Volume 30
Number 9
May 1, 1991

Inorganic Chemistry

Communications

Very High Field Magnetization and Zero-Field Splitting within the Excited State of a $Cu^{II}Ni^{II}$ Binuclear Compound

The $Cu^{II}Ni^{II}$ comopunds with $S_{Cu} = {}^1/_2$ and $S_{Ni} = 1$ local spins represent a rather ideal case of a heteropair.[1] The intramolecular interaction leads to two pair states characterized by the spins $S = {}^1/_2$ and $S = {}^3/_2$, the former being the lowest if, as is most often the case, this interaction is antiferromagnetic. The doublet–quartet energy gap can then be determined rather accurately through magnetic susceptibility measurements, and useful information on the structure of the doublet ground state can be deduced from low-temperature EPR spectra. This complementarity between magnetic and EPR techniques has been successfully exploited in several cases,[1,2] in particular for the compound $Cu(salen)Ni(hfa)_2$, where salen is *N*,*N'*-ethylenebis(salicylaldiminato) and hfa is hexafluoroacetylacetonato.[3] The structure of this compound is recalled in Figure 1. Copper(II) is in a N_2O_2 planar environment, and nickel(II), in a O_6 distorted octahedral environment. The CuO_2Ni bridging network is bent with a dihedral angle of 141.4°. Moreover, two CuNi units of this kind are related through a symmetry center, giving rise to a $[CuNi]_2$ entity with a Cu···Cu separation of 3.432 Å. The magnetic data reveal a doublet–quartet energy gap equal to 35.4 cm^{-1}. The EPR spectrum is entirely associated with the $[CuNi]_2$ entity. Indeed, this spectrum is that of the triplet state arising from the very weak interaction between two doublet pair states. A polarized neutron diffraction study has provided insight into the spin density distribution for this compound.[4] Although much is already known about $Cu(salen)Ni(hfa)_2$, an important piece of information is still missing, namely, the zero-field splitting (ZFS) within the excited quartet state, giving rise to two Kramers doublets separated by an energy gap Δ. This ZFS is primarily due to the local anisotropy of the nickel(II) ion but may also arise from dipolar and anisotropic interactions.[5,6] Δ cannot be determined by either magnetic susceptibility measurements or EPR spectra. Indeed, the ZFS within the excited $S = {}^3/_2$ state is without any detectable influence on the susceptibility curve, and in the temperature range where the $S = {}^3/_2$ state is thermally populated, the EPR spectrum vanishes. In this communication, we will show that very high field magnetization data determine Δ. To the best of our knowledge, such an approach has not been used before.

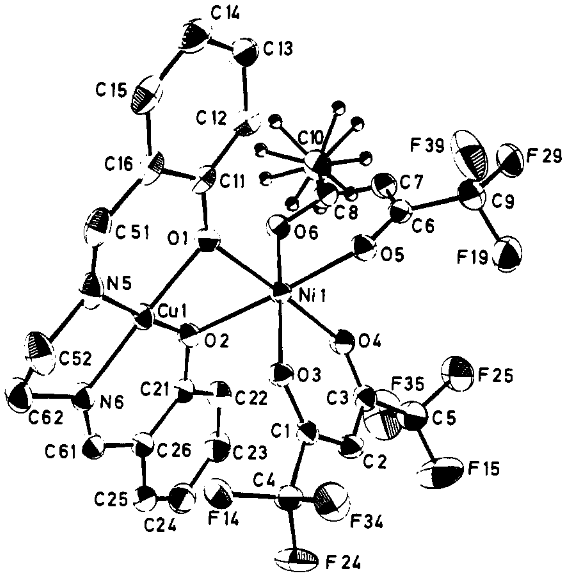

Figure 1. Perspective view of $Cu(salen)Ni(hfa)_2$.

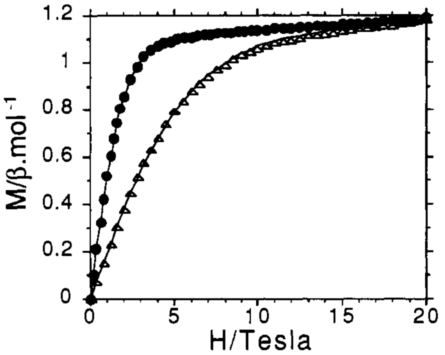

Figure 2. Experimental (●, 1.42 K; Δ, 4.2 K) and calculated (—) magnetization *M* versus field *H* plots for $Cu(salen)Ni(hfa)_2$ in the field range 0–20 T.

Basically, the method is the following. The doublet and quartet spin states couple through the local anisotropy of the nickel(II) ion. At low temperature, only the ground state is significantly populated but the nature of this state depends on the degree of $S = {}^1/_2$, $S = {}^3/_2$ mixing, i.e. on the nickel(II) local anisotropy on the one hand and on the doublet–quartet energy gap on the other hand. It follows that this local anisotropy can be extracted from the magnetization curve when this curve is recorded in a large magnetic field range. Indeed, the applied field tends to stabilize the excited quartet state with respect to the ground doublet state.

