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Ferromagnetic Interactions between t_{2g}^3 and e_g^2 Magnetic Orbitals in a $Cr^{III}Ni^{II}_3$ Tetranuclear Compound

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It has been suggested for a long time that the exchange interaction between chromium(III) and nickel(II) ions, with both in octahedral surroundings, might be ferromagnetic. This would arise from the orthogonality of the three t_{2g} orbitals occupied by the unpaired electrons of Cr(III) and the two e_g orbitals occupied by the unpaired electrons of Ni(II). The first compound with Cr(III)–Ni(II) interactions has been synthesized. This compound is $\{Cr[(ox)Ni(Me_6\text{-}[14]ane\text{-}N_4)]_3\}(ClO_4)_3$ ($CrNi_3$), where ox is the oxalato bridge $C_2O_4^{2-}$ and Me_6-[14]ane-N_4 is (±)-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane. Spectroscopic data together with chemical analysis have indicated that a central Cr(III) ion is linked to three Ni(II) ions through oxalato bridges. The magnetic susceptibility, studied in the 1.3–300 K temperature range, has confirmed that the Cr(III)–Ni(II) interactions were actually ferromagnetic so that the ground spin state of $CrNi_3$ is $S = S_{Cr} + 3S_{Ni} = {}^9/_2$. The magnetic data have been interpreted quantitatively. The interaction parameter $J(\mathcal{H} = -JS_{Cr}S_{Ni})$ has been found to be equal to 5.3 cm^{-1}. The magnetization, measured in the 0–6 × 10^4 G field range, has confirmed the spin multiplicity of the ground state. The orbital mechanism of the Cr(III)–Ni(II) interaction has been discussed.

Introduction

In the last few years, a great deal of effort has been devoted to the design of high-spin molecules. Several strategies have been proposed along this line. One of them consists of imposing a ferromagnetic interaction between nearest neighbor magnetic centers owing to the strict orthogonality of the magnetic orbitals.[1] The classical example of such a situation is provided by the $CuVO(fsa)_2en{\cdot}CH_3OH$ dinuclear compound exhibiting a spin-triplet ground state stabilized by ca. 120 cm^{-1} with respect to the spin-singlet excited state.[2] A recent ab initio calculation confirms that the cornerstone of the ferromagnetic interaction observed in $CuVO(fsa)_2en{\cdot}CH_3OH$ is actually the orthogonality of the two magnetic orbitals centered on the copper and vanadium atoms, respectively.[3] The stabilization of the state of highest spin multiplicity due to the orthogonality has also been observed in a copper(II)–chromium(III) compound[4] and in several metal ion–organic radical species[5–7] as well as in some organic diradicals.[8]

To our knowledge, it was mentioned for the first time by Ginsberg in 1971 that the interaction in the pair chromium(III)–nickel(II) might be expected to be ferromagnetic.[9] Indeed, Cr(III) in octahedral surroundings has three unpaired electrons occupying the three low-lying t_{2g} orbitals and Ni(II), also in octahedral surroundings, has two unpaired electrons occupying the two e_g high-lying orbitals. At this time, Ginsberg wrote "a complex for testing this prediction has not yet been reported and it is well worth seeking." To be complete, we must specify that Ginsberg had in mind a complex consisting of two octahedra sharing a corner, e.g. $[L_5CrONiL_5]^{3+}$ with a 180° Cr–O–Ni linkage. The overall symmetry is then C_{2v}, assuming that the ligand L is spherical. The t_{2g} orbitals of Cr(III) transform as $a_2 + b_1 + b_2$ and the e_g orbitals of Ni(II) as $2a_1$. For any pair of interacting magnetic orbitals, the strict orthogonality is obeyed and the interaction should be ferromagnetic. For two octahedra sharing an edge, Ginsberg suggested that the interaction should be antiferromagnetic.

