AN ESR STUDY OF COVALENT BINDING IN COPPER DIETHYLDISELENOCARBAMATE

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ABSTRACT

Single crystal ESR investigations of copper (II) diethyl-diselenocarbamate, diluted in the corresponding zinc complex, are reported in this paper. The g and C hyperfine tensors have non-coinciding principal axes. While the maximum Cu hyperfine splitting direction is normal to the plane of the ligands, the maximum g-value direction is located in the plane of the ligands. The g-values for this complex are very close to the free spin value; the g *shifts are the lowest reported for Cu (II) complexes. Hyperfine structure from the* ^{77}*Se isotope* ($7 \cdot 5\%$ *abundant) has been observed and the Se hyperfine principal values are used to estimate the coefficients of the Se* 4s *and* 4p *orbitals in the ground molecular orbital of the unpaired electron. These indicate a high degree of delocalization of the unpaired electron over the complex. A consistent explanation of the results is given in terms of the large delocalization of the unpaired electron and the high spin-orbit constant of the ligand.*

Key words: ESR: Cu diethyldiselenocarbamate: Covalent binding.

INTRODUCTION

We have been investigating for some time, the effects of covalent binding in sulphur co-ordinated copper complexes [1–3]. These studies motivated similar investigations in copper complexes bonded to the much heavier ligand atom Se. Cu dialkyldiselenocarbamates are among the few stable Se bonded Cu (II) complexes. These were taken up for study since the results on the corresponding thio complexes are available for comparison. Both complexes have similar geometry; the Cu atom is surrounded by four ligand atoms roughly at the corners of a square. Covalent binding effects can be investigated through superhyperfine (s.h.f.) structure study, more easily in the case of selenium than in the case of sulphur because of the higher relative abundance of the magnetic isotope of Se, ^{77}Se ($7 \cdot 5\%$ abundant).

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Therefore, a detailed ESR study of single crystals of copper diethyl-diselenocarbamate (desc) isomorphously diluted with the zinc complex was undertaken a few years ago[4]. A preliminary report on the work was published, but all the features of the ESR spectra had not been explained. Attempts were being made to study the effects of Ni dilution also. Two groups of workers[5,6] meanwhile published ESR results on Cu di-*n*-butyldiselenocarbamate Cu (dbsc)$_2$, diluted in the corresponding Ni complex. In both Cu (desc)$_2$ and Cu (dbsc)$_2$ the g- and Cu hyperfine (h.f.) tensors have non-coinciding principal axes. The g-shifts in these complexes are the lowest reported so far for Cu complexes. A large degree of delocalization of the unpaired electron is indicated by the magnitude of the ^{77}Se hyperfine interaction. In this paper we report our investigations on Cu, Zn (desc)$_2$ and compare them with the results for Cu, Ni (dbsc)$_2$ and attempt an explanation of the unusual features of the ESR spectrum in the two cases in terms of the large delocalization of the unpaired electron and the high spin-orbit coupling constant of the ligand.

EXPERIMENTAL

ESR investigations were carried out with an X-band spectrometer using 100 KHz modulation. Single crystals of Cu (desc)$_2$ isomorphously diluted with Zn (desc)$_2$[7] were grown from chloroform solutions. Preliminary X-ray examination in our laboratory indicated that Cu (desc)$_2$ is isomorphous with Cu diethyldithiocarbamate (detc). Mixed crystals of the thio and seleno complexes could also be grown without difficulty. Crystals of Cu (desc)$_2$ belong to the monoclinic space group $P2_1/c$ with $a = 10{\cdot}02$, $b = 11{\cdot}06$, $c = 17{\cdot}03$ Å, $\beta = 111°$, $z = 4$.

RESULTS

A recording of the ESR spectrum with the magnetic field in the *ac* plane is reproduced in Fig. 1. In addition to the strong hyperfine lines from Cu nuclei (^{63}Cu and ^{65}Cu isotopes), the spectrum shows a number of weak lines due to ^{77}Se nuclei ($I = \frac{1}{2}$).

Angular variation studies showed that the axes of the g- and Cu h.f. tensors do not coincide in this crystal. In the *ac* plane the maximum h.f. splitting direction is 70° away from the direction of maximum g-value ($g_{\max}$). The maximum and minimum g-value directions in the *ac* plane, $g_{\max}$ and $g_{\min}$ were noted. Angular variation study in three orthogonal planes (*ac*,

$g_{max}\,b$ and $g_{min}\,b$ planes) yielded the g-tensor which was diagonalized to give the principal g-values $g_u = 2{\cdot}0076$, $g_v = 2{\cdot}0228$ and $g_w = 2{\cdot}0581$.

