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^{33}S Hyperfine Interactions in the Single-Crystal ESR Spectra of $(n\text{-}Bu_4N)_2[^{63}Cu(mnt)_2]$*

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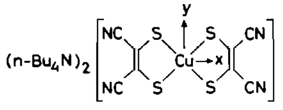
Several single-crystal ESR studies have been made on Cu(II) complexes having CuS_4 coordination spheres [1–12]. However, with the exception of Cu(II) bis(diethyl-dithiocarbamate) [12] and Cu(II) bis(diethyl-dithiophosphate) [10] no results have been reported concerning the ^{33}S ligand hyperfine structure (hfs) in these complexes. Especially the use of complete ligand hfs data provides direct information about the electronic ground state and the extent of electron spin delocalization over the ligand orbitals in these highly covalent Cu(II) chelates.

The single-crystal ESR spectra of $(n\text{-}Bu_4N)_2[Cu(mnt)_2]$ (I) were studied by Maki *et al.* [1] and Plumlee *et al.* [8]. We observed ^{33}S hfs in natural abundance (^{33}S: 0.74%, I = 3/2) in the single-crystal ESR spectra of $(n\text{-}Bu_4N)_2[^{63}Cu(mnt)_2]$, diamagnetically diluted in the corresponding Ni(II) chelate. In this paper a detailed analysis of the ^{33}S hfs is given.



(I)

Experimental

The ligand and the Cu(II) and Ni(II) complexes were prepared as described in [13]. $(n\text{-}Bu_4N)_2[^{63}Cu(mnt)_2]$ was obtained using ^{63}Cu enriched $CuCl_2 \cdot 6H_2O$ (97.8% ^{63}Cu, 2.2% ^{65}Cu). Well-formed single-crystals containing 0.1–0.5 mol% $(n\text{-}Bu_4N)_2[^{63}Cu(mnt)_2]$ in the corresponding diamagnetic Ni(II) complex were grown by slow solvent evaporation from acetone solutions.

Unfortunately, complete structural data of the tetra-n-butylammonium salt of $[Ni(mnt)_2]^{2-}$ are not available from the literature. However, structural studies made by Forrester *et al.* [14] and Plumlee *et al.* [8] have shown that the $(n\text{-}Bu_4N)_2[M(mnt)_2]$ complexes with M = Co, Ni and Cu are isomorphous containing one molecule in a triclinic unit cell. As a result the MS_4 unit of these complexes was found to be planarly arranged (nearly D_{2h} symmetry).

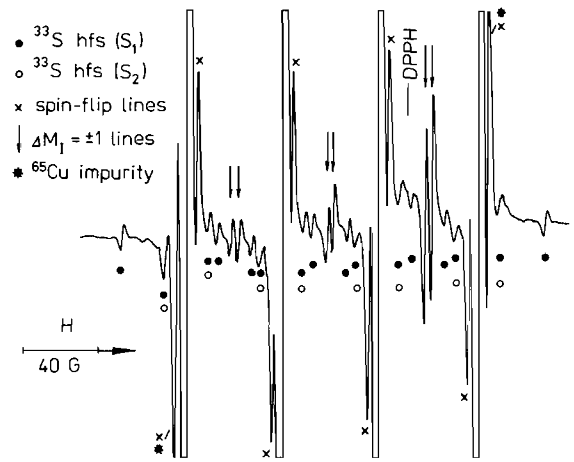


Figure 1. X band ESR spectrum of $(n\text{-}Bu_4N)_2[^{63}Cu(mnt)_2]$ in a $(n\text{-}Bu_4N)_2[Ni(mnt)_2]$ single-crystal at T = 298 K. H ∥ $A_z^{S_2}$. Only one set of ^{33}S hfs lines is to be seen; the other one is overlapped by the more intense lines of the spectrum.

The ESR spectra were recorded on an "E-112" spectrometer (Varian, USA) in the X band at room temperature.

Results and Discussion

In the ESR spectra of $[Cu/Ni(mnt)_2]^{2-}$ the absorption peaks of one $[Cu(mnt)_2]^{2-}$ anion were observed. Each Cu hfs line is flanked symmetrically by two sets of four ^{33}S satellites. The intensity of each satellite line is approximately 0.4% of the ^{63}Cu peaks. These satellites arise from molecules with one ^{33}S atom only. Such cases in which more than one ^{33}S atom are present in a $(n\text{-}Bu_4N)_2[Cu(mnt)_2]$ molecule can be neglected because of the low natural abundance of ^{33}S. A representative spectrum is shown in Figure 1.

In addition to the ^{33}S hfs lines in the spectra each Cu hfs line is flanked by another more intense satellite doublet. Similar lines have been observed also in the single-crystal spectra of Cu(II) bis(diethyl-dithiophosphate) [10] and Cu(II) bis(diethyl-dithiocarbamate) [12]. In the latter case we attributed erroneously these extra lines to ^{13}C hfs interactions. However, their field dependence indicates that they are due to a weak dipolar interaction between the unpaired electron and the magnetic moment of neighbouring protons and, therefore, correspond to a simultaneous electron and proton spin flip as discussed in [10]. In order to obtain more detailed

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*Mnt = 1,2-dicyanoethylene-1,2-dithiolate.

