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Vol. 56 January 1974 No. 1

Journal of the Indian Institute of Science

Volume 56 *Number* 1 *January* 1974

CONTENTS

FORTHCOMING PAPERS

V. V. Subba Rao : Studies on the Properties of Homogeneous Sand Mixes.

R. Hariharan and S. N. Rao : System Identification from Step Response.

Miss *Glory John and S. K. Chatterjee* : Effects of Environment on the Surface wave-Characteristics of a Dielectric-Coated Conductor.

Mrs. R. Chatterjee : Electro-Magnetic Boundary Value Problem of the Dielectric-Coated Conducting Sphere excited by Delta-Function Electric and Magnetic Sources.

M. R. Chidambara and N. Viswanadhan : Some New Applications of the Solution of $AX + XB = -Q$.

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(*vi*) Invited articles.

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Volume 56 *Number* 2 *February* 1974

CONTENTS

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Mrs. R. Chatterjee: Electro-Magnetic Boundary Value Problem of the Dielectric Coated Conducting Sphere excited by Delta-Function Electric and Magnetic Sources.

K. Rajaiah and Akella Kameswara Rao: Use of Hyperbolic Trigonometric Series in Rectangular Cartesian Co-ordinates for Problems with Arbitrary Rectilinear Boundaries.

P. Subramanian and M. S. Murthy: A Modified Vapour Phase Chromatographic Analysis for Residence time Distribution Studies.

G. Usha Devi and G. S. Krishna Rao: N-Nitroso-N-Benzyl-P-Toluene-sulphonamide.

M. R. Chidambara and N. Viswanadhan: Some New Applications of the Solution of $AX + XB = -Q$.

C. L. Khetrapal: NMR Spectroscopy of Molecules Dissolved in Liquid Crystal Solvents.

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Volume 56 *Number* 3 *March* 1974

CONTENTS

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A. Thomas : Design of Kinetic Translation Stage

G. B. Ghase : Variation of Residual Polarisation Voltage with Temperature in Some Mangamite Electrets

C. L. Khetrapal : NMR Spectroscopy of Molecules Dissolved in Liquid Crystal Solvents

M. R. Chidambara and N. Viswanadham : Some New Applications of the Solution of the Equation $AX + XB = -Q$

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Volume 56 *Number* 4 *April* 1974

CONTENTS

FORTHCOMING PAPERS:

V. Krishnan: Discrete Fourier Transform and Fast Fourier Algorithm.

K. Shankaran and D. N. Sheshadri: Volume Change of Mixing.

B. V. Dasarthy: A New Clustering Approach for Pattern Recognition.

E. S. R. Gopal, R. Ramachandra, M. V. Lele, P. Chandrashekar and N. Nagarajan: A Novel Volume Dialetometer for Thermal Expansion in Liquid Mixtures.

O. P. Gandhi: Orientational and Frequency Effects on Whole Animal Absorption of R. F. Energy.

B. S. Ramprasad and (Miss) Radha: A Simple Method of Fabricating Lineary Graded Films.

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Volume 56 *Number* 5 *May* 1974

CONTENTS

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Volume 56 *Number* 6 *June* 1974

CONTENTS

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Volume 56 *Number* 7 *July* 1974

CONTENTS

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G. N. Ramachandran: Some open questions regarding peptide conformation

M. R. Chidambara and A. P. Sivaprasad: A digital Kalman filter for radar tracking with filter gains independent of sampling interval

S. K. Bhattacharyya: Stress system in a rotating aeleotropic shaft in finite strain and its numerical study

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Volume 56 *Numbers* 8, 9 & 10 *August. Sept. & Oct.* 1974

CONTENTS

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M. A. Viswamitra, A. M. Shaikh and K. Jayalakshmi Ramanuja: High Temperature X-ray Crystallography; Devices for single crystal

M. Nayak: The influence of end friction on elastic parameters obtained in triaxial tests

V. S. Vaidyanathan: Certain concepts of biological membrane transport

E. Hussain, M. R. Nandagopal and B. R. Prabhakar; Effect of humidity on breakdown voltages of gaps and insulators

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Volume 56 *Numbers* 11 & 12 *Nov. & Dec.* 1974

