Ligand ENDOR Study of the Trigonal Bipyramidal Copper Complexes, [Cu(tren)NH$_3$](ClO$_4$)$_2$ and [Cu(tren)NCS]SCN in the Powder State (tren = tris(2-aminoethyl)amine)

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The HFC and NQC constants for all the coordinating atoms of the ligand tren, tris(2-aminoethyl)amine, in the trigonal bipyramidal (tbp) copper complexes [Cu(tren)NH$_3$](ClO$_4$)$_2$ 1 and [Cu(tren)NCS]SCN 2 have been determined from the angle selected ENDOR study in the powder state. The spin distribution and the metal ligand bonding nature in the copper (tbp) complexes are discussed.

ENDOR analyses of the tetragonal copper complexes have been reported by many authors.[1] From the ENDOR analyses, metal-ligand bondings have been discussed by evaluating nitrogen HFC values. However, untill now no ENDOR data of trigonal bipyramidal (tbp) copper complexes have been reported. Recently an ESEEM study of tbp copper compounds with substituted imidazoles has been reported,[2] where the HFC and NQC of the remote nitrogens have been determined, but no direct information about the metal nitrogen bonding was obtained. ENDOR can provide us with information about the metal-ligand bonding nature from the HFC and NQC of coordinating atoms. Tripodal ligand forms tbp complexes with transition metals.[3] We are trying to clarify the electronic features of some tbp copper complexes of the tripodal ligand tren by EPR and ENDOR analysis and for the first time we report ENDOR analysis results of the tbp copper complexes.

EPR and ENDOR spectra were taken by dopping the compound (2-3%) in the corresponding zinc complex powder, using a Varian E-112 X-band EPR spectrometer equipped with a Varian E-1700 ENDOR unit at 4-10 K. Both the compounds showed completely different EPR spectra ($g_\perp > g_\parallel$) from those of the tetragonal copper complexes. From the EPR spectra the complexes are suggested to have a ground states with d_{z^2} unpaired spin orbital. The HFC and NQC values for both axial and equatorial nitrogens were determined from the ENDOR spectra observed at the "$g_\parallel$ extreme" and "$g_\perp$ region" of the EPR spectra referring to the angle selected ENDOR data. Some of the angle selected ENDOR spectra of 1 are shown in Figure 1. The proton and nitrogen signals were distinguished by taking the ENDOR spectra at two different microwave (mw) frequencies, 9.1218 and 9.4066 GHz for 1 and 9.1273 and 9.3999 GHz for 2, for the same point of EPR spectrum. The change of mw frequency causes shifts of ENDOR signals according to the changes of Zeeman frequencies. By this technique we identified three types of nitrogen signals for 1 and four types of nitrogen signals for 2. The ENDOR frequencies of these signals were analyzed by the first order approximation.[1a] The assignments of nitrogen signals were made as follows. From the shape of the d_{z^2} orbital function (C_3 axis of tbp is along the z direction) it is expected that the axial nitrogens will have larger HFC values than those of the equatorial nitrogens. In 2 the two axial nitrogens have different HFC values; signals at the lower frequency region were assigned to the tren nitrogen by comparing the HFC and NQC values with those of [Cu(tren)Br]BPh$_4$ which has no nitrogen donor ligand at the 5th position of tbp. The HFC values of the two sets of overlapping signals for two axial nitrogens in 1 are nearer; here also the signals at lower frequency region were assigned to tren nitrogen as the HFC and NQC values are comparable to those in 2. Due to the shorter Cu-N bond length,[4] the NH$_3$ nitrogen may possess higher spin density relative to that at the tren nitrogen; this is also consistent with the above assignment for the nitrogen signals of 1. The HFC and NQC values for the nitrogens are listed in Table 1. From the angle dependent

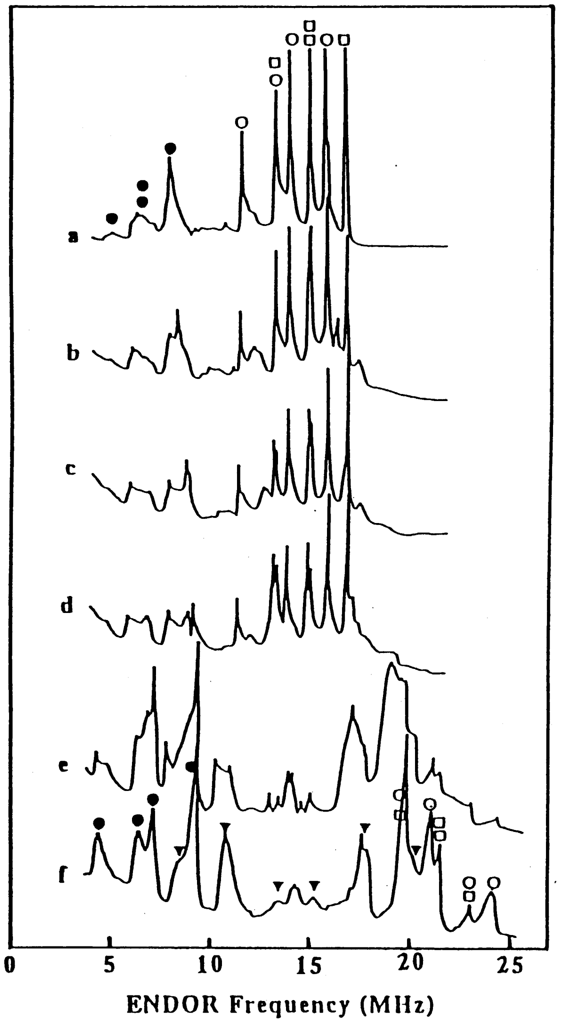

Figure 1. Powder ENDOR spectra of 1 at the magnetic fields a) 284.1 b) 294.8 c) 305.9 d) 316.9 e) 330.9 and f) 338.4 mT at temperature 4-6K and at mw frequency 9.1218 GHz, showing the signals of protons (▾), equatorial nitrogens (●), axial NH$_3$ nitrogen (□) and axial tren nitrogen (○).

