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The First Ferromagnetic Tetranuclear Nickel(II) Complex with a μ-Azido Bridge. Structure and Magnetic Properties of $[Ni_4(\mu\text{-}N_3)_4(2\text{-oxo-1,3-diaminopropane})_2(2\text{-hydroxo-1,3-diaminopropane})_2](ClO_4)_2$

Joan Ribas,*,† Montserrat Monfort,† Ramon Costa,† and Xavier Solans‡

Departament de Química Inorgânica, Universitat de Barcelona, Diagonal, 647. 08028-Barcelona, Spain, and Departament de Cristal.lografia i Mineralogia, Universitat de Barcelona,
Martí Franqués, s/n 08028-Barcelona, Spain

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The first ferromagnetic tetranuclear Ni(II) complex with an end-on μ-azido bridge has been synthesized. This compound has the formulation $[Ni_4(\mu\text{-}N_3)_4(2\text{-oxo-1,3-diaminopropane})_2(2\text{-hydroxo-1,3-diaminopropane})_2](ClO_4)_2$. The X-ray crystal structure has been solved. The complex $C_{12}H_{38}N_{20}Ni_4O_4[ClO_4]_2$ crystallizes in the monoclinic system, space group $C2/c$, with $a = 27.238(3)$ Å, $b = 8.712(1)$ Å, $c = 19.208(2)$ Å, $\beta = 134.10(2)°$, $V = 3273(1)$ Å^3, $Z = 4$, $R = 0.030$ and $R_w = 0.039$. The four Ni(II) atoms are in a distorted octahedral environment and are related by an S_4 symmetry axis forming a quasi-perfect square. The oxygen atom of the amine ligands (OHpn and Opn) also acts as a bridging ligand between two Ni(II) ions. The magnetic properties of this new complex have been studied. The curve $\chi_M T$ vs T indicates a ferromagnetic coupling between Ni(II) ions. Using the Hamiltonian $H = -J(S_1S_2 + S_2S_3 + S_3S_4 + S_4S_1)$, the J value obtained is +21.3 cm^{-1}. Anisotropic perturbation containing both an axial Zeeman effect and ZFS acting within the $S = 4$ ground state has also been studied.

Introduction

The azido group is a versatile bridging ligand which can coordinate two Ni(II) ions in either end-on[1-3] or end-to-end fashion.[4,5] Although both kinds of complexes are structurally and magnetically well characterized, the few compounds reported to date are dinuclear systems. No magnetostructural correlations have been performed in order to explain their different behavior according to the coordination of the azide to Ni(II) (ferromagnetic or antiferromagnetic, respectively), although there are several well-documented studies about analogous Cu(II) complexes. Kahn and co-workers introduced the concept of spin polarization to explain the antiferromagnetic behavior in $1,3\text{-}N_3Cu_2$ complexes and the ferromagnetic behavior in $1,1\text{-}N_3Cu_2$ complexes.[6-8] Very recently we have begun a systematic research into Ni(II) systems with N_3^- acting as a bridge, using several amines as blocking ligands (bidentate,[9] tridentate,[10] or tetradentate[11]) and different counteranions. With these ligands we have reported the first simple[9,11] and alternating[10] antiferromagnetic 1D Ni(II)-azido complexes and the first simple ferromagnetic Ni(II) azido compound.[9] In all cases, 1,3-coordination gives antiferromagnetic behavior and 1,1-coordination gives ferromagnetism.

In order to extend this study we have tried to synthesize new polynuclear species with C- or N-substituted amines, like 2-hydroxo- or 2,2′-dimethyl-1,3-diaminopropane. In this paper we present the synthesis, X-ray structure, and magnetic behavior of the first ferromagnetic tetranuclear Ni(II) complex with a mixed OH^- and N_3^- bridge obtained by using the 2-hydroxo-1,3-diaminopropane (OHpn) as blocking ligand. The ferromagnetic behavior observed agrees with $1,1\text{-}N_3$ coordination between nearest Ni(II) ions. The oxygen atom of the amine ligands (OHpn and Opn) also acts as bridging ligand between two Ni(II) ions. Each oxygen atom shares a proton with the oxygen atom of a neighboring ligand, leading to (O–H–O) pairs and our (averaged) formulation of equal number of OHpn and Opn^- ligands.

