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Low-Lying Electronic Energy Levels in a Series of Heterobinuclear Complexes Containing Octahedral Nickel(II) and Tetrahedral Metal(II) (Copper, Cobalt, and Manganese) Species

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A series of complexes of general formula Ni(CTH)MCl_4 (CTH = *dl*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane; M = Zn, Cu, Co, Mn) have been synthesized. An X-ray crystal structure determination was performed on the zinc derivative at room temperature. Ni(CTH)$ZnCl_4$ crystallizes in the monoclinic system, space group $C2/c$, with lattice constants $a = 19.048$ (3) Å, $b = 9.540$ (3) Å, $c = 12.853$ (3) Å, $\beta = 101.38$ (5)°, and $Z = 4$. Least-squares refinement of the structure led to a conventional R factor of 0.029. The structure consists of dinuclear units Ni(CTH)$ZnCl_4$ in which the nickel(II) ion is octahedrally coordinated by four nitrogen atoms of the macrocyclic ligand and by two chlorine atoms. The latter are bridge-bonded to the Zn(II) ion, which is tetrahedrally coordinated. Magnetic susceptibility measurements down to 4.2 K were performed with the copper, cobalt, and manganese derivatives. A ferromagnetic coupling was observed in the Ni–Cu derivative, a weak antiferromagnetic coupling was observed in the Ni–Mn derivative, and essentially no coupling was observed in the Ni–Co derivative. This behavior has been related to the available exchange pathways connecting the magnetic orbitals on nickel with those on the tetrahedral metal ions.

Introduction

Heterobinuclear complexes are still a relatively rare species in the zoo of magnetically coupled systems,[2,3] although a few well-characterized series of pure[4-15] and doped[16-23] compounds have been reported in the last few years. The advantage of studying a series of heterobinuclear as compared to homobinuclear complexes is that unusual sets of magnetic orbitals can be brought in close proximity, yielding, in principle, new pathways to exchange interactions. Indeed ferromagnetic coupling, which was relatively rare up to some years ago, has now been observed in quite a few cases for pairs or triples containing different metal ions.[4,5,24,25]

Table I. Summary of Crystal Data, Intensity Collection, and Structure Refinement[a]

formula	$C_{16}H_{32}N_4Cl_4NiZn$
fw	546.3
space group	$C2/c$
a, Å	19.048 (3)
b, Å	9.540 (3)
c, Å	12.853 (3)
β, deg	101.38 (5)
V, Å^3	2289.7
Z	4
d, g cm^{-3}	1.584
cryst size, mm	0.25 × 0.25 × 0.16
μ(Mo Kα), cm^{-1}	22.75
transmission factors, max-min	0.69-0.55
scan type	ω-2θ
scan width ($\Delta\omega$), deg	1.00 + 0.3(tan θ)
scan speed, deg min^{-1}	3
bkgd/scan time ratio	0.5
data colln range	$+h,k,l$ ($h + k = 2n$)
no. of data with $F_o^2 \geq 3\sigma(F_o^2)$	1664
no. of variables	173
R	0.029
R_w	0.030

[a] Agreement factors are defined as follows: $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = |\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2|^{1/2}$. The weighting scheme is defined by $w = 1/\sigma_F^2$; $\sigma_F = \sigma_I[I(Lp)]^{-1/2}$; $\sigma_I = |\sigma_c^2 + (0.02N_{net})^2|^{1/2}$. Programs used in the crystallographic calculations are given in ref 27. Atomic scattering factors were taken from a standard source.[28]

In order to synthesize heterobinuclear species a good starting point is that of metal complexes with empty coordination sites, which can then be occupied by a ligand capable of bridging two different metal ions. One possible candidate to this is the square-planar α-form of the (*dl*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)nickel(II) diperchlorate, Ni(CTH)$(ClO_4)_2$, which was reported to form paramagnetic adducts

