

# Substituent and solvent effects in the spectra and structure of some mixed-ligand copper(II) chelates containing $\beta$ -ketoenols

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## Abstract

The infrared and the ligand-field excitation spectra of a series of new mixed-ligand copper(II) chelates that encompass *N,N*-dimethyl-*N'*-ethyl-ethylenediamine (dmeen) and the anion of a substituted  $\beta$ -ketoenol (1,3-dione) were obtained in the solid state and in solution. Information related to the electronic excitation spectra, the IR spectra, the molar conductivity and the magnetic properties of the newly obtained and characterised chelates are presented and discussed. The molar conductivity in nitromethane reveals a predominance of electrostatic interactions between the  $[\text{Cu}(\beta\text{-dione})\text{dmeen}]^+$  entity and bulky polyatomic anions that counterbalance the positive charge while the IR spectra disclose that the bidentate ligands form chelate rings with copper as the common vertex. The resulting  $\text{CuN}_2\text{O}_2$  chromophore attains a square-coplanar structure and exhibits a tendency for axial ligation which is enhanced when electron-attracting substituents are attached to the  $\beta$ -dionato moiety. The tendency for axial ligation is partially fulfilled when suitable nucleophiles are present. Covalent interactions prevail when chloride is present and upon coordination it presumably occupies the apex of a square-pyramidal structure. Chain-like bidentate anions enable copper(II) to achieve coordination saturation and when configuration requirements demand it, they distort the square-planar arrangement of the initial  $\text{CuN}_2\text{O}_2$  chromophore forming distorted octahedral structures. Covalent solute-solvent interactions are revealed by shifts in the ligand-field excitation spectra that are enhanced as the nucleophilicity of the solvent increases. Linear dependence of the ligand-field excitation maximum on solvent parameters related to donor properties is generally observed.

## Introduction

Spectra are a plentiful source of valuable information on the factors influencing the structure and the reactivity of chemical entities. Spectral investigations of copper(II) chelates of 1,3-ketoenols ( $\beta$ -diones) and those of acyclic and aromatic 1,2-diamines and 1,2-diimines (enR) have made a significant contribution towards the present understanding of the factors determining the stereochemistry, the stability and the properties of these very important classes of coordination compounds [1–4]. Modification of spectral bands have supplied information on charge redistribution whenever functional groups were incorporated into a chelate ring. While substituents attached to the  $\beta$ -dionato moiety affect the Lewis acidity of the omnipresent square-planar  $\text{CuO}_4$  chromophore, shifts in the spectra of  $[\text{Cu}(\text{enR})_2]^{2+}$  species disclosed that extensive N-substitution and bulky groups in enR cause, in addition to electronic, steric interactions which in view of the small size of the copper(II) ion may become exceedingly strong to the extent of exclusion of the second enR molecule from

bond formation thus rendering the  $[\text{Cu}(\text{enR})_2]^{2+}$  entity unattainable [5, 6]. Additional absorptions observed in the spectra of the products resulting from the contemporaneous reaction of copper(II) salts with  $\beta$ -ketoenols and certain N-substituted 1,2-diamines (and 1,2-diimines) have revealed bonding interactions and ternary chelate formation [7–9]. Steric hindrance and inability to form the  $[\text{Cu}(\text{enR})_2]^{2+}$  species have been put forward to explain the existence of ternary chelates, the formation of which is not always facile. In many cases compounds other than the cationic chelates prevail and the electron distribution in  $\beta$ -ketoenol has been invoked to explain the observed reactivity [10–12]. Easing the steric interactions so that the species  $[\text{Cu}(\text{enR})_2]^{2+}$  can be formed, is a means to facilitate the study of electronic factors affecting ternary chelate formation. The influence of electronic effects in this class of mixed-ligand chelates may be best investigated by attaching the substituents as far away from the coordination sites of the  $\beta$ -dionato moiety as possible, that is in the carbon atom flanked by the carbonyl groups. This obviates any undue imbalance in charge distribution and the remoteness of substituents in the  $\gamma$ -position precludes any steric interference with the coordinated enR ligand.

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However, substitution of 1,3-diones in the  $\gamma$ -position is subject to limitations because of the spatial requirements of the approaching group. Besides, not all  $\gamma$ -substituted 1,3-ketoenols are stable as free ligands. The latter is partly rectified by taking advantage of the ability of coordinated  $\beta$ -diones to activate the  $\gamma$ -position and to undergo electrophilic substitution reactions. This and the lability of copper(II) open up new possibilities in the investigation of ternary chelate formation. In this way the stability of the mixed-ligand chelates relative to the  $[\text{Cu}(\text{enR})_2]^{2+}$  species and the  $\text{Cu}(\beta\text{-dionato})_2$  compounds may be further investigated. While the stability, the Lewis acidity and the electron distribution in the  $\text{Cu}(\beta\text{-dionato})_2$  chelates may be varied almost at will as a result of the electronic effects of the substituents within the  $\beta$ -dionato moiety, such subtle variations in enR are unattainable because of the proximity of the substituents to the coordination site. Nevertheless it is feasible to select a 1,2-diamine so that while the steric interactions are extensive, the species  $[\text{Cu}(\text{enR})_2]^{2+}$  can be isolated. A suitable choice for enR appears to be *N,N*-dimethyl-*N'*-ethyl-ethylenediamine, dmeen, since it affords  $[\text{Cu}(\text{dmeen})_2]^{2+}$  only under favourable experimental conditions [9].

In the present study the spectra of a series of  $[\text{Cu}(\beta\text{-dionato})(\text{dmeen})]^+$  chelates were obtained and analysed in order to investigate (i) the reactivity of the  $[\text{Cu}(\text{dmeen})_2]^{2+}$  species towards  $[\text{Cu}(\beta\text{-dionato})_2]$  chelates, (ii) the electronic interactions of the substituents with the chelate rings, (iii) the ensuing changes in group vibrations, (iv) the effect of the substituents on the physicochemical properties of the ground state and (v) the changes in spectral bands as a result of substituent, counterion and solvent effects. Further it was aimed to seek interrelations between experimentally obtained quantities and parameters describing the interactions induced by the solvents. For the compounds studied see Table 1.

## Experimental

### Reagents

The copper(II) salts were procured from Merck. *N,N*-Dimethyl-*N'*-ethyl-ethylenediamine (dmeen) and the  $\beta$ -ketoenols, 2,4-pentanedione (acacH), 3-methyl-2,4-pentanedione ( $\text{CH}_3\text{-acacH}$ ), 3-chloro-2,4-pentanedione ( $\text{Cl-acacH}$ ), 1-phenyl-1,3-butanedione (bzacH), 1,3-diphenyl-1,3-propanedione (dibenzoylmethane, dbmH), 4,4,4-trifluoro-1-phenyl-1,3-butanedione (bztFH), 1,1,1-trifluoro-2,4-pentanedione (tfacH), and 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (hfacH), were purchased from Aldrich, EGA-Chemie and Lancaster Synthesis. The  $\beta$ -ketoenols that are not commercially available, e.g. 3-cyano-2,4-pentanedione, were prepared by Fack-

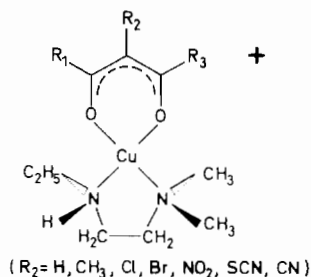
ler's procedure as detailed elsewhere [13, 14]. Copper(II)  $\beta$ -ketoenolates employed as starting compounds were prepared by standard methods. Activation of the  $\gamma$ -position and electrophilic substitution reactions were performed employing Collman's method [14, 15]. The ternary chelates,  $[\text{Cu}(\beta\text{-dionato})\text{dmeen}]^+$ , were prepared by established procedures [7, 9].

### Physical measurements and determinations

The methods used in the measurement of physical properties, the spectra (solid state and solution) and magnetic susceptibilities have been described before [9]. The magnetic moments,  $\mu_{\text{eff}}$ , of the new compounds listed in Table 1 are in the range of 1.69–2.00 BM, suggesting that the central ion retains its  $d^9$  configuration and the copper(II) chelates are magnetically dilute. These values are also consistent with the copper ion being in a non-degenerate ground state.

