

## ESR study of mixed ligand complexes of copper with dialkyl-diselenophosphate as one of the ligands\*

G KRISHNAMOORTHY, B S PRABHANANDA and  
P M SOLOZHENKIN†

Chemical Physics Group, Tata Institute of Fundamental Research, Bombay 400 005

†Institute of Chemistry, Academy of Sciences Tajik SSR, Dushanbe, USSR

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**Abstract.** A large number of mixed ligand complexes of copper with di-*i*-propyl-diselenophosphate as one of the ligands have been prepared by ligand exchange reactions and have been identified using electron spin resonance. From the measured ESR parameters in chloroform solutions it was concluded that (i) the measured  $g_0$  (and not  $A_{Cu}$ ) could be used to identify the mixed ligand complexes (in addition to ligand hyperfine splittings) (ii) the changes in spin transfer to  $^{77}Se$  and  $^{31}P$  on the same ligand dSeP are uncorrelated suggesting that the dominant mechanism of spin transfer to near neighbours  $^{77}Se$  is different from that to the next neighbour  $^{31}P$ . (iii) Observations on  $^{31}P$  splittings show that on formation of mixed ligand complex, the spin density on one ligand increases at the expense of other.

**Keywords.** Mixed ligand complex; electron spin resonance; ligand hyperfine; cupric complexes; spin transfer.

### 1. Introduction

The study of mixed ligand complexes has attracted the attention of several authors in the recent past. The stability of such complexes (Dietzch *et al* 1977 and references cited therein) and the change in electron delocalisation on forming a mixed ligand complex by a ligand exchange reaction (Prabhananda *et al* 1977, Krishnamoorthy and Prabhananda 1978 and references cited therein) have been the main subjects of these studies. In the case of cupric and vanadyl complexes, the characteristic features of their ESR spectra have been used to, identify the complexes, estimate their concentrations and determine the degree of electron delocalisation. Such studies have proved quite useful in understanding the mechanism of spin transfer to ligands (Krishnamoorthy and Prabhananda 1978). In the present work, mixed ligand complexes of Cu(II) with sulfur and selenium containing ligands have been prepared and the change in electron delocalisation is studied using the  $^{77}Se$  and  $^{31}P$  ligand hyperfine splittings observed in the ESR spectra in chloroform solutions at 25°C.

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## 2. Experimental

The various ligands used in the present work di-*i*-propyl diseleno-phosphate (dSeP), diethyldithiocarbamate (dtc), xanthate (xan), diethyldithiophosphate (dtp), diphenyldithiophosphinate (dtpi), *N*-benzoyl-*N'*-diethylthiocarbamide (btc), thiopicoline anilide (TPA) along with their abbreviated names are shown in figure 1. The potassium salt KdSeP and (dSeP)<sub>2</sub> were obtained from Dr Melink. Other ligands had been prepared following the procedures used in earlier work (Prabhananda *et al* 1972, Anufryanko *et al* 1964, Krishnamoorthy and Prabhananda 1978). Cupric acetate (enriched to > 99% with <sup>63</sup>Cu) was used in the preparation of cupric complexes. Cu(I) dSeP was first obtained from the reaction of cupric acetate with KdSeP. Cu(II)(dSeP)<sub>2</sub> was prepared by warming a chloroform solution of Cu(I)dSeP and (dSeP)<sub>2</sub> in molar proportion. The cupric complexes Cu(dtc)<sub>2</sub>, Cu(xan)<sub>2</sub>, Cu(dtp)<sub>2</sub>, Cu(dtpi)<sub>2</sub>, Cu(btc)<sub>2</sub> and Cu(TPA)<sub>2</sub> were prepared as described in earlier works (Anufryanko *et al* 1964, Krishnamoorthy and Prabhananda, 1978). The mixed ligand complex Cu(dtc)(dSeP) was obtained by the ligand exchange reaction.

