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Spectroscopic and electrochemical aspects of copper(II) chelates containing 1,2-diamines and β-ketoenols

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Abstract

The IR and electronic excitation spectra of a series of new copper(II) chelates containing the anion of a β-ketoenol (β-dione) and *N,N*-dimethyl-*N'*-ethyl-ethylenediamine (dmeen) were obtained in the solid state and in solution. Electrochemical measurements indicate enhanced stability of the ternary chelates. Their spectra suggest, in conjunction with other physicochemical measurements, that the chelate rings in the $[Cu(\beta\text{-dionato})(dmeen)]^+$ entity are coplanar. The substituents within the β-ketoenolato moiety induce electronic effects that affect the energy levels of the molecules, influence the extent of covalent interactions between the metal centre and bulky weakly coordinating anions, change the ligand field strength and may alter the course of the reaction. Solvatochromic shifts demonstrate the Lewis acidity inherent in these chelates and the tendency of the copper(II) ion to achieve coordination saturation. As good linear correlation between the donor number of a series of solvents and the energy of ligand field transitions pertains, such ternary chelates may be employed to assess the Lewis basicity of liquids.

Introduction

Spectroscopic investigations of metal(II) chelates with β-ketoenols (β-diones) and of those with aromatic and acyclic 1,2-diamines (enR) have made a significant contribution to the present understanding of the factors influencing the structure and properties of these very important classes of coordination compounds. The copper(II) chelates have been employed extensively in such studies and many features of both classes have been elucidated [1–5]. The square planar structure of the CuO_4 chromophore is omnipresent in the bis(β-dionato) copper(II) compounds with the metal ion as common vertex in the two six-membered chelate rings in which extensive electron delocalization occurs. Substituents within the β-dionato moiety engender steric and, more significantly, electronic effects that influence the charge density on the carbonyl oxygens, the electronic structure and the stability of these compounds [1–4]. Electronic absorption spectra and X-ray diffraction studies involving $[Cu(enR)_2]^{2+}$ chelates revealed the predominant planarity of the CuN_4 chromophore, the *gauche* conformation of the methylene groups and the 'strain' of the five-membered chelate rings [5]. In view of the relatively small size of the copper(II) ion, the steric interactions of the N-alkyl groups may become exceedingly strong to the extent of exclusion of the second diamine molecule from bond formation [6–9]. Under such circumstances other species, including solvent molecules, may bind to copper(II). The simultaneous presence of bidentate oxygen-bearing ligands, such as the glycinato, oxalato, cinnamato, acetylacetonato ions, with 1,2-diamine (or 1,2-diimine) affords ternary chelates [10–13]. These coordination compounds, in addition to occasional thermochromism, exhibit remarkable solvatochromic properties that may be employed to study solvent characteristics. The chelates involving *N,N,N',N'*-tetramethyl-ethylenediamine (Me_4en) and β-ketoenols have been studied to some extent [10–12]. Interesting possibilities arise when the steric restrictions emanating from the N-alkyl groups are eased and the substituents within the β-dionato moiety are altered so that the effects, steric and electronic, induced by the groups present compete for bond formation. Steric hindrance may be reduced by varying, for instance, some of the alkyl groups in substituted ethylenediamines. Such a variant is an isomer of Me_4en, the *N,N*-dimethyl-*N'*-ethyl-ethylenediamine (dmeen). This 1,2-diaminoethane derivative and a series of β-ketoenols have been employed in the work currently in progress to form mixed-ligand chelates.

The present study involving mixed-ligand copper(II) chelates of ethylenediamine derivatives and β-ketoenols was undertaken in order to investigate: (i) the influence of the substituents in bond formation, (ii) the electronic interactions of the moieties present and their influence on the reaction mechanism, (iii) the changes in electron population in the ground state brought about by the

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substituents, (iv) the ensuing consequences in group vibrations, (v) the shifts incurred in spectral bands as a result of substituent and solvent effects, and (vi) the effect of the ligands and the environment on electrochemical processes and reduction potentials. Further it was aimed to seek interrelations between experimentally obtained quantities and parameters describing the interactions induced by the substituents and the solvents. For this purpose a series of compounds obtained from the reaction of divalent transition metals with mixtures of ethylenediamine derivatives (enR) and β-ketoenols was employed. In this paper, the first of the series, some spectroscopic properties and the electrochemical behaviour of certain copper(II) chelates are reported and discussed.

Experimental

Reagents

The copper(II) salts were procured from Fluka. Ethylenediamine (1,2-diaminoethane), en, and its N-alkyl derivatives (enR), *N*-methylethylenediamine, Meen; *N,N,N'*-trimethyl-ethylenediamine, Me_3en; *N,N,N',N'*-tetramethylethylenediamine, Me_4en; *N,N*-dimethyl-*N'*-benzyl-ethylenediamine, Me_2ben; and *N,N*-dimethyl-*N'*-ethyl-ethylenediamine, dmeen, were obtained from Aldrich. The β-ketoenols, 2,2,6,6-tetramethyl-3,5-heptanedione (dipivaloylmethane, Hdpm), 2,4-pentanedione (acetylacetone, Hacac), 3-methyl-2,4-pentanedione (Me-acac), 1-phenyl-1,3-butanedione (benzoylacetone, Hbzac), 1,1,1-trifluoro-2,4-pentanedione (Htfac), 1-phenyl-4,4,4-trifluoro-1,3-butanedione (Hbztf), 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (Hhfac) and 1,3-diphenyl-1,3-propanedione (dibenzoylmethane, Hdbm) were purchased from Aldrich and Lancaster Synthesis. The β-ketoenols (β-diones) not commercially available were prepared as their sodium salts by Claisen condensation according to previously reported methods [4, 14].

Preparation of the cationic chelates

The $[Cu(enR)(\beta\text{-dionato})]^+$ ternary chelates were prepared by placing equimolar quantities of β-ketoenol and the selected *N*-alkyl-ethylenediamine (enR) in a separatory funnel containing a small amount of ethanol. Then an equimolar to either ligand quantity of copper(II) salt was added, followed by sodium carbonate sufficient to neutralize the β-dione. After shaking the mixture vigorously for a while and letting the carbon dioxide out, the solution was left unperturbed for about 15 min and subsequently was concentrated either in a water bath or by bubbling through nitrogen. The crude product separated out was recrystallized from ethanol and, subsequently, from CH_2Cl_2/isopropanol. Use of sodium salts of β-dione rendered the addition of sodium carbonate unnecessary. In certain cases sodium hydroxide or sodium acetate were employed instead of Na_2CO_3. An alternative preparative procedure involved the reaction of the appropriate β-dione with the dimeric copper(II) chelate $[Cu_2(dmeen)_2(OH)_2](ClO_4)_2$ (structure II). This μ-hydroxo bridged chelate was prepared according to the method reported by Meek and Ehrhardt [8] for the corresponding chelate of *N,N,N',N'*-tetramethyl-ethylenediamine, Me_4en, by dissolving the copper salt in 80% ethanol and adding the appropriate amount of dmeen. Another method was employed for the preparation of $[Cu(CH_3\text{-acac})dmeen]ClO_4$. In this case an equimolar quantity of $Cu(CH_3\text{-acac})_2$ was added to an aqueous solution of $[Cu(dmeen)_2](ClO_4)_2$ and the mixture was stirred until complete dissolution of the water insoluble $Cu(CH_3\text{-acac})_2$ was effected. Slow evaporation of the solvent afforded dark blue–violet crystals. The chelate $[Cu(dmeen)_2](ClO_4)_2$ was obtained by dissolving $Cu(ClO_4)_2 \cdot 6H_2O$ in dry alcohol and dehydrating the solution with 2,2-dimethoxypropane for 1 h prior to the addition of *N,N*-dimethyl-*N'*-ethyl-ethylenediamine (dmeen). The diamine, dmeen, was added dropwise in a slight excess of the stoichiometric amount while stirring continuously.