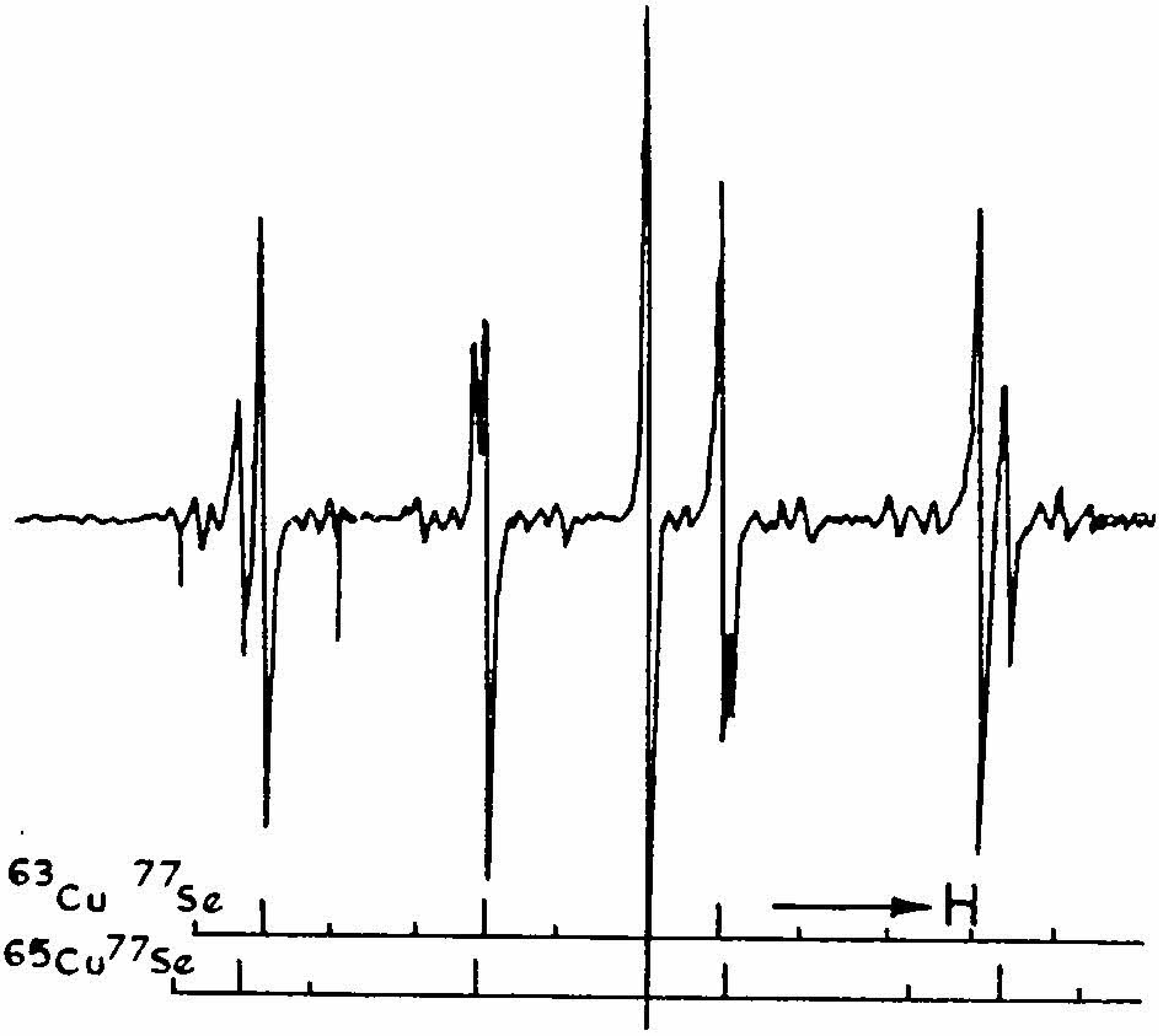

FIG. 1. ESR spectrum of Cu, Zn (desc)$_2$ with H lying in the ac-plane.

