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Counterion effects in the spectra and structure of solvatochromic copper(II) chelates containing 1,2-diamines and β-ketoenols

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Abstract

The contemporaneous reaction of copper(II) 'salts' with certain β-diones and N-substituted 1,2-diaminoethanes (enR) is reported. The influence of γ-position derivatives of 2,4-pentanedione, X-acacH (X = H, CN, NO_2), is described and the contribution of anions to the stability, the stereochemistry and the electronic structure of the resulting mixed-ligand chelates is discussed. Spectroscopic observations disclose that the bidentate ligands form chelate rings with copper(II) as common vertex. Whenever the $[Cu(\beta\text{-dionato})enR]^+$ entity pertains, the IR and the electronic excitation spectra, in conjunction with other physicochemical measurements, suggest that the CuN_2O_2 chromophore attains a virtually square-planar structure. Copper(II) in the $[Cu(\beta\text{-dionato})enR]^+$ entity lacks coordination saturation and, in addition to electrostatic interactions that prevail when bulky polyatomic anions counterbalance the positive charge, it is capable of forming covalent bonds with neutral molecules and charged species such as the halides and pseudohalides. The basal CuN_2O_2 plane is distorted upon coordination of unidentate ligands residing on the apex of the resulting square-pyramidal structure. Further increase in the coordination number of copper(II) by bidentate anions or neutral molecules leads to tetragonally distorted octahedral structures. This change in the symmetry of the field induced on copper(II) is revealed by spectral shifts that also disclose covalent interactions in the encounters of the CuN_2O_2 chromophore with polar or polarisable molecules. These interactions are enhanced with increasing ability of the attacking species to act as an electron pair donor. Linear dependence of the ligand field excitation maxima on the donicity of the attacking species is established. Rearrangement involving rapture of the Cu–O bond and formation of the CuN_4 chromophore accompanies the addition of *N,N*-dimethylethylenediamine, Me_2en, to $Cu(CN\text{-acac})_2$. The charge in the resulting $[Cu(Me_2en)_2]^{2+}$ entity is neutralised by the anion of the 3-cyano-2,4-pentanedione, CN-acac⁻, that binds to copper(II) through the nitrogen atom coordinating as nitrile. The coordination of a β-ketoenol as unidentate ligand through an atom other than oxygen or carbon has no precedence.

Introduction

The chemistry of metal chelates of β-ketoenols (β-diones) continues to attract unabated interest not only because the ligands may coordinate in a variety of modes but also because of the uncommon properties and the unusual and interesting reactivity of the products [1–6]. For instance, when the β-dione coordinates through the carbonyl oxygens it is susceptible to electrophilic attack and may undergo substitution reactions by activation of the carbon atom that is flanked by the carbonyl groups [6]. The metal centre, on the other hand, is capable of redox reactions and addition reactions, in cases in which coordination saturation is lacking. Considering the labile copper(II) ion, it reacts with the anions of β-ketoenols to form neutral compounds with the metal ion as common vertex in two virtually coplanar six-membered chelate rings. The copper(II) β-ketoenolates, $Cu(\beta\text{-dionato})_2$, in addition to condensation and electrophilic substitution reactions altering the structure of the ligand, undergo ligand replacement as well as ligand exchange reactions [2, 5]. Furthermore, since copper(II) usually has coordination numbers towards oxygen (and nitrogen) greater than four, the square-planar CuO_4 chromophore of the neutral bis(β-dionato)copper(II) exhibits tendency for axial ligation and with neutral donor molecules undergoes addition reactions behaving as a Lewis acid [1]. Electron attracting substituents imbedded in the β-dionato moiety enhance the tendency for coordination saturation [1, 7]. A similar tendency is also evident in compounds containing the square-planar CuN_4 chromophore, such as the chelates resulting from the reaction of copper(II) with acyclic (and cyclic) 1,2-diamines, enR. In this case, the nature of interactions of the CuN_4 chromophore that carries a double positive charge, depends [8, 9] on the effective ligand field strength of