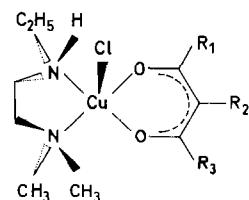
The new mixed-ligand copper(II) chelates are deeply coloured crystals or crystalline powders corresponding to the general formula  $\text{Cu}(\text{enR})(\beta\text{-dionato})\text{Y}$  ( $\text{Y} = \text{Cl}^-$ ,  $\text{ClO}_4^-$ ,  $\text{NO}_3^-$ ) and are stable in the air, both in the solid state and in organic solvents. The solutions of the perchlorates in nitrobenzene and nitromethane are electrically conductive with molar conductivity values indicative of 1:1 electrolytes ( $\Lambda_{\text{M}} = 20\text{--}29 \text{ S cm}^2 \text{ M}^{-1}$  in the former and  $\Lambda_{\text{M}} = 80\text{--}106 \text{ S cm}^2 \text{ M}^{-1}$  in the latter solvent). When nitrates are employed a drop in the molar conductivity is observed ( $\Lambda_{\text{M}} = 33 \text{ S cm}^2 \text{ M}^{-1}$  in nitromethane and  $\Lambda_{\text{M}} = 6.8 \text{ S cm}^2 \text{ M}^{-1}$  in nitrobenzene), suggesting that the covalent interactions of the nitrate anion are extensive [16]. Replacement of the polyatomic anions and neutralisation of the  $[\text{Cu}(\beta\text{-dionato})\text{dmeen}]^+$  species by chloride renders the nitromethane solutions virtually non-conductive ( $\Lambda_{\text{M}} = 18.7 \text{ S cm}^2 \text{ M}^{-1}$ ) indicating predominance of covalent interactions. These results imply a change in the coordination number of copper(II) and the concomitant change in structure.

The structure of the  $\text{CuO}_2\text{N}_2$  chromophore in the  $[\text{Cu}(\beta\text{-dionato})\text{enR}]^+$  species, in which a potentially chiral centre at the nitrogen bearing the ethyl group has been created, is believed to be planar (structure I). When the relatively small chloride anion is also



Structure I

bonded to copper(II), thermodynamic considerations suggest that the compounds should attain a distorted square-pyramidal structure with the metal ion elevated above the basal plane (structure II). The tendency to



Structure II

accommodate the unidentate ligand on the apex of the square pyramid should be attributed to crystal field stabilisation energy (CFSE), the loss of which would have been greater than the gain in configurational stability resulting from a trigonal pyramidal arrangement. Although geometric isomers are envisaged when the  $\beta$ -ketoenol is non-symmetric ( $R_1 \neq R_3$ ), no attempt was made to separate the *cis* from the *trans* isomers or establish predominance of either isomer.

The compounds prepared, their melting points and elemental analyses are listed in Table 1.

## Results and discussion

The reaction of copper(II) ions with mixtures of acetylacetone (2,4-pentanedione) and *N,N*-dimethyl-

*N'*-ethyl-ethylenediamine (dmeen) results in the creation of ternary chelates [7–9]. Copper(II) reacts with 1,2-diamines as well as with  $\beta$ -ketoenols in a stepwise fashion and follows an Eigen–Wilkins pathway in which metal–ligand bond formation is sequential. Spectroscopic evidence suggests that the ligands coordinate through the atoms possessing an unshared lone pair of electrons and chelate rings are formed. The species formed at the early stages of the reaction appear to possess discriminating qualities towards other ligands. Actually the  $[\text{Cu}(\text{acac})]^+$  entity shows preference to certain 1,2-diamines (enR), while the  $[\text{Cu}(\text{dmeen})]^{2+}$  species prefers the coordination of  $(\text{CH}_3\text{COCHCOCH}_3)^-$  (acac<sup>-</sup>) or, more generally,  $\beta$ -ketoenolato anions  $(\text{R}'\text{COCXCOR})^-$  (Table 1). Formation of the  $[\text{Cu}(\text{acac})\text{dmeen}]^+$  entity indicates enhanced stability relative to that of either the chelate  $\text{Cu}(\text{acac})_2$  or the  $[\text{Cu}(\text{dmeen})_2]^{2+}$  species.

Mixed-ligand chelates are also obtained when one or both methyl groups of acacH are replaced by phenyl ones as the spectra and the elemental analyses of the products indicate (Table 1). Difficulties were encountered, however, when the trifluoro derivative of acetylacetone (tfacH) was employed and in attempts to prepare the corresponding ternary chelate, under the experimental conditions described, other products were isolated, with  $[\text{Cu}(\text{tfac})_2\text{dmeen}]$  prevailing. Adduct formation is not uncommon regarding  $\text{Cu}(\beta\text{-dionato})_2$  che-

TABLE 1. Yield, melting points and elemental analyses of copper(II) chelates with *N,N*-dimethyl-*N'*-ethyl-ethylenediamine and  $\beta$ -ketoenols

No.	Compound	R <sup>1</sup>	X(R <sup>2</sup> )	R <sup>3</sup>	Colour	Yield (%)	m.p. (°C)	C (%)	N (%)	H (%)
1	[Cu(acac)dmeen]ClO <sub>4</sub>	CH <sub>3</sub>	H	CH <sub>3</sub>	violet	83	121–123	35.09 (34.90)	7.36 (7.40)	6.21 (6.12)
2	[Cu(acac)dmeen]NO <sub>3</sub>	CH <sub>3</sub>	H	CH <sub>3</sub>	blue	68	102–106	38.26 (38.74)	12.40 (12.33)	6.64 (6.90)
3	[Cu(CH <sub>3</sub> -acac)dmeen]ClO <sub>4</sub>	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	blue	81	122–123	37.00 (36.71)	7.22 (7.14)	6.67 (6.41)
4	[Cu(CH <sub>3</sub> -acac)dmeen]NO <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	blue–violet	78	122–125	41.07 (40.94)	11.59 (11.94)	6.74 (6.29)
5	[Cu(Cl-acac)dmeen]ClO <sub>4</sub>	CH <sub>3</sub>	Cl	CH <sub>3</sub>	blue–green	81	124–126	32.13 (31.99)	6.59 (6.78)	5.29 (5.36)
6	[Cu(Cl-acac)dmeen]NO <sub>3</sub>	CH <sub>3</sub>	Cl	CH <sub>3</sub>	blue	88	115–119	35.45 (35.18)	12.04 (11.11)	5.83 (5.90)
7	[Cu(Br-acac)dmeen]ClO <sub>4</sub>	CH <sub>3</sub>	Br	CH <sub>3</sub>	blue	72	123–125	28.56 (28.87)	6.23 (6.12)	4.76 (4.84)
8	[Cu(CN-acac)dmeen(H <sub>2</sub> O)]NO <sub>3</sub>	CH <sub>3</sub>	CN	CH <sub>3</sub>	royal blue	87	103–105	36.15 (37.52)	14.13 (14.60)	6.76 (6.29)
9	[Cu(NO <sub>2</sub> -acac)dmeen]ClO <sub>4</sub>	CH <sub>3</sub>	NO <sub>2</sub>	CH <sub>3</sub>	blue	91	141–143	31.93 (31.26)	10.07 (9.95)	5.27 (5.24)
10	[Cu(NO <sub>2</sub> -acac)dmeen]NO <sub>3</sub>	CH <sub>3</sub>	NO <sub>2</sub>	CH <sub>3</sub>	blue	78	155–157	35.01 (34.22)	13.63 (14.54)	5.22 (5.74)
11	[Cu(NO <sub>2</sub> -acac)dmeen]Cl	CH <sub>3</sub>	NO <sub>2</sub>	CH <sub>3</sub>	green	31	167–169	35.18 (36.74)	12.23 (11.69)	5.87 (6.16)
12	[Cu(SCN-acac)dmeen]ClO <sub>4</sub>	CH <sub>3</sub>	SCN	CH <sub>3</sub>	blue–green	49	< 141	34.11 (33.08)	9.43 (9.65)	5.18 (5.09)
13	[Cu(bzac)dmeen]ClO <sub>4</sub>	C <sub>6</sub> H <sub>5</sub>	H	CH <sub>3</sub>	violet	90	171–172	44.15 (43.61)	6.40 (6.36)	5.82 (5.71)
14	[Cu(bzac)dmeen]NO <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>	H	CH <sub>3</sub>	blue–green	77	183–187	48.4 (47.67)	10.35 (10.43)	6.33 (6.25)
15	[Cu(Cl-bzac)dmeen]ClO <sub>4</sub>	C <sub>6</sub> H <sub>5</sub>	Cl	CH <sub>3</sub>	blue–green	54	< 188	39.91 (40.45)	5.97 (5.90)	4.98 (5.09)
16	[Cu(NO <sub>2</sub> -bzac)dmeen]ClO <sub>4</sub>	C <sub>6</sub> H <sub>5</sub>	NO <sub>2</sub>	CH <sub>3</sub>	grey–green	91	163–165	38.92 (39.57)	8.84 (8.66)	5.06 (4.98)
17	[Cu(SCN-bzac)dmeen]ClO <sub>4</sub>	C <sub>6</sub> H <sub>5</sub>	SCN	CH <sub>3</sub>	blue–green	56	< 188	40.58 (41.03)	8.68 (8.50)	5.03 (4.86)
18	[Cu(dbm)dmeen]ClO <sub>4</sub>	C <sub>6</sub> H <sub>5</sub>	H	C <sub>6</sub> H <sub>5</sub>	dark green	89	243–245	51.22 (50.13)	5.64 (5.57)	5.36 (5.41)
19	[Cu(dbm)dmeen]NO <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>	H	C <sub>6</sub> H <sub>5</sub>	dark blue	81	191–193	55.83 (54.22)	8.83 (9.04)	5.52 (5.84)
20	[Cu(Cl-dbm)dmeen]ClO <sub>4</sub>	C <sub>6</sub> H <sub>5</sub>	Cl	C <sub>6</sub> H <sub>5</sub>	grey–green	91	183–185	45.30 (46.95)	5.08 (5.22)	4.79 (4.87)
21	[Cu(bztf)dmeen]ClO <sub>4</sub>	C <sub>6</sub> H <sub>5</sub>	H	CF <sub>3</sub>	blue	84	194–196	38.59 (38.85)	5.57 (5.66)	4.51 (4.48)
22	[Cu(dmeen) <sub>2</sub> Cl]Cl				bright green	67	142–144	38.57 (39.26)	15.14 (15.27)	8.84 (8.78)
23	[Cu(dmeen)Cl <sub>2</sub> ]				turquoise	64	152–153	28.44 (28.71)	11.39 (11.16)	6.60 (6.42)