Experimental Section

Materials. 2-Hydroxo-1,3-diaminopropane (OHpn) (Aldrich), nickel perchlorate (Fluka), and sodium azide (Fluka) were purchased and used without further purification.

Synthesis. *Caution*! Perchlorate salts of metal complexes with azide and organic ligands are potentially explosive. Only a small amount of material should be prepared, and it should be handled with caution.

When a solution of 10 mmol of NaN_3 was added to an aqueous solution containing 5 mmol of $Ni(ClO_4)_2(aq)$ and 5 mmol of 2-hydroxo-1,3-diaminopropane (OHpn), blue-violet crystals were obtained after several days by slow evaporation.

Spectral and Magnetic Measurements. IR spectra were recorded on a Perkin-Elmer 1330 IR spectrophotometer. Magnetic measurements were carried out on a polycrystalline sample (40 mg) with a pendulum type magnetometer–susceptometer (MANICS DSM-8) equipped with an Oxford Helium continuous flow cryostat, working in the 4.2–300 K range, and a Drusch EAF 16UE electromagnet. The magnetic field was approximately 1.5 T. The diamagnetic correction was evaluated as 428×10^{-6} cm^3 mol^{-1} from Pascal's tables. To guarantee the results in the low temperature range, magnetic measurements were repeated with a Quantum Design MPMS SQUID susceptometer operating at a magnetic field of 0.5 T between 2 and 300 K. The sample was tested for para- and ferromagnetic impurities up to 5 T at room temperature. EPR spectra were recorded on powder sample at X-band frequency with a Varian 109 spectrometer at helium temperature.

X-ray Crystallography. A prismatic crystal ($0.1 \times 0.1 \times 0.2$ mm) was selected and mounted on a Philips PW-1100 diffractometer. Unit cell

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† Departament de Química Inorganica.

‡ Departament de Cristal.lografia i Mineralogia.

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Table I. Crystallographic data for $[Ni_4(\mu\text{-}N_3)_4(Opn)_2(OHpn)_2](ClO_4)_2$

formula	$C_{12}H_{38}N_{20}Ni_4O_4(ClO_4)_2$
fw	960.31
space group	*C*2/*c*
a, Å	27.238(3)
b, Å	8.712(1)
c, Å	19.208(2)
β, deg	134.10(2)
V, Å^3	3273(1)
Z	4
$d_{calc.}$ g/cm^3	1.948
μ(Mo Kα), cm^{-1}	25.08
λ(Mo Kα), Å	0.710 69
T, °C	room temp
scan method	ω
no. of params refined	248
R^a	0.030
$R_w{}^b$	0.039

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$ ^{b} $R_w = \sum_w||F_o| - |F_c||/\sum_w|F_o|$.

parameters were determined from automatic centering of 25 reflections ($8° \leq \theta(\text{Mo}) \leq 12°$) and refined by the least-squares method. Intensities were collected with graphite monochromatized Mo Kα radiation using the ω scan technique. A total of 2621 reflections were measured in the range $2° \leq \theta \leq 25°$, 2074 of which were assumed as observed applying the condition $I \geq 2.5\sigma(I)$. Three reflections were measured every 2 h as orientation and intensity control; significant intensity decay was not observed. Lorentz–polarization and absorption corrections were made. The crystallographic data, conditions employed for the intensity data collection, and some features of the structure refinement are listed in Table I. The structure was solved by Patterson synthesis, using the SHELXS computer program[12] and refined by the full-matrix least-squares methods, with the SHELX76 computer program.[13] The function minimized was $\sum w||F_o| - |F_c||^2$, where $w = \sigma^2(F_o)$. f, f' and f'' were taken from ref 14. The positions of 18 H atoms were computed, the remaining H atoms were located from a difference synthesis, and all were refined with an overall isotropic temperature factor, using a riding model. The final *R* factor was 0.030 ($R_w = 0.039$) for all reflections observed. Number of refined parameters was 248. Maximum shift/esd = 0.1 and maximum and minimum peaks in final difference synthesis were +0.3 and –0.3 eÅ^3, respectively. Final atomic coordinates are given in Table II.