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Table II. Positional Parameters for Ni(CTH)ZnCl$_4$[a]

atom	*x*	*y*	*z*
Ni	0	1697 (1)	2500
Zn	0	-2080 (1)	2500
Cl1	-927 (1)	-3442 (1)	2670 (1)
Cl2	-416	-449 (1)	1197 (1)
N1	752 (1)	1876 (2)	1481 (2)
N2	618 (1)	3104 (2)	3542 (2)
C1	300 (2)	3118 (4)	4496 (2)
C2	1413 (2)	2847 (3)	3798 (3)
C3	1790 (2)	3884 (4)	4633 (3)
C4	1733 (2)	2950 (3)	2808 (3)
C5	1548 (2)	1869 (3)	1924 (3)
C6	1973 (2)	2214 (4)	1056 (3)
C7	1746 (2)	389 (4)	2323 (3)
C8	506 (2)	3116 (3)	813 (3)

[a] Coordinates multiplied by 10^4. Standard deviations in the last significant digits are in parentheses.

with tetrachlorozincate ions.[26] Since this behavior must be related to the formation of cis-octahedral nickel(II) complex, we decided to characterize this complex and to prepare other analogous ones with $CuCl_4^{2-}$, $CoCl_4^{2-}$, and $MnCl_4^{2-}$ with the aim of studying the variation of the magnetic properties of the adducts on varying the metal ion and the number of magnetic orbitals. We neglected the $NiCl_4^{2-}$ and $FeCl_4^{2-}$ derivatives, which also are formed, because the ground state of these tetrahedral ions are orbitally degenerate and therefore are expected to give comparatively complicated magnetic exchange patterns.

Experimental Section

Synthesis of the Complexes. All of the Ni(CTH)MX$_4$ derivatives have been synthesized by mixing acetonitrile solutions containing stoichiometric amounts of the α-form of the Ni(CTH)(ClO$_4$)$_2$ complex and the appropriate tetraethylammonium tetrachloro metal complex. A precipitate appeared after a few minutes. It was filtered on a sintered glass funnel, washed with acetonitrile–diethyl ether mixtures, and dried in vacuo.

These compounds analyzed satisfactorily for Ni(CTH)MCl$_4$. Anal. Calcd for $C_{16}H_{36}N_4Cl_4NiCu$: C, 35.03; H, 6.61; N, 10.21. Found: C, 35.39; H, 6.77; N, 10.49. Calcd for $C_{16}H_{36}N_4Cl_4NiCo$: C, 35.33; H, 6.67; N, 10.30. Found C, 35.65; H, 6.83; N, 10.47. Calcd for $C_{16}H_{36}N_4Cl_4NiMn$: C 35.39; H, 6.72; N, 10.38. Found: C, 35.37; H, 6.85; N, 10.32. Calcd for $C_{16}H_{36}N_4Cl_4NiZn$: C, 34.92; H, 6.59; N, 10.18. Found C, 35.17; H, 6.74; N, 10.22.

The compounds can be also prepared by mixing a solution of the nickel macrocyclic complex in acetone with a methanolic solution of the appropriate metal chloride. The addition of few drops of concentrated hydrochloric acid induced the crystallization of the complexes.

Crystals suitable for X-ray analysis were obtained only for Ni(CTH)ZnCl$_4$ by recrystallization from *N,N*-dimethylformamide–ethanol or *N,N*-dimethylformamide–butan-1-ol mixture. The C, H, N analysis is in agreement with those of the powder.

X-ray Structure Determination of Ni(CTH)ZnCl$_4$. A crystal of Ni(CTH)ZnCl$_4$, shaped as a monoclinic prism and of appropriate dimensions of 0.25 × 0.25 × 0.16 mm, was used for crystal data and intensity data collection.

Diffraction data were collected on a Philips PW 1100 automated diffractometer equipped with a Mo X-ray tube and a graphite monochromator. Details on crystal data and intensity data collection are given in Table I. The orientation matrix and unit cell parameters were obtained from 21 machine-centered reflections with $8 \leq \theta \leq 12$. Intensities of three check reflections measured every 120 minutes revealed no decay over the duration of data collection. Data were corrected for Lorentz and polarization effects, as well as for absorption.

The systematic absences *hkl* ($h + k = 2n$) and *h*0*l* ($h, l = 2n$) indicated two possible space groups: *Cc* and *C*2/*c*. The structure was solved in the *C*2/*c* space group by locating the Ni and Zn atoms with direct methods. All the remaining non-hydrogen atoms were located by Fourier and difference Fourier maps and least-squares refinement.