lates, especially when strong electron-attracting substituents are incorporated in the  $\beta$ -dionato moiety [11]. In order to glean more information on the behaviour of  $[\text{Cu}(\text{tfac})_2\text{dmeen}]$ , the spectral changes were monitored as dmeen was added to a solution of  $\text{Cu}(\text{tfac})_2$  in  $\text{CH}_2\text{Cl}_2$ . An hyperchromic effect and a bathochromic shift accompanies the addition of dmeen which reach a maximum when the dmeen-to-copper(II) ratio becomes 1:1. The extinction coefficient at maximum absorption seems impervious to further addition of dmeen (Fig. 1).

The irregular behaviour of  $\text{tfac}^-$  towards  $[\text{Cu}(\text{dmeen})\text{Y}]^+$  is difficult to interpret. Steric inhibition cannot be invoked to explain the observed reactivity since the size of the fluorine atoms is comparable to the hydrogen ones. Furthermore, replacement of the methyl groups by the bulkier  $-\text{C}(\text{CH}_3)_3$  ones did not inhibit the preparation of  $[\text{Cu}(\text{dpm})\text{dmeen}]^+$  demonstrating that bulky substituents attached to the carbonyl carbons are of no consequence [9]. The exclusion of steric interactions as the reason of the change in reactivity of  $\text{tfac}^-$  leaves as only credible explanation for the observed behaviour the change in electron distribution effected by the electron-withdrawing  $-\text{CF}_3$  group. However, Fukuda *et al.* [7a] employing  $N,N,N',N'$ -tetramethyl-1,2-diamineethane,  $\text{Me}_4\text{en}$ , succeeded in preparing the corresponding mixed-ligand chelates,  $[\text{Cu}(\text{tfac})\text{Me}_4\text{en}]^+$ . Their results clearly indicate that additional factors, such as the degree of N-substitution, also influence the course of the reaction.

In an attempt to probe further the influence of electronic effects engendered by substituents within the  $\beta$ -dionato moiety on the formation and stability of ternary chelates in which  $N,N$ -dimethyl- $N'$ -ethyl-ethylenediamine participates, a series of  $\beta$ -ketoenols were employed containing various substituents. Insertion of substituents in the  $\gamma$ -position alters the electron dis-

tribution in the  $\beta$ -dionato moiety. Nevertheless, a symmetrical electron population is maintained at the coordination sites, regardless of the direction the substituents shift the electron density. The adversity encountered when employing  $\text{tfac}^-$ , in which the electron-withdrawing group  $-\text{CF}_3$  is present, suggested the use of substituents that attract electrons. It is true that insertion of the strongly electron-attracting  $-\text{CF}_3$  group in copper(II) ketoenolates enhances the Lewis acidity of the square planar  $\text{CuO}_4$  chromophore, and shifts the reduction potentials to more positive values [14]. Enhancement of the Lewis acidity and shift of the reduction potentials to more positive value can also be achieved by attaching in the  $\beta$ -dionato moiety other substituents such as the chloride [10]. The 3-chloro-2,4-pentanedione afforded  $[\text{Cu}(\text{Cl-acac})\text{dmeen}]^+$  in high yield. Similar behaviour was observed when the slightly bulkier bromide replaced the chloride (van der Waals radii:  $-\text{Cl}=0.180$  nm,  $-\text{Br}=0.195$  nm,  $-\text{CF}_3=0.200$  nm). In so far as the Hammett  $\sigma$  functions express the electronic effects that appear to be operative in the  $\text{Cu}(\beta\text{-dionato})_2$  chelates, the resultant inductive and resonance effect of the  $-\text{CF}_3$  group is far stronger than that exercised by either the chloride or the bromide ( $\sigma_p$ :  $\text{CF}_3=0.54$ ,  $\text{Cl}=0.23$ ,  $\text{Br}=0.23$ ,  $\sigma_m$ :  $\text{CF}_3=0.43$ ,  $\text{Cl}=0.37$ ,  $\text{Br}=0.39$ ). Employment of substituents with  $\sigma_p$  and  $\sigma_m$  values higher than that for  $-\text{CF}_3$ , for instance the cyano and the nitro group ( $\sigma_p$ :  $\text{CN}=0.66$ ,  $\text{NO}_2=0.78$ ,  $\sigma_m$ :  $\text{CN}=0.56$ ,  $\text{NO}_2=0.71$ ), culminated in the formation and the isolation of the corresponding mixed-ligand chelates (Table 1). An unambiguous manifestation of the enhanced stability of these ternary chelates, regardless of the electronic effects of the substituents in the  $\gamma$ -position, constitutes the method employed to obtain the  $[\text{Cu}(\text{CH}_3\text{-acac})\text{dmeen}]^+$  and  $[\text{Cu}(\text{NO}_2\text{-acac})\text{dmeen}]^+$  species. While  $\text{Cu}(\text{CH}_3\text{-acac})_2$  and  $\text{Cu}(\text{NO}_2\text{-acac})_2$  are water insoluble, their addition in equimolar quantities to an aqueous solution of  $[\text{Cu}(\text{dmeen})_2]^{2+}$  culminates in complete dissolution and formation of the corresponding mixed-ligand chelates. Organic solvents may be equally well employed. The hyperchromic effect and the other changes incurred in the electronic spectra upon mixing solutions of  $[\text{Cu}(\text{dmeen})_2]^{2+}$  and  $\text{Cu}(\text{NO}_2\text{-acac})_2$  amply demonstrate the mutual ligand exchange and the formation of a new compound (Fig. 2).