In the framework of our program on the high-spin molecules and the molecular-based ferromagnets,[10,11] we have attempted for some time to synthesize a compound with Cr(III)–Ni(II) interactions. In this paper, we report on the first compound of this kind, namely $\{Cr[(ox)Ni(Me_6\text{-}[14]ane\text{-}N_4)]_3\}(ClO_4)_3$, hereafter abbreviated as $CrNi_3$, where ox is the oxalato bridge $C_2O_4^{2-}$ and Me_6-[14]ane-N_4 is (±)-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane. We successively describe the synthesis, the spectroscopic characterization, and the magnetic properties of this compound. We will show that $CrNi_3$ has a $S = {}^9/_2$ ground spin state, arising from the ferromagnetic nature of the Cr(III)–Ni(II) interactions.

Experimental Section

Syntheses. $[Ni(Me_6\text{-}[14]ane\text{-}N_4)](ClO_4)_2$[12] and $K_3[Cr(ox)_3]{\cdot}3H_2O$[13] were synthesized as previously described. $CrNi_3$ was obtained as follows: 10^{-3} mol of $[Ni(Me_6\text{-}[14]ane\text{-}N_4)](ClO_4)_2$ was dissolved in 30 mL of a 50/50 mixture of acetonitrile and methanol. The solution was violet. One then added dropwise 10 mL of an aqueous solution containing 0.33 × 10^{-3} mol of $K_3[Cr(ox)_3]{\cdot}3H_2O$. After 30 min, $CrNi_3$ precipitated as a light gray-blue polycrystalline powder. The precipitate was washed with water and methanol, and dried under vacuo.

Anal. Calcd for $C_{54}H_{108}N_{12}O_{24}Cl_3CrNi_3$: C, 39.45; H, 6.62; N, 10.22; Cl, 6.47; Cr, 3.16; Ni, 10.71. Found: C, 39.13; H, 6.70; N, 9.99; Cl, 6.14; Cr, 3.18; Ni, 10.51.

$\{[Ni(Me_6\text{-}[14]ane\text{-}N_4)]_2(ox)\}(ClO_4)_2$, for which the electronic spectrum has been compared to that of $CrNi_3$, was obtained as follows: 10^{-3} mol of $[Ni(Me_6\text{-}[14]ane\text{-}N_4)](ClO_4)_2$ was dissolved in 20 mL of a 50/50 acetonitrile–water mixture. One then added 10^{-3} mol of sodium oxalate dissolved in 20 mL of warm water. The solution immediately became blue. The acetonitrile was gently evaporated under vacuo at room temperature, and the expected compound precipitated as a blue polycrystalline powder.

Anal. Calcd for $C_{34}H_{72}N_8O_{12}Cl_2Ni_2$: C, 41.95; H, 7.46; N, 11.51; Cl, 7.28. Found: C, 41.91; H, 7.40; N, 11.70; Cl, 7.27.

Magnetic Measurements. In the 4.2–270 K temperature range, these were carried out with a Faraday-type magnetometer equipped with a helium continuous-flow cryostat. $HgCo(NCS)_4$ was used as a susceptibility standard. Diamagnetic correction was taken as −670 × 10^{-6} cm^3

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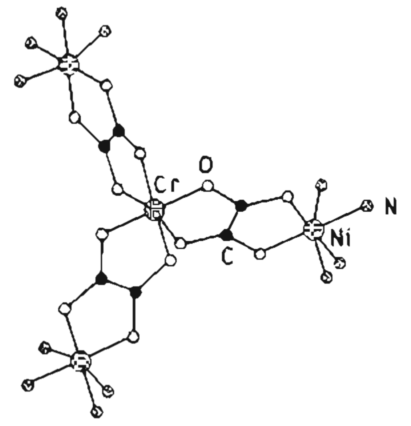


Figure 1. Schematic representation of the tetranuclear cation in $CrNi_3$. For the sake of clarity, the macrocycles bound to the Ni(II) ions have not been represented.