CONTENTS

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M. A. Viswamitra, A. M. Shaikh and K. Jayalakshmi Ramanuja: High temperature X-ray crystallography: Devices for single crystal analysis

V. S. Vaidyanathan: Certain concepts of biological membrane transport

M. Nayak and R. J. Srinivasan: Influence of foundation roughness on stresses and displacements under foundations

C. Venkatesan and R. Krishnan: Dual phase damping in simple shock mounts

M. D. Wagh and S. V. Kanetkar: Estimation of errors in image restoration

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EDITORIAL

The Editorial Committee is happy to announce that the *Journal of the Indian Institute of Science* will be a monthly publication starting from this issue in January. It is our effort to make it a leading journal of science and technology, retaining at the same time, in some measure, the flavour of the Indian Institute of Science.

The Editorial policy, as outlined in the inside cover pages, is to ensure that the Journal shall have different types of articles, having a broad coverage of original research papers, review articles, short notes, and book reviews. It is also our endeavour to see that an article, once it is accepted for publication, would be published as quickly as possible. As a matter of policy, it has been decided that no page or publication charges will be levied by the Journal. Reprints of articles will, however, be available at a nominal charge.

The Editor and his colleagues hope that the members of the Institute would send their best publications to our own Journal, and they seek the fullest support and encouragement from the academic staff of the Institute in their endeavour to step up the activities of the Journal to a high standard.

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A NEW NON-PARAMETRIC FEATURE SELECTION CRITERION—'EFFECT'*

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ABSTRACT

The problem of feature selection in the field of pattern classification of multi-dimensional feature vectors is essentially one of dimensionality reduction. A new non-parametric technique for choosing an optimum subset of features from the given feature set is proposed in this study. This technique is based on the concept of inter-class and intra-class distances and tests conducted reveal the efficacy of this new Effective Figure of Merit Criterion—'EFFECT'.

Key Words: Feature Selection, Pattern Recognition, Non-Parametric Methods, Estimated Probability of Misrecognition.

1. INTRODUCTION

Numerous parametric and non-parametric techniques of feature selection have been proposed in the Literature [1-4] from time to time. Many of these methods are based on the concept of inter-class and intra-class distances of the different pattern classes. Deuser [5] proposed one such technique called the Hybrid Multispectral Feature Selection Criterion. Tests conducted using this criterion on Iris data [6] brought out the unsuitability of the technique for implementation in multispectral feature selection problems of interest to remotely sensed earth resources data analysis and the like. Results of these preliminary tests on comparison with the results of actual classification of the test data using non-parametric recursive algorithms (such as the Ho–Kashyap Algorithm [7] and maximum likelihood classification methods [8]) revealed that the Hybrid Figure of Merit obtained for different feature subsets were highly disproportionate to the corresponding actual classification efficiencies obtained using the same feature subsets. The Hybrid Figure of Merit in addition had no lower and upper bounds

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* Presented at the National Systems Conference held in June 1973, at the Indian Institute of Science, Bangalore.

on the actual values and this proves to be a drawback when a choice has to be made among the possible feature subsets. Such a comparison between feature subsets is most effective if the figure of merit is based on a normalized scale. This lack of normalized scale of merit together with the major conceptual shortcoming of not accounting for the inter-feature correlations arising within the feature subset brought out the need for a new criterion of feature selection. Investigations carried out towards this end has led to a new and more meaningful criterion for feature selection which takes into account the effect of inter-feature correlations. This is conceptually significant in that one of the basic aims of transformation techniques employed in feature selection problems is to obtain an orthogonal system of coordinates (which form the components of the feature vector) minimizing the cross correlation between features, *i.e.*, to choose such (transformation of) features as will diagonalize the covariance matrices of the training sample sets of the different pattern classes. The new figure of merit is bounded and rates the different feature subsets on a universal 0–1 scale, thus allowing a direct comparison amongst these different feature subsets. Results derived by application of this new criterion to Iris test data have verified the superiority of this criterion over the Hybrid Figure of Merit Criterion. Also, as a further evaluation of this new criterion, comparison relating to a parametric feature selection method (based on Gaussian assumptions) was made using the same test data. Results showed a fair agreement between the two approaches relative to the actual classification efficiencies, with the new criterion showing a far better correlation than the parametric method (which possibly could be attributed to the doubtful validity of the Gaussian assumptions). These are presented and discussed in the sequel in detail.