Symmetrical charge distribution pertains upon replacement of the methyl groups of acetylacetonate by phenyl ones and dibenzoylmethane (dbmH) and its derivatives X-dbmH also afford ternary chelates. The phenyl groups not only induce changes in the spectra but also modify additional physicochemical properties and the stability of the mixed-ligand chelates in solution. While the  $[\text{Cu}(\text{X-acac})\text{dmeen}]^+$  chelates are recrystallisable from water, dissolution of the  $[\text{Cu}(\text{X-}$

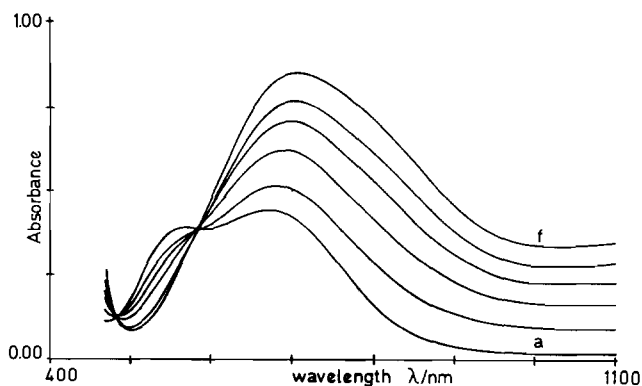


Fig. 1. Spectral changes accompanying the addition of  $N,N$ -dimethyl- $N'$ -ethylethylenediamine, (dmeen), to a  $10^{-3}$  M solution of  $\text{Cu}(\text{tfac})_2$  in dichloromethane. (a)  $10^{-3}$  M  $\text{Cu}(\text{tfac})_2$ , (f)  $10^{-3}$  M  $\text{Cu}(\text{tfac})_2$  dmeen.

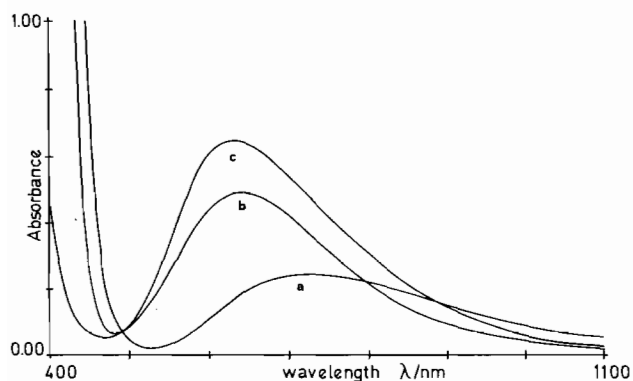


Fig. 2. Ligand-field excitation spectra of  $5 \times 10^{-3}$  M solutions in DMSO of  $\text{Cu}(\text{NO}_2\text{-acac})_2$  (a),  $\text{Cu}(\text{dmeen})_2(\text{ClO}_4)_2$  (b) and  $[\text{Cu}(\text{NO}_2\text{-acac})\text{dmeen}]\text{ClO}_4$  (c).

$\text{dbm)dmeen}]^+$  series in this solvent results in their decomposition.

Inequality in electron population in the  $\beta$ -dionato moiety has not necessarily an adverse effect in ternary chelate formation, neither symmetrical charge distribution in  $\beta$ -dione suffices to impose mixed-ligand chelate formation. Despite the symmetrical electron population in hexafluoroacetylacetone, addition of this ligand in admixture with dmeen to an ethanolic solution of  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  did not yield the expected ternary chelate and resulted in a variety of products. Among the products isolated the adduct  $[\text{Cu}(\text{hfac})_2\text{dmeen}]$  was predominant. Benzoylacetone (bzacH) although lacking the symmetry of, say, hexafluoroacetylacetone, nevertheless is capable of ternary chelate formation. Removal of electron density from the carbonyl oxygens by attaching substituents in the methinic carbon atom is also of no consequence to mixed-ligand chelate formation. It seems that the  $-\text{CF}_3$  group has a destabilising effect. This destabilising effect, however, is ameliorated when groups capable of extending the delocalization are present in the  $\beta$ -dionato moiety. For instance 1-phenyl-4,4,4-trifluoro-1,3-butanedione, bztfH, in which the methyl group of tfacH has been replaced by a phenyl one, readily produces ternary chelates.

Copper(II) in the  $\text{CuO}_2\text{N}_2$  chromophore lacks coordination saturation and in view of its tendency to achieve coordination numbers greater than four when it is bonded to nitrogen or oxygen, it is receptive to covalent interactions when species known for their ability to coordinate become available.

The interactions of the square-planar  $\text{CuO}_2\text{N}_2$  chromophore are not depended solely on the nature of the species neutralising the positive charge. Electronic effects engendered by substituents in the  $\beta$ -dionato moiety alter the electron density at the coordination sites and the repercussions are evidenced in the changes of certain physicochemical properties. For instance, the presence of electron-withdrawing substituents culminates in en-

hancement of covalent interactions as the drop in conductivity suggests. An unexpected deviation of the established pattern was observed when 3-cyano-2,4-pentanedione was reacted with  $[\text{Cu}(\text{dmeen})(\text{NO}_3)_2]$ . Instead of enhancement of the covalent interactions of the nitrate group and diminution in the degree of dissociation, an increase in molar conductivity was observed that reached a value indicative of a 1:1 electrolyte ( $\Lambda_M = 83 \text{ S cm}^2 \text{ M}^{-1}$  in nitromethane). Stoichiometric analyses suggested the presence of one water molecule per copper(II) ion. Coordination of water molecules to copper(II) participating in the  $\text{CuN}_2\text{O}_2$  chromophore consisting of 1,2-diamine and two perturbed carbonyl oxygens has been reported for a neutral binuclear compound [17]. Strong absorption bands at about  $3500 \text{ cm}^{-1}$  (Fig. 3) corroborate the existence of coordinated water in  $[\text{Cu}(\text{CN-acac})\text{dmeen}(\text{H}_2\text{O})]\text{NO}_3$ , so the coordination number of copper(II) in this compound is also greater than four. Confirmation of the presence of coordinated water in an apical position perpendicular to the basal plane was accrued from preliminary X-ray structure determination.

#### Infrared spectra

Certain absorption bands that are characteristic of the  $[\text{Cu}(\beta\text{-dionato})_2]$  chelates and the  $[\text{Cu}(\text{dmeen})_2]^{2+}$  species persist in the IR spectra of the mixed-ligand chelates while the disappearance of other bands in conjunction with the emergence of absorptions in specific regions of the spectrum are indicative of the bonds formed and the entities present in the newly obtained chelates. The bands are distinguished into those emanating from the ligands and those associated with the counterion.