Results

IR and Analytical Data. The most characteristic bands are those attributable to azido ligand and perchlorate anion. The ν_{as} azide at 2040 cm^{-1} (s, br) and the perchlorate bands at 1100 cm^{-1} (s, br) and 620 cm^{-1} (m) are found. The other two bands of the N_3^- group (ν_s and δ) are masked by the amine and perchlorate bands. The elemental analyses (C, N, H, Cl, Ni) for different syntheses were consistent with the product formulation: $C_{12}H_{38}N_{20}Ni_4O_4(ClO_4)_2$. Anal. Calcd/Found. C, 15.01/15.1; H, 3.98/3.9; N, 29.17/29.3; Ni, 24.45/24.5; Cl, 7.38/7.4.

Table II. Final Atomic Coordinates (×10^4) and Equivalent Isotropic Thermal Parameters (Å^2) and Their Estimated Standard Deviations for $[Ni_4(\mu\text{-}N_3)_4(Opn)_2(OHpn)_2](ClO_4)_2$

	x/*a*	*y*/*b*	*z*/*c*	$B_{EQ}{}^a$
Ni(1)	40479(1)	35492(2)	22359(1)	1.81(1)
Ni(2)	43400(1)	34758(2)	8824(1)	1.72(1)
N(1)	4763(1)	4424(1)	3667(1)	2.27(5)
N(2)	4787(1)	5665(1)	3963(1)	2.71(6)
N(3)	4814(1)	6908(1)	4237(1)	3.98(7)
N(4)	3619(1)	2578(1)	890(1)	2.17(4)
N(5)	3341(1)	1319(1)	613(1)	2.78(6)
N(6)	3084(1)	132(2)	359(1)	4.30(7)
N(7)	3355(1)	5270(2)	1690(1)	3.01(6)
C(8)	3631(1)	6688(1)	1636(1)	2.77(6)
C(9)	3950(1)	6268(1)	1258(1)	2.02(5)
O(10)	4402(1)	5018(1)	1796(1)	2.03(3)
C(11)	3402(1)	5996(2)	187(1)	2.73(6)
N(12)	3691(1)	5092(2)	–131(1)	2.55(5)
N(13)	3679(1)	1863(1)	2525(1)	2.75(6)
C(14)	4292(1)	1065(2)	3435(1)	2.86(6)
C(15)	4801(1)	719(1)	3369(1)	1.86(5)
O(16)	4882(1)	2011(1)	2990(1)	1.77(4)
C(17)	5490(1)	319(1)	4372(1)	2.54(6)
N(18)	5802(1)	1727(1)	4969(1)	2.33(4)
Cl	26710(2)	22641(5)	–24895(3)	3.13(2)
O(1)	3152(1)	3535(1)	–2064(1)	4.58(7)
O(2)	2664(1)	1770(2)	–1793(1)	4.76(7)
O(3)	2016(1)	2812(1)	–3310(1)	4.45(5)
O(4)	2859(1)	1087(2)	–2787(1)	4.91(7)

^{a} ($B_{EQ} = 8\pi^2/_3\sum_i\sum_j U_{ij}A^*{}_jA^*{}_iA_jA_i$).

