that this idea of degenerate states must be retained for defining spin frustration in isolated systems. Only in such cases may spin frustration lead to a peculiar physical behavior which might have some similarity with the high-spin−low-spin crossover phenomenon; the system hesitates as for the nature of its ground state.[1] Along this line, an equilateral triangle of antiferromagnetically coupled $S = 1$ isotropic spins is not frustrated. The ground state is a nondegenerate spin singlet, whatever the magnitude of the antiferromagnetically interaction may be. Even when a local spin $^3/_2$ [$Cr(CN)_6^{3-}$] is added at the center of the equilateral triangle, the ground state remains nondegenerate; it is a spin quartet, whatever the nature of the rad- - -$Cr(CN)_6$ interaction may be. We intend to come back to the concept of spin frustration for isolated molecular species in a subsequent paper.

Conclusion

Our goal when beginning this work was to design open-shell molecular assemblies in which the intermolecular ferromagnetic interactions would be maximalized. The compounds described in this paper are not ferromagnets. First, they have a very strong two-dimensional character, while long-range ordering is usually a three-dimensional property. Moreover, the antiferromagnetic interaction characterized by J_2 gives rise to a nonmagnetic ground state. However, for one of the three compounds, $rad_6Cr(CN)_6I_3{\cdot}2H_2O$, three out of four intermolecular interactions are ferromagnetic. Two of them, characterized by J_1 and J_4, have been created in a controlled fashion. The presence of J_2, if it prevents the compound to exhibit a spontaneous magnetization, leads to an exceptional situation of spin frustration.

Until now, most of supramolecular chemists have worked with closed-shell units. When they exceptionally handle chemical groups bearing unpaired electrons, they usually do not care about the physics associated with these electrons. Our feeling is that the supramolecular chemistry of open-shell units deserves to be explored further. Such a chemistry could combine the aesthetic appeal of the supramolecular assemblies and the excitement of new physics.

Supporting Information Available: Tables of atomic coordinates, bond lengths, bond angles, and anisotropic thermal parameters for compounds $(rad)_6M(CN)_6I_3{\cdot}2H_2O$ (M = Cr, Fe, Co) and $\chi_M T$ versus T curves for the same compounds (24 pages). This material is contained in many libraries on microfiche, immediately follows this article is the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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