^{33}S AND ^{13}C HYPERFINE INTERACTIONS IN THE SINGLE-CRYSTAL EPR SPECTRA OF ^{63}Cu(II) BIS(DIETHYL-DITHIOCARBAMATE)

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Abstract—A detailed analysis of the ^{33}S and ^{13}C ligand hyperfine interactions observed in the single-crystal EPR spectra of ^{63}Cu-labelled copper(II)bis(diethyl-dithiocarbamate), diamagnetically diluted by the corresponding Ni(II)-complex, is reported. The ^{33}S hyperfine tensors are nearly axial symmetric; the unique axes are found to lie along the Cu–S bond directions. The observation of two different sets of ^{33}S splitting parameters is in agreement with the presence of a rhombic distortion of the planar ligand field. The ^{13}C hyperfine tensor is isotropic within experimental error. The bonding situation of the electronic ground state is discussed. In order to explain the unusually small linewidths observed the electron spin-lattice relaxation time was measured in the temperature-range $2 \leq T \leq 77$ K.

INTRODUCTION

The EPR spectra of Cu(detc)$_2$ (detc = diethyl-dithiocarbamate) doped into single-crystals of the corresponding Ni(II) and Zn(II) chelates were studied by different authors[1–5]. However, with exception of the isotropic ^{33}S splitting observed for Cu(II)-diisopropyl-dithiocarbamate in liquid solution[6] no results are reported concerning the ^{33}S ligand hyperfine structure (hfs) in this complex. Attempts to resolve the ^{13}C hfs in Cu(detc)$_2$ were unsuccessful also[7]. However, especially the use of complete ligand hfs data provides direct information about the nature of the electronic ground state and the extent of electron spin delocalization over the ligand orbitals in this very covalent complex. In the single-crystal EPR spectra of ^{63}Cu(detc)$_2$ (I) we have observed hyperfine satellites due to ^{33}S and ^{13}C in natural abundance (^{33}S; 0.74%, I = 3/2; ^{13}C: 1.1%, I = 1/2).

(1)
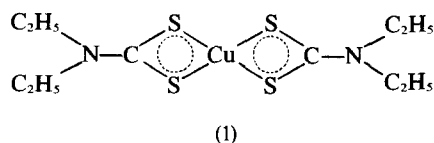
In this paper a detailed analysis of the ^{33}S and ^{13}C hfs of ^{63}Cu(detc)$_2$ diamagnetically diluted by the corresponding Ni(II) chelate is given. Furthermore, the temperature-dependence of the electron spin–lattice relaxation time for Cu(detc)$_2$ was investigated in order to explain the unusually small EPR linewidths observed, which enabled use to resolve the small hfs interactions described in this work.

EXPERIMENTAL

Single crystals containing 0.3 mol% ^{63}Cu(detc)$_2$ in the corresponding diamagnetic Ni(II) complex were grown by solvent evaporation from CHCl$_3$ solutions. ^{63}Cu(detc)$_2$ was prepared as described by Cavell and Sugden[8] using ^{63}Cu enriched CuCl$_2 \cdot 6$H$_2$O (97.8% ^{63}Cu, 2.2% ^{65}Cu). The complete structures of both complexes have been determined by X-ray diffraction[9]. Ni(detc)$_2$ crystallizes monoc-

linic, space group P2$_1$/c with two molecules in the unit cell. The 4-coordinating sulfur atoms around the Ni^{2+} are planar arranged; the central part of the molecule has nearly D_{2h} symmetry.

The EPR spectra were recorded on a "THN-251" X-band spectrometer (Firma "Thomson", France) at room temperature. In order to derive the principal values of the ^{33}S and ^{13}C hfs tensors spectra were recorded about every 10° in the three perpendicular planes defined by the directions of the principal axes of the g tensor of one of the sites in the unit cell of the crystal. Measurements of the electron spin–lattice relaxation time T_1 were made on a 28.8 GHz spectrometer as described earlier[10] in the temperature range $2 \leq T \leq 77$ K using the pulse saturation technique. The pulse width was varied between 200 μs and 10 ms. T_1 was measured on Ni(detc)$_2$ single-crystals containing 1.0 ± 0.1 mol-% ^{63}Cu(detc)$_2$. The magnetic field was directed along the normal to the plane through the four sulfur atoms of the formula unit, that is, H$\|g_z$, A$_z^{Cu}$. The magnetic field was controlled by a NMR marker; polycrystalline DPPH was used as g-marker.

RESULTS

In general the single-crystal spectra depict the absorption signals of two magnetically nonequivalent molecules. If the magnetic field is located in the crystallographic ac-plane or parallel to the b axis, the two structural units of the unit cell are magnetically equivalent and the absorption signals coincide. The principal values of the g- and the ^{63}Cu hfs tensor derived are listed in Table 1; they agree with those measured by Weeks and Fackler[2].

Using higher amplification small satellite lines due to ^{33}S and ^{13}C are observed. In general the presence of the ^{33}S isotope gave rise to two quartets of satellites. Each satellite has an intensity of 0.35–0.4% of the ^{63}Cu peaks and an intensity of approx. 16% of the ^{65}Cu peaks. These satellites are due to molecules with one ^{33}S atom only. Such cases in which more than one ^{33}S atom are present in a Cu(detc)$_2$ molecule can be neglected because of the low natural abundance of ^{33}S. A representative spectrum showing the ^{33}S satellite lines is reproduced in Fig. 1, the magnetic field is located in the crystallographic ac plane so that the two molecules in the unit cell are magnetically equivalent.