Preparation of $[Cu(\beta\text{-dionato})_2(dmeen)_x]$ adducts

The synthesis of the $[Cu(\beta\text{-dionato})_2(dmeen)_x]$ adducts (listed in Table 1) was achieved by adding the appropriate amount of dmeen in a solution of $[Cu(\beta\text{-dionato})_2$ in benzene, acetone, ethanol or CH_2Cl_2 and allowing the crystals to be formed upon slow evaporation of the solvent. Although Kuska and coworkers [3] reported the preparation of $[Cu(\beta\text{-dionato})(\beta\text{-dionato})']$ chelates and thus the possibility of forming $[Cu(\beta\text{-dionato})(\beta\text{-dionato})'(dmeen)_x]$ addition compounds with the anion of a different β-ketoenol in the place of the counterion exists, no attempt was made to prepare such chelates since they may be present in equilibrium with the $[Cu(\beta\text{-dionato})_2(dmeen)_x]$ species.

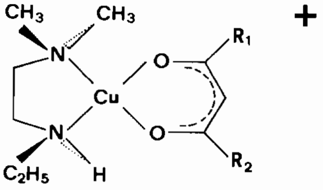
Physical measurements and determinations

Carbon, hydrogen and nitrogen were determined by microanalysis using a Perkin-Elmer 240B elemental analyser. Melting points were determined on a Reichert heated plate apparatus and are uncorrected (Table 1). Molar conductivities were measured on a WTW conductivity bridge employing a calibrated dip-type cell. The measurements were obtained in approximately 10^{-3} M solutions of analytical grade nitrobenzene and nitromethane. Magnetic susceptibility measurements in powdered samples were performed at 25 °C employing the Faraday method on a home-built balance calibrated against $Hg[Co(SCN)_4]$. Diamagnetic corrections were estimated from Pascal's constants and employing the experimental values obtained for dmeen and (RCOCHCOR′)Na. The effective magnetic moments, μ_{eff}, were calculated using the expression

$$\mu_{eff}/m_B = 48.98(T\chi_M^{corr})^{1/2} \quad (T = 928\ K)$$

Electronic spectra in solution were measured on a Shimatzu 160A spectrophotometer using 10 mm teflon stoppered quartz cells. The solid state electronic spectra were obtained from nujol mulls. IR spectra were obtained by the KBr disc technique and were recorded on a Perkin-Elmer 1430 spectrophotometer with a range 4000–200 cm^{-1} calibrated against polystyrene.

The cyclic voltammetry experiments were carried out at 25.0±0.2 in DMSO (BDH) solutions using $NaNO_3$ as supporting electrolyte. The apparatus comprised a BANK Wenking model LB81 potentiostat and a Wenking model VSG 72 function generator connected to a Hitachi VC-6030 digital storage oscilloscope and a Philips model PM8043 recorder. A three-compartment cell, immersed in a thermostated water bath, was used to carry out measurements. The compartments were separated by sintered glass. The working electrode was carbon fibres (Celanese, Celion GY-70SE) immersed to a depth of 25 mm corresponding to 1 mg. A SSCE electrode was employed as reference and a platinum foil served as the counter electrode. Oxygen was removed by purging the solution with pure nitrogen saturated with solvent vapours. Further details are given elsewhere [15].



Structure I

The new ternary copper(II) chelates are deeply coloured crystals or crystalline powders corresponding to the general formula Cu(enR)(β-dionato)Y (Y = ClO_4^-, NO_3^-) and are stable in air, both in the solid state and in organic solvents. The structure of these chelates, as the evidence suggests, seems to be planar (structure I). Although geometric isomers are envisaged when the β-ketoenol is non-symmetric ($R_1 \neq R_2$), no serious attempt was made to separate the *cis* from the *trans* isomers. The compounds prepared, their melting points and elemental analyses are listed in Table 1.

Results and discussion

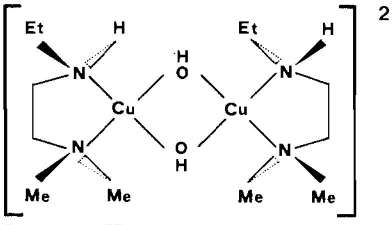
The IR spectra of the new coordination compounds in conjunction with the elemental analyses (Table 1) indicate that the simultaneous reaction of copper(II) with ethylenediamine N-derivatives (enR) and β-ketoenols affords compounds containing both ligands. In the absence of β-ketoenol the bis(diamino)copper(II) chelate, $[Cu(enR)_2]^{2+}$, may be formed. The magnetic moment of the ternary compounds listed in Table 1

TABLE 1. Yield, melting points and elemental analyses of copper(II) chelates with β-ketoenols and *N,N*-dimethyl-*N*′-ethyl-1,2-diamineethane (dmeen) and related ligands