#### Ligand spectra

In the IR spectra of  $[\text{Cu}(\text{dmeen})\text{Cl}_2]$  and  $[\text{Cu}(\text{dmeen})_2\text{Cl}]\text{Cl}$  several bands appear in the region  $1600\text{--}700 \text{ cm}^{-1}$  that are also observed, albeit with minor shifts, in the spectra of the free base, *N,N*-dimethyl-*N'*-ethyl-ethylenediamine. Taking into consideration the existence of the  $(\text{CH}_2\text{NR}^1\text{R}^2)$  groups and the spectra of 1,2-diaminoethane chelates [18, 19], the absorption

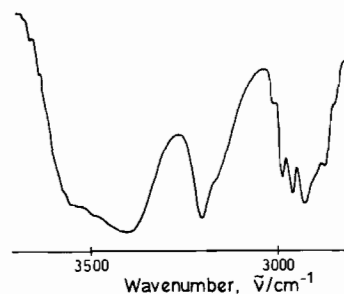


Fig. 3. IR absorptions of  $[\text{Cu}(\text{CN-acac})\text{dmeen}(\text{H}_2\text{O})]\text{NO}_3$  in a KBr matrix in the region  $2800$  to  $4000 \text{ cm}^{-1}$ .

at  $1040\text{ cm}^{-1}$  is probably due to the stretching vibration of the carbon–nitrogen bond. The abundance of  $-\text{CH}_2-$  groups suggests that certain strong bands may originate from the angle vibrations of this group and the intense absorptions at  $1475\text{--}1440\text{ cm}^{-1}$  are very likely associated with the scissoring vibrations,  $\delta(\text{CH}_2)$ , while the broad band at  $1140\text{ cm}^{-1}$  most probably emanates from a twisting motion. The band at  $794\text{ cm}^{-1}$  that in the spectra of free dmeen appears broader and is split in two ( $785$  and  $756\text{ cm}^{-1}$ ) may be due to the rocking vibration,  $\rho_r(\text{CH}_2)$ . The stretching vibrations of the  $\text{N}-\text{CH}_2$  group, and the prominent bands in the region  $2850 \pm 100\text{ cm}^{-1}$  that are associated with it, are more important since they serve as an indication of coordination of dmeen. Upon covalent bond formation these absorptions apparently lose intensity, become shifted to higher frequencies and mingle with other C–H absorption bands.

Dependence on coordination is also exhibited by the intense band occurring at  $3230 \pm 30\text{ cm}^{-1}$  which is associated with the  $\text{N}-\text{H}$  vibration and is observed at  $3330\text{ cm}^{-1}$  in the free ligand. As the lone pair of electrons of the donor atom (nitrogen) become involved in the metal–ligand bond, the transfer of electron density to the metal and the ensuing polarisation of the ligand involves electron depopulation of the  $\text{N}-\text{H}$  bond which culminates in a shift to lower frequencies. The occurrence of the  $\text{N}-\text{H}$  vibration in a region that neither the  $\beta$ -diones nor the anions employed absorb, is of diagnostic value since most bands are masked by the more intense absorptions of the other entities present in the  $[\text{Cu}(\beta\text{-dionato})\text{dmeen}]\text{Y}$  species (Table 2).

Formation of a six-membered chelate ring comprising the copper(II) and the  $\beta$ -dionato moiety is disclosed by the intense absorptions in the region  $1650\text{--}1500\text{ cm}^{-1}$  and in addition to the changes in frequency of the  $\text{C}=\text{O}$  and  $\text{C}=\text{C}$  vibrational modes incurred upon formation of the metal–oxygen bonds there are frequency shifts engendered by substituents within the  $\beta$ -dionato moiety due to the well documented receptiveness of the  $\text{C}=\text{O}$  and the conjugated  $\text{C}=\text{C}$  bonds to mass and electronic effects [3, 20]. Insertion of substituents in the methylene carbon atom of acacH culminates in a merge of the bands emanating from the perturbed double bonds. Replacement of one  $\beta$ -dionato chelate ring by that of the 1,2-diamine diminishes the extent of conjugation and the repercussions of the presence of the 1,2-diamine on the aforementioned perturbed double bonds become evident when the frequencies of the vibrational modes are compared with the corresponding ones in the bis( $\beta$ -dionato)copper(II) chelates. For example, while the absorption due to the perturbed  $\text{C}=\text{O}$  in  $\text{Cu}(\text{bzac})_2$  peaks at  $1561\text{ cm}^{-1}$ , upon formation of the mixed-ligand species the band is shifted to  $1592\text{ cm}^{-1}$  (Table 2).

### Counterion spectra

Corroboration of the variable nature of the interactions of the bulky  $\text{ClO}_4^-$  group with the  $\text{CuO}_2\text{N}_2$  chromophore, implied by the molar conductivity values, is obtained from the IR spectra. The presence of the  $\text{ClO}_4^-$  group is declared by the very broad intense band with a poorly defined maximum observed in the spectrum of  $[\text{Cu}(\text{bzac})\text{dmeen}]\text{ClO}_4$  at  $1087\text{ cm}^{-1}$ , notwithstanding other groups that also absorb in the same region. This band which corresponds to the triply degenerate asymmetric stretching vibration ( $T_2$ ) of the tetrahedral  $\text{ClO}_4^-$  group does not appear in the spectrum of  $[\text{Cu}(\text{bzac})\text{dmeen}]\text{NO}_3$  (Fig. 4). The existence of the nitrates is disclosed by the intense absorption at  $1387\text{ cm}^{-1}$  attributed to the  $\nu_3(E')$  vibration while a weak band at  $825\text{ cm}^{-1}$  is associated with the  $\nu_2(A_2'')$  vibration. The nitrate may exist as a counterion or it may form covalent bonds acting as a unidentate, bidentate or even bridging ligand. Although some covalency is indicated by the molar conductivity values and credence to this is given by the broad nature of the band at  $1387\text{ cm}^{-1}$ , the unfortunate positioning of the vibrations of the  $\beta$ -dionato moiety does not enable us to discern unambiguously the mode of existence of the nitrates in the solid state. Such a dilemma does not occur when chloride counterbalances the charge of the cationic species and a band observed at  $325\text{ cm}^{-1}$  is attributed to the copper–chloride bond.

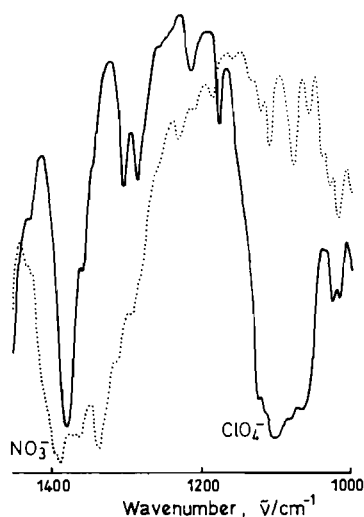
### Ligand field excitation spectra

The diffuse reflectance spectra of  $[\text{Cu}(\text{acac})\text{dmeen}]\text{ClO}_4$ , which is typical of the  $[\text{Cu}(\beta\text{-dionato})\text{dmeen}]^+$  series, is characterised by a broad structureless band (envelope) in the visible at about  $1.800\text{ }\mu\text{m}^{-1}$  (Fig. 2). The same envelope appears when the spectrum is obtained employing solutions in 1,2-dichloroethane and other non-coordinating solvents. In the series, the position of the maximum absorption depends on the substituents attached to the  $\beta$ -dionato moiety, the solvent and, more importantly, on the species neutralising the charge of the  $[\text{Cu}(\beta\text{-dionato})\text{dmeen}]^+$  entity.  $[\text{Cu}(\text{acac})\text{Me}_4\text{en}]\text{ClO}_4$  exhibits an absorption maximum at  $1.850\text{ }\mu\text{m}^{-1}$ . The shift induced by substituting  $\text{Me}_4\text{en}$  for dmeen suggests that the steric and electronic effects due to groups in the 1,2-diamine constitute an additional factor affecting the excitation energies (Table 3).

