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A Single Crystal EPR Study of $(n\text{-}Bu_4N)$ [Cu/Ni(mnt)(et$_2$dtp)]

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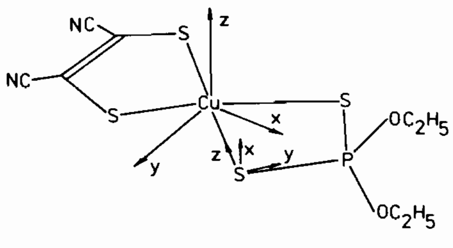
Several attempts have been made to explain the formation of copper mixed ligand complexes containing unsaturated dichalcogeno-ligands [1]. Beside kinetic studies calorimetric and EPR measurements as well as quantum chemical calculations were used to investigate the different ligand exchange behaviour of the parent complexes and the properties of the resulting mixed ligand chelates. Especially the results of calorimetric studies and of EHT calculations suggest that in cases where the mixed ligand complex is formed exclusively (combination of a four- and a five-membered ring chelate) the complex formation is caused by an energy gain based on the whole electronic system. EPR single crystal investigations are well suited for detecting variations of the electronic structure of the mixed ligand chelate in comparison to the parent compounds. The use of complete ligand hyperfine structure (hfs) data provides direct information about the 'electronic ground state' and the extent of electron spin delocalization over the ligand orbitals.

In this paper we report a single crystal EPR study on ^{63}Cu doped $(n\text{-}Bu_4N)$ [Ni(mnt)(et$_2$dtp)] (mnt = 1.2-dicyanoethylene-1.2-dithiolate; et$_2$dtp = O.O′-diethyldithiophosphate) (I). The corresponding parent complexes were studies by several authors. The EPR single crystal spectra of $(n\text{-}Bu_4N)_2$[Cu(mnt)$_2$] were investigated by Maki *et al.* [2] and Plumlee *et al.* [3]. In a recent paper [4] we reported the ^{33}S hfs data for this compound diluted in the corresponding Ni(II) complex. Attanasio *et al.* [5] studied Cu(et$_2$dtp)$_2$ likewise doped in the corresponding Ni(II) chelate.



Experimental

The complexes $(n\text{-}Bu_4N)_2$[Ni(mnt)$_2$] and Ni(et$_2$dtp)$_2$ were prepared according to standard literature methods. The mixed ligand chelate $(n\text{-}Bu_4N)$ [Ni(mnt)(et$_2$dtp)] was synthesized by refluxing equimolar amounts of the parent complexes in an acetone/chloroform solution for three hours. The reaction mixture was reduced *in vacuo* and the product was precipitated by adding isopropanol. The complex was recrystallized in acetone and isolated in the above described manner. Suitable single-crystals of $(n\text{-}Bu_4N)$[Ni(mnt)(et$_2$dtp)], doped with copper, can be grown by slow evaporation of an acetone/ethanol solution (ratio 5:1) containing the diamagnetic host and approximately 1% of ^{63}Cu enriched $CuCl_2 \cdot 2H_2O$.

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

Results and Discussion

In the EPR spectra of [Cu/Ni(mnt)(et$_2$dtp)]$^-$ the absorption signals of one [Cu(mnt)(et$_2$dtp)]$^-$ anion were observed. Each Cu hfs peak shows a doublet splitting caused by the interaction of the unpaired electron with one ^{31}P nucleus. These hfs lines are flanked symmetrically by four quartets of very weak signals which arise from molecules with one ^{33}S ligator atom (^{33}S: natural abundance 0.74%, $I = 3/2$). The four sets of ^{33}S ligand hfs signals indicate that the ^{33}S atom can be located in four non-equivalent positions. The intensity of each ^{33}S satellite is approximately 0.2% of the ^{31}P peaks. Due to the low intensity the ^{33}S hfs signals could be detected only in small intervals of the recorded angular dependencies using very high gains. In addition the ^{31}P hfs lines are flanked by spin flip satellites suggesting that protons of the $(n\text{-}Bu_4N)^+$ cation come close to the copper atom [4, 5]. A representative spectrum is shown in Fig. 1.