Table I. Frequencies (10^3 cm^{-1}) of the Electronic Transitions Observed in $K_3[Cr(ox)_3]$ (1), $\{[Ni(Me_6\text{-}[14]ane\text{-}N_4)]_2(ox)\}(ClO_4)_2$ (2), and $\{Cr[(ox)Ni(Me_6\text{-}[14]ane\text{-}N_4)]_3\}(ClO_4)_3$ ($CrNi_3$)

	1[a]	2[b]	$CrNi_3$[b]
Cr: $^4A_2 \rightarrow {}^2E + {}^2T_2$	14.4		14.4
$\rightarrow {}^4T_2$	17.7		17.5[c]
$\rightarrow {}^4T_1$	24.0		23.9
Ni: $^3A_2 \rightarrow {}^3T_2$		10.4	10.7
$\rightarrow {}^1E$		15.7	15.6
$\rightarrow {}^3T_1$		17.2	17.5[c]
$\rightarrow {}^3T_1(F)$		27.2	27.8

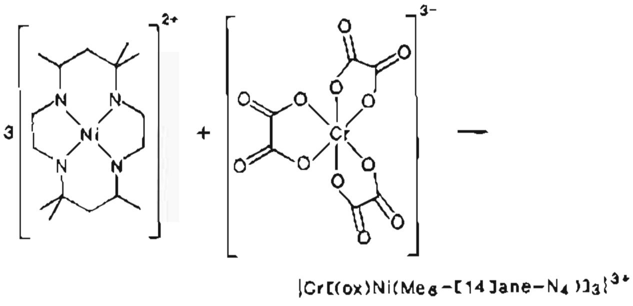
[a] In aqueous solution. [b] In a 50/50 acetonitrile–methanol solution. [c] The two transitions $^4A_2(Cr) \rightarrow {}^4T_2(Cr)$ and $^3A_2(Ni) \rightarrow {}^3T_1(Ni)$ are merged.

mol^{-1}. In the 1.23–4.2 K temperature range, the data were obtained with a mutual inductance bridge. Magnetization data were recorded with a laboratory-made apparatus working according to the extraction method.

Electronic Spectra. They were recorded with a Cary 2300 spectrometer in solution at room temperature.

Spectroscopic Properties

$CrNi_3$ is synthesized according to the scheme



In spite of our endeavors, we have not been able to grow single crystals suitable for X-ray diffraction. However, the spectroscopic data together with the chemical analysis and the magnetic properties (see below) indicates unambiguously that the structure of the tetranuclear cation is as drawn in Figure 1. A central Cr(III) ion in an octahedral environment is linked to three Ni(II) ions through oxalato bridges. Each Ni(II) ion achieves an hexacoordination with the terminal macrocycle. Me_6-[14]ane-N_4 is known to give a folded tetracoordination in the presence of a bidentate anion.[12] The infrared spectrum shows the bands characteristic of the bridging oxalato ligand ($\nu_{C\text{-}O}$ = 1675 cm^{-1} and $\nu_{O\text{-}C\text{-}O}$ = 805 cm^{-1}) as well as those of the Me_6-[14]ane-N_4 ligand. $\{[Ni(Me_6\text{-}[14]ane\text{-}N_4)]_2(ox)\}(ClO_4)_2$ also exhibits an infrared spectrum typical of an oxalato-bridged nickel(II) dinuclear complex similar to that reported by Hendrickson and co-workers.[14]

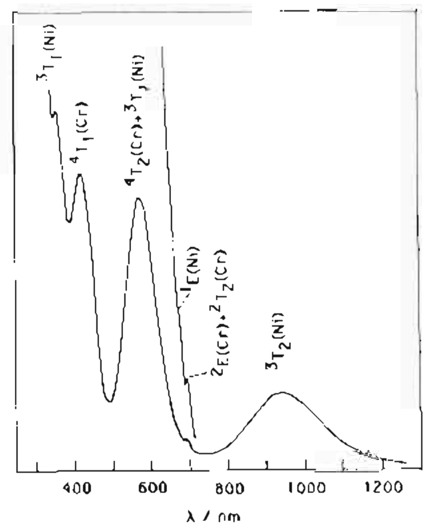


Figure 2. Electronic spectrum of $CrNi_3$ in solution in a 50/50 acetonitrile–methanol mixture.