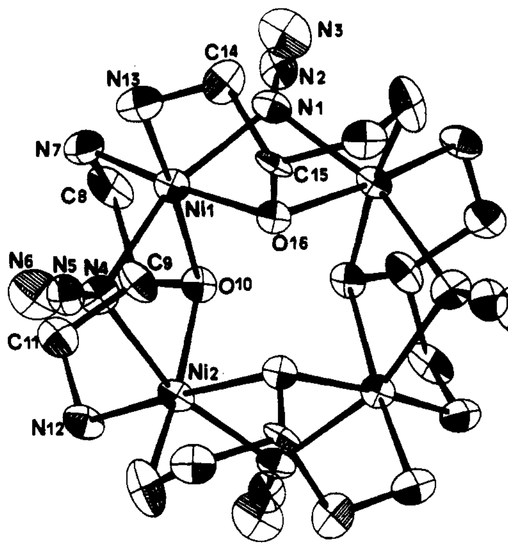

Figure 1. Molecular structure of $[Ni_4(\mu\text{-}N_3)_4(Opn)_2(OHpn)_2]^{+2}$, showing the labeling scheme.

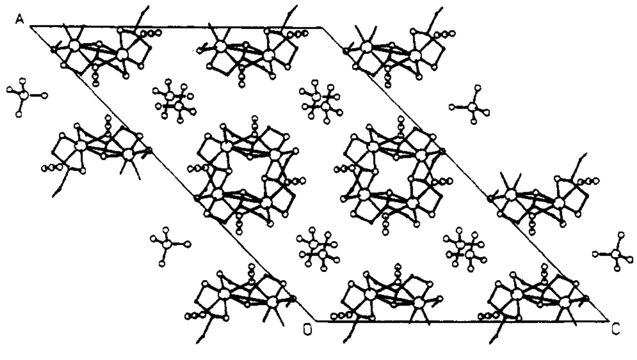

Figure 2. Packing diagram for the tetranuclear $[Ni_4(\mu\text{-}N_3)_4(Opn)_2(OHpn)_2](ClO_4)_2$.

Crystal Structure. The structure consists of the $[Ni_4(\mu\text{-}N_3)_4(Opn)_2(OHpn)_2]^{2+}$ cations isolated from each other by ClO_4^- anions. The structures of the tetranuclear unit and the packing diagram are shown in Figures 1 and 2 respectively. The bond lengths and angles are gathered in Table III. In the structure each Ni(II) atom is in a distorted octahedral environment which is coordinated by two azido ligands in trans configuration, two μ-O groups of two different amine ligands, and two N atoms of two different amines. The four Ni(II) atoms are related by a S_4 axis and form a quasi-perfect square: two distances are 3.203 Å and the other two, 3.205 Å; the pairs of angles are alternated, 90.20 and 89.75°. The longest distance to the mean plane formed by the four Ni atoms is 0.032(1) Å. This symmetry element repeats the unit Ni(μ-N_3)(μ-O)Ni, which is the most important from the magnetic point of view. A schematic representation is given in Figure 3. Ni(1)–O(10)–Ni(2)–N(4) form an asymmetrical unit with four similar distances (from 2.101 to 2.135 Å) and two sets of very different angles: near 76 and 98°, respectively.

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Table III. Main Bond Lengths (Å) and Angles (deg) for $[Ni_4(\mu\text{-}N_3)_4(Opn)_2(OHpn)_2](ClO_4)_2$[a]