2. ANALYSIS

Let C_i $(i = 1, m)$ represent the 'm' pattern classes into which any given feature vector x, of maximum dimension 'n', is to be assigned. The purpose of this or any other feature selection criterion is to determine the optimal subset of r features $(r \leqslant n)$ out of the possible $(2^n - 1)$ feature subsets for the ensuing classification (decision) process. Let $x(j,i,p)$ represent the j-th feature $(j \leqslant r)$ of the p-th training sample of class C_i $[p \leqslant L(i)$ where $L(i)$ is the total number of training samples from class $C_i]$. To appreciate the physical significance of this non-parametric feature selection criterion, consider two pattern classes C_1 and C_2. Assuming that two training samples from each of these classes are available, one can visualize that the decision or classification process becomes more efficient with increase

in the inter-class (between samples of the two different classes) Euclidean distance in the corresponding feature space. On the other hand, an increase in the intra-class (between samples of the same class) Euclidean distances tends to decrease the efficiency of classification. Therefore, the optimum subset of features is one that maximizes the inter-class distance while minimizing the intra-class distance in the Euclidean feature space. An obvious candidate criterion is, hence, the difference of inter-class and intra-class distance. This non-parametric method (being based on no specific parametric assumption about the distributions) can be made more meaningful physically by attaching suitable weights to these distances to account for possible differences in the ease of measuring (and hence the cost) of certain features over some others or such other physical or problem dependent considerations. This is the basis for Deuser's criterion, which can be written as:

Hybrid Figure of Merit of a set of r features

$$H = \sum_{j=1}^{r} SUM(j)$$

$$= \sum_{j=1}^{r} [SUM1(j) - a(j)\, SUM2(j)]$$

Here

$$SUM1(j) = \sum_{i=2}^{m} \sum_{i_1=1}^{i-1} k_{ii_1} \sum_{p=1}^{L(i)} \sum_{p_1=1}^{L(i_1)} [x(j, i, p) - x(j, i_1, p_1)]^2$$

$$SUM2(j) = \sum_{i=1}^{m} k_i \sum_{p=2}^{L} \sum_{p_1=1}^{p-1} [x(j, i, p) - x(j, i, p_1)]^2$$

k_{ii_1}, k_i, $a(j)$ are the appropriate weights defined from physical constraints of the problem.

The particular subset of r features which maximises this criterion was considered as the best 'r' features. (A particularly interesting exercise in FORTRAN coding was called for to automatically consider all possible combinations). However, this does not allow for a direct comparison over different sized feature subsets (r_1, $r_2 \ldots n$), *i.e.*, over all the possible subsets of features. To overcome this and other deficiencies, attempts were made to define a new criterion and this is discussed in the sequel.

A careful analysis of Deuser's criterion reveals that no consideration is given to the effect of interfeature correlation, which increases the scatter of the classes in the feature space and hence is a significant factor in problems with highly correlated features. Also, no attempt at defining a bounded universal scale of merit is made in his analysis, thus lacking a necessary and basic ingredient of any figure of merit concept. To meet these conceptual omissions, the following new criterion is proposed.

3. Effective Figure of Merit Criterion

Let $J = \{J_i : i = 1, \ldots n\}$ be the set of features under consideration.

Let $Q(J)$ be the complement of $\mathcal{P}(J)$ with respect to Φ where $\mathcal{P}(J)$ is the power set (set of all subsets) of J and Φ is the null set.