$Cu(salen)Ni(hfa)_2$ was prepared as previously described.[1] The molar magnetization *M* was measured as a function of the magnetic field *H* at 1.42 and 4.2 K by means of a fluxmetric

---

[1] Kahn, O. *Struct. Bonding* (*Berlin*) **1987**, *68*, 89 and references therein.

[2] Morgenstern-Badarau, I.; Rerat, M.; Kahn, O. *Inorg. Chem.* **1982**, *21*, 3050.

[3] Journaux, Y.; Kahn, O.; Morgenstern-Badarau, I.; Galy, J.; Jaud, J.; Bencini, A.; Gatteschi, D. *J. Am. Chem. Soc.* **1985**, *107*, 6305.

[4] Gillon, B.; Cavata, C.; Schweiss, P.; Journaux, Y.; Kahn, O.; Schneider, D. *J. Am. Chem. Soc.* **1989**, *111*, 7124.

[5] See, for instance: Willett, R. D.; Gatteschi, D.; Kahn, O. Magneto-Structural Correlations in Exchange Coupled Systems. *NATO ASI Ser. C* **1985**, *140*.

[6] Bencini, C.; Gatteschi, D. *Mol. Phys.* **1985**, *54*, 969.

0020-1669/91/1330-1965$02.50/0 © 1991 American Chemical Society

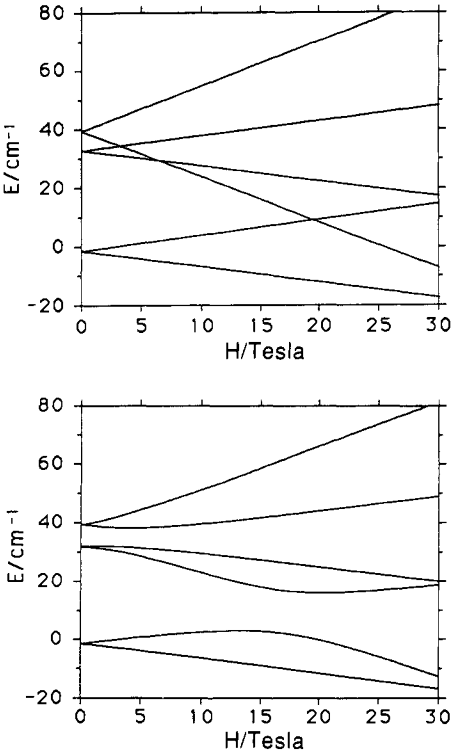

Figure 3. Variation of the low-lying-state energies versus the field H for Cu(salen)Ni(hfa)$_2$: (top) H parallel to the z direction of **D**; (bottom) H perpendicular to the z direction of **D** (see text).

method. The M versus H plots are shown in Figure 2. The sample was extracted in a constant magnetic field between compensated pick-up coils connected in series opposition. The integrated signal of the induced voltage was proportional to M. The continuous magnetic field up to 20 T was produced by a water-cooled Bitter magnet. The calibration and the sensitivity of the apparatus were previously described in detail.[7] The molar magnetization M_u along the direction u of the magnetic field H_u is given by

$$M_u = N[\sum_i(-\partial E_{i,u}/\partial H_u)\exp(-E_{i,u}/kT)]/[\sum_i \exp(-E_{i,u}/kT)] \qquad (1)$$

where the $E_{i,u}$'s are the energies of the six levels in the presence of the field. The average molar magnetization is then calculated as[8]

$$M = (4\pi)^{-1}\int_{\text{space}} M_{\theta,\phi}\sin\theta\, d\theta\, d\phi \qquad (2)$$

The energies $E_{i,u}$ are obtained by diagonalization of the spin Hamiltonian (3) by using the $|S, M_S\rangle$ functions associated with

$$\mathcal{H} = -JS_{Cu}\cdot S_{Ni} + S_{Ni}\cdot\mathbf{D}\cdot S_{Ni} + \beta H\cdot(\mathbf{g}_{Cu}\cdot S_{Cu} + \mathbf{g}_{Ni}\cdot S_{Ni}) \qquad (3)$$

the pair states as a basis set, where J is the isotropic interaction parameter, $\mathbf{g}_{Cu}$ and $\mathbf{g}_{Ni}$ are the local Zeeman tensors, and **D** is the nickel(II) local anisotropy tensor. In (3), the ZFS within the quartet pair state is assumed to arise entirely from the nickel(II) local anisotropy. In other words, dipolar and anisotropic interactions are neglected. This assumption does not affect the determination of Δ.