Ni(2)–Ni(1)	3.206(1)	N(12)–Ni(2)	2.026(1)
N(1)–Ni(1)	2.116(1)	$N(1)^i$–Ni(2)	2.111(1)
N(4)–Ni(1)	2.136(1)	$O(16)^i$–Ni(2)	2.102(1)
N(7)–Ni(1)	2.039(1)	$N(18)^i$–Ni(2)	2.065(1)
O(10)–Ni(1)	2.102(1)	N(2)–N(1)	1.203(2)
N(13)–Ni(1)	2.062(1)	N(3)–N(2)	1.183(2)
O(16)–Ni(1)	2.116(1)	N(5)–N(4)	1.223(2)
N(4)–Ni(2)	2.123(1)	N(6)–N(5)	1.150(2)
O(10)–Ni(2)	2.121(1)		
N(4)–Ni(1)–N(1)	161.6(1)	N(12)–Ni(2)–N(4)	94.0(1)
N(7)–Ni(1)–N(1)	95.1(1)	N(12)–Ni(2)–O(10)	82.5(1)
N(7)–Ni(1)–N(4)	98.0(1)	$O(16)^i$–Ni(2)–$N(1)^i$	76.5(1)
O(10)–Ni(1)–N(1)	92.2(1)	$O(16)^i$–Ni(2)–N(4)	92.4(1)
O(10)–Ni(1)–N(4)	76.8(1)	$O(16)^i$–Ni(2)–O(10)	95.1(1)
O(10)–Ni(1)–N(7)	82.3(1)	$O(16)^i$–Ni(2)–N(12)	172.3(1)
N(13)–Ni(1)–N(1)	95.0(1)	$N(18)^i$–Ni(2)–$N(1)^i$	98.0(1)
N(13)–Ni(1)–N(4)	94.9(1)	$N(18)^i$–Ni(2)–N(4)	93.9(1)
N(13)–Ni(1)–N(7)	102.3(1)	$N(18)^i$–Ni(2)–O(10)	170.2(1)
N(13)–Ni(1)–O(10)	171.1(1)	$N(18)^i$–Ni(2)–N(12)	101.2(1)
O(16)–Ni(1)–N(1)	76.1(1)	$N(18)^i$–Ni(2)–$O(16)^i$	82.3(1)
O(16)–Ni(1)–N(4)	90.0(1)	$Ni(2)^i$–N(1)–Ni(1)	98.5(1)
O(16)–Ni(1)–N(7)	170.7(1)	N(2)–N(1)–Ni(1)	129.5(1)
O(16)–Ni(1)–O(10)	94.9(1)	N(2)–N(1)–$Ni(2)^i$	119.5(1)
O(16)–Ni(1)–N(13)	81.8(1)	N(3)–N(2)–N(1)	177.7(2)
N(4)–Ni(2)–$N(1)^i$	162.4(1)	Ni(2)–N(4)–Ni(1)	97.6(1)
O(10)–Ni(2)–$N(1)^i$	90.5(1)	N(5)–N(4)–Ni(1)	122.2(1)
O(10)–Ni(2)–N(4)	76.7(1)	N(5)–N(4)–Ni(2)	128.5(1)
N(12)–Ni(2)–$N(1)^i$	96.2(1)	N(6)–N(5)–N(4)	179.5(1)

[a] Symmetry code i = $1 - x, y, 0.5 - z$.

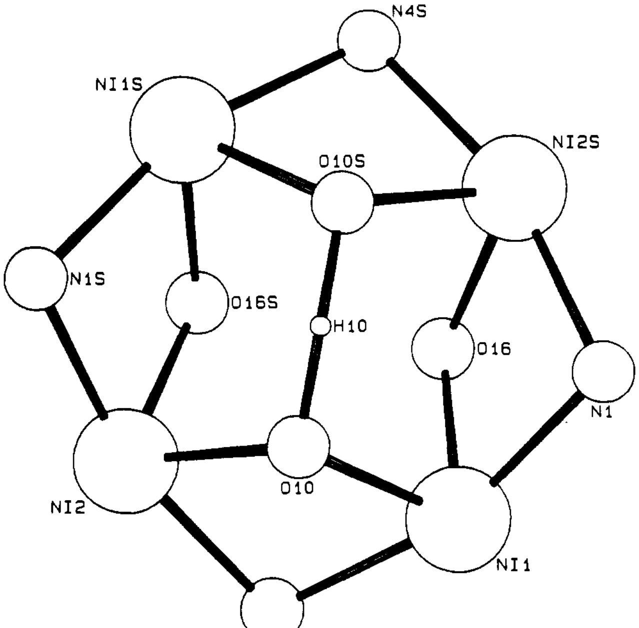

Figure 3. Schematic representation of the central core of the $[Ni_4(\mu\text{-}N_3)_4(Opn)_2(OHpn)_2]^{+2}$ displaying the quasi-perfect square formed about the four Ni(II) atoms.