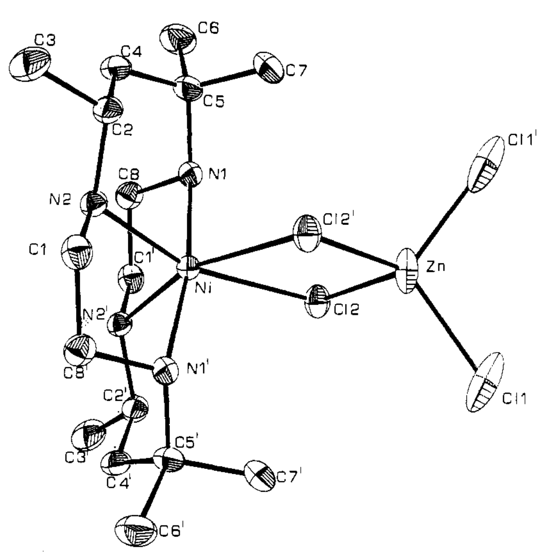

Figure 1. Perspective view of Ni(CTH)ZnCl$_4$.

Table III. Bond Distances (Å) and Bond Angles (deg) for Ni(CTH)ZnCl$_4$[a]

Ni-N1	2.13 (4)	Ni-N2	2.09 (4)
Ni-Cl2	2.66 (3)	Ni-Zn	3.60 (3)
Zn-Cl1	2.24 (1)	Zn-Cl2	2.31 (3)
N1-Ni-N2	88.9 (1)	N1-Ni-N1'	170.8 (1)
N1-Ni-N2'	85.2 (1)	N2-Ni-N2'	100.0 (1)
N1-Ni-Cl2	80.1 (1)	N2-Ni-Cl2	163.2 (1)
Cl1-Zn-Cl1'	108.9 (1)	Cl1-Zn-Cl2	107.3 (1)
Cl1-Zn-Cl2'	119.0 (1)	Cl2-Zn-Cl2'	95.2 (1)
Ni-Cl2-Zn	92.6 (1)	Cl2-Ni-Cl2'	79.7 (1)

[a] Standard deviations in the last significant digits are in parentheses.

Hydrogen atoms were located in calculated positions (C–H = 1.08 Å) and introduced in structure factor calculations with isotropic thermal parameters, which were allowed to vary.

The residual peaks in the last difference Fourier map were less than 0.3 e Å^{-3}. Final atomic positional parameters for non-hydrogen atoms are collected in Table II. Atomic positional parameters for hydrogen atoms and thermal parameters for non-hydrogen atoms are available as supplementary material (Tables SI and SII). A listing of observed and calculated structure factors is also available.

The isomorphism of the Ni–Cu to the Ni–Zn derivative was checked on some poor single crystals, which allowed us only to measure the unit cell, because for $\theta \geq 12°$ a marked decrease of the intensty was observed.

Powder diffraction patterns of the Ni–Co and Ni–Mn derivatives show that these also are isomorphous with Ni(CTH)ZnCl$_4$.

Results

Description of the Structure of Ni(CTH)ZnCl$_4$. An ORTEP plot of Ni(CTH)ZnCl$_4$ is shown in Figure 1. The X-ray crystal structure confirms that a cis-octahedral adduct has indeed been formed in such a way that a dinuclear species containing nickel(II) and tetrahedral zinc(II) is present in the lattice. The two metal ions are bridged by two chlorine atoms, and the overall symmetry of the complex is C_2. Relevant bond distances and angles around the two metal ions are shown in Table III. The coordination of the nickel(II) chromophore is similar to that previously reported[29-31] for cis-octahedral adducts of $(NiCTH)^{2+}$. The nickel(II) ion is octahedrally coordinated to the four nitrogen atoms of the CTH ligand and to two chlorine atoms of $ZnCl_4^{2-}$. The C_2 symmetry of the complex requires that Ni, N2, N2′, Cl2, and Cl2′ define a plane, the equatorial plane of the distorted octahedron.

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Table IV. Absorption Maxima ($cm^{-1} \times 10^{-3}$) of Electronic Spectra of $Ni(CTH)MCl_4$ Complexes

$Ni(CTH)ZnCl_4$		8.7 (sh)		17.0
		9.9		
$Ni(CTH)CuCl_4$	7.4	10.3		17.9 (sh)
	7.1[a]	10.4[a]		17.9[a]
$Ni(CTH)CoCl_4$	6.5	9.8	14.9	16.4
$Ni(CTH)MnCl_4$		8.7 (sh)		16.7
		9.9		

[a] At liquid-nitrogen temperature.