We define B the best feature subset of J as

$$B = S \ni \underset{S \epsilon Q(J)}{E(S)} \text{ is maximum,}$$

where, $E(S)$: The Effective Figure of Merit of a feature subset

$S = \{s_j : j = 1, \ldots r\}$ $r = m(S)$ is given by

$$\mathrm{E}(\mathrm{S}) = [P(S)/(1 \cdot 0 + C(S)]^{\frac{1}{2}}$$

$$P(S) = \left[1 \cdot 0 - \prod_{j=1}^{r} (1 \cdot 0 - F(s_j))\right]$$

$$C(S) = SUM3(S) / \sum_{j=1}^{r} (SUM1(s_j) - SUM2(s_j)); \quad r \geqslant 2$$

$$= 0 \qquad ; \quad r = 1$$

$$F(s_j) = (SUM1(s_j) - SUM2(s_j))/SUM1(s_j).$$

Here,

$$SUM1(s_j) = \sum_{i_1=2}^{m} \sum_{i_2=1}^{i_1-1} K_{i_1 i_2} \sum_{p_1=1}^{L(i_1)} \sum_{p_2=1}^{L(i_2)} (x(s_j, i_1, p_1) - x(s_j, i_2, p_2))^2$$

$$SUM2(s_j) = \sum_{i=1}^{m} K_i \sum_{p_1=2}^{L(i)} \sum_{p_2=1}^{p_1-1} (x(s_j, i, p_1) - x(s_j, i, p_2))^2$$

$$SUM3(S) = \sum_{i=1}^{m} \sum_{p=1}^{L(i)} \sum_{j_1=2}^{r} \sum_{j_2=1}^{j_1-1} |d_{j_1} d_{j_2}|$$

$$d_j = x(s_j, i, p) - \left[\sum_{p=1}^{L(i)} x(s_j, i, p)/L(i)\right]$$

An estimate of the probability of misrecognition can be determined as $EPOMR(S) = (m - 1)\left(1 - E^2(S)\right)/m$.

This effective figure of merit unlike Deuser's Hybrid Figure of Merit, allows comparison over different sizes of subsets, and more proportionate comparison within the combinations possible of a given subset size. It can even represents a rational basis for comparing different feature selection problems. As a further evaluation of this criterion, comparison with a suitable parametric feature selection method was thought of. The existing parametric feature selection technique based on the assumption of Gaussian distributions and equal covariance matrices for the pattern classes, was considered here. The high classification efficiency obtained for the test data through maximum likelihood classification procedures based on Gaussian assumptions indicated that the Gaussian assumption may be justifiable to an extent. The statistical analysis of the Iris data showed that the sample covariance matrices for the two classes were unequal, but close enough to justify the use of the above parametric approach provided some suitable modifications to the method could be made to account for the difference between the covariance matrices of the two classes of Iris data. Two alternatives were considered: (i) Average the covariance matrices and computing the inverse of this averaged covariance matrix for further analysis, (ii) Computing the inverses of the covariance matrices of the two classes individually and averaging the inverse matrices for further analysis.

Let M_i, K_i; $(i = 1, 2)$ be the mean vectors and covariance matrices of the classes 1 and 2 respectively. Under Gaussian assumption, the divergence criterion, for two class problem with equal covariance matrices K, can be written as

$$D(C_1, C_2) = (M_1 - M_2)^T K^{-1} (M_1 - M_2)$$

and the features are selected on the basis of the magnitude of D for the different feature subsets. Here, the covariances matrices being unequal, the measure is not necessarily optimal. However, an equivalent inverse covariance matrix can be defined in view of the fact K_1 and K_2 are not very different in their values and towards this end two possibilities are considered:

(i) $K_e^{-1} = [(K_1 + K_2)/2]^{-1}$: inverse of the average,

(ii) $K_e^{-1} = (K_1^{-1} + K_2^{-1})/2$: average of the inverses.

is computed through both these approaches. The results of experiments along these directions with Iris test data is presented and discussed in the next section.