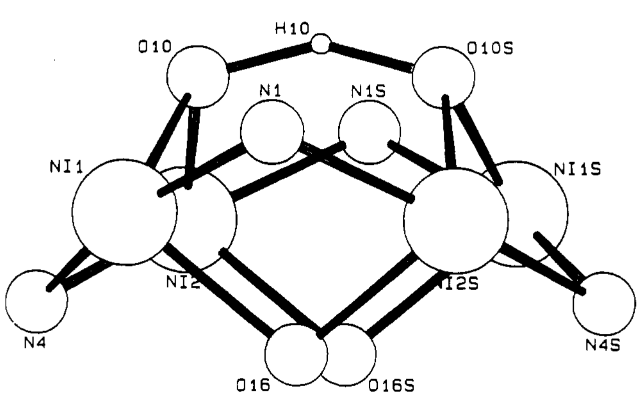

Figure 4. Alternate view of the central skeleton of $[Ni_4(\mu\text{-}N_3)_4(Opn)_2(OHpn)_2]^{+2}$, showing the distorded tetrahedron arrangement of the four oxygen atoms.

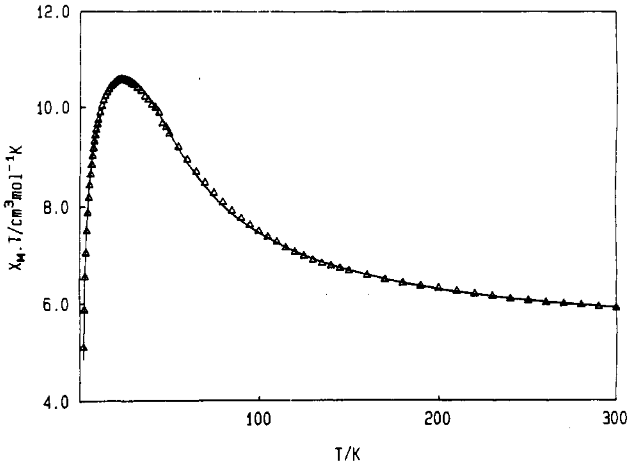

Figure 5. Experimental (▲) and calculated (—) temperature dependence of $\chi_M T$ for the tetranuclear $[Ni_4(\mu\text{-}N_3)_4(Opn)_2(OHpn)_2](ClO_4)_2$.

The dihedral angle between Ni(1)–O(10)–Ni(2) and Ni(1)–N(4)–Ni(2) is 24.16°. The symmetry of the central core results in a distorted tetrahedron arrangement of the four oxygen atoms (Figure 4). These atoms are symmetrically linked two by two by a hydrogen atom. Only the position of H(10) (Figure 4) has been determined exactly. The other H atom, between O(16) and O(16S), is assumed in the related position taking into account the symmetry and the total charge of the tetranuclear entity (+2), which forces two of the four OH^- to be deprotonated. This fact (deprotonation of some of the OH groups in aminoalcohol ligands) has scarcely been studied in Ni(II) derivatives but it has been extensively reported for analogous Cu(II) complexes.[15-18] Finally, the four N-azido atoms linked to Ni(II) [N(1), N(4), N(1S) and N(4S)] are not coplanar but are arranged two above and two below the Ni_4 plane (Figure 4).