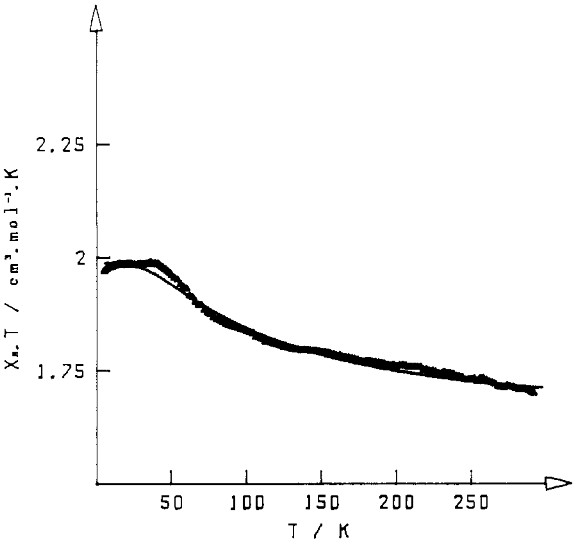

Figure 2. Experimental (▵) and theoretical (- - -) temperature dependencies of χ_MT for $Ni(CTH)CuCl_4$.

The bonds with the axial nitrogen atoms are slightly longer than those with the equatorial ones (2.13 (4) vs. 2.04 (4) Å). The Ni–Cl bonds are on the long edge side of those usually found in octahedral nickel chloride complexes.[32] The axial nitrogen atoms, N1 and N1′, are slightly pushed away from the perpendicular to the equatorial plane, making an angle N1–Ni–N1′ of 170.8 (1)°.

The $ZnCl_4^{2-}$ ion is tetrahedral as expected, with the bonds with the bridging chlorides slightly longer than those with the terminal chlorides (2.31 (3) vs. 2.24 (1) Å). The Ni–Cl2–Zn bridge angles are 92.6 (2)°.

The structures of the other derivatives of this series are presumably similar, as suggested by the isomorphism of the crystals. Relatively large variations can be expected for $Ni(CTH)CuCl_4$, in which the coordination around copper is presumably compressed tetrahedral as observed in several mononuclear[33] and dinuclear[34] copper chloride derivatives.

Electronic Spectra. The frequency maxima in the diffuse reflectance spectra of $Ni(CTH)MCl_4$ (M = Mn, Co, Cu, Zn, Ni) are given in Table IV. In all of them are present bands at 9000–10 000 and 16 000–17 000 cm^{-1}, which can be attributed to the octahedral nickel chromophores.[35] They remain roughly constant, showing that no major distortion in the nickel(II) coordination environment occurs through the series. The similarity of these absorptions to those of simple mononuclear nickel(II) complexes confirm that the ground state is a spin triplet with no orbital degeneracy. This statement is confirmed by sample angular overlap calculations, which suggest that the ground state is split in zero magnetic field by ca. 10 cm^{-1}. The other bands can be attributed to the tetrahedral MCl_4 chromophores (M = Cu, Co). In fact the spectrum of $Ni(CTH)CuCl_4$ is dominated by the bands of the $CuCl_4$ moiety: in the long wavelength limit the d–d transitions are obscuring those of nickel, while at high frequency it is the Cu–Cl charge transfer that largely overlaps to the nickel ν_2 transition. The electronic spectra are in agreement with a distorted tetrahedral configuration of the $CuCl_4$ moiety.[36]

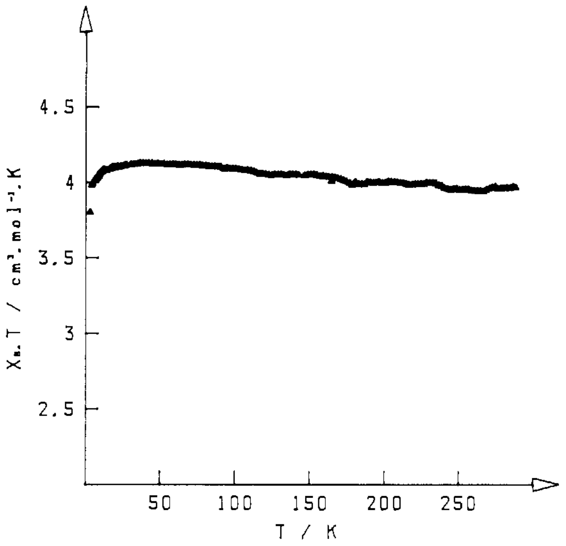

Figure 3. Experimental (▵) and theoretical (- - -) temperature dependencies of χ_MT for $Ni(CTH)CoCl_4$.