4. Discussion of Results of Experiments with Iris Data

The two class Iris data [6] consisting of 100 four-dimensional training samples was used as a base for this experiment designed to make a comparative study of the Hybrid and Effective Figure of Merit. The Hybrid and Effective Figures of Merit were computed using the Iris data for all the possible 15 feature combinations. To obtain a basis for comparative evaluation of these two figures of merit, the actual classification efficiencies under each of these 15 feature combinations were estimated using a new non-parametric method of feature classification. (This technique can be used either independently or as an extension to existing techniques such as the *Ho*–Kashyap algorithm. The classification results listed in Table I were obtained using the new method as an extension to *Ho*–Kashyap algorithm. It was found that the classification efficiencies, under this approach, turned out to be considerably higher than under either the *Ho*–Kashyap algorithm without extension or the maximum likelihood approach with the assumption of Gaussian distributions, for all feature combinations).

A careful perusal of Table I brings to light the relative superiority of the new Effective Figure of Merit over the Hybrid Figure of Merit. This point can be dramatically brought home by considering, for example, the cases of features 3 and 4. The Hybrid Figure of Merit for feature 3 is about 350 per cent of that for feature 4 thus indicative of a very high superiority of feature 3 over feature 4. But the fact, as can be seen from actual classification, is that not only the feature 3 is not superior to feature 4 by this order of magnitude, but actually is even slightly less efficient than feature 4. This indeed is very clearly broughtout by the new figure of merit. Similarly, comparison of the results among other cases of interest such as features 1 and 4 reinforce the superiority of the new figure of merit. The bounded (0–1) scale of merit of the new method, in addition to allowing good relative evaluation of different feature subsets, does also give beforehand a fair measure (a sort of lower bound) of the classification efficiencies that can be expected in the corresponding feature space. Indeed except for the case of feature subsets (1, 2, 4) and (1, 4) the order of merit as derived from the Effective Figure of Merit criterion is exactly the same as that derived by actual classification of the data and even there the measure of classification

TABLE I

A comparative study of the new Effective figure of merit with Deuser's hybrid figure of merit and modified (parametric) divergence criterion using Iris data

Features used	Effective figure of merit	Estimated probability of mis-recognition	Estimated classification on efficiency (%)	Actual observed classification efficiency (%)	Deuser's hybrid figure of merit	Divergence D (C_1, C_2) using parametric feature selection criteria	
						$K_e^{-1} = \bar{K}_e^{\,1}$	$K_e^{-1} = K^{-1}$
1, 2, 3, 4	0·9834	0·0165	98·35	98	6564·92	14·219	15·853
1, 3, 4	0·9833	0·0166	98·34	98	6460·88	17·207	19·207
2, 3, 4	0·9794	0·0204	97·96	98	5502·17	22·974	24·445
3, 4	0·9770	0·0227	97·73	97	5398·13	25·109	26·848
1, 2, 4	0·9466	0·0520	94·80	96	2391·78	18·262	29·925
1, 4	0·9399	0·0583	94·17	95	2287·74	21·496	34·128
1, 2, 3	0·9346	0·0633	93·67	97	5339·22	11·637	16·956
1, 3	0·9234	0·0737	92·63	96	5235·88	11·533	16·315
2, 4	0·9178	0·0788	92·12	95	1329·03	12·378	22·856
4	0·9020	0·0932	90·68	94	1224·99	14·759	26·107
2, 3	0·8961	0·0985	90·15	94	4277·17	23·012	29·307
3	0·8742	0·1179	88·21	93	4173·13	22·054	27·718
1, 2	0·7017	0·2538	74·62	75	1166·79	3·976	4·048
1	0·6267	0·3036	69·64	73	1062·75	3·976	4·259
2	0·4164	0·4133	58·67	63	104·04	0·712	0·740

efficiency derived from the criterion compares favourably with the actual classification efficiency. This is of value in comparing various feature selection and classification problems which are of a similar nature. Table II shows the results of the new feature selection technique as applied to Iris data, wherein the various feature subsets are ordered according to the values of the corresponding effective figure of merit. Depending on the ease (and hence the cost) of measurement of different sizes of feature subsets, the optimum size of feature subset can be chosen. Then, using Table II, the best feature subset within the chosen subset size may be selected.