Compound	R^1	R^3	Yield (%)	Melting point (°C)	C (%)	H (%)	N (%)
$[Cu(bdo)dmeen]ClO_4$	H	CH_3	73	110–112	33.2 (33.06)	5.85 (5.83)	7.64 (7.71)
$[Cu(ppdo)dmeen]ClO_4$	H	C_6H_5	78	108–110	41.8 (42.25)	5.39 (5.44)	6.60 (6.57)
$[Cu(npdo)dmeen]ClO_4$	H	$C_{10}H_7$	81	103–105	48.4 (47.90)	5.25 (5.29)	5.82 (5.88)
$Cu(acac)dmeen]ClO_4$	CH_3	CH_3	82	120–121	35.0 (34.92)	6.13 (6.13)	7.53 (7.41)
$[Cu(apm)dmeen]ClO_4$	CH_3	$C(CH_3)_3$	76	125–128	39.8 (40.00)	7.00 (6.95)	6.70 (6.67)
$[Cu(bzac)dmeen]ClO_4$	C_6H_5	CH_3	79	173–175	43.9 (43.64)	5.68 (5.72)	6.29 (6.36)
$[Cu(dbm)dmeen]ClO_4$	C_6H_5	C_6H_5	69	243–245	50.1 (50.20)	5.39 (5.42)	5.61 (5.58)
$[Cu(bzpm)dmeen]ClO_4$	C_6H_5	$C(CH_3)_3$	84	139–141	48.1 (47.30)	6.77 (6.48)	5.85 (5.81)
$Cu(dpm)dmeen]ClO_4$	$C(CH_3)_3$	$C(CH_3)_3$	78	159–161	44.6 (44.15)	7.70 (7.63)	6.00 (6.06)
$[Cu(bztf)dmeen]ClO_4$	C_6H_5	CF_3	86	104–106	39.2 (38.87)	4.52 (4.49)	5.59 (5.67)
$[Cu(CH_3\text{-}acac)dmeen]ClO_4$	CH_3	CH_3	81	122–123	37.0 (36.71)	7.22 (7.14)	6.67 (6.41)
$[Cu(bzac)Meen]ClO_4$	C_6H_5	CH_3	73	175–177	39.5 (39.20)	4.88 (4.81)	6.91 (7.03)
$[Cu(acac)Me_3en]ClO_4$	CH_3	CH_3	83	152–154	32.6 (32.97)	5.75 (5.81)	7.74 (7.69)
$[Cu(dpm)dmeen]NO_3$	$C(CH_3)_3$	$C(CH_3)_3$	28	139–141	40.0 (48.03)	8.37 (8.30)	9.92 (9.89)
$[Cu(bzac)dmeen]NO_3$	C_6H_5	CH_3	77	183–187	47.4 (47.69)	6.21 (6.25)	10.35 (10.43)
$[Cu(bztf)_2dmeen]$	C_6H_5	CF_3	76	91–95	61.3 (62.19)	6.79 (6.83)	5.74 (5.58)
$[Cu(bztf)_2dmeen_2]$	C_6H_5	CF_3	73	87–89	51.7 (52.92)	6.29 (6.11)	7.98 (7.71)
$[Cu(dmeen)_2](ClO_4)_2$			76	179–181	28.9 (29.12)	6.45 (6.52)	11.27 (11.32)
$[Cu(dmeen)_2](NO_3)_2$			65	191–192	34.1 (34.32)	7.72 (7.68)	19.89 (20.01)
$[Cu(dmeen)_2(OH)_2](ClO_4)_2$			77	129–132	24.4 (24.33)	5.83 (5.79)	9.38 (9.46)

are in the range of 1.69–2.00 m_B 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 ions being in a non-degenerate ground state. The solutions of the perchlorate series in nitromethane ($\Lambda_M = 80\text{–}106$ S cm^2 M^{-1}) and in nitrobenzene ($\Lambda_M = 20\text{–}29$ S cm^2 M^{-1}) are electrically conductive and the corresponding molar conductivity values indicate that the new compounds are 1:1 electrolytes that dissociate appreciably. The behaviour of $[Cu(dpm)(dmeen)]NO_3$ in these solvents is quite different and the low molar conductivity values ($\Lambda_M = 33$ S cm^2 M^{-1} in nitromethane and $\Lambda_M = 6.8$ S cm^2 M^{-1} in nitrobenzene) suggest that the covalent interactions of the nitrate anion are extensive. Increase in the coordination number of copper(II) and possible change of structure are envisaged in cases in which strong tendency for coordination characterizes the anion. Preliminary results indicated that the NO_3^- and ClO_4^- groups are readily replaced by anions such as the halides and pseudohalides.

Substituted 1,2-diamines, especially those having tertiary amino groups, induce enhanced coordination stability when incorporated into a chelate ring (the chelate effect). In accordance with the reactivity of copper(II) towards other 1,2-diamines [5–9] the reaction of copper(II) with *N*,*N*-dimethyl-*N*′-ethyl-ethylenediamine apparently proceeds in two main steps. Molecular models in which the methylene groups attain *gauche* conformation and the van der Waals volumes of the groups comprising the diamine molecule are taken into account, indicate increased strain in the formation of $[Cu(dmeen)_2]^{2+}$ species as compared to $[Cu(dmeen)]^{2+}$ since the small size of Cu^{2+} permits close proximity of the approaching ligand to the coordinated one. However, while the preparation of $[Cu(dmeen)_2]^{2+}$ under favourable experimental conditions is facile, the reaction of copper(II) with *N*,*N*,*N*′,*N*′-tetramethylethylenediamine, Me_4en, affords invariably the μ-hydroxo bridged binuclear copper(II) chelate [8], $[Cu_2(Me_4en)_2(OH)_2]^{2+}$. Comparison of the behaviour of the two diamines (Me_4en and dmeen) towards copper(II) suggests that, if only steric interactions were operative, the repulsion between the N-alkyl groups on adjacent ligands are reduced and the strain induced by the fourth methyl group is eased when replaced by the hydrogen atom, to the extent that even an ethyl group may be accommodated in geminal to hydrogen position. The spatial requirements of the N-alkyl groups in these copper(II) chelates are reconciled when the ligands adopt configuration with the ethyl groups opposite the hydrogen atoms. Other arrangements are thermodynamically less stable for reasons of steric hindrance. The importance of steric inhibition is further demonstrated when the ethyl group is replaced by a bulkier one, for instance the benzyl group, although its electronic effects make it not the most judicious choice to study size effects. The reaction of copper(II) with *N*,*N*-dimethyl-*N*′-benzyl-ethylenediamine also results in formation of the corresponding binuclear chelate as suggested by Pfeiffer and Glaser [6] and other investigators [7–9] when steric hindrance prevails. The hydroxo bridge is revealed by the intense peak at 3424 cm^{-1} and the Cu–Cu magnetic interaction is evidenced by the magnetic moments ($\mu_{eff} = 1.54$ m_B). It should be noted that the μ-hydroxo bridged binuclear chelate $[Cu_2(dmeen)_2(OH)_2]^{2+}$ (structure II) is obtained when the reaction of copper(II) with the appropriate amount of dmeen takes place in 80% ethanol.



Structure II

The 1:1 copper(II)–dmeen chelate, $[Cu(dmeen)]^{2+}$, appears to possess discriminating qualities towards other ligands and the tendency of the 1:1 copper(II)–diamino species to preferably coordinate to oxygen-containing anionic compounds is a more general one. In the present investigation the preference of $[Cu(dmeen)]^{2+}$ towards coordination to some β-ketoenols should additionally be attributed to the difficulty of copper(II) ion to accommodate just as easily the second dmeen molecule. $[Cu(dmeen)_2]^{2+}$ is in most cases less stable, as would have been expected on the grounds of steric effects, than the ternary chelate which is formed in good yield on addition of the anion of a β-ketoenol to a solution of $[Cu(dmeen)]^{2+}$. The reduction of charge in $[Cu(dmeen)(\beta\text{-dionato})]^+$ suggests that enthalpy (coulombic) and entropy (decrease of the extent of orientation of solvent molecules) effects favour the formation of ternary chelates. Coordination of the β-ketoenol takes place through the carbonyl oxygen atoms and an additional chelate ring (a six-membered one) is formed with the copper(II) ion as common vertex. In these compounds the σ-bonding in the metal–oxygen bond is covalent in nature and it is extensively delocalized over both the copper and the β-ketoenol orbitals.