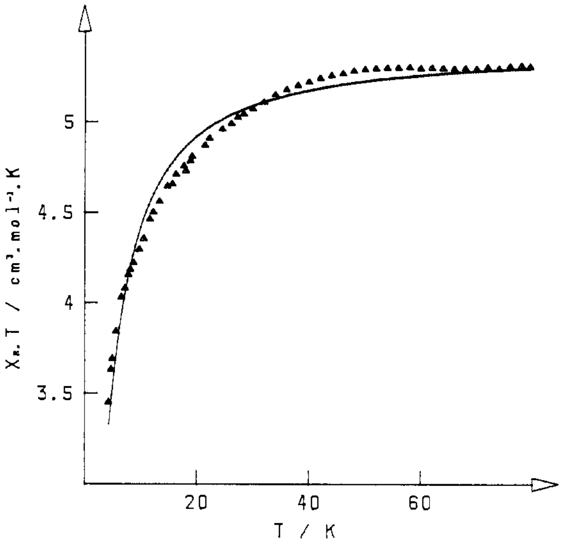

Figure 4. Experimental (▵) and theoretical (- - -) temperature dependencies of χ_MT for $Ni(CTH)MnCl_4$.

Magnetic Properties. General Data. The magnetic properties of the three compounds $Ni(CTH)MCl_4$ (M = Cu, Co, Mn) are represented in Figures 2–4 in the form of the product χ_MT of the molar magnetic susceptibility by the temperature.

M = Cu. As the sample is cooled down from room temperature, χ_MT increases and then reaches a plateau from 40 K with χ_MT = 1.98 $cm^3\ mol^{-1}$ K. The two low-lying states for a copper–nickel pair are a spin doublet and a spin quartet. The magnetic behavior clearly shows that the spin quartet is the lowest. Below 40 K only this $S = {}^3/_2$ state is thermally populated, and the magnetic susceptibility follows the Curie law expected for an isolated quartet state, namely $\chi_MT = 5N\mu_B{}^2g_{3/2}{}^2/4k$, with the $g_{3/2}$ factor associated with this state equal to 2.05. The theoretical expression of χ_MT is

$$\chi_MT = \frac{N\mu_B{}^2}{4k}\,\frac{g_{1/2}{}^2 + 10g_{3/2}{}^2\exp(3J/2kT)}{1 + 2\exp(3J/2kT)} \qquad (1)$$

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where the symbols have their usual meaning and where the zero-field splitting within the quartet state is neglected. Here the spin Hamiltonian was used in the form $\hat{\mathbf{H}} = -J\mathbf{S}_1\cdot\mathbf{S}_2$.

$g_{1/2}$ and $g_{3/2}$ may be related to the local g_{Cu} and g_{Ni} values according to[3]

$$g_{1/2} = -{}^1\!/_3 g_{Cu} + {}^4\!/_3 g_{Ni} \qquad g_{3/2} = {}^1\!/_3 g_{Cu} + {}^2\!/_3 g_{Ni} \tag{2}$$

The population of the excited doublet state, even in the high-temperature range, is not sufficient to allow an independent determination of $g_{1/2}$, which is strongly correlated to J. Therefore, we preferred to impose the value of $g_{1/2}$. For $g_{1/2} = g_{3/2}$, the least-squares fitting of the experimental data leads to $= 99$ cm^{-1}. Since g_{Ni} is expected to be larger than g_{Cu} (roughly 2.25 and 2.10 respectively), $g_{1/2}$ is expected to be slightly larger than $g_{3/2}$. Any value of $g_{1/2} > g_{3/2}$ leads to $J < 99$ cm^{-1}. For instance, for $g_{1/2} = 2.20$, J is found equal to 69 cm^{-1}. In fact, as for all the ferromagnetically coupled polymetallic systems, the energy gaps between the low-lying states cannot be determined accurately from the magnetic data. In the present case, we can only assert that the splitting $3J/2$ between doublet and quartet is in the range 100–150 cm^{-1}.