When H is parallel to the z direction of **D**, only the $|{}^1/_2, \pm{}^1/_2\rangle$ and $|{}^3/_2, \pm{}^1/_2\rangle$ functions with the same M_S couple through **D**, so that M_S remains a good quantum number. On the other hand, when H is perpendicular to the z direction, the $|{}^1/_2, M_S\rangle$ and $|{}^3/_2, M_S'\rangle$ functions with $M_S \neq M_S'$ couple as well, and the off-diagonal matrix elements are proportional either to **D** or to $\beta\Delta\mathbf{g}H$ ($\Delta\mathbf{g} = \mathbf{g}_{Cu} - \mathbf{g}_{Ni}$). The most important interaction takes place between $|{}^1/_2, {}^1/_2\rangle$ and $|{}^3/_2, -{}^3/_2\rangle$ in the field range where the two levels are close to each other. This mixing between ground doublet and excited quartet pair states through **D** leads to magnetization curves that, even at low temperature, are significantly different from what would be expected for a rigorously pure doublet ground state (e.g. a mononuclear copper(II) compound). In particular, instead of showing a saturation magnetization $M_S = g_{1/2}/2\ \mu_B$, $g_{1/2}$ being the Zeeman factor for the doublet state, the M versus H plot continuously increases when H increases. This situation may be explained as follows: In the absence of **D**, the $|{}^1/_2, -{}^1/_2\rangle$ and $|{}^3/_2, -{}^3/_2\rangle$ levels would intersect for a field value of $-3J/2\beta g_{1/2}$ (around 40 T), with an abrupt transition in the M versus H plot. Due to the coupling of the pair states through **D**, this transition is much smoother and starts at relatively low field.

To fit the two magnetization curves, we used the J scalar, and the $\mathbf{g}_{Cu}$ and $\mathbf{g}_{Ni}$ tensors as deduced from magnetic susceptibility and EPR data,[9] and we determined the **D** tensor by minimizing R defined as $\sum(M^{obs} - M^{calc})^2/\sum(M^{obs})^2$. The three parameters of the problem are then the axial D ($=3D_{zz}/2$) and rhombic E ($=|D_{xx} - D_{yy}|/2$) local anisotropy parameters as well as the angle θ between the local z axes of the $\mathbf{g}_{Cu}$ and **D** tensors.[10] The lowest R value ($=8 \times 10^{-6}$) was obtained for $D = 12.5$ cm^{-1}, $E/D = 0.06$, and $\theta = 67°$. The ZFS splitting Δ ($=2(D^2 + 3E^2)^{1/2}/3$) within the quartet state of the Cu^{II}Ni^{II} pair is then equal to 8.4 cm^{-1}. The variations of the low-lying-state energies versus the field for both H parallel and perpendicular to the z direction of **D** are shown in Figure 3. This figure emphasizes the mixing of the $|S, M_S\rangle$ functions in the perpendicular case. This is particularly true for $|{}^1/_2, {}^1/_2\rangle$ and $|{}^3/_2, -{}^3/_2\rangle$. At very high field, $|{}^1/_2, {}^1/_2\rangle$ becomes $|{}^1/_2, -{}^3/_2\rangle$ and $|{}^3/_2, -{}^3/_2\rangle$ becomes $|{}^3/_2, {}^1/_2\rangle$. Although this is not the main goal of this communication, it worth mentioning that the large nickel(II) local anisotropy explains why the triplet state for the [CuNi]$_2$ entity is significantly split in zero field. Indeed, the magnitude of this splitting detected in the EPR spectrum is expected to vary as D/J on the one hand and as the interpair interaction J_{AB} on the other hand.[3]

To conclude, very high field magnetization data at low temperatures have provided a quantitative piece of information on the spectrum of the low-lying states that has been impossible to deduce from any other technique. This approach is an important new step in the field of the molecular magnetism.

Registry No. Cu(salen)Ni(hfa)$_2$, 71073-29-5.

Laboratoire de Chimie Inorganique
URA No. 420
Université de Paris-Sud
91405 Orsay, France

Pierre Bergerat
Olivier Kahn*

Service National des Champs Intenses
UPR No. 5021, CNRS
38042 Grenoble, France

Maurice Guillot

Received August 9, 1990

---

(7) Picoche, J. C.; Guillot, M.; Marchand, A. *Physica B* **1989**, *155*, 407.

(8) Day, E. P.; Kent, T. A.; Lindahl, P. A.; Münck, E.; Orme-Johnson, W. H.; Roder, H.; Roy, A. *Biophys. J.* **1987**, *52*, 837.

(9) $J = -23.6$ cm^{-1}; $g_z = 2.24$ is along the direction perpendicular to the copper basal plane, and g_x and $g_y = 2.025$ are in the basal plane; $\mathbf{g}_{Ni}$ is isotropic with the principal value $g_{Ni} = 2.26$.

(10) Due to the weak rhombicity of **D**, the relative orientations of D_{xx} and D_{yy} with respect to the principal directions of $\mathbf{g}_{Cu}$ do not play any role.

Synthesis and Structural Characterization of $[Hg_7Se_{10}]^{4-}$ and $[Hg_7Se_9]_n^{4n-}$: Novel Metal-Chalcogenide Frameworks

In our investigation of the coordination chemistry of Q_x^{2-} (Q = Se, Te) ligands we have used late transition metals and relatively long polychalcogenide ligands in M:Q_x^{2-} (x = 4, 5) ratios of 1:2 and 1:3.[1] This combination of reagents usually yields mononuclear

0020-1669/91/1330-1966$02.50/0 © 1991 American Chemical Society