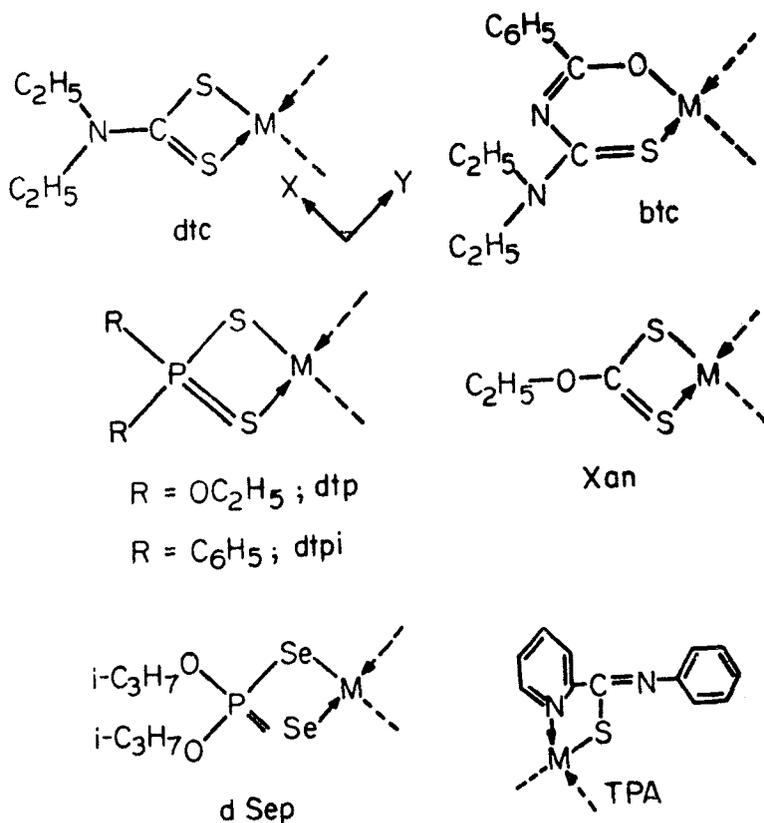
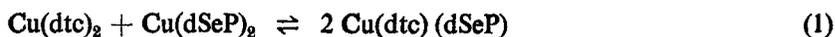