The electron distribution in the reacting β-ketoenols apparently influences bond formation since difficulties were encountered when polyfluorinated β-ketoenols were employed to form ternary chelates. Preliminary quantum chemical calculations suggest a destabilizing effect of the terminal $-CF_3$ group. Only the use of 1-phenyl-4,4,4-trifluoro-1,3-butanedione ($PhCOCH_2COCF_3$, Hbztf) met with success and [Cu(dmeen)-

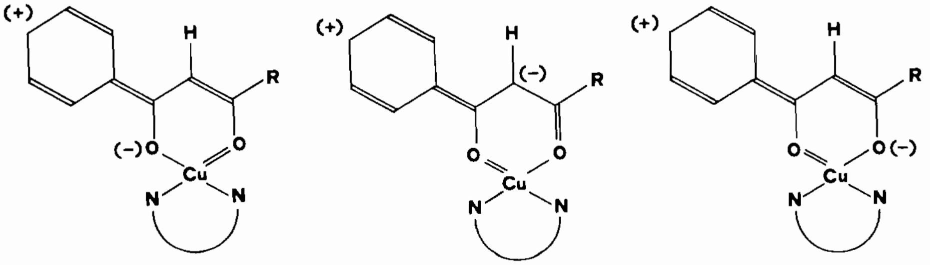
(bztf)]$^+$ was obtained in high yield. The reaction of [Cu(dmeen)]$^{2+}$ with either tfac$^-$ or hfac$^-$ failed to produce the expected ternary chelates under the conditions described This is in contrast to the behaviour of copper(II) towards these ligands in the presence of *N,N,N',N'*-tetramethyl-ethylenediamine [10]. The formation of the corresponding ternary chelates, [Cu(Me$_4$en)(tfac)]$^+$ and [Cu(Me$_4$en)(hfac)]$^+$, excludes steric hindrance as the reason for the change in the reaction path. Rather the NH group seems to affect profoundly the mechanism of the reaction in conjunction with the electronic structure of β-ketoenols since the latter influences their mode of bonding. In β-ketoenols the carbonyl groups flanking the methylene carbon are susceptible to both resonance and field (pure field and inductive) effects brought about by substituents attached to the carbon atoms of the afore-mentioned groups. The spontaneity of the formation of [Cu(acac)dmeen]$^+$ suggests that electron-repelling groups, i.e. $-CH_3$, $-C(CH_3)_3$, facilitate coordination of the β-ketoenol. On the other hand, the presence of electron-attracting substituents in hfac$^-$ makes the β-ketoenol more acidic and renders the electron density on the carbonyl oxygen atoms such that other reaction paths are favoured [16, 17], as the isolation of [Cu(hfac)$_2$dmeen] among the reaction products indicates. Similar behaviour of hfac$^-$ was observed [17] when it was added in admixture with 1,2-dipiperidinoethane to an ethanolic solution of $Cu(ClO_4)_2 \cdot 6H_2O$.

The sensitivity of formation of the ternary chelates to various effects is further manifested in the case of the anions tfac$^-$ and bzac$^-$. These ligands may be thought of as resulting from acac$^-$ by replacing one methyl group with $-CF_3$ (in tfac$^-$) or with a phenyl group (bzac^{-1}). The reduction of charge in the oxygen atoms of tfac$^-$ by the field effect of the $-CF_3$ group is substantial and bond formation between copper(II) in [Cu(dmeen)]$^{2+}$ and the acidic β-ketoenol probably takes a different path. The field effect created by the phenyl group in bzac$^-$ also reduces the electronic charge on the carbonyl oxygen but to a lesser extent. At the same time the mutual coplanarity of the phenyl group with the chelate ring [18] facilitates resonance interaction and the ensuing charge accumulation on the oxygen atoms (structure III) strengthens the Cu–O bond. The importance of this delocalization becomes apparent in the case of bztf$^-$ where the resonance interaction of the phenyl ring cancels out the field effect of the $-CF_3$ group. The resulting extensively delocalized π-system allows the formation of [Cu(bztf)dmeen]$^+$ which is obtained in good yield. The relative importance of steric and electronic effects is further demonstrated in the case of similarly structured ligands. While the attempts to form ternary chelates of ethylenediamine did not afford the desired products, the compounds [Cu(acac)Me$_3$en]ClO$_4$ and [Cu(bzac)-Meen]ClO$_4$ were prepared without undue difficulty.

It is known that copper(II) ion has a tendency towards oxygen or nitrogen to attain a coordination number greater than four. The [Cu(enR)$_2$]$^{2+}$ species form adducts and so do the bis(β-dionato)copper(II) compounds in order to achieve coordination saturation [16]. Incorporation of electron-attracting substituents lowers the stability of the copper(II) β-ketoenolates while at the same time increases their strength as Lewis acids thus enhancing their affinity for axial ligation. Consequently more stable addition compounds are obtained. Addition of dmeen to solutions of some Cu(β-dionato)$_2$ chelates, a.g. Cu(dbm)$_2$, Cu(tfac)$_2$, Cu(bztf)$_2$, Cu(hfac)$_2$, caused a bathochromic shift and an hyperchromic effect in the electronic excitation spectra and resulted in adduct formation. The [Cu(β-dionato)$_2$dmeen] adducts may be regarded as an interesting variant of the [Cu(β-dionato)dmeen]$^+$ species in which the (positive) charge is counterbalanced by the β-ketoenol anion. In certain cases, as described above, the stability of the neutral species is greater than that of the cationic ones. The structure of these addition compounds is thought to be pseudooctahedral with no coplanar chelate rings as suggested [19] for Cu(hfac)$_2$bipy. Confirmation of the existence of the addition compounds and the cationic chelates was also obtained from the electrochemical experiments.

Electrochemical measurements

Recourse to the electrochemical behaviour of solvated copper(II) and the Cu(β-dionato)$_2$ chelates at the carbon fibre electrode in acetonitrile [4] leads to expectation of two one-electron cathodic waves in the cyclic voltammograms of the present series. Considering a typical



member of the present series, e.g. [Cu(bzac)dmeen]$^+$, its electrochemical behaviour in DMSO at the same electrode (carbon fibre) appears rather complicated because of the small additional peaks in the region 0.0 to -0.4 V (Fig. 1). The coordinating solvent, the lability of copper(II) and the presence of other ions at high concentration, such as the NO_3^-, insinuate the possibility of complex equilibria in the system under consideration. In an attempt to assign the observed peaks to specific processes, the cyclic voltammograms of $Cu(NO_3)_2$ were recorded (Fig. 2). The two peaks appearing during the cathodic scan are not difficult to assign. The first peak at -0.06 V (peak a) should be attributed to one-electron reduction of the solvated copper(II) to $Cu^+(s)$, while the second peak at -0.57 V (peak b) is apparently associated with the reduction of $Cu^+(s)$ and the subsequent deposition of metallic copper to the carbon fiber, as the appearance of the anodic peak at 0.04 V (peak b′) during the reverse scan suggests. Addition of the 1,2-diamine (dmeen) sufficient to form the $[Cu(dmeen)_2]^{2+}$ species or, otherwise, employment of the actual chelate itself, shifts, as expected, the reduction potentials to -0.12 and -1.04 V, respectively. The shifts to more negative potentials are associated with coordination that results in lower energy orbitals due to ligand field stabilization.