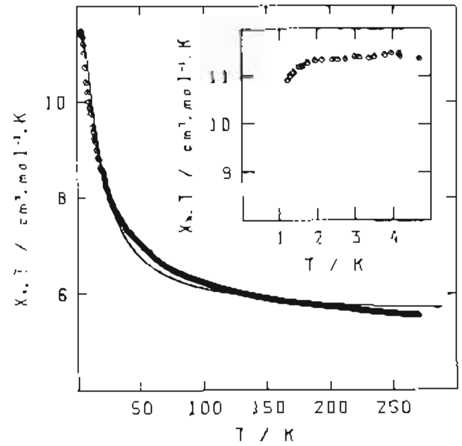


Figure 3. Experimental (Δ) and calculated (—) temperature dependences of $\chi_M T$ for $CrNi_3$.

The electronic spectrum of $CrNi_3$ in a 50/50 acetonitrile–methanol solution is given in Figure 2 with the assignments of the transitions. The frequencies are gathered in Table I and compared to those of $K_3[Cr(ox)_3]$ and $\{[Ni(Me_6\text{-}[14]ane\text{-}N_4)]_2(ox)\}(ClO_4)_2$. This spectrum shows the two sets of transitions associated with the chromium(III) and the nickel(II) ions, respectively. The first set is almost unchanged with respect to the spectrum of $K_3[Cr(ox)_3]$,[15] and the latter is also very similar to the spectrum of the compound $\{[Ni(Me_6\text{-}[14]ane\text{-}N_4)]_2(ox)\}(ClO_4)_2$ where the Ni(II) ion has the same surroundings as in $CrNi_3$. The spin-forbidden transitions are not enhanced,[13] in contrast with what has been observed in other coupled heteropolymetallic systems with the same type of bis-bidentate bridges.[16]

Magnetic Susceptibility and Magnetization

The molar magnetic susceptibility χ_M of $CrNi_3$ was investigated in the $1.3 < T/K < 270$ temperature range, and the results are shown in Figure 3 in the form of an $\chi_M T$ versus T plot. At 270 K, $\chi_M T$ is equal to 5.52 cm^3 mol^{-1} K, which corresponds to what is expected for one Cr(III) ion and three Ni(III) ions magnetically isolated. When the compound is cooled, $\chi_M T$ increases in a continuous fashion down to ca. 6 K and then reaches a plateau or a broad maximum with $\chi_M T$ = 11.3 (1) cm^3 mol^{-1} K. Below 2 K, $\chi_M T$ seems to decrease very slightly and is equal to 10.9 cm^3 mol^{-1} K at 1.23 K. This $\chi_M T$ versus T plot clearly shows that the Cr(III)–Ni(II) interactions are ferromagnetic so that the ground state has the spin $S = {}^9/_2$. The value of the maximum

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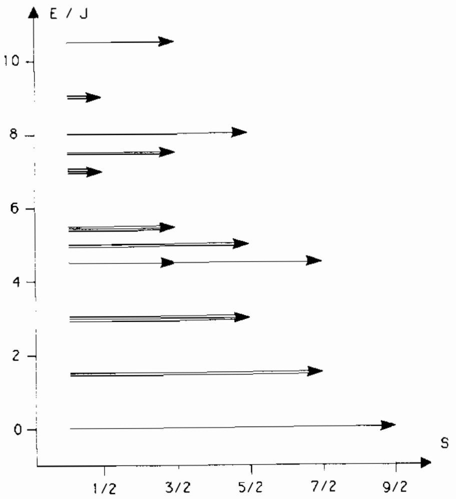

Figure 4. Low-lying spin states in $CrNi_3$.

of $\chi_M T$ is close to what is expected for a $S = {}^9/_2$ ground state in the temperature range where only this state is thermally populated. Indeed, in this temperature range, we should have

$$\chi_M T = 33N\beta^2 g_{9/2,3}{}^2/4k \tag{1}$$

$g_{9/2,3}$ is the Zeeman factor associated with this ground state, and the other symbols have their usual meaning.