Figure 1. Ligands used in the present work

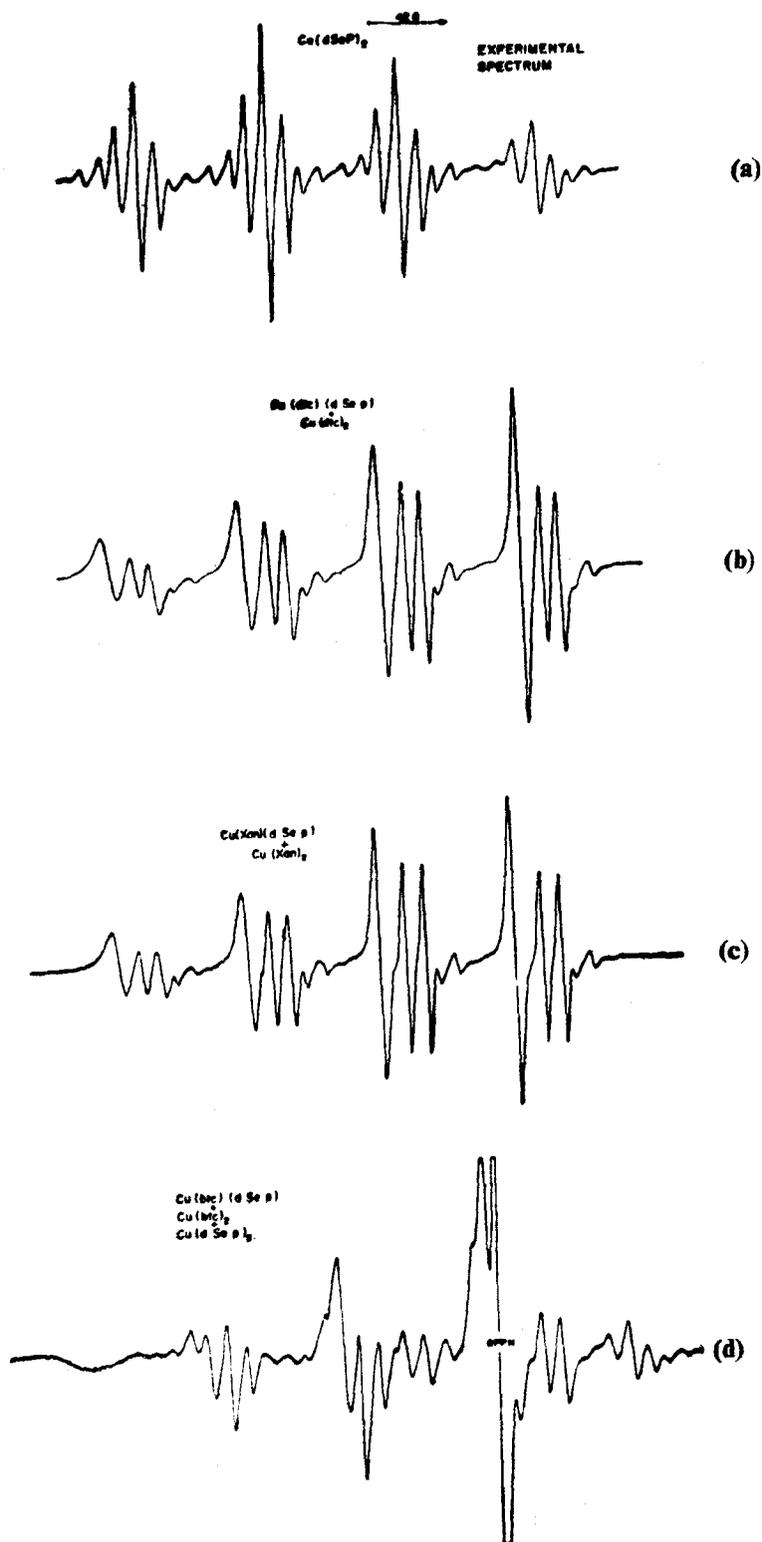


Figure 2. ESR spectra obtained from chloroform solutions of (a)  $\text{Cu}(\text{dSeP})_2$ ; equilibrium mixtures used in the preparation of (b)  $\text{Cu}(\text{dte})(\text{dSeP})$ , (c)  $\text{Cu}(\text{xan})(\text{dSeP})$  (d)  $\text{Cu}(\text{btc})(\text{dSeP})$  at  $25^\circ\text{C}$

The mixed ligand complexes  $\text{Cu}(\text{xan})(\text{dSeP})$ ,  $\text{Cu}(\text{btc})(\text{dSeP})$ ,  $\text{Cu}(\text{TPA})(\text{dSeP})$ ,  $\text{Cu}(\text{dtp})(\text{dSeP})$  and  $\text{Cu}(\text{dtpi})(\text{dSeP})$  were also prepared by similar reactions. However, excess ligands  $\text{dtp}^-$  and  $\text{dtpi}^-$  were present in the solutions in the preparation of last two complexes. The chloroform solutions were degassed before taking their ESR spectra. The ESR spectrometer used is described elsewhere (Prabhananda *et al* 1972).  $g_0$  have been measured taking DPPH as the standard.

### 3. Results

The ESR spectrum of  $\text{Cu}(\text{dSeP})_2$  obtained in the present work (figure 2a) was essentially the same as that reported earlier (Larin *et al* 1972) except that the spectrum due to complexes with  $^{65}\text{Cu}$  isotope was absent in the present preparations making the interpretations easier. Apart from the hyperfine splittings from the two equivalent  $^{31}\text{P}$ , the ESR spectrum shows the splittings from one  $^{77}\text{Se}$  in  $\sim 30\%$  of the complexes consistent with the expectations from the natural abundance of  $^{77}\text{Se}(\sim 7.5\%)$  (since  $\text{dSeP}$  is bidentate).

Figures 2(b-d) show the spectra from equilibrium mixtures obtained at the end of five minutes of mixing the cupric complexes (see table 1), used for the preparation of mixed ligand complexes  $\text{Cu}(\text{dte})(\text{dSeP})$ ,  $\text{Cu}(\text{xan})(\text{dSeP})$  and  $\text{Cu}(\text{btc})(\text{dSeP})$  at concentrations convenient for ESR measurements. Knowing the ESR spectra of complexes used in the preparations and noting that the spectra of these mixed ligand complexes should show hyperfine splitting from one  $^{31}\text{P}$ , we can easily identify the lines due to the mixed ligand complexes which do not have the isotope  $^{77}\text{Se}$ . Similarly, figures 3(a-c) give the ESR spectra obtained from the equilibrium mixtures (table 1) used in the preparation of  $\text{Cu}(\text{dtp})(\text{dSeP})$ ,  $\text{Cu}(\text{dtpi})(\text{dSeP})$  and  $\text{Cu}(\text{TPA})(\text{dSeP})$ . In these cases, the spectra of mixed ligand complexes could be identified by noting that the lines split into doublets by the  $^{31}\text{P}$  in  $\text{dSeP}$ , are further split into doublets by the  $^{31}\text{P}$  in  $\text{dtp}$  or  $\text{dtpi}$  and into triplets by the  $^{14}\text{N}$  in TPA.