The turning points of the Cu h.f. splitting in the principal planes of the g-tensor indicated that one of the principal axes of the Cu h.f. tensor m coincides with the g_v direction and the h.f. splitting in this direction is found to be the maximum. The other two principal directions l and n are located in the uw plane making angles of about 40° with the u and w directions respectively (Fig. 2). The principal hyperfine constants are: $A_l = 26{\cdot}6 \times 10^{-4}\,cm^{-1}$; $A_m^{63} = 127{\cdot}7 \times 10^{-4}\,cm^{-1}$; $A_m^{65} = 136{\cdot}9 \times 10^{-4}\,cm^{-1}$ and $A_n = 44{\cdot}6 \times 10^{-4}\,cm^{-1}$.

Since the directions of maximum g-value and maximum Cu h.f. splitting do not coincide, the problem arises as to which corresponds to the z-direction of the spin Hamiltonian. To find this out mixed crystals were grown with Cu, Zn (detc)$_2$ in which the g- and A tensors coincide. ESR spectrum of this mixed crystal showed that the maximum h.f. direction corresponds to the normal to the Cu–Se$_4$ plane.

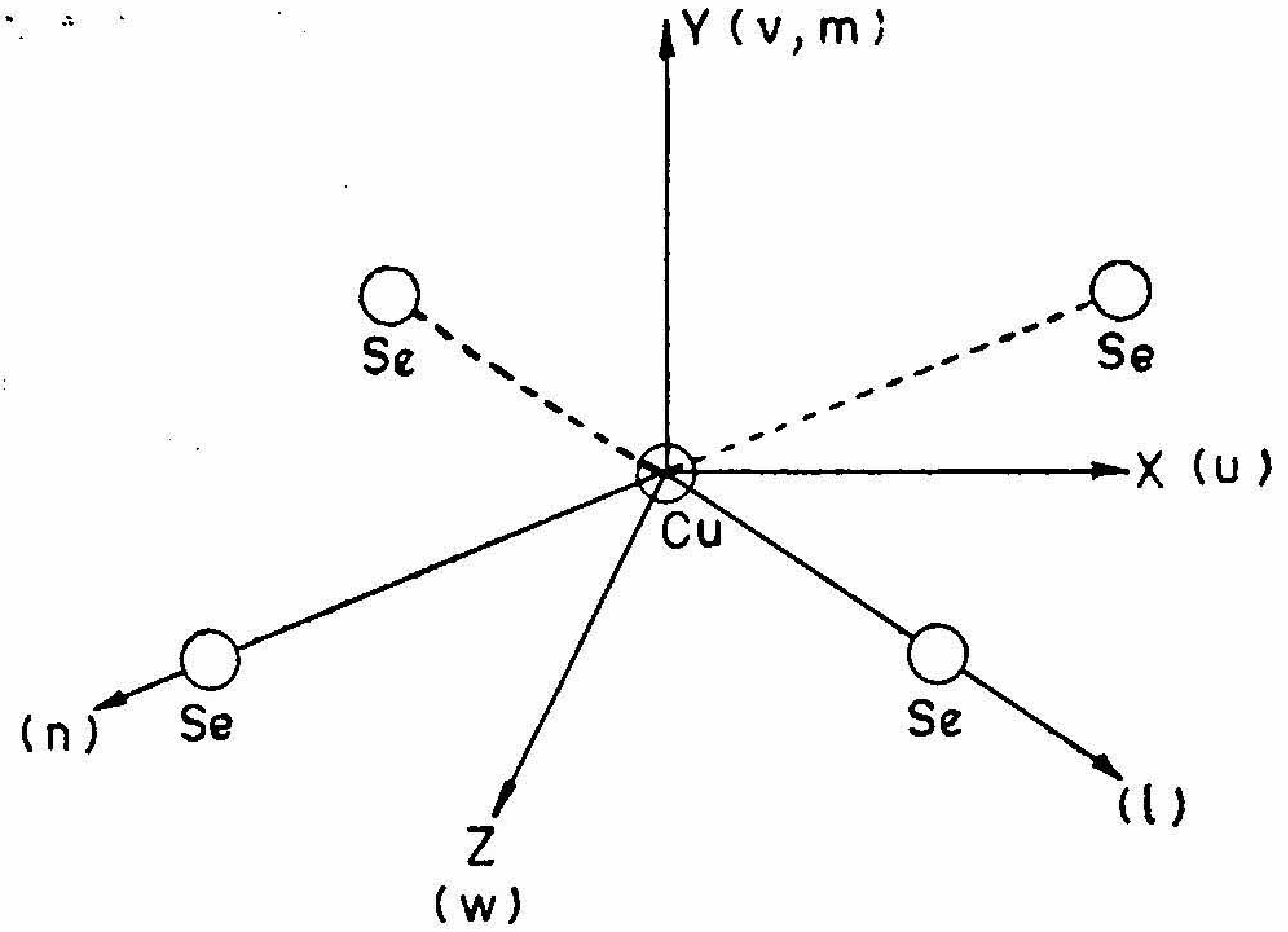

FIG. 2. Relative orientation of the g and Cu hyperfine tensors and the coordinate system used for the discussion of ESR results. The Cu and the four Se atoms are in the XZ plane.

S.h.f. structure from ^{77}Se nuclei has been analysed. The measured Se h.f. separation along the maximum Cu h.f. direction is 27×10^{-4} cm^{-1}. Assuming the s.h.f. interaction to be axial about the bond direction, this is taken as the principal value B^{Se}. Tracking the lines in the vu plane, the maximum separation measured along the u direction is 75×10^{-4} cm^{-1}. Noting that this direction is 40° from the bond direction l, the hyperfine separation A^{Se} along the bond direction is calculated to be 95×10^{-4} cm^{-1}.

Measurements made with a benzene solution of the complex gave the values: $g = 2{\cdot}0246$, $A^{Cu} = 75 \times 10^{-4}$ cm^{-1} and $A^{Se} = 42 \times 10^{-4}$ cm^{-1}.

DISCUSSION

The following points may be noted from a comparison of our experimental results with those of Van Rens *et al.*[5] and Kirmse *et al.*[6].

(i) In both complexes the g-values, Cu and Se h.f. tensors have roughly tetragonal symmetry in their respective principal axes frames with only small rhombic components.

(ii) The g-values are very close to the free spin value. The g-shifts are the lowest reported for cupric complexes. One of the g-values for Cu, Ni $(dbsc)_2$ is less than $2{\cdot}0023$.

(iii) The principal axes of the Cu and Se h.f. tensors are oriented as is normally found in other Cu (II) complexes, but unusually, in both complexes, the direction of maximum *g*-value is in the plane of the ligands.