TABLE II

Results of feature selection for Iris data using the effective figure of merit criterion

Feature subsets listed in the descending order of merit			
Subset dimension	1	2	3
Figures in parentheses indicate the best classification efficiencies obtained in the corresponding feature subspace	4 (94%)	3, 4 (97%)	1, 3, 4 (98%)
	3 (93%)	1, 4 (95%)	2, 3, 4 (98%)
		1, 3 (96%)	
	1 (73%)	2, 4 (95%)	1, 2, 4 (92%)
		2, 3 (94%)	
	2 (63%)	1, 2 (75%)	1, 2, 3 (97%)

Table 1, also gives the divergence values $D(C_1, C_2)$ computed using the psuedo equivalent inverse covariance matrices as detailed earlier. While the divergence values are relatively lower for subsets which have significantly lower actual classification efficiencies, comparison of divergence values between subsets, which are not too far apart in terms of their actual classifica-

tion efficiencies, does not reflect well on the reliability of this criterion. This may possibly be due to the doubtful validity of the Gaussian assumptions. Further the results in Table I show that averaging the covariance matrices before computing the inverse gives far better ordering of the different subsets. This is also more meaningful from physical and mathematical considerations.

One can also notice that agreement between the Effective Figure of Merit Criterion and the modified version of the Divergence Criterion is good for single features and fair for feature subsets of two dimensions. However, as the size of the feature subset increases, the agreement becomes poorer. This probably is due to the fact that errors due to assumption of equal covariance matrices and averaging become more and more predominent as the size of the feature subsets increase. Also, the validity of the assumption of multivariate Gaussian distribution tend to reduce with increasing dimensionalities. However, the non-parametric Effective Figure of Merit Creterion being independent of such assumptions has the same over all reliability. Thus the eflectiveness and reliability of the new creterion is clearly demonstrated by these tests conducted with the well known Iris data.

References

1. Wee, W. G. .. On feature selection in a class of distribution-free pattern classifiers. *IEEE Trans. on Information Theory*, IT–16, 1970, pp. 47–55.

2. Fu, K. S., Min, P. J. and Li, T. J. On feature selection in pattern recognition. *Proc. of the 6th Annual Allerton Conference on Circuits and Systems Theory*, 1968, pp. 10–19.

3. Min, P. J., Landgrebe, D. A. and Fu, K. S. On feature selection in multiclass pattern recognition. *Proc. of the 2nd Annual Princeton Conference on Information Sciences and Systems*, 1968, pp. 453–457.

4. *IEEE Trans. on Computers*: Special Issue on feature extraction and selection in Pattern recognition, 1971, C–20, No. 9.

5. Deuser, L. M. .. A hybrid multispectral feature selection criterion. *IEEE Conference Record of the Symposium on Feature Extraction and Selection in Pattern Recognition*, 1970, pp. 223.

6. Fischer, R. A. .. The use of multiple measurement in taxonomic problem. *Ann. Eugenics*, 1936, 7, 179–187.

7. Ho, Y. C. and Kashyap, R. L. A class of itirative procedures for non-linear inequalities. *J. SIAM Control*, 1966, 4, 112–115.

8. ——— and Agrawala, A. K. On pattern classification algorithms—introduction and survey. *IEEE Trans. on Automatic Control*, 1968, AC–13, pp. 676–690.

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 (7·5% 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 (7·5% 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 $g_w = 2{\cdot}0581$.