M = Co. For this compound, χ_MT is essentially constant and equal to 4.00 ± 0.05 cm^3 mol^{-1} K, which closely corresponds to what is expected for the sum of an octahedral nickel(II) ion and a tetrahedral cobalt(II) without interaction. In other words, the magnetic properties of Ni(CTH)CoCl$_4$ do not reveal any interaction between the two metal centers.

M = Mn. The $\chi_M T$ vs. T plot for Ni(CTH)MnCl$_4$ is constant and equal to 5.30 cm^3 mol^{-1} K from room temperature down to 40 K and then decreases in a continuous manner to reach 3.4 cm^3 mol^{-1} K at 4.2 K. When the $\chi_M T$ vs. T curve is extrapolated below 4.2 K, one obtains a $\chi_M T$ value close to 2.0 cm^3 mol^{-1} K at 0 K. This magnetic behavior is characteristic of a weak antiferromagnetic interaction between the $S_{Mn} = {}^5/_2$ single-ion ground state for manganese(II) and $S_{Ni} = 1$ single-ion ground state for nickel(II), giving a $S = {}^3/_2$ ground state, a $S = {}^5/_2$ first excited state at $-5J/2$, and a $S = {}^7/_2$ second excited state at $-6J$. The theoretical expression of $\chi_M T$ is

$$\chi_M T = \frac{N\mu_B^2}{4k} \times \frac{10g_{3/2}^2 + 35g_{5/2}^2 \exp(5J/2kT) + 84g_{7/2}^2 \exp(6J/kT)}{2 + 3\exp(5J/2kT) + 4\exp(6J/kT)} \tag{3}$$

where $g_{3/2}$, $g_{5/2}$, and $g_{7/2}$ are related to the local values according to

$$g_{3/2} = -{}^2\!/_5 g_{Ni} + {}^7\!/_5 g_{Mn} \qquad g_{5/2} = {}^4\!/_{35} g_{Ni} + {}^{31}\!/_{35} g_{Mn}$$
$$g_{7/2} = {}^2\!/_7 g_{Ni} + {}^5\!/_7 g_{Mn} \tag{4}$$

In (3), we again neglected the zero-field splitting within the low-lying states. The least-squares fitting of the experimental data with relation 3 leads to $J = -1.18$ cm^{-1} and an average g value of 2.01. Since the magnitude of the interaction is weak, the zero-field splitting is certainly not without influence on the magnetic properties, so that another model could also lead to a satisfactory fitting of the magnetic data. The important point, however, is that these data show unambigously that the metal ions interact in an antiferromagnetic fashion. Indeed, if the manganese(II) and nickel(II) ions were uncoupled, the magnetic behavior would be, as in Ni(CTH)CoCl$_4$, the sum of the magnetic behaviors of the isolated ions. For manganese(II), the zero-field splitting is extremely small[37] and without influence on the magnetic properties above 4.2 K. It follows that, in absence of interaction, the contribution $(\chi_M T)_{Mn}$ due to the manganese(II) ion would be $35N\mu_B^2g^2/12k$, i.e. close to 4.38 cm^3 mol^{-1} K. To this contribution, one would have to add the contribution $(\chi_M T)_{Ni}$ due to the nickel(II) ion. Actually, the observed value of $\chi_M T$ at 4.2 K is much below 4.38 cm^3/mol^{-1}/K. Moreover, it is quite remarkable that the limit of $\chi_M T$ in Ni(CTH)MnCl$_4$ at 0 K is the same as that of $\chi_M T$ in Ni(CTH)CuCl$_4$. Both complexes exhibit a quartet ground state. In the former compound, this $S = {}^3/_2$ state arises from an antiferromagnetic interaction. In the latter, it arises from a ferromagnetic interaction.

Finally it must be observed that the tendency to a decrease of $\chi_M T$ at very low temperatures observed for these compounds may be due to weak antiferromagnetic interactions between the heterobinuclear complexes. However they do not affect the previous discussion of the data obtained at higher temperatures.