(iv) The numerical values of the *g*- and Cu h.f. tensors are similar for Cu, Zn $(desc)_2$ and Cu, Ni $(dbsc)_2$.

(v) The *g*-tensor axes are differently oriented in the two complexes. In Cu, Zn $(desc)_2$, the only coincident principal axes of the *g*- and A^{Cu} tensors is along the normal to the Cu–Se_4 plane while in Cu, Ni $(dbsc)_2$ it is in the molecular plane.

Since the principal axes of the *g*- and Cu h.f. tensors do not coincide, the molecular orbital theory developed by Maki and McGarvey[8] and Kivelson and Neiman[9] is not directly applicable. However, the symmetry of the Cu and Se h.f. tensors indicate the ground orbital of the unpaired electron to be the antibonding σ-orbital. The present results may be understood by noting that the unpaired electron is highly delocalized over the ligand atoms. Under these circumstances the *g*-values are ditermined by the overall symmetry of the complex over which delocalization is effective; h.f. tensors have symmetry axes decided by the local symmetry provided by the immediate neighbourhood of the nuclear site because of the r^{-3} dependence of the anisotropic part of the h.f. interaction. This accounts for the normal orientation of the A^{Cu} and A^{Se} tensors. In addition to the large delocalization, another special feature is the spin orbit coupling constant of Se which is much larger than that for other ligands studied; in fact, it is larger than that for Cu.

An estimate of covalency in the complex may be obtained from ligand h.f. data. The isotropic and anisotropic parts of the h.f. interaction, determined from experimental h.f. parameters, are: $a^{Se} = 49 \cdot 67 \times 10^{-4}$ cm^{-1} and $b^{Se} = 22 \cdot 67 \times 10^{-4}$ cm^{-1}. These are assumed to arise from spin densities ρ_s and ρ_p in the Se 4*s* and 4*p* orbitals, which can be estimated by comparing the experimental h.f. parameters with theoretically calculated values. For the two sets of theoretical values calculated by Whiffen[10] and Hurd and Coodin[11] the values of ρ_s and ρ_p estimated are $\rho_s = 0 \cdot 011$ and $0 \cdot 008$, $\rho_p = 0 \cdot 18$ and $0 \cdot 138$ respectively. The values of σ-overlap integrals for the Se 4*s* and 4*p* orbitals with the metal *d*-orbital taken from Boudreaux *et al.*[12] are: $S_s = 0 \cdot 036$, $S_p = 0 \cdot 05$. The values of α_1^2, the square of the coefficient of the metal *d*-orbital in the ground molecular orbital of the unpaired electron, calculated from the values of ρ_s, ρ_p, S_s and S_p, are $0 \cdot 29$ and $0 \cdot 48$ for the two sets[10,11] of the estimated spin densities on Se. The values of α_1^2