The principal values of all tensors of the spin-Hamiltonian derived from the single crystal measurements are listed in Table I. However, it is difficult to determine the positions of the principal g, A^{Cu}, A^{P} values in the molecular frame because no structural data for the host complex are available. Structural studies on $(n\text{-}Bu_4N)$[Cu(mnt)(et$_2$dtc) [6] have shown that the bonding angles and distances differ only slightly from those observed for $(n\text{-}Bu_4N)_2$[Cu(mnt)$_2$] [3] and Cu(et$_2$dtc)$_2$ [7]. Even in the used host lattice $(n\text{-}Bu_4N)$ Ni(mnt)(et$_2$dtp) the metal and the ligand atoms should be arranged like in the [Ni(mnt)$_2$]$^{2-}$ [8] and Ni(et$_2$dtp)$_2$ [9] chelates.

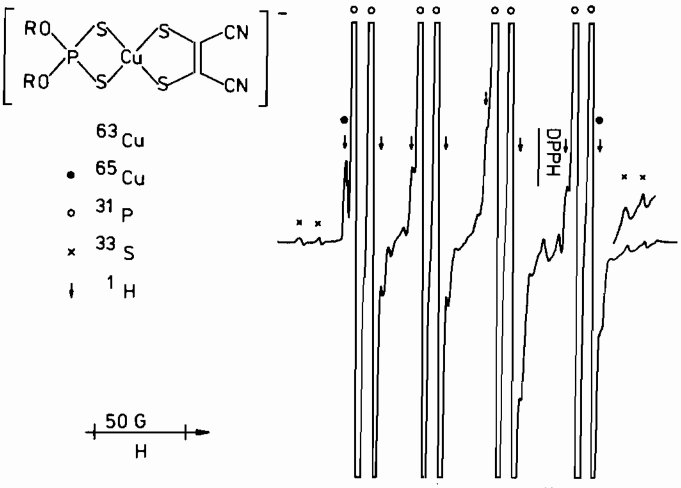


Fig. 1. Single crystal X band EPR spectrum of (n-Bu$_4$N)[^{63}Cu/Ni(mnt)(et$_2$dtp)] recorded in the xy plane at T = 298 K.

TABLE I. Principal Values of the g Tensor, the ^{63}Cu hfs and the ^{31}P hfs (Coupling constants in 10^{-4} cm^{-1}).

g	A(^{63}Cu)	A(^{31}P)
g_1 = 2.088	A_1 = −158.4	A_1 = 8.3
g_2 = 2.026	A_2 = −38.9	A_2 = 8.0
g_3 = 2.023	A_3 = −36.1	A_3 = 7.4
g = 2.046	A = −77.8	A = 7.9

[a] Experimental errors: g_1, g_2, g_3 ± 0.001; A_1^{Cu} ± 0.5; A_2^{Cu}, A_3^{Cu} ± 1.0; A_1^P, A_2^P, A_3^P ± 0.2.

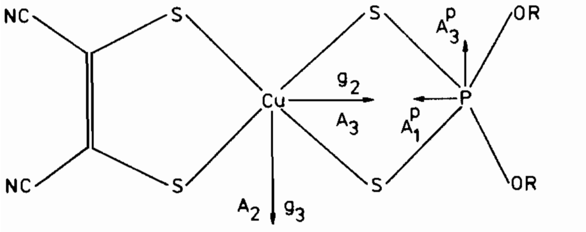


Fig. 2. Orientation of the principal axes of the g, ^{63}Cu hfs and the ^{31}P hfs tensors in [Cu(mnt)(et$_2$dtp)]$^-$ assuming that A_1^P points in the direction of the copper atom. A_1^{Cu}, g_1 and A_2^P lie perpendicular to the molecular plane.