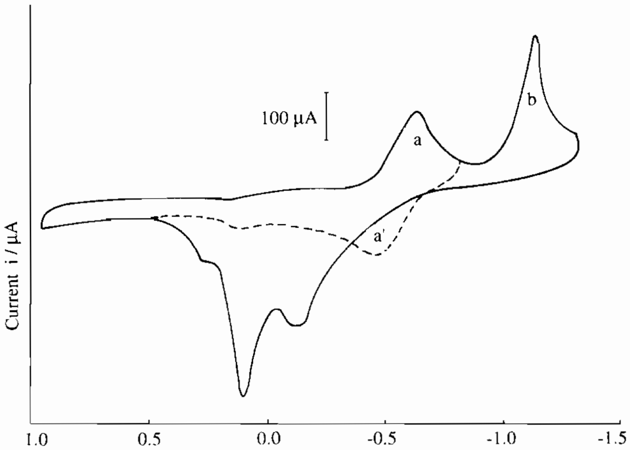


Fig. 1. Cyclic voltammogram ($\nu = 100$ mV s^{-1}) of $[Cu(bzac)(dmeen)]NO_3$ in DMSO at the carbon fibre electrode.

More informative proved to be the cyclic voltammograms of $Cu(bzac)_2$ (Fig. 3), a substance in which attachment of DMSO takes place, as the spectra and the isolation of the corresponding addition compound of $Cu(tfac)_2$ suggests. Addition of $Cu(NO_3)_2$ to solutions of $Cu(bzac)_2$ leads to enhancement of peaks a and especially b. The same peaks are suppressed upon addition of Nabzac. It seems reasonable to assume that while peak a stems from the solvated copper(II), $Cu^{2+}(s)$, peak b should be associated with the acquisition of one electron by the species $[Cu(bzac)(NO_3)]$ (Fig. 3). Replacement of the nitrates by an additional anion of 1-phenyl-1,3-butanedione, bzac$^-$, causes a further shift of the potential to negative values, so that the one-electron reduction of $Cu(bzac)_2$ to $[Cu(bzac)_2]^-$ occurs at -0.81 V (peak c). The reduction of the latter species and deposition of elemental copper on the carbon fibre occurs at -1.11 V (peak d). The cyclic voltammograms of equimolar mixtures of $Cu(bzac)_2$ and $[Cu(dmeen)_2](NO_3)_2$ were identical to those obtained employing pure ternary chelate, suggesting that ligand exchange occurs readily. The cathodic peak at -0.64 V and the corresponding anodic peak at -0.47 V in Fig. 1 (peaks a and a′) should be associated with one-electron transfer to $[Cu(bzac)(dmeen)]NO_3$ and the

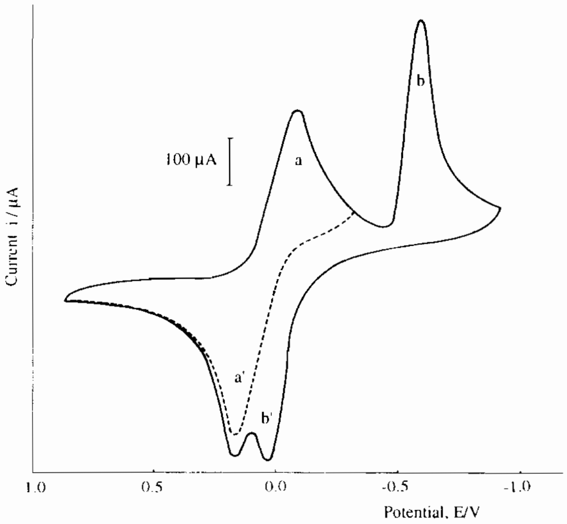


Fig. 2. Cyclic voltammogram ($\nu = 100$ mV s^{-1}) of $Cu(NO_3)_2$ in DMSO at the carbon fibre electrode.

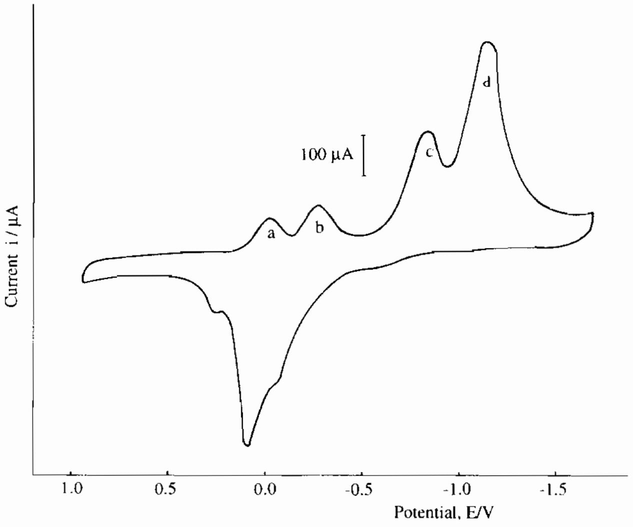


Fig. 3. Cyclic voltammogram ($\nu = 100$ mV s^{-1}) of $Cu(bzac)_2$ in DMSO at the carbon fibre electrode.

reverse process, respectively. Acquisition of a second electron at −1.14 V (peak b, Fig. 1) is followed by rapid loss of the ligands and deposition of elemental copper onto the carbon fibre. Reversal of the potential scan induces electrodissolution and conversion of metallic copper to Cu(II) state, as the anodic peaks indicate. A detailed account on the electrochemical behaviour of this class of mixed-ligand chelates and the factors influencing redox potentials will be given in a forthcoming report [15].

Infrared spectra

In the IR spectra of the ternary compounds a plethora of bands appears stemming from the chemical entities present in the newly obtained chelates. Bond formation is revealed by absorptions in specific regions of the spectra and the disappearance of certain bands that are observed in spectra of the free ligands. Assignment of bands to specific vibrations is facilitated by comparison with the spectra of the [Cu(β-dionato)$_2$] chelates, the IR spectrum of [Cu(en)$_2$]$^{2+}$ and the spectra of model compounds [5, 20–27]. The bands are distinguished in those due to the ligands and in those emanating from the counterion (Table 2).

Counterion spectra

The broad band observed at about 1400 cm^{-1} in the spectrum of [Cu(dpm)dmeen]NO$_3$, notwithstanding other groups that also absorb in the same region, should be attributed to the NO$_3^-$ group because it does not appear in the spectra of, for example, [Cu(acac)dmeen]ClO$_4$ or [Cu(dmeen)$_2$](ClO$_4$)$_2$ (Fig. 4). In the solid state FT-IR spectra of [Cu(bzac)dmeen]NO$_3$ a double medium-intensity band with peaks at 1752 and 1729 cm^{-1} indicates that the NO$_3^-$ group behaves as monodentate ligand [27].