calculated are the lowest reported for cupric complexes. More spin density is transferred to the Se ligands than is retained in the metal orbital. In the above discussion we have not taken into account the 3*d*-orbitals on the Se atoms. These would contribute directly to the anisotropic h.f. interaction and indirectly to isotropic h.f. coupling by core polarization. We have also omitted the exchange polarization and covalency of the bonding orbitals.

For comparable a_1, Se binding should be more effective than *S* binding in leading to near free-spin *g*-values because of the larger spin-orbit coupling constant of Se. In the unquenching of orbital momentum caused by spin-orbit interaction, the spin-orbit effects on the ligands partially cancel out the effect from the metal atom, thus resulting in a smaller *g*-shift. This effect is not so pronounced in the case of lighter ligands with smaller spin-orbit parameters. Ligand effects are so large in Se complexes that in Cu, Ni $(dbsc)_2$ they are even stronger than the spin-orbit interaction on Cu and one of the *g*-shifts becomes negative.

With such large covalency it would, therefore, not be correct to use molecular orbitals of D_{4h} or D_{2h} symmetry with the *z*-axis normal to the plane of the ligands. Some spin density may be found even outside the $CuSe_4$ framework. The symmetry of the surroundings of the Cu-Se_4 unit as a whole cannot be greater than two-fold. The D_{2h} symmetry for perfect planar arrangement of atoms will be lowered by distortions. The results in the present case can be qualitatively explained by assuming a two-fold axis with the quantizing direction in the co-ordination plane. Assuming the symmetry of the complex to be C_{2h} (similar results would be obtained for C_2) the *z*-axis is taken to be along the maximum *g*-direction g_w in the ligand plane (Fig. 2). The *x*-axis is taken along g_u and the common principal axis direction ($v = m$) is taken as the *y*-axis.

Considering the unpaired electron to be in the antibonding orbital between the metal atom and the ligands, the ground orbital would be that involving the d_{xz} orbital on the metal atom. Under low symmetry, irreducible representations have low dimensionality; more than one orbital belongs to the same irreducible representation. Both d_{xz} and d_{yz} orbitals belong to B_g symmetry in C_{2h}. The ground state of the unpaired electron should, therefore, be written as a linear combination of the metal d_{xz} and d_{yz} orbitals and appropriate linear combinations of Se 4*s* and 4*p* orbitals, *viz.*,

$$B_g = a_1 d_{xz} - \frac{a_2}{2}(\sigma^1 + \sigma^2 + \sigma^3 + \sigma^4)$$

$$+ a_3 d_{yz} - \frac{a_4}{2}(p_y{}^1 - p_y{}^2 - p_y{}^3 + p_y{}^4)$$

where σ^i is the suitable hybridized combination of 4*s* and 4*p* orbitals on the Se ligand *i*.

To calculate the *g*-values, the spin-orbit admixture into the B_g orbital is to be evaluated. The l_z operator admixes d_{yz} into d_{xz}. This gives a contribution to g_z. The l_x operator connects the d_{xy} orbital with the d_{xz} orbital. The l_y operator takes the d_{xz} orbital into a linear combination of $d_{3z^2-x^2}$ and $d_{x^2-y^2}$. d_{x^2}, d_{y^2}, d_{z^2} and d_{xy} all belong to the A_g representation in C_{2h}. Spin-orbit admixture is most effective with the l_y operator along the normal to the $CuSe_4$ plane so that *g*-shift due to spin-orbit effects is maximum along the *y*-direction. Similar but smaller contributions are obtained along the *z*- and *x*-direction. There is an extra contribution to the *g*-shift along the *z*-direction coming from the crystal field admixture of d_{yz}. A knowledge of the exact strength of the crystal field is necessary to calculate this effect. It is, however, apparent from experimental results that this effect is appreciable. The *g*-value is, therefore, maximum along the *z*-axis and g_y is greater than g_x.