Only one similar Ni_4 square planar complex, with a tetranucleating macrocyclic ligand is reported in the literature.[19] In this case, the four Ni(II) ions are linked by a central OH group. Another very symmetrical tetranuclear Ni(II) complex has also been described,[20] but owing to the square-planar coordination of each Ni(II) ion, it is diamagnetic. To our knowledge, all other tetranuclear complexes of Ni(II) reported to date have a "cubane"-like structure[20-26] (weakly ferromagnetic) or are very irregular[27] (antiferromagnetic).

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Magnetic Results. The magnetic behavior of the tetranuclear complex is shown in Figure 5 as the plot of the $\chi_M T$ product vs temperature (K). The value of $\chi_M T$ increases upon cooling from 5.90 cm^3 K mol^{-1} at 300 K to a maximum of 10.58 cm^3 K mol^{-1} at 23 K. This description corresponds to the pattern of a moderately ferromagnetic coupling, in which the highest value is consistent with that expected for an $S = 4$ ground state arising from the intramolecular interactions between the four Ni(II) ions. Further cooling causes the $\chi_M T$ product to fall to a minimum of 0.49 cm^3 K mol^{-1} at 2 K. Both zero-field splitting effects and intermolecular antiferromagnetic interactions could be responsible for this decrease. The latter supposition is not in agreement with the structural data, in which the tetranuclear entities are found to be isolated from each other by the perchlorate anions.

The experimental magnetic data have been fitted using the Van Vleck equation, with an error function defined as

$$R = [(\chi_M T)_{\mathrm{exp}} - (\chi_M \mathrm{T})_{\mathrm{calc}}]^2/(\chi_M T)_{\mathrm{exp}}^{\ 2}$$

The zero-order energy eigenvalues were calculated using the isotropic Heisemberg Hamiltonian for an square-like coupled Ni_4 cluster:

$$H_0 = -J(S_1S_2 + S_2S_3 + S_3S_4 + S_4S_1)$$

In this Hamiltonian we assume, with regard to both structure and symmetry, that all the J values between adjacent Ni(II) atoms are equal and that the two j values between diagonal Ni(II) atoms are negligible.

The expression of the molar susceptibility derived from this Hamiltonian, is

$$\chi_M = (2Ng^2\beta^2/kT)(30 + \exp 9x + 7 \exp 7x + 11 \exp 5x + 26 \exp 4x + 5 \exp 3x + 28 \exp 2x)/(9 + \exp 10x + 3 \exp 9x + 11 \exp 7x + \exp 6x + 13 \exp 5x + 24 \exp 4x + 5 \exp 3x + 14 \exp 2x)$$

where $x = J/kT$.

In order to account for the ZFS hypothesis, the first and second order energy expansion coefficients were calculated from an anisotropic perturbation containing both axial Zeeman effect and ZFS acting within the $S = 4$ ground state:

$$H' = \beta H(g_{\parallel}S_z + g_{\perp}S_{x(y)}) + D[S_z^{\ 2} - {}^1/_3S(S+1)]\delta_{S=4,S}$$

This formulation assumes that the spin states do not interact through the Ni(II) anisotropy ($|J| > |D|$). This leads to the $S = 4$ ground state being the most populated at the low temperatures where the effect is detected.

The best fit parameters are found as $J = +\ 21.3$ cm^{-1}, $g_{\parallel} = 2.65$, $g_{\perp} = 2.08$ and $|D| = 6.0$ cm^{-1}. The agreement factor R is equal to 5.4×10^{-5}.

EPR. The new tetranuclear complex is EPR silent from room temperature to ca. 20 K. At 4 K (X-band) the main feature is the presence of a very broad band ($\delta H_{pp} \approx 2500$ G) centered around 1850 G, with an asymmetrical derivative-shape. This low-field value (g = 3.60) at liquid helium temperature can only be explained by an allowed transition inside the $S = 4$ ground state, the only thermally populated state.