About 15% of the mixed ligand complexes are expected to give ESR spectra with additional splittings due to one  $^{77}\text{Se}$  (which has spin 1/2). In the case of  $\text{Cu}(\text{dte})(\text{dSeP})$  and  $\text{Cu}(\text{xan})(\text{dSeP})$ , these could be easily identified on the high field side of

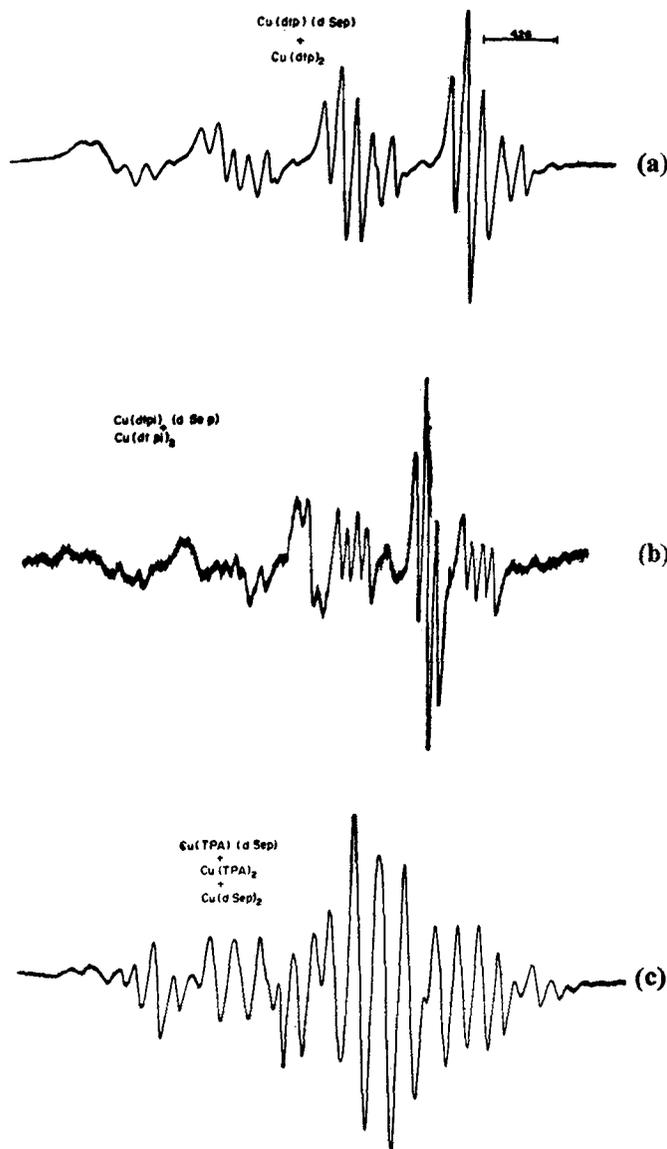
Table 1. Concentration of the various cupric complexes used in the preparation of mixed ligand complexes and their proportion in equilibrium mixtures