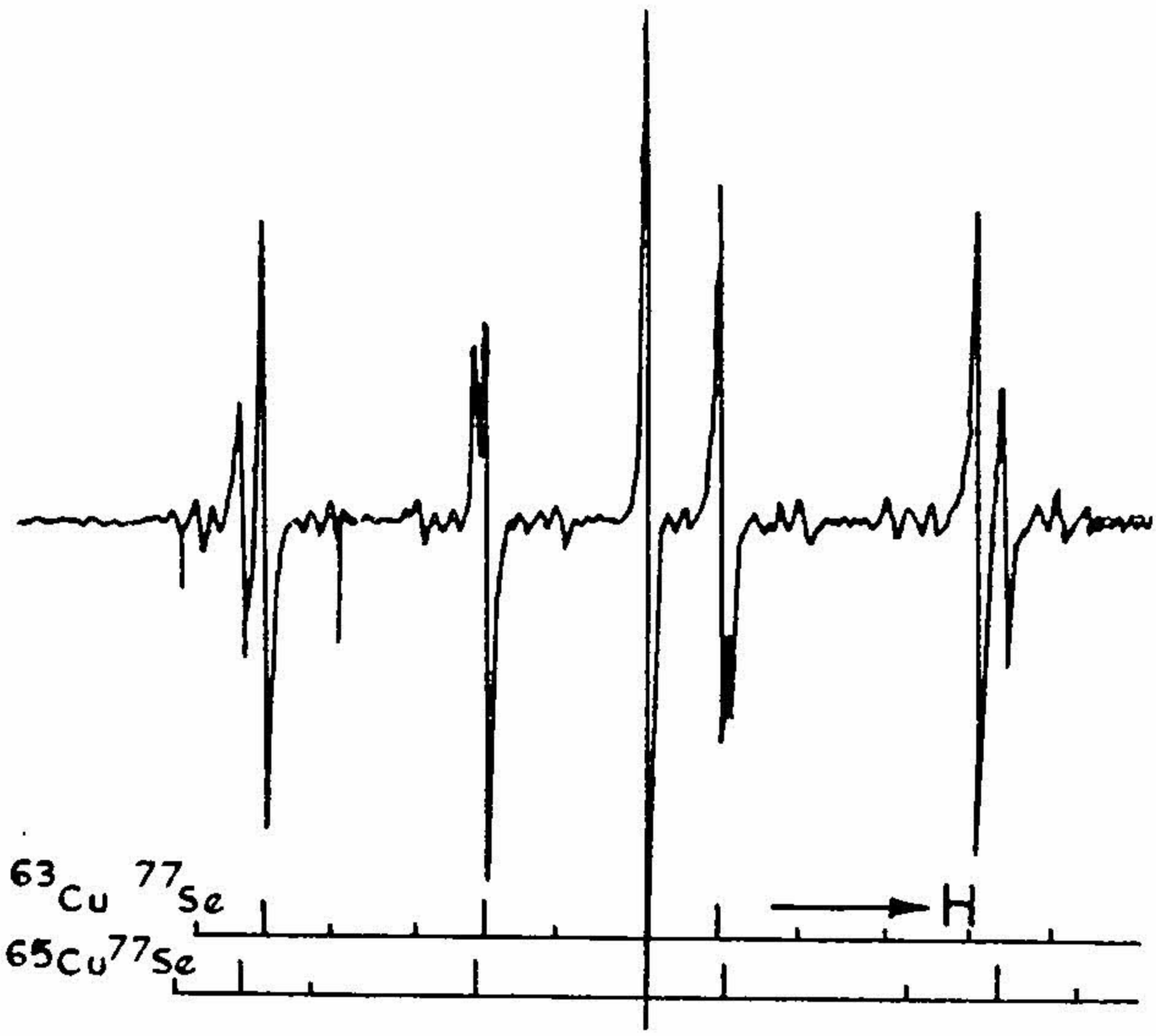

FIG. 1. ESR spectrum of Cu, Zn (desc)$_2$ with H lying in the ac-plane.

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.