To fit qualitatively the magnetic data, we first derived the theoretical expression of the magnetic susceptibility χ_M arising from the spin Hamiltonian:

$$\mathcal{H} = -JS_{Cr}(S_{Ni1} + S_{Ni2} + S_{Ni3}) + D[S_z{}^2 - (1/3)S(S + 1)\delta_{S,9/2}\delta_{S',3} + \beta[g_{Cr}S_{Cr} + g_{Ni}(S_{Ni1} + S_{Ni2} + S_{Ni3})]H \tag{2}$$

with

$$S' = S_{Ni1} + S_{Ni2} + S_{Ni3} \qquad S = S' + S_{Cr} \tag{3}$$

In (2), we take into account an axial zero-field splitting within the ground state, the corresponding parameter being D. (2) is valid only if $|D|$ is much weaker than $|J|$. Otherwise, it is necessary to introduce the Ni(II) local anisotropy as well as anisotropic and antisymmetric exchange terms in the spin Hamiltonian.[1] Moreover, the local g factors g_{Cr} and g_{Ni} are assumed to be isotropic. The g factors $g_{S,S'}$ associated with the spin states are easily calculated by using well-known algebra.[17-19] The low-lying spin states in zero field deduced from (2) are represented in Figure 4 where each state is indicated by an arrow, the length of which is equal to its spin. The parameters were calculated by minimizing R defined as

$$R = \sum[(\chi_M T)^{obs} - (\chi_M T)^{cal}]^2/\sum[(\chi_M T)^{obs}]^2$$

and found as $J = 4.5$ cm^{-1}, $g_{Cr} = 2.10$, $g_{Ni} = 2.14$, and $D = 1.1 \times 10^{-3}$. The R factor is then equal to 5×10^{-3}, which does not correspond to an excellent agreement. Moreover, several other sets of slightly different values of the parameters lead to almost equal R values. In a second attempt, we neglected the zero-field splitting, which in any case is found to be very small as compared to J, and we assumed that weak intermolecular interactions could affect the experimental data. To account for these interactions, we used the molecular field exchange model as shown in (4) where

$$\chi'_M = \chi_M/(1 - zJ'A) \tag{4}$$

χ'_M is the corrected magnetic susceptibility actually measured and zJ' the product of the molecular field exchange constant by the number of interacting nearest neighbors. χ_M is given by

$$\chi_M = (N\beta^2/4kT)\Big[165g_{9/2,3}{}^2 + 168g_{7/2,2}{}^2 \exp(3x) + 105g_{5/2,1}{}^2 \exp(6x) + \big(10g_{3/2,0}{}^2 + 84g_{7/2,1}{}^2\big) \exp(9x) + 70g_{5/2,2}{}^2 \exp(10x) + 30g_{3/2,1}{}^2 \exp(11x) + 3g_{1/2,1}{}^2 \exp(14x) + 20g_{3/2,2}{}^2 \exp(15x) + 35g_{5/2,3}{}^2 \exp(16x) + 2g_{1/2,2}{}^2 \exp(18x) + 10g_{3/2,3}{}^2 \exp(21x)\Big]\Big/[5 + 8 \exp(3x) + 9 \exp(6x) + 6 \exp(9x) + 6 \exp(10x) + 6 \exp(11x) + 3 \exp(14x) + 4 \exp(15x) + 3 \exp(16x) + 2 \exp(18x) + 2 \exp(21x)] \tag{5}$$

with

$$x = -J/2kT$$

A is deduced from (5) by replacing all the $g_{S,S'}$ factors by one. In (5), the second-order Zeeman terms proportional to $(g_{Cr} - g_{Ni})^2$ have been neglected. We have checked that the total magnitude of these additional terms with the local g values mentioned below is weaker than the experimental uncertainty on $\chi_M T$, i.e. about 0.05 cm^3 mol^{-1} K. The parameters were found as $J = 5.3$ cm^{-1}, $g_{Cr} = 2.05$, $g_{Ni} = 2.17$, and $zJ' = -0.079$ cm^{-1}. R is then equal to 5×10^{-4}, i.e. 1 order of magnitude better than before. As is generally true in the case of ferromagnetic interaction, the uncertainty on J may be rather large, of the order of 1 cm^{-1}. The sign of the Cr(III)–Ni(II) exchange parameter, on the other hand, is unambiguous.