Mixed ligand complex $\text{Cu}(\text{X})(\text{Y})$	Initial concentration $[\text{Cu}(\text{X})_2] \times 10^3 \text{ M}$	Initial concentration $[\text{Cu}(\text{Y})_2] \times 10^3 \text{ M}$	Proportion of cupric complexes in equilibrium mixtures <sup>c</sup>
$\text{Cu}(\text{dte})(\text{dSeP})$	2.4	6.5	2.4 : 1.0 : $\sim 0$
$\text{Cu}(\text{xan})(\text{dSeP})$	2.5	13.0	0.7 : 1.0 : $\sim 0$
$\text{Cu}(\text{btc})(\text{dSeP})$	5.7	52.0	1.3 : 0.8 : 1.0
$\text{Cu}(\text{dtp})(\text{dSeP})^a$	7.0	29.0	5.9 : 7.7 : 1.0
$\text{Cu}(\text{dtpi})(\text{dSeP})^b$	5.0	60.0	4.5 : 5.2 : 1.0
$\text{Cu}(\text{TPA})(\text{dSeP})$	8.0	18.0	2.9 : 5.9 : 1.0

<sup>a</sup>Equilibrium mixture had 0.18 M  $\text{dtpH}$  also

<sup>b</sup>Equilibrium mixture had 0.04 M  $\text{dtpiH}$  also

<sup>c</sup> $[\text{Cu}(\text{X})(\text{Y})] : [\text{Cu}(\text{X})_2] : [\text{Cu}(\text{Y})_2]$  determined from the analysis of ESR spectra



**Figure 3.** ESR spectra obtained from the equilibrium mixtures in chloroform used in the preparation of (a)  $\text{Cu(dtp)(dSeP)}$  (b)  $\text{Cu(dtpi)(dSeP)}$  (c)  $\text{Cu(TPA)(dSeP)}$ .

the spectra, where the overlap of lines was minimum. In the case of other four complexes these were identified by comparing the observed spectra with computer simulated spectra in the high field region (figures 4 a-d). The relative concentrations of the paramagnetic complexes present in the equilibrium mixtures (table 2) were also estimated by this procedure. (It was found necessary to increase the widths of lines due to  $\text{Cu(dSeP)}_2$  by  $\sim 10\%$  in these simulations. This is understandable since the lines are expected to be broadened due to the rapid ligand exchange taking place in the equilibrium mixtures. Line width variations among the different hyperfine lines were also included in the computer simulations).