EPR Spectra. The polycrystalline powder EPR spectra of Ni(CTH)CoCl$_4$ at 4.2 K show a very broad absorption ranging from 0 to 0.5 T, with what could be a perpendicular feature (effective $S = {}^1/_2$) at $g = 6$ and another one at $g = 2$. A broader signal is observed also at $g = 1.3$.

The polycrystalline powder EPR spectra of Ni(CTH)MnCl$_4$ show essentially a broad signal centered at $g \sim 2$, with a broad additional absorption at ca. 0.2 T. Given the weak coupling observed in these two compounds, which leaves several different levels occupied even at the lowest temperature available, it seems safe not to attempt any interpretation of these essentially featureless spectra.

No EPR spectra could be detected for the Ni(CTH)CuCl$_4$ derivative. We have no good explanation for this surprising behavior. Indeed quite a few examples of Ni–Cu EPR spectra are available in the literature,[3,10,13,14,19,21,22,38,40] even in a case where the ground state was $S = {}^3/_2$ as in the present case. Relaxation effects might be responsible for the lack of spectra, connected with the nature of the zero-field splitting of the ground $S = {}^3/_2$ state for the pair, but we do not feel inclined to speculate further in this direction.

Discussion

The largest magnetic coupling in this series of complexes is that of the Ni–Cu pair, which is ferromagnetic, while only a weak antiferromagnetic coupling is operative in the Ni–Mn pair, with essentially no coupling for the Ni–Co pair. To our knowledge this is the first case for which a ferromagnetic coupling is reported for a discrete copper(II)–nickel(II) pair, while a weak ferromagnetic coupling was suggested for Ni–Cu pairs obtained by doping[22] tetrakis(μ-benzoato-*O*,*O'*)bis(quinoline)dicopper(II) with nickel(II).

The experimental result in this series of Ni(CTH)MCl$_4$ compounds is at first glance surprising because it is generally assumed that the ferromagnetic exchange pathways increase with the number of unpaired electrons present in the couple,[41] so that one might anticipate a stronger ferromagnetic interaction in the Ni–Mn derivative than in the Ni–Co and Ni–Cu derivatives. Apparently this prediction is completely at variance from the experimental results, so that the whole problem must be reanalyzed in deeper detail.

In the last few years it has been shown that ferromagnetic coupling is by no means as uncommon[4,5,24,25] as was previously assumed and that effective strategies can be conceived in order to synthesize molecular compounds displaying such a type of coupling.[42] Since it is well-known that ferromagnetic coupling can arise when the magnetic orbitals are orthogonal to each other, this condition can be achieved in two ways: accidental and strict orthogonality. In the former case the relative orientation of the two interacting magnetic orbitals is such that the overlap is zero, but this is not dictated by symmetry requirements, while in the latter case the magnetic orbitals belong to different irreducible representations of the molecular point group. Small variations in the geometrical parameters, which can occur in a series of homologous complexes, may remove the condition of accidental

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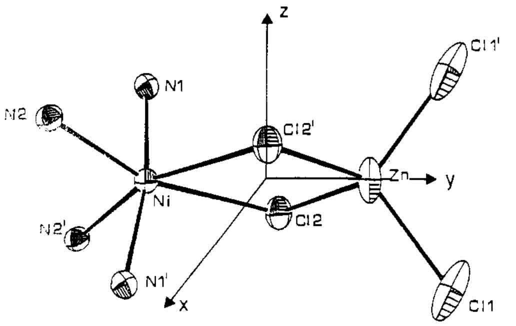

Figure 5. Sketch of Ni(CTH)MCl_4 complexes with the molecular reference frame.

orthogonality, reintroducing a nonzero antiferromagnetic component in the coupling, while strict orthogonality can be removed only if the symmetry requirement is removed, i.e. if the homology of the terms of the series is removed. A beautiful example of the first type of behavior is that of the bis(μ-hydroxo)-bridged copper(II) complexes,[43,44] in which the coupling varies from ferro- to antiferromagnetic depending on the value of the Cu-O-Cu angle. The relative insensitivity of the strict orthogonality condition to the value of the bridging angle has been shown in the case of Cu-VO pairs[5,24] and in the coupling between ground and excited states of copper(II) ions monitored by EPR spectra.[45]

In order to decide whether the ferromagnetic coupling observed in the Ni-Cu pairs is determined by either strict or accidental degeneracy and which are the factors determining the large decrease in the ferromagnetic coupling when the cobalt(II) and manganese(II) derivatives are considered, a detailed analysis of the magnetic orbitals is now at order.