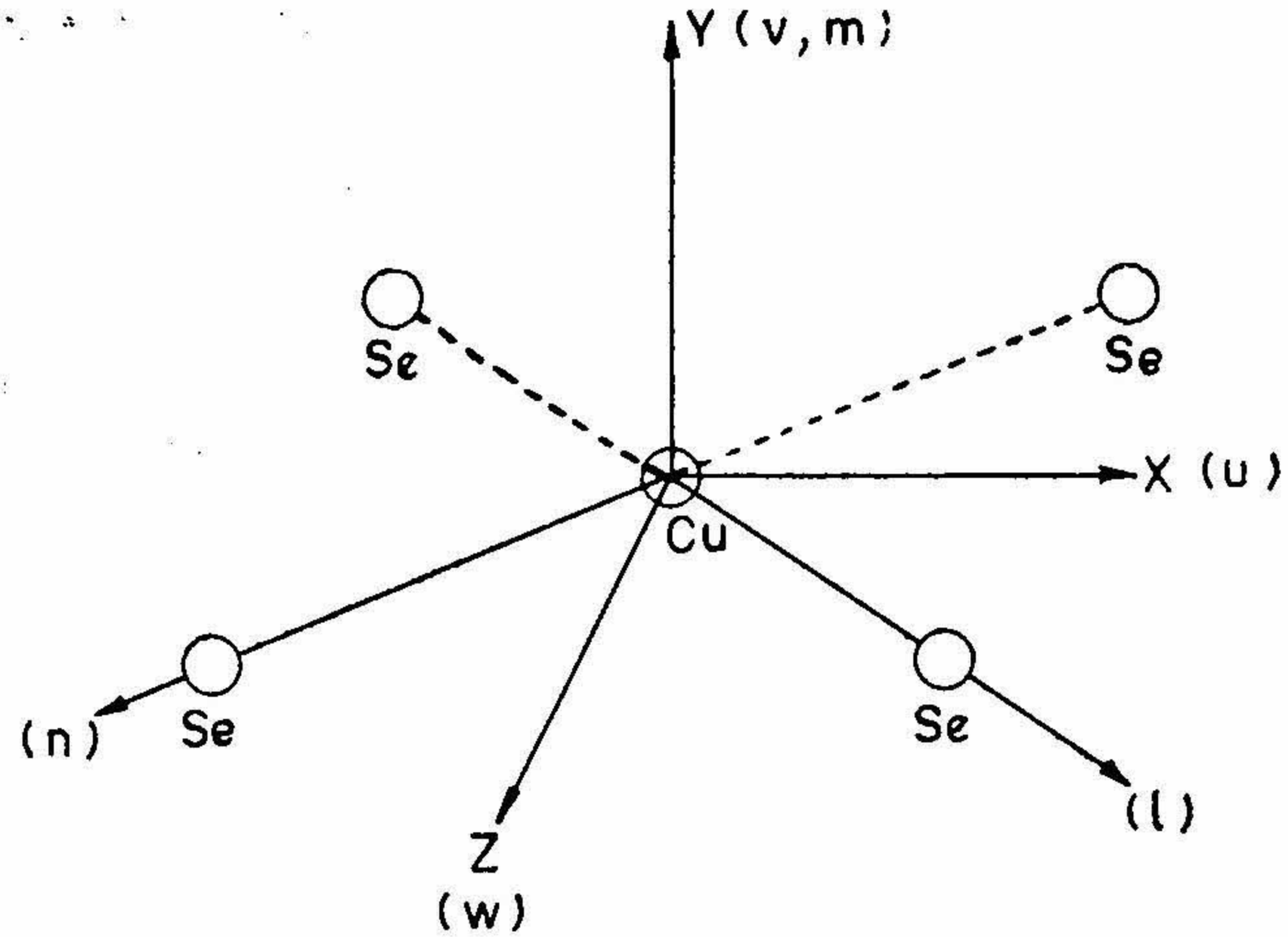

FIG. 2. Relative orientation of the g and Cu hyperfine tensors and the coordinate system used for the discussion of ESR results. The Cu and the four Se atoms are in the XZ plane.

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 $27 \times 10^{-4}\,cm^{-1}$. 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 $75 \times 10^{-4}\,cm^{-1}$. Noting that this direction is 40° from the bond direction l, the hyperfine separation A^{Se} along the bond direction is calculated to be $95 \times 10^{-4}\,cm^{-1}$.

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 2·0023.

(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 $4s$ and $4p$ 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 $4s$ and $4p$ 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 α_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 $Cu\text{-}Se_4$ 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 $4s$ and $4p$ 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 $d_{3z^2-r^2}$ 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 $Cu\text{-}Se_4$ 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 pcwder 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.