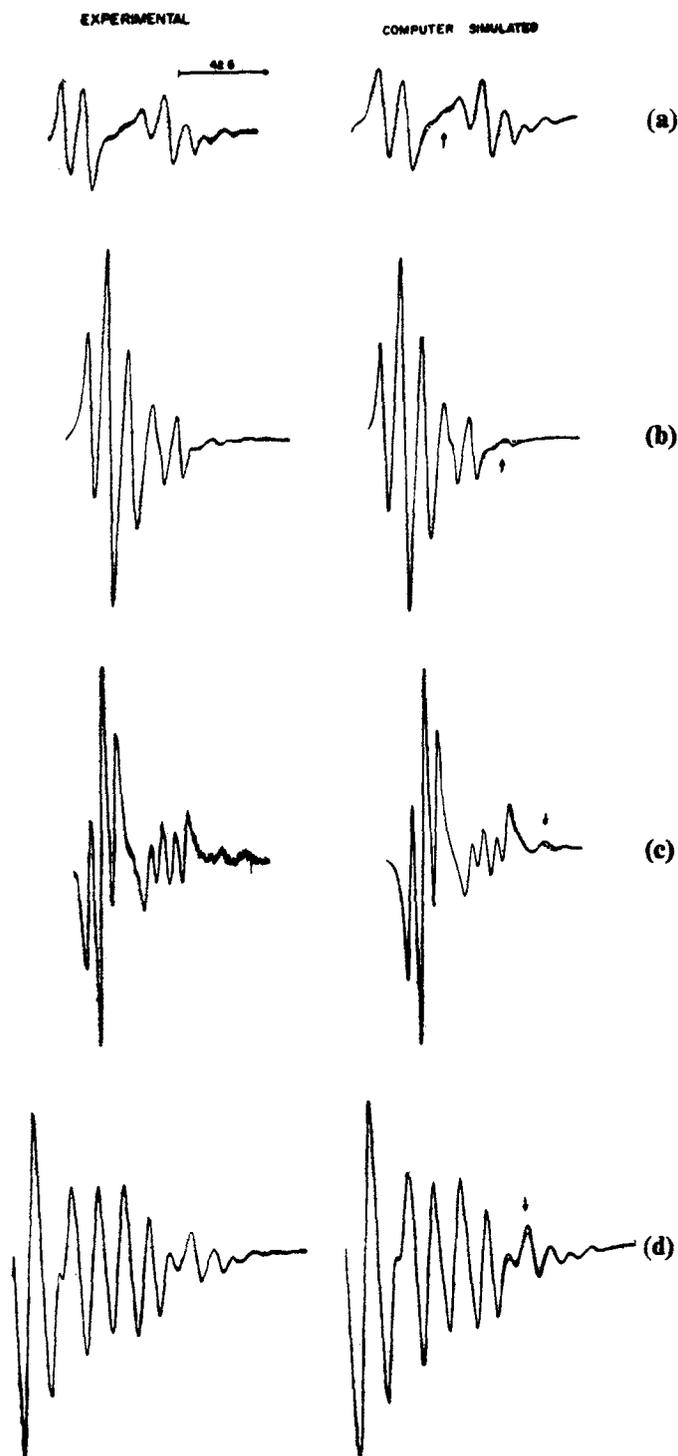


Figure 4. Experimental and computer simulated ESR spectra (in the high field region) of equilibrium mixtures used in the measurement of  $A_p$ ,  $A_{Se}$ ,  $A_p$  in (a) Cu(btc)(dSeP) (b) Cu(dtp)(dSeP) (c) Cu(dtpi)(dSeP) (c) Cu(TPA)(dSeP) Broken lines in the simulated spectra correspond to  $A_{Se} = 0$  for the mixed ligand complex. The presence of the  $^{77}\text{Se}$  split lines have been checked by varying the relative concentrations of the complexes used in the preparation.

**Table 2.** The ESR parameters of the cupric complexes used in the present work, measured at 25° C in chloroform solutions

Complex	$A_P$ Gauss	$A_N$ Gauss	$A_{Se}$ Gauss	$A_{Cu}$ Gauss	$g_0$
Cu(dSeP) <sub>2</sub>	10.8	—	38.0	75.7	2.0279
Cu(dtp) <sub>2</sub>	9.6	—	—	72.0	2.0487
Cu(dtp)(dSeP)	8.8 12.4 <sup>a</sup>	—	36.0	74.6	2.0374
Cu(dtc) <sub>2</sub>	—	—	—	78.0	2.0480
Cu(dtc)(dSeP)	10.2	—	34.6	77.7	2.0360
Cu(xan) <sub>2</sub>	—	—	—	75.1	2.0480
Cu(xan)(dSeP)	10.7	—	34.1	75.7	2.0354
Cu(dtpi) <sub>2</sub>	6.2	—	—	68.0	2.0552
Cu(dtpi)(dSeP)	5.6 12.3 <sup>a</sup>	—	34.9	72.6	2.0406
Cu(btc) <sub>2</sub>	—	—	—	79.7	2.0826
Cu(btc)(dSeP)	11.0	—	46.5	75.7	2.0559
Cu(TPA) <sub>2</sub>	—	15.4	—	68.0	2.0776
Cu(TPA)(dSeP)	9.5	13.2	39.6	73.0	2.0487
Errors	± 0.3	± 0.5	± 0.5	± 2.0	± 0.002

<sup>a</sup> $A_P$  associated with dSeP.

The values of  $g_0$  and hyperfine splittings from the metal,  $A_{Cu}$  and the ligands,  $A_P$ ,  $A_{Se}$  measured from the spectra at 25°C in chloroform are given in table 2. Measurements of  $A_P$  and  $A_{Se}$  were restricted to high field region, where the lines were better resolved.

#### 4. Discussion

##### 4.1. $g_0$ and $A_{Cu}$ in mixed ligand complexes

From the observations of spin densities on the ligands in mixed ligand complexes using NMR (Eaton and Phillips 1965) and using ESR (Krishnamoorthy and Prabhananda 1978), one can expect the unpaired d-electron density on the metal in Cu(X)(Y) to be the average of that in Cu(X)<sub>2</sub> and Cu(Y)<sub>2</sub>. The ligand field splittings are also expected to show such average values. If the ligand field splittings are not very different in Cu(X)<sub>2</sub> and Cu(Y)<sub>2</sub>, then we can see from the standard expressions for  $g_0$  ( $= \frac{1}{3} g_{\parallel} + \frac{2}{3} g_{\perp}$ , see Prabhananda *et al.*, 1972) that the observed  $g_0$  for Cu(X)(Y),  $g_{xy}$  is the average of that for Cu(X)<sub>2</sub> and Cu(Y)<sub>2</sub>;  $g_{xy} \simeq (g_x + g_y)/2$ . The values of  $g_0$  listed in table 2 show such a behaviour.