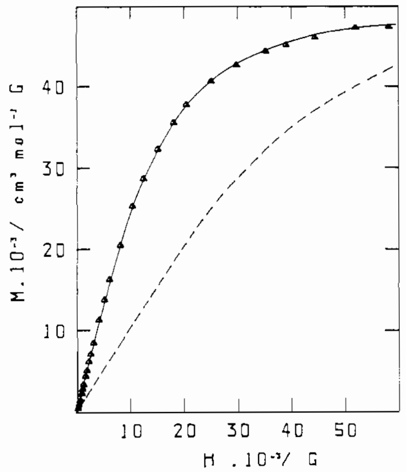

Figure 5. Magnetization M versus magnetic field H plots for $CrNi_3$: (▲) experimental data; (—) calculated curve for a $S = {}^9/_2$ state with a g factor equal to 1.97; (- -) calculated curve for a chromium(III) ion with $S_{Cr} = {}^3/_2$ and three nickel(II) ions with $S_{Ni} = 1$ uncoupled plotted with $g_{Cr} = g_{Ni} = 1.97$.

In order to confirm that $CrNi_3$ has a $S = {}^9/_2$ ground state, we measured the molar magnetization M up to 6×10^4 G at 4.2 K. The results shown in Figure 5 follow reasonably well the theoretical expression[20]

$$M = Ng_{9/2,3}\beta SB(y) \tag{6}$$

with

$$y = g_{9/2,3}\beta SH/kT \tag{7}$$

in which $B(y)$ is the Brillouin function. The best agreement is obtained for $g_{9/2,3} = 1.97$. The saturation magnetization M_S is estimated as 4.8×10^4 cm^3 mol^{-1} G. It must be pointed out that the value of M_S alone does not indicate that the ground state of $CrNi_3$ is $S = {}^9/_2$. In the absence of Cr(III)–Ni(II) interaction, M_S would be equal to $N\beta(3g_{Ni} + 3g_{Cr}/2)$, which is almost identical with the value expected for a $S = {}^9/_2$ state. However, the magnetization versus field plots are very different according to whether the Cr(III) and Ni(II) ions are ferromagnetically coupled

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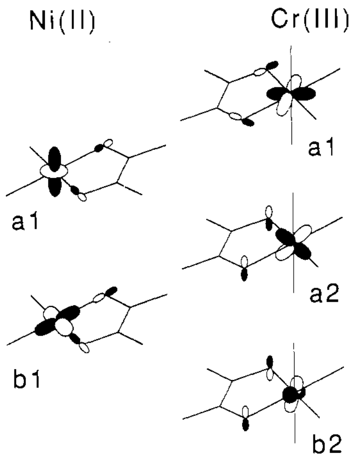

Figure 6. Schematic representation of the magnetic orbitals centered on the Cr(III) ion and the Ni(II) ions in $CrNi_3$.

or not coupled. This difference is emphasized in Figure 5.

Discussion and Conclusion

We want first to turn back to the symmetry considerations and to analyze the nature of the magnetic orbitals involved in the Cr(III)–Ni(II) interactions within $CrNi_3$.

J in (2) refers to a Cr(III)–Ni(II) pair. Therefore, it is justified to consider the symmetry of the Cr(ox)Ni bridging network, close to C_{2v}, instead of the overall symmetry of $CrNi_3$, close to C_{3v}. In this C_{2v} symmetry, the unpaired electrons of Cr(III) occupy orbitals transforming as $a_1 + a_2 + b_2$ and those of Ni(II) orbitals transforming as $a_1 + b_1$. These orbitals are shown in Figure 6. J may be written as a sum of J_{ij}'s contributions involving pairs of interacting orbitals as[1]

$$J = \tfrac{1}{3}(J_{a1a1} + J_{a1b1} + J_{a2a1} + J_{a2b1} + J_{b2a1} + J_{b2b1}) \qquad (8)$$