The main feature in the [Cu(β-dionato)dmeen]ClO$_4$ series is the very broad intense band with a poorly defined maximum corresponding to the triply degenerate asymmetric stretching vibration (T$_2$) of the tetrahedral ClO$_4^-$ group observed at 1090 cm^{-1} in the spectrum of KClO$_4$. The presence of the ClO$_4^-$ group is further manifested by the theoretically forbidden very weak absorption at ~930 cm^{-1} which is due to the non-degenerate symmetric stretching vibration (A$_1$) that becomes weakly allowed owning to distortion of the tetrahedral ClO$_4^-$ ion in a crystal field of lower symmetry than itself.

Changes in the shape and the position of bands stemming from the counterion are observed upon replacement of electron-repelling groups existing within the β-dionato moiety by increasingly electron-attracting substituents. Considering the tendency of the four-coordinate copper(II) to achieve coordination saturation, these changes suggest that the counterion–copper(II) interactions may not be purely ionic. Such interactions have been observed in [Cu(enR)$_2$]$^{2+}$ chelates and the term 'semi-coordination' has been used [5f] to describe the phenomenon. Whenever coordination of the perchlorato group occurs, it attains a lower symmetry and the degeneracy of certain vibrations is reduced with consequent splitting of the bands ob-

TABLE 2. Wavenumber of the $\mathrm{C}\underline{\cdots}\mathrm{O}$, $\mathrm{C}\underline{\cdots}\mathrm{C}$ and N–H stretching vibrations of a series of [Cu(β-dionato)dmeen]ClO$_4$ chelates and related compounds

Compound	R^1	R^2	R^3	$\mathrm{C}\underline{\cdots}\mathrm{O}$ $\tilde{\nu}$ (cm^{-1})	$\mathrm{C}\underline{\cdots}\mathrm{C}$ $\tilde{\nu}$ (cm^{-1})	N–H $\tilde{\nu}$ (cm^{-1})
[Cu(bdo)dmeen]ClO$_4$	H	H	CH$_3$	1595	1530	3230
[Cu(ppdo)dmeen]ClO$_4$	H	H	C$_6$H$_5$	1590	1565	3240
[Cu(npdo)dmeen]ClO$_4$	H	H	C$_{10}$H$_7$	1600	1570	3260
[Cu(acac)dmeen]ClO$_4$	CH$_3$	H	CH$_3$	1588	1530	3230
[Cu(apm)dmeen]ClO$_4$	CH$_3$	H	C(CH$_3$)$_3$	1590	1555	3220
[Cu(bzac)dmeen]ClO$_4$	C$_6$H$_5$	H	CH$_3$	1592	1560	3225
[Cu(dbm)dmeen]ClO$_4$	C$_6$H$_5$	H	C$_6$H$_5$	1605	1555	3220
[Cu(bzpm)dmeen]ClO$_4$	C$_6$H$_5$	H	C(CH$_3$)$_3$	1590	1545	3230
[Cu(dpm)dmeen]ClO$_4$	C(CH$_3$)$_3$	H	C(CH$_3$)$_3$	1590	1570	3230
[Cu(bztf)dmeen]ClO$_4$	C$_6$H$_5$	H	CF$_3$	1615	1578	3215
[Cu(CH$_3$-acac)dmeen]ClO$_4$	CH$_3$	CH$_3$	CH$_3$	1585	1585	3230
[Cu(bzac)Meen]ClO$_4$	C$_6$H$_5$	H	CH$_3$	1595	1565	3225
[Cu(acac)Me$_3$en]ClO$_4$	CH$_3$	H	CH$_3$	1585	1530	3215
[Cu(dpm)dmeen]NO$_3$	C(CH$_3$)$_3$	H	C(CH$_3$)$_3$	1590	1568	3190
[Cu(bzac)dmeen]NO$_3$	C$_6$H$_5$	H	CH$_3$	1594	1565	3190
[Cu(bztf)$_2$dmeen]	C$_6$H$_5$	H	CF$_3$	1625	1574	3275
Cu(bztf)$_2$dmeen$_2$]	C$_6$H$_5$	H	CF$_3$	1625	1574	3270
[Cu(dmeen)$_2$](ClO$_4$)$_2$						3225
[Cu(dmeen)$_2$](NO$_3$)$_2$						3190
[Cu$_2$(dmeen)$_2$(OH)$_2$](ClO$_4$)$_2$						3372

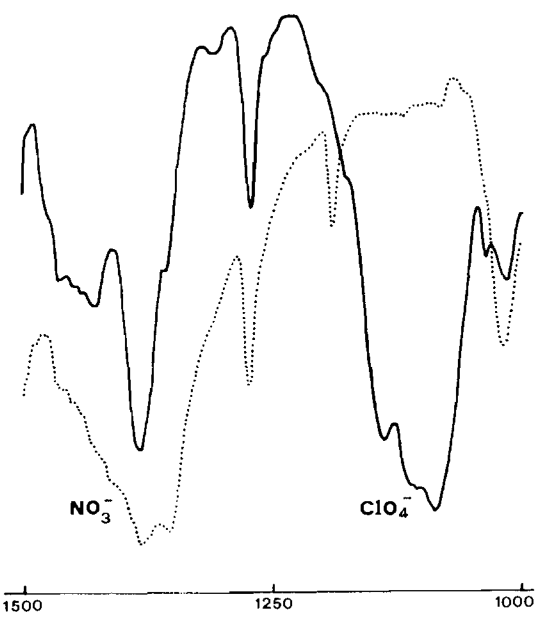


Fig. 4. Bands in the IR spectra of [Cu(acac)dmeen]Y (Y = NO_3^-, ClO_4^-) emanating from the counterion.

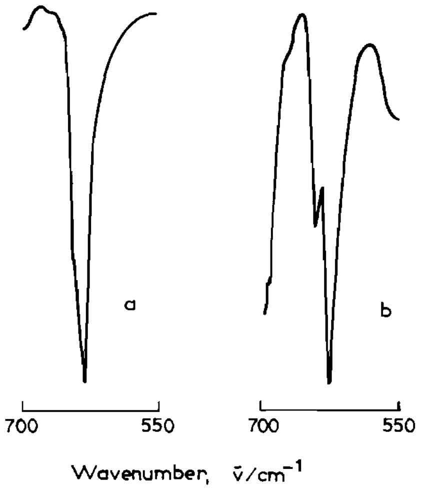


Fig. 5. Bands in the IR spectra of [Cu(dpm)dmeen]ClO_4 (a) and [Cu(dbm)dmeen]ClO_4 (b) due to the counterion.

served in the free ClO_4^-. Information on the mode of existence of the ClO_4^- group should be obtained from bands that, in the absence of other vibrations absorbing in the same region, can be unambiguously assigned to that entity. Apparently the band at 1087 cm^{-1} cannot serve that purpose since the diamine also absorbs in the same region. More informative is the sharp intense band occurring in the spectrum of [Cu(dpm)dmeen]ClO_4 at 626 cm^{-1} (Fig. 5a) which is due to the degenerate asymmetric bending vibration of the ClO_4^- group [26b] and is indicative of persisting T_d symmetry. This band remains unsplit in the spectrum of [Cu(acac)dmeen]ClO_4 while upon insertion of electron-delocalizing groups, i.e. $-C_6H_5$, a splitting is evident as in the spectrum of [Cu(dbm)dmeen]ClO_4 (Fig. 5b), suggesting involvement of the perchlorato group in partial covalent bonding between one of its oxygens and copper(II) and reduction of the symmetry of the perchlorato group to C_{3v}.