The magnetic orbitals in nickel(II) are xy and z^2 in the reference frame depicted in Figure 5. Since the dinuclear species has C_2 symmetry, these two orbitals can be classified within that point group as A and B respectively. The ground state for the compressed tetrahedron around copper is a linear combination of xy and yz, both of B character. Therefore in the Ni-Cu pair two pathways are possible, the one involving the nickel(II) z^2 being weakly ferromagnetic. The pathway involving nickel(II) xy is expected to yield either ferro- or antiferromagnetic contribution, depending on the Ni-Cl-Cu angle. For angles close to 90° accidental orthogonality may occur, yielding ferromagnetic coupling. Therefore we suggest that the observed value of J is largely determined by the accidental orthogonality of the xy orbitals on nickel and copper.

The magnetic orbitals on cobalt correspond to the three t_2 orbitals of tetrahedral symmetry, therefore to the B combination of copper, so two others must be added, one of type B and the other of type A. Finally the five magnetic orbitals of manganese are obtained by adding to the three of cobalt two more of A symmetry. As far as symmetry is concerned, several strictly orthogonal ferromagnetic pathways are introduced (those involving an A orbital on one center and a B orbital on the other) together with others (those involving either A or B type orbitals on both centers) that can be either ferro- or antiferromagnetic depending on the Ni-Cl-M angle. The large decrease in the ferromagnetic coupling on passing from copper to cobalt and manganese shows that the antiferromagnetic contributions are taking over. This may be due to small angular variations in the series and to the fact that the condition of accidental orthogonality can be met for a pair of orbitals at an angle different from that of another pair.

It is therefore apparent that in the present series of complexes the accidental orthogonality or nonorthogonality of magnetic orbitals is determining the observed large variation in the magnetic properties. These results show how difficult it can be to elaborate strategies for obtaining strong ferromagnetic coupling based on accidental orthogonality of magnetic orbitals and how only the strict orthogonality relation yields a valuable way to synthesize compounds of which the ground state is the state of the highest spin multiplicity.

Registry No. Ni(CTH)$ZnCl_4$, 101224-31-1; Ni(CTH)$CuCl_4$, 101224-32-2; Ni(CTH)$CoCl_4$, 101224-33-3; Ni(CTH)$MnCl_4$, 101224-34-4.

Supplementary Material Available: Listings of hydrogen atom positional parameters (Table SI), anisotropic thermal parameters for nonhydrogen atoms (Table SII), and observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

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Crystal Structure of (Azacapten)cobalt(II) Diperchlorate and Strain Energy Minimization Analyses of the (Azacapten)cobalt(III) and (Azacapten)cobalt(II) Cations

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[Co^{II}(azacapten)]$(ClO_4)_2$, $C_{14}H_{30}Cl_2CoN_4O_8S_3$, crystallizes in the orthorhombic space group $Pna2_1$, with a = 20.684 (8) Å, b = 12.820 (5) Å, c = 8.826 (5) Å, and Z = 4. The complex cation is disordered with both enantiomers occupying the same site. The average Co(II)-N and Co(II)-S bond lengths are 2.08 and 2.31 Å, respectively. The cation adopts a lel_3 conformation, which molecular mechanics calculations suggest is the geometry of lowest strain energy. Molecular mechanics calculations also indicate that the relatively short Co(II)-N bond length is not a consequence of ligand constraints but is most likely due to the low-spin electronic state of the complex.

Introduction

The preparation and structure of a cobalt encapsulating macrobicyclic ligand with three nitrogen and three sulfur donors have been reported recently.[1] This ligand, 1-methyl-3,13,16-trithia-6,8,10,19-tetraazabicyclo[6.6.6]eicosane (azacapten), like previously reported hexaamine cryptates,[2,3] so tightly binds the metal that on reduction to Co(II) a stable nonlabile complex is obtained. Consequently, reactions of Co(III) and Co(II) azacapten complexes can be studied in the absence of ligand-exchange processes.

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