The copper(II) ion in  $[\text{Cu}(\text{dmeen})_2]^{2+}$  and other  $[\text{Cu}(\text{enR})_2]^{2+}$  chelates, in which steric interactions are of no consequence to the  $\text{CuN}_4$  chromophore, effectively exists in a square-planar environment with a  $^2B_{1g}$  ground state. Hathaway [2e] investigating the ligand-field spectra of copper(II) chelates of known structure in which copper(II) is bonded to nitrogen or oxygen, concluded that absorption in the  $1.8$  to  $2.0\text{ }\mu\text{m}^{-1}$  region correlates

TABLE 2. Characteristic bands in the IR spectra of some copper(II) chelates with *N,N*-dimethyl-*N'*-ethyl-ethylenediamine and  $\beta$ -ketoenols

No.	Compound	R <sup>1</sup>	X(R <sup>2</sup> )	R <sup>3</sup>	$\bar{\nu}(\text{N-H})$ (cm <sup>-1</sup> )	$\bar{\nu}(\text{C=O})$ (cm <sup>-1</sup> )	$\bar{\nu}(\text{C}\equiv\text{C})$ (cm <sup>-1</sup> )	$\bar{\nu}(\text{R}^2)$ (cm <sup>-1</sup> )	$\bar{\nu}(\text{M-O,N})$ (cm <sup>-1</sup> )
1	[Cu(acac)dmeen]ClO <sub>4</sub>	CH <sub>3</sub>	H	CH <sub>3</sub>	3230	1585	1530		450
2	[Cu(acac)dmeen]NO <sub>3</sub>	CH <sub>3</sub>	H	CH <sub>3</sub>	3150	1590	1530		445
3	[Cu(CH <sub>3</sub> -acac)dmeen]ClO <sub>4</sub>	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	3235		1585		460
4	[Cu(CH <sub>3</sub> -acac)dmeen]NO <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	3150		1582		460
5	[Cu(Cl-acac)dmeen]ClO <sub>4</sub>	CH <sub>3</sub>	Cl	CH <sub>3</sub>	3220		1575		445
6	[Cu(Cl-acac)dmeen]NO <sub>3</sub>	CH <sub>3</sub>	Cl	CH <sub>3</sub>	3145		1582		445
7	[Cu(Br-acac)dmeen]ClO <sub>4</sub>	CH <sub>3</sub>	Br	CH <sub>3</sub>	3220		1570		445
8	[Cu(CN-acac)dmeen(H <sub>2</sub> O)]NO <sub>3</sub>	CH <sub>3</sub>	CN	CH <sub>3</sub>	3230		1615	2210	430, 475
9	[Cu(NO <sub>2</sub> -acac)dmeen]ClO <sub>4</sub>	CH <sub>3</sub>	NO <sub>2</sub>	CH <sub>3</sub>	3235		1600	1518, 1330	440
10	[Cu(NO <sub>2</sub> -acac)dmeen]NO <sub>3</sub>	CH <sub>3</sub>	NO <sub>2</sub>	CH <sub>3</sub>	3160		1605	1515, 1330	445
11	[Cu(NO <sub>2</sub> -acac)dmeen]Cl	CH <sub>3</sub>	NO <sub>2</sub>	CH <sub>3</sub>	3100		1640	1330	420, 480
12	[Cu(SCN-acac)dmeen]ClO <sub>4</sub>	CH <sub>3</sub>	SCN	CH <sub>3</sub>	3230		1570	2150	445
13	[Cu(bzac)dmeen]ClO <sub>4</sub>	C <sub>6</sub> H <sub>5</sub>	H	CH <sub>3</sub>	3220	1592	1560		445
14	[Cu(bzac)dmeen]NO <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>	H	CH <sub>3</sub>	3300	1595	1565		445
15	[Cu(Cl-bzac)dmeen]ClO <sub>4</sub>	C <sub>6</sub> H <sub>5</sub>	Cl	CH <sub>3</sub>	3240	1585	1560		465
16	[Cu(NO <sub>2</sub> -bzac)dmeen]ClO <sub>4</sub>	C <sub>6</sub> H <sub>5</sub>	NO <sub>2</sub>	CH <sub>3</sub>	3240	1595	1575	1520, 1330	468, 448
17	[Cu(SCN-bzac)dmeen]ClO <sub>4</sub>	C <sub>6</sub> H <sub>5</sub>	SCN	CH <sub>3</sub>	3240	1605	1570	2180	480
18	[Cu(dbm)dmeen]ClO <sub>4</sub>	C <sub>6</sub> H <sub>5</sub>	H	C <sub>6</sub> H <sub>5</sub>	3240	1598	1550		462
19	[Cu(dbm)dmeen]NO <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>	H	C <sub>6</sub> H <sub>5</sub>	3150	1598	1550		465
20	[Cu(Cl-dbm)dmeen]ClO <sub>4</sub>	C <sub>6</sub> H <sub>5</sub>	Cl	C <sub>6</sub> H <sub>5</sub>	3230		1532		465
21	[Cu(bztf)dmeen]ClO <sub>4</sub>	C <sub>6</sub> H <sub>5</sub>	H	CF <sub>3</sub>	3240	1615	1575		480
22	[Cu(dmeen) <sub>2</sub> Cl]Cl				3180				445
23	[Cu(dmeen)Cl <sub>2</sub> ]				3150				445

Fig. 4. Absorption bands in the IR spectra of [Cu(bzac)dmeen]Y (Y=NO<sub>3</sub>, ClO<sub>4</sub>).

with a square-coplanar geometry of the CuN<sub>4</sub> chromophore. The similarities in spectroscopic behaviour of the [Cu( $\beta$ -dionato)dmeen]<sup>+</sup> and the [Cu(enR)<sub>2</sub>]<sup>2+</sup> species regarding the interactions with solvents and the influence of anions such as Cl<sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, suggest a square-coplanar structure of the CuN<sub>2</sub>O<sub>2</sub> chromophore. Considering that the field induced by coordinated oxygen atoms is weaker than that due to nitrogen ones,

ligand-field absorptions of the CuN<sub>2</sub>O<sub>2</sub> chromophore at wavenumbers higher than 1.70  $\mu\text{m}^{-1}$  should be thought of as an indication of square-planar geometry.

The relative energy of the d orbitals of the central atom, as it is known, depends on the geometry of the field created by the ligands. When copper(II) is surrounded by atoms in a square-planar arrangement, for instance in the [Cu( $\beta$ -dionato)dmeen]<sup>+</sup> entity, its d orbitals are no longer degenerate (Fig. 5). The non-degeneracy of the d orbitals leads to expectation of more than one band provided the energy separation of the orbitals is appreciable and the molecules exist in a low vibrational state. Instead, one broad structureless absorption is observed in room temperature electronic excitation spectra suggesting that the d orbitals are rather closely spaced. Attempts to analyse the envelope into Gaussian components proved meaningless since no unique set of bands was found because of the inadequacy of information regarding bandwidths and intensities.

Bathochromic shifts accompany the dissolution of the [Cu( $\beta$ -dionato)dmeen]Y chelates in basic solvents and the same effect is observed when nucleophilic anions replace bulky polyatomic ones. Copper(II) in the CuN<sub>2</sub>O<sub>2</sub> chromophore lacks coordination saturation and therefore is receptive to covalent interactions. Insertion in the  $\beta$ -dionato moiety of electron-attracting substituents enhances the Lewis acidity of the CuN<sub>2</sub>O<sub>2</sub>

TABLE 3. Ligand-field band maxima in the electronic excitation spectra of some copper(II) chelates with *N,N*-dimethyl-*N'*-ethyl-ethylenediamine and  $\beta$ -ketoenols