Table 1. HFC and NQC values (MHz) for the axial and equatorial nitrogens[a]

Compounds	^{N}A(equatorial)	c	^{N}A(axial)	c	^{N}A(axial)	c
1	----[b]	---[b]	41.5	1.8	44.7	1.3
	13.5	1.4	27.9	1.3	30.7	0.9
2	----[b]	----[b]	42.3	1.7	49.8	1.0
	16.2	1.8	28.3	1.2	44.0	0.4
	18.9[c]	2.5[c]				

[a] The values in the first line are parallel principal values and those in the second line are the perpendicular principal values.

[b] Reliable values were not obtained.

[c] The perpendicular princepal values of HFC and NQC values for second type of equatorial nitrogen.

Table 2. Isotropic and anisotropic HFC values (MHz) and spin densities for the axial nitrogens

Compounds	^{N}Aiso	^{N}Aaniso	ρ_{2s}	ρ_{2p}	$\rho_{2s}+\rho_{2p}$	ρ_{2p}/ρ_{2s}
1	33.1	10.5	0.021	0.11	0.13	5.4
	35.4[a]	9.3[a]	0.023[a]	0.09[a]	0.11[a]	4.0[a]
2	33.5	10.4	0.021	0.11	0.13	5.0
	46.0[b]	3.8[b]	0.029[b]	0.04[b]	0.07[b]	1.3[b]

[a,b] The HFC values and spin densities for NH_3 and NCS nitrogens, respectively.

ENDOR signals of 1 (Figure 1) it is clear that the anisotropy of the equatorial nitrogens is small and that of the axial nitrogens is relatively large. The anisotropy of the NCS nitrogen in 2 is much less than that of the NH_3 nitrogen in 1 (Table 2). This is due to the fact that the lone pair orbitals of NCS and NH_3 are in the sp and sp^3 hybridized states, respectively. The experimentally obtained value of ρ_{2p}/ρ_{2s} for NCS is consistent with its hybridization type. On the other hand, the ρ_{2p}/ρ_{2s} values of the axial tren nitrogens are larger than that of regular sp^3, which may be explained from the change in sp ratio with structure around the nitrogen. The sp ratio of the lone pair orbitals varies sharply with the change of bond angle (α) of the coordinating nitrogens as shown in Figure 2. The calculated spin density ratios (~5) for the axial nitrogens correspond to an angular distortion of about 3° from regular sp^3 geometry. This value of angular distortion coincides with that shown by M. Dugan *et al.*[4] for the apical nitrogen of tren in 1.

In case of the equatorial nitrogens it was difficult to read the parallel principal values from the powder type spectral pattern. Since all the equatorial nitrogens are sp^3-hybridized the total spin at the equatorial nitrogens was evaluated, assuming $\rho_{2p} \sim 3\rho_{2s}$.

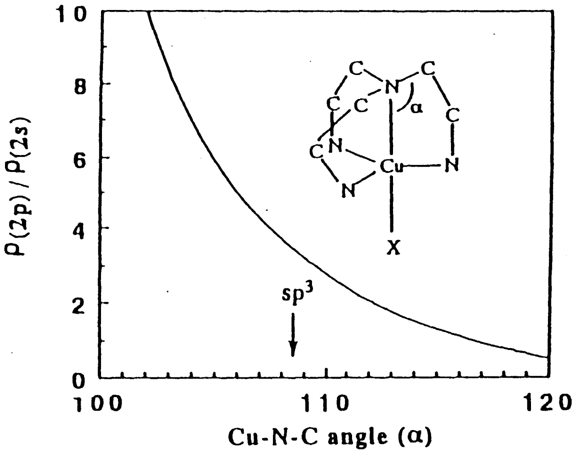

Figure 2. Calculated sp ratio as a function of Cu-N-C (α) angle, based on the equations in reference 6

Two sets of signals were observed for the equatorial nitrogens in 2, indicating inequivalency of the equatorial nitrogens, though the rhombicity was not clear from the EPR spectrum. P.C. Jain *et al*.[5] have reported the slight distortion from the exact C_3 symmetry by the X-ray crystallographic method. Therefore, the ENDOR method can be useful to prove the rhombicity. From the total spin density at 2p and 2s orbitals of all the nitrogens we can say that about 38% of the spin is distributed among the coordinating nitrogens, which is substantially greater than that in case of tetragonal copper complexes. The main characteristics is that in the tbp compounds most of the spin is distributed in the axial bonds. We could observe ENDOR signals for both of the axial and equatorial nitrogens. It was possible to determine the spin distribution among all the coordinating atoms of the tbp compounds.

References and Notes

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