Ligand spectra

Formation of a six-membered chelate ring comprising the copper(II) and the β-dionato moiety is disclosed by the intense absorptions in the region 1650–1500 cm^{-1}, attributed to the perturbed C⎓O and the conjugated C⎓C bonds. The assignment of bands follows the proposals of Bellamy and Branch [20] and are based on the irrefutable experimental evidence provided by Pinchas *et al.* [21] and subsequent investigators [22, 23]. The susceptibility of the C⎓O and the conjugated C⎓C bonds to mass and electronic effects has been established by many investigators (see ref. 23). In addition to the changes in frequency of the C⎓O and C⎓C⎓C vibrational modes incurred upon formation of the metal–oxygen bonds, frequency shifts are observed, besides those engendered by substituents attached to the chelate ring (Table 2).

Comparison of the IR spectra of the ternary chelates with those of the bis(β-dionato)copper(II) compounds and the dmeen adducts reveals that the influence of the coordinated diamine (dmeen) to certain vibrations of the β-dionato moiety is quite important while the effect of the counterions ClO_4^- and NO_3^- only marginal. Figure 6 depicts the frequency shifts and intensity changes in the 1700–1400 cm^{-1} region of the spectrum of Cu(bztf)$_2$ effected when, under appropriate conditions, the 1,2-diamine forms an adduct or ternary chelate. Similar changes are observed in the spectra of the other ternary chelates and are not restricted in the region just mentioned. For instance, in the spectrum of Cu(acac)$_2$ the band attributed to the perturbed C⎓O is shifted from 1578 to 1590 cm^{-1} while the frequency of the band stemming from the conjugated C⎓C bonds remains unchanged. The band at 1548 cm^{-1}, which is considered to be a combination band between the IR active and the inactive out-of-plane CH vibrations, γ(C–C–H), loses intensity and becomes a barely discernible shoulder of the band at 1590 cm^{-1}. The band at 780 cm^{-1} due to the afore-mentioned IR active out-of-plane CH vibrations, also diminishes in intensity and is shifted to 795 cm^{-1}.

Changes are also observed in bands emanating from the coordinated dmeen. The assignment of the multitude of bands that are observed in he IR spectra of [Cu(dmeen)$_2$]Y_2 (Y = ClO_4^-, NO_3^-) is facilitated by the work of Powell and Sheppard [24] and subsequent investigators [5, 24–26]. The prominent bands in the IR spectrum of the free base, dmeen, in the region

Fig. 6. Differences in the IR spectra of [Cu(bztf)dmeen]ClO$_4$ (–··–) and Cu(bztf)$_2$ (– – –), and changes incurred upon adduct formation, [Cu(bztf)$_2$dmeen] (——).

2850 ± 100 cm^{-1} that are associated with the N–CH$_2$ group serve as an indication of coordination of *N*,*N*-dimethyl-*N*′-ethyl-ethylenediamine. Upon coordination of dmeen they become shifted to higher frequencies while their intensity diminishes. In the region 1600 to 600 cm^{-1} four bands of medium intensity that appear in the spectra of the free base also persist and remain unshifted in the spectra of [Cu(dmeen)$_2$]Y$_2$. It is very likely that the bands at 1380, 1250 and 790 cm^{-1} are associated with the wagging, twisting and rocking vibrations of the CH$_2$ group, respectively, while the fourth band at 958 cm^{-1} probably originates from the stretching vibration of the C–C bond of the diamino ligand.

Of interest is the single band of medium intensity that in the free dmeen peaks at 3310 cm^{-1} and does not appear in the IR spectra of the bis(β-dionato)copper(II) chelates. Upon coordination the frequency of this band is shifted to lower wavenumbers. In [Cu(dmeen)$_2$]Y$_2$ the extent of the shift depends on the anion Y. For example in [Cu(dmeen)$_2$](ClO$_4$)$_2$ it is observed at 3225 cm^{-1} while in [Cu(dmeen)$_2$](NO$_3$)$_2$ the band occurs at only 3190 cm^{-1}. The association of this band with the N–H stretching vibration is apparent. In [Cu(dpm)dmeen]NO$_3$ a broad band appears in the place of the sharp band (at 3225 cm^{-1}) and the position of the maximum, although difficult to define, is also shifted to lower frequencies. The broadening of the band suggests extensive interactions of the hydrogen atom with the NO$_3^-$ oxygen and, possibly, hydrogen bond formation.

Electronic excitation spectra

There are distinct differences between the electronic absorption spectra of the ternary copper(II) chelates and the corresponding bis(β-dionato)copper(II) ones, both in the bands occurring in the visible and in those observed at higher transition energies. While two or more ligand field bands are discernible in the electronic excitation spectra of the Cu(β-dionato)$_2$ compounds at wavelengths longer than 500 nm, the reflectance spectra of [Cu(β-dionato)dmeen]$^+$ species are characterized by a broad structureless band (envelope) in the same region (Fig. 7). It is likely that this envelope comprises the bands emanating from transitions within the metal d orbitals whose degeneracy is lifted. The same envelope appears when the spectra are obtained employing 1,2-dichloroethane solutions and, disregarding the occasional blue shift, it shows similarities with the spectra of [Cu(dmeen)$_2$]$^{2+}$ and other [Cu(enR)$_2$]$^{2+}$ chelates in which the copper ion effectively exists in a square-planar environment with a $^2B_{1g}$ ground state [2, 5]. The shift of the extremum of the envelope of the [Cu(β-dionato)dmeen]$^+$ species is much smaller and in the opposite direction to that observed in the spectra of the μ-hydroxo-bridged dimer (Table 3).

Small but discernible shifts in the extremum of the envelope attend the replacement of the substituents within the β-dionato moiety. Electron-donating substituents shift the extremum of the envelope to higher excitation energies while a bathochromic shift accompanies the insertion of electron-withdrawing groups (Table 3). The nature of the counterion also influences the position of the extremum. Replacement of the