In (8), all the J_{ij}'s are positive, since they involve orthogonal orbitals, except J_{a1a1}. This contribution, however, may be expected to be rather small. Indeed, the $a_1(z^2)$ orbital centered on nickel is weakly delocalized in the plane of the oxalato bridge. Among the positive contributions, J_{a1b1} is certainly the most important since the a_1 orbital centered on chromium and the b_1 orbital centered on nickel are both situated in the plane of the bridging network and may efficiently interact. It can be noticed here that the interaction between Cu(II) and VO^{2+} ions through the oxalato ligand in (tmen)Cu(ox)VO(ox) with tmen = *N,N,N′,N′*-tetramethylethylenediamine also involves orthogonal b_1 and a_1 magnetic orbitals.[21] The interaction parameter J, however, has been found to be almost negligible ($J < 1$ cm^{-1}). The more efficient character of the ferromagnetic exchange pathway in $CrNi_3$ could be due to the fact that the a_1 magnetic orbital around Cr(III) would be more delocalized toward the oxygen atoms of the bridge than the a_1 magnetic orbital of VO^{2+}. Indeed, Cr(III) is certainly located in the plane of the oxalato bridge whereas the V(IV) ion is pulled out of this plane toward the oxygen atom of the vanadyl group.

To conclude, we recall that one of our goals is to design molecular-based ferromagnets.[10,11] Our strategy along this line consists of synthesizing high-spin molecules or chains and then assembling them in a ferromagnetic fashion within the crystal lattice. To obtain high-spin molecules, we are exploring two different approaches. The former is the achieving of ferromagnetic interactions due to the orthogonality of the magnetic orbitals. $CrNi_3$ provides a spectacular example of the possibilities of this approach. A $S = {}^9/_2$ ground state, if no longer unique,[22–24] is still quite unusual. The latter strategy consists of polarizing high peripheral spins due to antiferromagnetic interactions with a small central spin. We have attempted to apply this approach by using manganese(II) instead of nickel(II) in the synthesis process in order to obtain $CrMn_3$. Since the Cr(III)–Mn(II) interaction is expected to be antiferromagnetic,[1–4] the ground state of $CrMn_3$ would be characterized by the spin $S = 3S_{Mn} - S_{Cr} = 6$. Unfortunately, we have not yet succeeded in synthesizing such a compound.

Registry No. **1**, 14217-01-7; **2**, 117686-66-5; $CrNi_3$, 117709-37-2; $[Ni(Me_6\text{-}[14]\text{-}ane\text{-}N_4)](ClO_4)_2$, 52553-45-4.

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Electronic Structure and Enhanced Reactivity of Carbon Dioxide Coordinated with a Rhodium(I) Complex. An ab Initio MO Study

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An ab initio MO study has been carried out on $RhCl(AsH_3)_4(CO_2)$ and the isolobal adduct $(NH_3)(CO_2)$. Although $RhCl(AsH_3)_4(CO_2)$ has a pseudooctahedral structure with a $4d^8$ electron configuration, the most stable state is calculated to be a singlet. This result agrees well with the experimentally reported diamagnetism. The reactivity of carbon dioxide for electrophilic attack is predicted to be much more enhanced in $RhCl(AsH_3)_4(CO_2)$ than in $(NH_3)(CO_2)$, which is rationalized in terms of the coordinate bonding nature of carbon dioxide. The coordinate bond of CO_2 to $RhCl(AsH_3)_4$ is described by three-orbital mixing of Rh d_{z^2} and CO_2 π and π^* orbitals; the main interaction is a charge transfer from the Rh d_{z^2} to the CO_2 π^* orbital, into which the CO_2 π orbital mixes in an antibonding fashion with the Rh d_{z^2} orbital. This orbital mixing accumulates the electron population on the O atom of CO_2, raises the CO_2 π and nonbonding π orbital energies, and increases the O p_π contribution in the HOMO. All of these results enhance the reactivity of CO_2 with electrophiles.

Introduction

There has been much current interest in the fixation of carbon dioxide into organic substances.[2] During the last decade, intensive efforts have been devoted to the preparation and the characterization of transition-metal carbon dioxide complexes,[3–10] because

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