TABLE I. Principal Values[a] of the ^{33}S hfs, ^{63}Cu hfs and the g Tensor (Coupling Constants in 10^{-4} cm^{-1}).

A(^{33}S)		g	A(^{63}Cu)
$A_z^{S_1} = 21.4$	$A_z^{S_2} = 22.0$	$g_z = 2.086$	$A_z = 161.1$
$A_y^{S_1} = 7.6$	$A_y^{S_2} = 7.9$	$g_y = 2.026$	$A_y = 39.0$
$A_x^{S_1} = 9.4$	$A_x^{S_2} = 9.4$	$g_x = 2.023$	$A_x = 38.0$
$\langle A^{S_1}\rangle = 12.8$[b]	$\langle A^{S_2}\rangle = 13.1$[b]		

[a] Experimental errors: A_z^S, $A_x^S \pm 0.2$; $A_y^S \pm 0.5$; $g_x, g_y, g_z \pm 0.001$; $A_z, A_y, A_x \pm 0.3$. [b] $\langle A^S\rangle = (A_x^S + A_y^S + A_z^S)/3$.

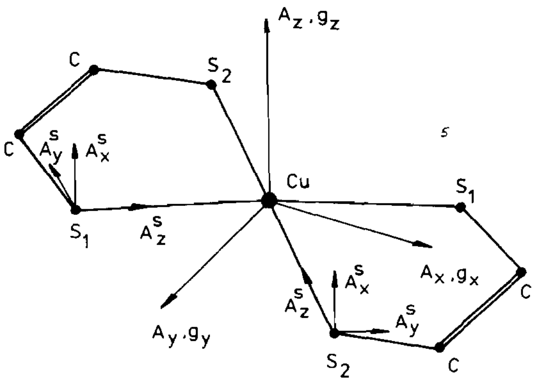

Figure 2. Orientations of the principal axes of the g, ^{63}Cu hfs and the ^{33}S hfs tensors in $(n\text{-}Bu_4N)_2[Cu(mnt)_2]$.

information we tried to get proton ENDOR spectra of $(n\text{-}Bu_4N)_2[Cu/Ni(mnt)_2]$ single-crystals with 0.3% Cu^{2+} (relative to Ni^{2+}) at T = 4.2 K. Unfortunately, due to very long electron spin–lattice relaxation times at 4.2 K ($T_1 \gtrsim 5$ s) the saturation of the Cu hfs transitions is nearly complete even for very low microwave powers preventing the observation of the ENDOR effect.

The principal values of the ^{33}S hfs tensor of both sets of S atoms are listed in Table I together with the derived g and A^{Cu} tensor values which agree with those measured by Maki *et al.* [1] within the experimental error. The directions of the principal axes of g, A^{Cu} and A^S in the molecular frame are shown in Figure 2. The ^{33}S hfs tensor components A_z^S and A_y^S were derived from the angular dependence measured in the x, y-plane of the molecule. A_x^S was determined from the spectrum obtained for H ∥ g_z. A_z^S points in the direction of the Cu atom and A_x^S lies perpendicular to the coordination plane. The angle between the directions of $A_z^{S_1}$ and $A_z^{S_2}$ is (90 ± 2)° which agrees well with the S_1–Cu–S_2 [8] and S_2–Co–S_2 [14] angles found for the Cu and Co complexes by X-ray studies. From the angular dependence of the ^{33}S hfs the following conclusions can be made: (a) two pairs of nonequivalent S atoms are present in the coordination sphere and (b) the inversion centre of the guest molecules is retained, when doped into $[Ni(mnt)_2]^{2-}$. These results agree with the above-made structural assumptions for $(n\text{-}Bu_4N)_2[Ni(mnt)_2]$.

Using the ^{33}S data the ligand contribution to the ground state of the molecule can be estimated according to [12]. The molecular orbital of the unpaired electron can be written as follows:

$$\psi_{B_{1g}} = \alpha\,|d_{xy}\rangle - \frac{\alpha^{S_1}}{\sqrt{2}}(-\sigma^1 + \sigma^3) - \frac{\alpha^{S_2}}{\sqrt{2}}(\sigma^2 - \sigma^4)$$

where

$$\sigma^{(i)} = (1 - n^2)^{1/2} s^{(i)} \mp n p^{(i)}.$$

The following values were obtained for the MO coefficients and the hybridization degree "n" of the S-3s and 3p orbitals:

$$\alpha^{S_1} = 0.58,\ n^{S_1} = 0.92;\ \alpha^{S_2} = 0.60,\ n^{S_2} = 0.92.$$

As found from ^{33}S data for the complex Cu(II) bis-(diethyl-dithiocarbamate) [12] the covalency of the metal–sulphur bond is very high. In contrast to the dithiocarbamate complex for $[Cu(mnt)_2]^{2-}$ the isotropic ^{33}S coupling is somewhat greater indicating an increase of the hybridization between the S-3s and 3p orbitals. The differences between the Cu–S–C bonding angles for $[Cu(mnt)_2]^{2-}$ and Cu(II) bis-(diethyl-dithiocarbamate) are mainly responsable for this result.

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