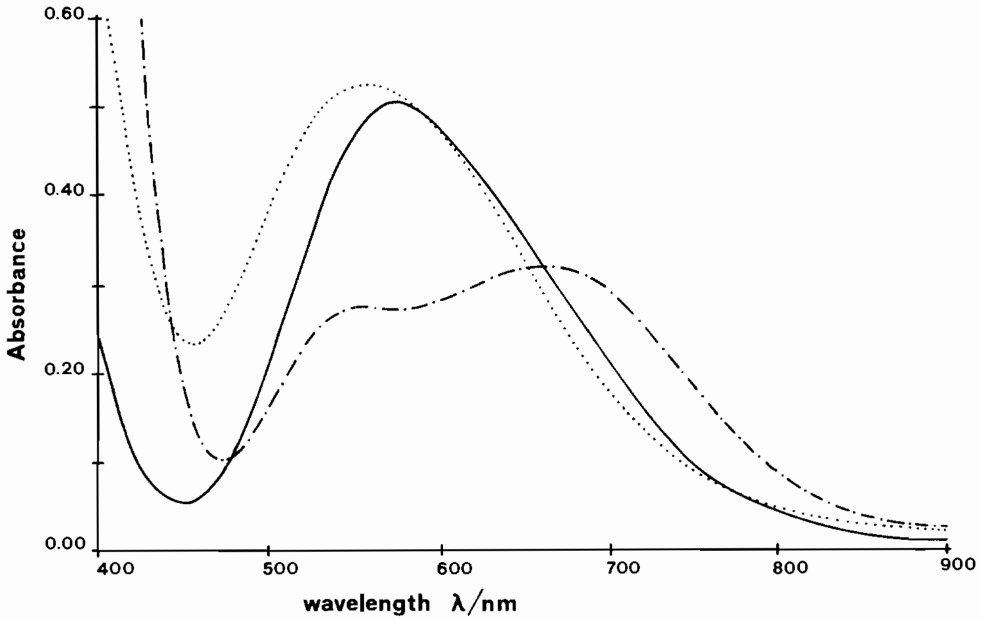


Fig. 7. Electronic absorption spectra of [Cu(acac)dmeen]ClO_4 (···), [Cu(dmeen)$_2$]$(ClO_4)_2$ (——) and Cu(acac)$_2$ (–·–) in CH_2Cl_2.

TABLE 3. Wavenumber of the ligand field band maxima in the electronic excitation spectra of a series of [Cu(β-dionato)dmeen]ClO_4 chelates and related compounds in solvents of different donor number

Compound	R^1	R^2	R^3	$C_2H_4Cl_2$ $\tilde{\nu}$ (μm^{-1})	C_2H_5OH $\tilde{\nu}$ (μm^{-1})	DMF $\tilde{\nu}$ (μm^{-1})	DMSO $\tilde{\nu}$ (μm^{-1})
[Cu(bdo)dmeen]ClO_4	H	H	CH_3	1.740	1.730	1.635	1.610
[Cu(ppdo)dmeen]ClO_4	H	H	C_6H_5	1.720	1.705	1.610	1.595
[Cu(npdo)dmeen]ClO_4	H	H	$C_{10}H_7$	1.725	1.705	1.630	1.605
[Cu(acac)dmeen]ClO_4	CH_3	H	CH_3	1.760	1.742	1.655	1.615
[Cu(apm)dmeen]ClO_4	CH_3	H	$C(CH_3)_3$	1.770	1.753	1.660	1.634
[Cu(bzac)dmeen]ClO_4	C_6H_5	H	CH_3	1.750	1.740	1.640	1.625
[Cu(dbm)dmeen]ClO_4	C_6H_5	H	C_6H_5	1.735	1.730	1.635	1.620
[Cu(bzpm)dmeen]ClO_4	C_6H_5	H	$C(CH_3)_3$	1.740	1.735	1.640	1.625
[Cu(dpm)dmeen]ClO_4	$C(CH_3)_3$	H	$C(CH_3)_3$	1.789	1.755	1.665	1.650
[Cu(bztf)dmeen]ClO_4	C_6H_5	H	CF_3	1.720	1.665	1.585	1.570
[Cu(CH_3-acac)dmeen]ClO_4	CH_3	CH_3	CH_3	1.759	1.770	1.680	1.638
[Cu(bzac)Meen]ClO_4	C_6H_5	H	CH_3	1.748	1.675	1.634	1.625
[Cu(acac)Me$_3$en]ClO_4	CH_3	H	CH_3	1.786	1.765	1.675	1.638
[Cu(dpm)dmeen]NO_3	$C(CH_3)_3$	H	$C(CH_3)_3$	1.688			
[Cu(bzac)dmeen]NO_3	C_6H_5	H	CH_3	1.667	1.655	1.625	1.620
[Cu(bztf)$_2$dmeen]	C_6H_5	H	CF_3	1.470	1.470		1.513
[Cu(bztf)$_2$dmeen$_2$]	C_6H_5	H	CF_3	1.444	1.495		1.485
[Cu(dmeen)$_2$]$(ClO_4)_2$				1.789	1.758		1.512
[Cu(dmeen)$_2$]$(NO_3)_2$				1.587	1.648	1.567	1.505
[Cu_2(dmeen)$_2$$(OH)_2$]$(ClO_4)_2$				1.859		1.745	1.703

ClO_4^- ion by NO_3^- also results in a small bathochromic shift indicative of the enhanced interactions of the latter ion with the central atom. The differences persist in solutions of non-coordinating solvents but they are gradually eliminated as the ability of the solvent for coordination is enhanced (Table 3). Actually as the coordinating ability of the solvent increases the extremum of the envelope is red-shifted and the shifts induced by solvents may well exceed any other shifts.

The solvent shifts, which are well documented in the case of Cu(β-dionato)$_2$ species [1], suggest that the axial interactions are not restricted to negatively charged ions and reflect the tendency of four-coordinated copper(II) to achieve coordination saturation. The shifts also suggest that the ternary chelates retain sufficient Lewis acidity to form addition compounds even with weak Lewis bases. A measure of the coordinating ability of a given solvent is Gutmann's 'donor number'

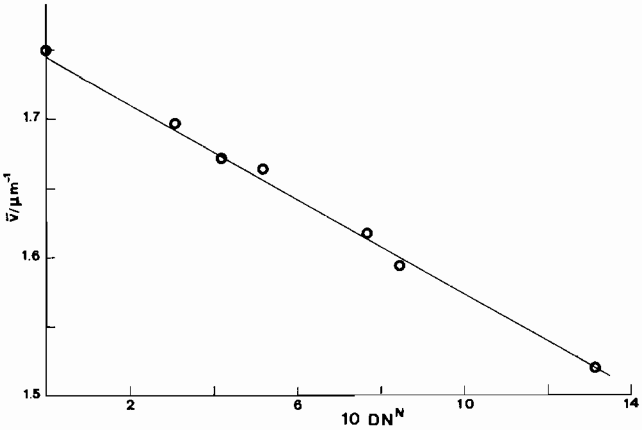


Fig. 8. Dependence of the excitation energy (band maxima) of the ligand field transitions of [Cu(bzac)dmeen]ClO_4 on the normalized donor number, DN^N, of the solvents.

('donicity') [28]. In order to further probe the Lewis acidity of the present series, the compound [Cu(bzac)dmeen]ClO_4 was arbitrarily selected and the spectra in the visible in a series of solvents were recorded. The wavenumber of the extremum of the envelope was plotted against the normalized donor number, DN^N, of the solvents employed. The straight line obtained (Fig. 8) suggests that a good correlation pertains between excitation maxima and solvent donor number (DN^N: 1,2-dichloroethane 0.00, acetonitrile 0.36, dimethylformamide 0.69, DMSO 0.77, pyridine 0.85, piperidine 1.31) so that this chelate, as well as the other members of the series, may be employed as a 'rule of thumb' for the spectroscopic estimation of Lewis basicity of liquids.

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