However, the isotropic part of the metal hyperfine constant  $A_{Cu}$  for the mixed ligand complex is not in general close to the average of the values for Cu(X)<sub>2</sub> and Cu(Y)<sub>2</sub>. This could signify a change in 4s- contribution, which could alter  $A_{Cu}$  by as much as 5 gauss with negligible change in  $g_0$  (within the limits of error, and being only a small fraction of the changes in  $g_0$ . (This can be seen using the papers by McGarvey 1967; Watson and Freeman 1961).

From the above mentioned observations it can be seen that the measured  $g_0$  could be used to identify the mixed ligand complexes, when the ligand hyperfine splittings are absent or unresolved.

#### 4.2. Mechanism of spin transfer to ligand

On the basis of arguments given in the previous papers from our laboratory (Krishnamoorthy and Prabhananda 1978) it can be seen that the spin transfer to near neighbours in cupric complexes with dtp, dSeP or similar ligands is to be associated with the covalent bonding involving the unpaired electron orbital  $d_{x^2-y^2}$  on the metal and the ligand orbitals. However, the spin transfer to next neighbours were suggested to be associated with the covalent bonding involving  $d_{xy}$  orbital and the ligand orbitals. The presence of unpaired spin in  $d_{xy}$  was attributed to configuration interaction mechanism.

It was also argued that the spin transfer to next neighbours via the near neighbours was not a dominant mechanism. The present work provides further support to this argument by enabling the observation of change in spin density on the near neighbour  $^{77}\text{Se}$  and the next neighbour  $^{31}\text{P}$  on the same ligand dSeP forming a mixed ligand complex. The observed decrease in both  $^{77}\text{Se}$  and  $^{31}\text{P}$  splittings in  $\text{Cu}(\text{dSeP})$  when compared to in  $\text{Cu}(\text{dSeP})_2$  could be accidental. The decrease in  $A_{\text{Se}}$  with an increase in  $A_{\text{P}}$  in  $\text{Cu}(\text{dtp})(\text{dSeP})$  and  $\text{Cu}(\text{dtpi})(\text{dSeP})$ ; negligible change in  $A_{\text{P}}$  with substantial decrease in  $A_{\text{Se}}$  in  $\text{Cu}(\text{xan})(\text{dSeP})$  and increase in  $A_{\text{Se}}$  in  $\text{Cu}(\text{btc})(\text{dSeP})$ ; decrease in  $A_{\text{P}}$  with a small increase in  $A_{\text{Se}}$  in  $\text{Cu}(\text{TPA})(\text{dSeP})$ ; show that changes in spin density on the Se is not directly correlated with that on  $^{31}\text{P}$  in dSeP. It can be concluded that the spin transfer to next neighbour  $^{31}\text{P}$  via the near neighbour Se is not the dominant reason for the observed  $^{31}\text{P}$  hyperfine splittings in cupric complexes with dSeP as ligands.

On the basis of mechanism proposed in our earlier work it can be expected that the spin transfer to ligands in vanadyl mixed ligand complexes show a behaviour opposite to that observed in cupric complexes. The observed increase in the  $^{31}\text{P}$  splittings in  $\text{VO}(\text{dSeP})$  when compared to in  $\text{VO}(\text{dSeP})_2$  by Baratova *et al* (to be published) is consistent with this expectation.

Furthermore, we see from the next neighbour  $^{31}\text{P}$  splittings in  $\text{Cu}(\text{dtp})(\text{dSeP})$  and  $\text{Cu}(\text{dtpi})(\text{dSeP})$  that the spin density on the next neighbour on one ligand increases at the expense of spin density on the next neighbour on the other ligand, consistent with our observations on the  $^{13}\text{C}$  enriched  $\text{Cu}(\text{dSeP})_2$  and  $\text{Cu}(\text{dSeP}^*)(\text{dtp})$  in our previous work (Krishnamoorthy and Prabhananda 1978).

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