No.	Compound	R <sup>1</sup>	X(R <sup>2</sup> )	R <sup>3</sup>	CH <sub>2</sub> Cl <sub>2</sub>	CH <sub>3</sub> CN	EtOH	DMF	DMSO
1	[Cu(acac)dmeen]ClO <sub>4</sub>	CH <sub>3</sub>	H	CH <sub>3</sub>	1.792	1.718	1.684	1.650	1.618
2	[Cu(acac)dmeen]NO <sub>3</sub>	CH <sub>3</sub>	H	CH <sub>3</sub>	1.692	1.715	1.669	1.647	1.615
3	[Cu(CH <sub>3</sub> -acac)dmeen]ClO <sub>4</sub>	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	1.858				
4	[Cu(CH <sub>3</sub> -acac)dmeen]NO <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	1.736	1.742	1.703	1.665	1.638
5	[Cu(Cl-acac)dmeen]ClO <sub>4</sub>	CH <sub>3</sub>	Cl	CH <sub>3</sub>	1.787	1.710	1.646	1.628	1.596
6	[Cu(Cl-acac)dmeen]NO <sub>3</sub>	CH <sub>3</sub>	Cl	CH <sub>3</sub>	1.649	1.661	1.642	1.607	1.582
7	[Cu(Br-acac)dmeen]ClO <sub>4</sub>	CH <sub>3</sub>	Br	CH <sub>3</sub>	1.786	1.694	1.672	1.622	1.596
8	[Cu(CN-acac)dmeen(H <sub>2</sub> O)]NO <sub>3</sub>	CH <sub>3</sub>	CN	CH <sub>3</sub>	1.638	1.666	1.612	1.597	1.583
9	(Cu(NO <sub>2</sub> -acac)dmeen]ClO <sub>4</sub>	CH <sub>3</sub>	NO <sub>2</sub>	CH <sub>3</sub>	1.733	1.668	1.643	1.602	1.578
10	[Cu(NO <sub>2</sub> -acac)dmeen]NO <sub>3</sub>	CH <sub>3</sub>	NO <sub>2</sub>	CH <sub>3</sub>	1.638	1.658	1.627		1.577
11	[Cu(NO <sub>2</sub> -acac)dmeen]Cl	CH <sub>3</sub>	NO <sub>2</sub>	CH <sub>3</sub>			1.490		1.479
12	[Cu(SCN-acac)dmeen]ClO <sub>4</sub>	CH <sub>3</sub>	SCN	CH <sub>3</sub>	1.712	1.661	1.613	1.583	1.584
13	[Cu(bzac)dmeen]ClO <sub>4</sub>	C <sub>6</sub> H <sub>5</sub>	H	CH <sub>3</sub>	1.775	1.706	1.676	1.634	1.612
14	[Cu(bzac)dmeen]NO <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>	H	CH <sub>3</sub>	1.667	1.706	1.667	1.623	1.623
15	[Cu(Cl-bzac)dmeen]ClO <sub>4</sub>	C <sub>6</sub> H <sub>5</sub>	Cl	CH <sub>3</sub>	1.730	1.598	1.593	1.576	1.550
16	[Cu(NO <sub>2</sub> -bzac)dmeen]ClO <sub>4</sub>	C <sub>6</sub> H <sub>5</sub>	NO <sub>2</sub>	CH <sub>3</sub>	1.712	1.661	1.593	1.593	1.550
17	[Cu(SCN-bzac)dmeen]ClO <sub>4</sub>	C <sub>6</sub> H <sub>5</sub>	SCN	CH <sub>3</sub>	1.504			1.500	
18	[Cu(dbm)dmeen]ClO <sub>4</sub>	C <sub>6</sub> H <sub>5</sub>	H	C <sub>6</sub> H <sub>5</sub>	1.775	1.704	1.662	1.623	1.614
19	[Cu(dbm)dmeen]NO <sub>3</sub>	C <sub>6</sub> H <sub>5</sub>	H	C <sub>6</sub> H <sub>5</sub>	1.658	1.702	1.662	1.618	1.618
20	[Cu(Cl-dbm)dmeen]ClO <sub>4</sub>	C <sub>6</sub> H <sub>5</sub>	Cl	C <sub>6</sub> H <sub>5</sub>	1.742	1.686	1.644	1.597	1.584
21	[Cu(bztf)dmeen]ClO <sub>4</sub>	C <sub>6</sub> H <sub>5</sub>	H	CF <sub>3</sub>	1.706	1.650	1.602	1.567	1.557
22	[Cu(dmeen) <sub>2</sub> Cl]Cl				1.422	1.406	1.452	1.397	1.420
23	[Cu(dmeen)Cl <sub>2</sub> ]				1.387	1.385	1.391	1.282	1.366

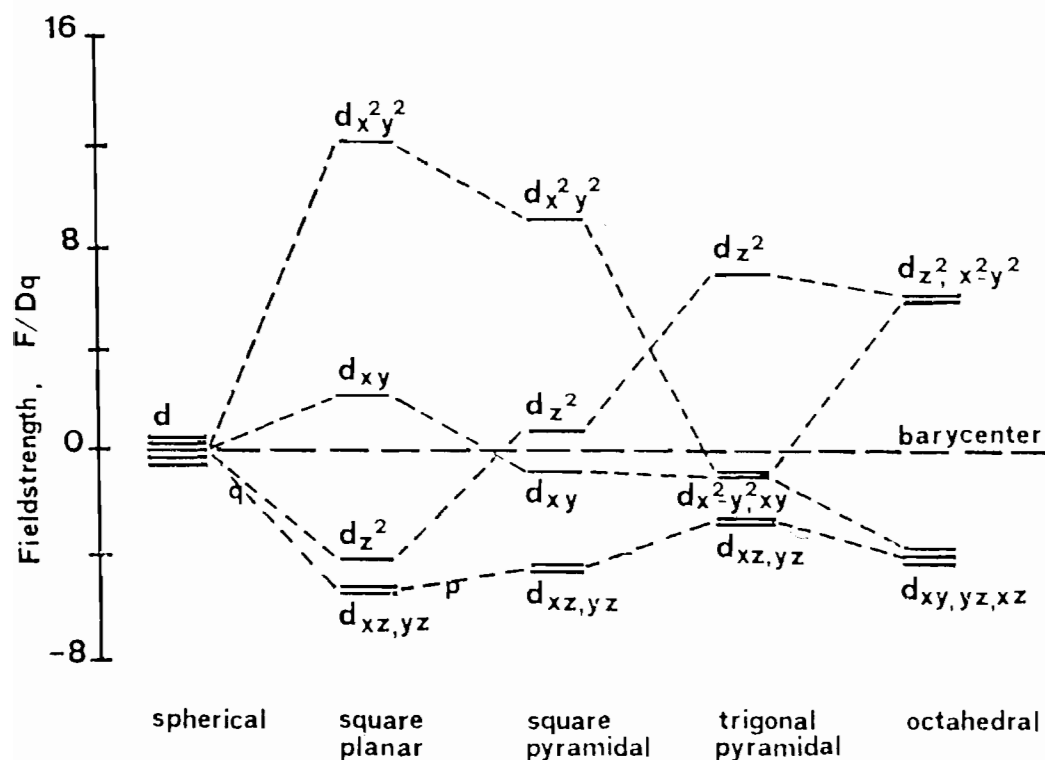


Fig. 5. The energy levels of the d orbitals in crystal fields of different geometries.



chromophore and promotes covalent interactions, the extent of which is controlled by the nucleophilicity of the approaching species. For example, the covalent interactions are reciprocated to a greater extent when the tetrahedral  $\text{ClO}_4^-$  group is replaced by the trigonal  $\text{NO}_3^-$  anion and are further enhanced in the presence of the nucleophilic chloride. When the covalent interactions prevail over the electrostatic ones, an increase in the coordination number of copper(II) is brought about and the concomitant change in the geometry of the field created by the ligands alters the energies of the d orbitals (Fig. 5). This naive interpretation of the spectral changes acquires credibility when the transition energies in the ligand-field spectra of the  $[\text{Cu}(\text{NO}_2\text{-acac})\text{dmeen}]\text{Y}$  species are considered. The ligand-field excitation of  $[\text{Cu}(\text{NO}_2\text{-acac})\text{dmeen}]\text{ClO}_4$  has a maximum at  $1.733 \mu\text{m}^{-1}$ . It is shifted to lower wavenumbers ( $1.638 \mu\text{m}^{-1}$ ) when the nitrates interact with Cu(II) in  $\text{CuN}_2\text{O}_2$  (*xy* plane), presumably along the *z* axis. When the interactions of copper(II) with the nucleophilic chloride become predominantly covalent and alter the geometry of the crystal field to square pyramidal, the excitation energy diminishes by about  $2500 \text{ cm}^{-1}$  with the band maximum observed at  $1.433 \mu\text{m}^{-1}$ . It is the geometry rather than the counterions that cause the observed shifts.

The dependence of the ligand-field band maxima on the geometry of the atoms in the immediate environment of copper(II) is reaffirmed once again in the case of  $[\text{Cu}(\text{tfac})_2\text{dmeen}]$ . This molecule apparently assumes an octahedral structure with the configuration requirements of the 1,2-diamine imposing coordination in the *cis* position and destroying the planarity of the  $\text{CuO}_4$  chromophore of  $\text{Cu}(\text{tfac})_2$ . The pervading electronic effects alter the Cu–O as well as the Cu–N distances with the distortion probably accentuated by the Jahn–Teller effect [21, 22]. As a result the molecule exhibits an absorption maximum at only  $1.410 \mu\text{m}^{-1}$  (Fig. 1).