When building the secular determinant for the ground state, we have considered axial symmetry and zero value for the rhombic distortion. Under these conditions, the high D value obtained from the magnetic data must hinder any transition between different non-Kramers states. Inside each doublet, transitions for H parallel to the z-axis are forbidden. Nevertheless, off-diagonal terms connecting the $|0\rangle$ and $|\pm 1\rangle$ levels appear for perpendicular fields. The mixing allows a transition inside the latter. According to the susceptibility fitting parameters, this resonance should be observed at around 4600 G. Nevertheless, no other signal is observed at such high fields.

A plausible explanation would be the existence of a non strictly null value for the rhombic splitting. This will lead to a mixing affecting all the states, and low-field transitions within them will result.[28] Unfortunately, the lacking of monocrystal EPR data prevents us from estimating the E parameter and the prediction of the corresponding transition field.

Discussion

Interpretation of the Magnetic Data. Only two Ni(II) complexes with a 1,1-N_3^- azido bridge have been previously reported,[4,5] both being ferromagnetically coupled, but no magnetostructural correlations have been made. The actual complex is the first to contain one 1,1-azido and one OH bridge. This case is very similar to that reported by Kahn and co-workers[7] for an analogous Cu(II) dinuclear compound also with one azido and one hydroxo bridging group. In that case, J was reported to be greater than 200 cm^{-1}. Extended Hückel calculations on idealized molecules demonstrate that, even if the gap between the d_{xy} orbitals is weak for certain Cu–N–Cu angles giving the so-called "accidental orthogonality", the ferromagnetism is found for all angles and distances. For this reason Kahn introduces the "spin polarization" concept as the key factor to explain the behavior of end-on azido bridges in complexes of this kind.[6,7] In this theory the in-plane II_g orbital (HOMO) of N_3^- with a node on the central nitrogen atom, is mainly considered. The electron on the bridging nitrogen atom (α spin, for example) is partially delocalized toward the two d_{xy} metal orbitals. Consequently, each unpaired electron of the two metal ions will have a great probability of β spin, which favors the triplet state. As a result, the coupling would be ferromagnetic whatever the values of distances and angles.

Our results seem to indicate that this effect is also the predominant factor which explains the ferromagnetic behavior in Ni(II) polynuclear complexes. According to the theory of Hoffmann[29] and Kahn,[30] if we consider four interacting octahedral Ni(II) ions, the J parameter of the spin Hamiltonian can be decomposed into a ferromagnetic term (j_f), which depends on the two-electron integrals, and an antiferromagnetic term (J_{af}), which depends on the splitting of the pairs of MO's derived from d_{z^2} and d_{xy} respectively. Only when J_{af} is zero or negligible (orthogonal orbitals) may j_f be predominant and the behavior ferromagnetic. In order to study this J_{af} contribution we have made extended Hückel calculations with the CACAO[31] program on an idealized tetranuclear molecule with two NH_3 molecules as terminal ligands on each Ni(II) ion. The two magnetic orbitals from each Ni(II) create eight molecular orbitals without any degeneracy. Taking into account the low symmetry of the molecule, all the molecular orbitals have a mixed contribution from the d orbitals of each Ni(II). The energy gap between the highest and lowest orbitals is more than 1 eV. While being mindful of the limitations of calculations of this kind, we may safely assume that in the present complex there is no orbital orthogonality that would lead to small or negligible values of J_{af} and hence that on these grounds the complex would be expected to be antiferromagnetic. The observed ferromagnetism, however, can be readily explained by spin polarization effects, and hence, we deduce that spin polarization may well be the key feature leading to ferromagnetism in our tetranuclear complex.

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Supplementary Material Available: Text giving experimental details of the structure determination and tables giving crystal data and details of the structure determination, atom coordinates, bond lengths, bond angles, anisotropic thermal parameters, and hydrogen atom locations (8 pages). Ordering information is given on any current masthead page.