Therefore the structural and electronic behaviour of the [Cu/Ni(mnt)(et$_2$dtp)]$^-$ units should be comparable with the parent complexes. If the ^{31}P hfs components point within small deviations in the same directions as observed for Cu/Ni(et$_2$dtp)$_2$ the principal axes of the g and A^{Cu} tensors can be located in the mixed ligand complex as shown in Fig. 2. The maximum components g_1 and A_1^{Cu} are directed along the normal to the molecular plane. This proves that the central part of the molecule is planar. The small components of the g and A^{Cu} tensor are located in the molecular plane. Surprisingly A_2^{Cu} points in the direction of g_3. The g and the A^{Cu} tensor axes coincide within the experimental error, which is nearly 5° for the equatorial components because of their low anisotropy. This assignment changes using the ^{33}S hfs for the location of the principal axes of the g and A^{Cu} tensor in the paramagnetic centre. However these data are somewhat uncertain due to the incompleteness of the values derived from the angular dependencies. The low intensity of the ^{33}S satellites and additional line overlappings by ^{33}S signals belonging to the second line of the ^{31}P splitting prevents the exact identification of the ^{33}S hfs in some orientations of the single crystal. From the measurements in the xy plane the large components of the ^{33}S tensors, which points in the direction of the copper atom, could be determined. Two of these four maximum values are nearly equivalent. The angle between the larger components was found to be 90° and between the smaller ones 85°. According to the structural assumptions they should belong to the sulphur atoms in the mnt and et$_2$dtp ligand, respectively. The A_3^S components were obtained from the spectrum recorded for H_z; A_2^S was calculated as described in [10]. Using these data, which are listed in Table II, the principal axes of all tensors can be located in the molecular plane as shown in Fig. 3.

In correspondence with the experimental results the MO of the unpaired electron consists mainly of the metal 3d$_{xy}$ and sulphur 3p$_z$ orbitals. With the help of the ^{33}S hfs data the ligand contribution to the MO of the unpaired electron can be estimated according to [10]. The values are listed together with the hybridization degree 'n' of the S-3s and 3p orbitals in Table II.

TABLE II. The ^{33}S hfs Tensors of the Systems: $(n\text{-}Bu_4N)_2[Cu/Ni(mnt)_2]$, $(n\text{-}Bu_4N)[Cu/Ni(mnt)(et_2dtp)]$ and $Cu/Ni(et_2dtp)_2$ (Coupling constants in 10^{-4} cm^{-1}) and the Corresponding MO Coefficients and Hybridizations Degrees.

	$(n\text{-}Bu_4N)_2[Cu/Ni(mnt)_2]$[a]		$(n\text{-}Bu_4N)[Cu/Ni(mnt)(et_2dtp)]$[b]				$Cu/Ni(et_2dtp)_2$[c]	
	S_1	S_2	S_1	S_2	S_3	S_4	S_1	S_2
A_1	22.0	21.4	25.2	23.7	19.7	18.2	19.6	19.6
A_2	9.4	9.4	11.5	10.4	9.5	9.0	6.5	6.4
A_3	7.9	7.6	8.2	8.2	8.2	8.2	4.9	4.7
A	13.1	12.8	15.0	14.1	12.5	11.8	10.2	10.2
2	0.36	0.34	0.46	0.44	0.39	0.37		
n	0.92	0.92	0.92	0.92	0.91	0.90		

[a] Ref. [4]. [b] Experimental errors: $A_1^S \pm 1.0$; $A_2^S \pm 2.0$; $A_3^S \pm 1.5$. [c] Ref. [5].

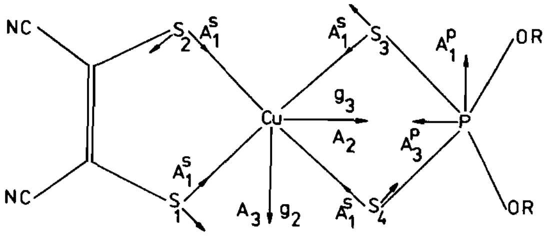


Fig. 3. Positions of the principal axes of the g, ^{63}Cu hfs and ^{31}P hfs tensor components in the molecular plane using the ^{33}S hfs data for the location of the tensors. A_1^{Cu}, g_1, A_2^P and A_3^S lie perpendicular to the molecular plane.

As can be seen from Table II the A_1^S values of the mnt S atoms are larger than those determined for $[Cu/Ni(mnt)_2]^{2-}$ whereas the A_1^S components of the S in the et_2dtp ligand are comparable with the values obtained for $Cu/Ni(et_2dtp)_2$. If the bonding angles and distances in the $[Cu/Ni(mnt)(et_2dtp)]^-$ are not different from those found for the corresponding parent chelates the larger values of the maximum S hfs components in the mnt ligand should be due to an increased electron spin density. This is supported by the almost isotropic ^{31}P hfs, which is smaller than in the $Cu/Ni(et_2dtp)_2$ system [5] suggesting a decrease of the electron spin density. These changes in the electronic system in comparison to the parent compounds may be one of the reasons for the stability of the investigated mixed ligand complex.

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