As already mentioned, the symmetry of the h.f. tensors can be explained by noting that the interaction falls off as r^{-3} and is therefore, determined largely by the local symmetry at the Cu nuclear site. Usually all ligand and overlap terms are neglected in the calculation of the hyperfine interaction with the metal atom. Therefore, for the discussion of the Cu h.f. structure axes, the symmetry can be considered to be D_{2h} with the unpaired electron in the d_{xz} orbital. Calculation of h.f. interaction then yields principal axes and values that agree with the experimental situation. A similar argument that the Se h.f. structure is determined by the symmetry at the concerned Se site shows the Se hyperfine structure to be roughly axial about the Cu-Se bond direction.

Though the *g*-tensor appears to be more peculiarly oriented in Cu, N (dbsc)$_2$, a similar argument explains the situation. The *g*-value along the *z*-direction in the Cu-Se$_4$ plane is maximum because of the crystal field admixture. The orientation of the other two *g*-tensor axes in the perpendicular plane would depend on the finer details of the geometry of the molecule and the orientation of the π-orbitals. A distortion of the ligands beyond Se out of the $CuSe_4$ plane with a trans geometry for the molecule, retaining a centre of symmetry at Cu, could explain the g-tensor orientation. It would perhaps be interesting to study by ESR Cu, Ni $(desc)_2$ and Cu, Zn $(bdsc)_2$ to determine the extent to which the alkyl groups affect the resonance properties.

CONCLUSION

It is shown how it is possible to understand the nature of the g and hyperfine tensors in highly covalent Cu complexes of low symmetry. However, accurate values of a large number of parameters, precise structural information and more reliable atomic parameters are necessary before quantitative calculations of g-shifts could be arrived at for these complexes.

REFERENCES

1. Ramasubba Reddy, T. and Srinivasan, R.	ESR and optical absorption studies in copper diethyldithiocarbamate. *Journal of Chemical Physics*, 1965, **43**, 1404–1409.
2. Kumari Cowsik, R. and Srinivasan, R.	ESR investigation of copper (II) bis-diethyldithiophosphate in single crystals. *Chemical Physics Letters*, 1972, **16**, 183–196.
3. ——— ..	ESR study of copper diethyldithiophosphate in single crystals. *Journal of Chemical Physics* (in press).
4. Ramasubba Reddy T. and Srinivasan, R.	ESR in copper diethyldiselenocarbamate. *Proceedings of the International Conference on Spectroscopy*, Bombay, 1967, **2**, 412.
5. Van Rens, J. G. M., Keijzers, C. P. and van Willigen, H.	Single crystal ESR study of a Cu (II) diethyldiselenocarbamate. An example of non-coincidning principal axes. *Journal of Chemical Physics*, 1970, **53**, 2858–2864.
6. Kirmse, R., Windsch, W. and Hoyer, E.	EPR investigations of copper (II)-*bis*-(di-*n*-butyldiselenocarbamate) in solution. *Chemical Physics Letters*, 1970, **4**, 565–566.
———, Wartewig, S., Windsch, W. and Hoyer, E.	Single crystal and powder EPR studies on copper (II) *bis* (di-*n*-butyldiselenocarbamate). *Journal of Chemical Physics*, 1972, **56**, 5273–5278.
7. Barnard, D. and Woodbridge, D. T.	Derivatives of NN-dialkyldiselenocarbamic acids. *Journal of the Chemical Society*, 1961, pp. 2922–2926.
8. Maki, A. H. and McGarvey, B. R.	Electron spin resonance in transition metal chelates. I. Copper (II) *bis*-acetylacetonate. *Journal of Chemical Physics*, 1958, **29**, 31–34.

9. Kivelson, D. and Neiman, R. ESR studies on the bonding in copper complexes. *Journal of Chemical Physics*, 1961, **35**, 149–155.

10. Whiffen, D. H. .. Information derived from anisotropic hyperfine couplings. *Journal de Chimie Physiuqe*, 1964, **61**, 1589–1591.

11. Hurd, C. M. and Coodin, P Atomic parameters for the interpretation of ESR and diamagnetic susceptibility data. *Journal of Physics and Chemistry of Solids*, 1967, **28**, 523–525.

12. Boudreaux, E. A., Cusachs, L. C. and Durean, L. D. *Numerical Tables of Two-centre Overlap Integrals*, W. A. Benjamin Inc., New York, 1970, pp. 86, 238.