The shifts induced by certain solvents equal those due to the counterion (Table 3). For instance, the extremum of the envelope that in the diffuse reflectance spectra of  $[\text{Cu}(\text{Cl-acac})\text{dmeen}]\text{ClO}_4$  occurs at  $1.820 \mu\text{m}^{-1}$  and remains virtually unchanged in 1,2-dichloroethane, is red shifted as the basicity of the solvent increases (Fig. 6). Interestingly, a hyperchromic effect is observed at the same time, suggesting further relaxation of the selection rules. Assuming that the approach of the solvent occurs along the *z* axis, the solvent molecules are repelled by the two electrons in the  $d_{z^2}$  orbital of copper(II) and only the more basic species can force their way in to form relatively strong bonds. Upon coordination they exert a *z* component field proportional to their position in the spectrochemical series. Thus while solvents of low basicity (e.g. 1,2-

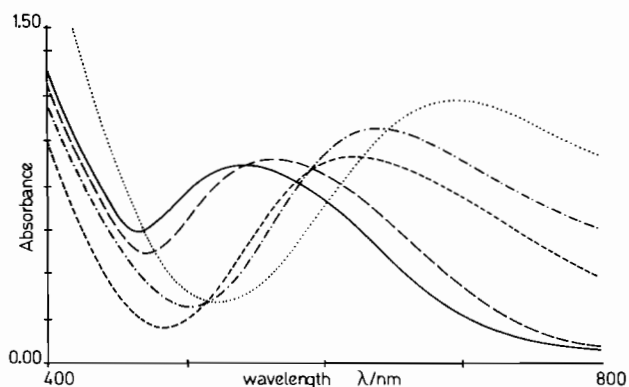


Fig. 6. Solvent shifts and hyperchromic effect in the ligand-field excitation spectra of  $8 \times 10^{-3} \text{ M}$   $[\text{Cu}(\text{Cl-acac})\text{dmeen}]\text{ClO}_4$ . Solvents: nitromethane (---), dichloromethane (---), DMSO (---), pyridine (---), piperidine (.....).

dichloroethane) have no effect in the band maxima, others that are considerably more basic induce large bathochromic shifts. Considering the position in the spectrochemical series of solvents and anions (*f* values:  $\text{Cl} = 0.78$ ,  $\text{CH}_3\text{CN} = 1.22$ ), the only plausible explanation for the observed shifts appears to be a tetragonal distortion culminating in a reduction of the energy separating the d orbitals.

Coordination compounds and in particular copper(II) chelates have been proposed as indicators for the determination of solvent properties including Lewis basicity [23]. In an attempt to learn more about the interactions of the  $[\text{Cu}(\beta\text{-dionato})\text{dmeen}]^+$  entity with solvents, the spectra of  $[\text{Cu}(\text{NO}_2\text{-acac})\text{dmeen}]\text{ClO}_4$  were obtained using a narrower bandpass and were examined in more detail. Since no solvent property can explain adequately the solute–solvent interactions [24], a wide variety of both protonic and non-protonic solvents was employed. The manifested Lewis acidity of the  $\text{CuN}_2\text{O}_2$  chromophore in the  $[\text{Cu}(\beta\text{-dionato})\text{dmeen}]^+$  entity towards solvents possessing atoms with at least one lone pair of electrons available, suggests that the solute–solvent interactions lead to electron pair donor/electron pair acceptor complexes (EPD/EPA complexes). When an occupied molecular orbital of adequately high energy in the EPD molecule and an unoccupied molecular orbital of sufficiently low energy in the EPA entity are present, then during the encounters these orbitals (of solute and solvent) overlap and a finite electron density is created between the approaching species. The intermolecular bonding is assumed to be a hybrid of electrostatic and covalency forces. An empirical semiquantitative measure of the nucleophilic properties of EPD solvents constitutes the so-called donor number (donicity) due to Gutmann [25]. Other investigators in analogous to Gutmann's approaches have proposed additional empirical scales [26, 27]. The observed solvent shifts and the behaviour

of many solvents towards the  $[\text{Cu}(\beta\text{-dionato})\text{-dmeen}]\text{ClO}_4$  series are in concordance with Gutmann's scale of the nucleophilic properties of electron pair donor solvents in which 1,2-dichloroethane takes zero value. Regression analysis of the band maxima of  $[\text{Cu}(\text{NO}_2\text{-acac})\text{dmeen}]\text{ClO}_4$  against various basicity scales of solvents indicated that better correlation obtains when the  $D_s$  values [27] are considered (Fig. 7). Deviations are observed indicative of the complex nature of the solute-solvent interactions. For example the maximum ligand-field absorption of  $[\text{Cu}(\text{Cl-acac})\text{dmeen}]\text{ClO}_4$  in nitromethane solution occurs at higher frequency ( $1.820 \mu\text{m}^{-1}$ ) than in 1,2-dichloromethane ( $1.787 \mu\text{m}^{-1}$ ) although the donor number,  $D_N$ , of the former is 2.6. It is not unlikely that the inconsistency in the absorption maxima may be due to the interactions of the  $\text{ClO}_4^-$  group with the  $[\text{Cu}(\text{X-acac})\text{dmeen}]^+$  entity. As the relative permittivity (dielectric constant) of nitromethane takes a much higher value, this solvent facilitates the dissociation of the cationic chelate. Thus reducing the axial interactions of the counteranion and eliminating the tetragonal distortion.

In conclusion, the mixed-ligand copper(II) compounds are more stable than the corresponding  $\text{Cu}(\beta\text{-dionato})_2$  chelates and the  $[\text{Cu}(\text{dmeen})_2]^{2+}$  species. As the IR spectra reveal, the ligands coordinate through the carbonyl oxygens of the  $\beta$ -dione and both nitrogen atoms of the 1,2-diamine with copper(II) becoming the common vertex of the two chelate rings. The electronic excitation spectra disclose that the resulting  $\text{CuN}_2\text{O}_2$  chromophore of the  $[\text{Cu}(\beta\text{-dionato})\text{dmeen}]^+$  entity attains a virtually square-coplanar geometry and the nature of its interactions with anions vary. The interactions are essentially electrostatic when bulky, non-linear polyatomic anions counterbalance the positive charge. Chloride, and possibly other halides and pseudohalides, increase the coordination number of copper(II) as

implied by the virtually non-conductive nitromethane solutions indicating predominance of covalent interactions, while the electronic excitation spectra suggest the likelihood of coordination taking place along an axis perpendicular to the  $\text{CuN}_2\text{O}_2$  plane. Shifts in the band maxima disclose that the covalent interactions of the  $[\text{Cu}(\beta\text{-dionato})\text{dmeen}]^+$  entity are not limited to charged species. In strongly nucleophilic solvents donor-acceptor interactions induce tetragonal distortion of the  $\text{CuN}_2\text{O}_2$  chromophore and the ligand field band maxima correlate linearly with parameters that characterise the solvents as electron pair donors.

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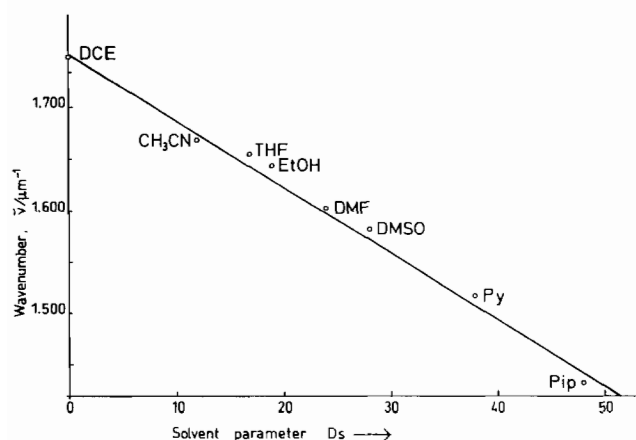


Fig. 7. Dependence of the ligand-field band maxima of  $[\text{Cu}(\text{NO}_2\text{-acac})\text{dmeen}]\text{ClO}_4$  on the solvent Donor scale,  $D_s$  value.

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