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the coordinated diamine and (disregarding steric inhibition) on the size, shape, structure, polarisability, nucleophilicity and π-acceptor capacity of the counterion. While the behaviour of the $[Cu(enR)_2]^{2+}$ and the bis(β-dionato)copper(II) chelates as Lewis acids has been extensively investigated, the species $[Cu(\beta\text{-dionato})enR]^+$ encompassing the ligands of the previous classes of copper(II) chelates, have attracted only limited attention [10–12]. The solvatochromism exhibited by the $[Cu(\beta\text{-dionato})enR]^+$ species and its electrochemical behaviour suggest that the nature of the interactions of the cationic chelate with anions is greatly influenced by groups attached to the ligands as well as the structure, spatial and electronic, of the anion. In view of the exceptional solubility and the remarkable solvatochromic properties of the $[Cu(\beta\text{-dionato})enR]^+$ entity, it appears that such chelates merit further consideration.

The present study involving mainly the $[Cu(X\text{-acac})enR]^+$ entity was undertaken in order to explore the factors controlling its stability, the nature of its bonding interactions with charged and neutral species, and in particular (i) the importance of the geometry of the counterion, (ii) the effect of substituents and the significance of isomerism of the 1,2-diamines, (iii) the functions of groups attached to the hindmost position of the β-dionato moiety and their influence on the Lewis acidity of the $[Cu(\beta\text{-dionato})enR]^+$ entity, (iv) the stereochemical modifications brought about by covalent interactions with nucleophiles, (v) the ensuing changes in electron population in the ground state, (vi) the accompanying adjustments in group vibrations, and (vii) the shifts incurred in spectral bands as a result of solvent effects. Attempting to eliminate complications arising from steric effects and imbalance in charge distribution imposed by asymmetry in the anion of the β-dione, only 2,4-pentanedione, acacH, and its derivatives 3-cyano-2,4-pentanedione, CN-acacH, and the anion of the putative 3-nitro-2,4-pentanedione, NO_2-acacH, were employed. The symmetric *N*,*N*′-dimethyl-1,2-diaminoethane, MeenMe, and the asymmetric *N*,*N*-dimethyl-1,2-diaminoethane, Me_2en, were selected and in admixture with the β-dione were reacted with copper(II) to form the $[Cu(X\text{-aca})enR]^+$ entity. The charge was neutralised by employing an extensive series of singly charged monoatomic as well as polyatomic anions, the latter being linear, trigonal, angular or rotund, some acting as unidentate and others as bidentate ligands. The compounds isolated and studied are listed in Table 1.

Experimental

Reagents

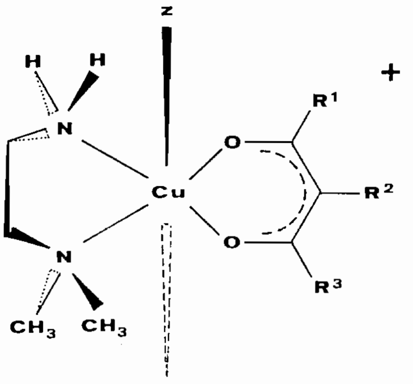
The copper(II) salts were procured from Fluka. Acetylacetone (2,4-pentanedione), acacH; *N*,*N*,*N*′,*N*′-tetramethyl-1,2-diaminoethane, Me_4en; *N*,*N*-dimethyl-1,2-diaminoethane, Me_2en; and its symmetric isomer *N*,*N*′-dimethyl-1,2-diaminoethane, MeenMe; were purchased from Aldrich. The synthesis of 3-cyano-2,4-pentanedione, CN-acacH, was performed by reacting acetylacetone with cyanogen according to the procedure described by Fackler [13]. The bis(3-nitro-2,4-pentanedionato) copper(II), $Cu(NO_2\text{-acac})_2$ was prepared by Collman's method [14, 15].

TABLE 1. Elemental analyses and physicochemical data of some copper(II) compounds, $Cu(CN\text{-acac})Me_2en(Z)$, and allied chelates

Compound	Colour	Yield (%)	m.p. (°C)	C (%)	H (%)	N (%)	Λ_M (S cm^2 M^{-1})	μ_{eff} (m_B)
$[Cu(acac)MeenMe]ClO_4$	dark violet	92	158–160	30.58 (30.86)	5.62 (5.47)	8.07 (8.00)	78	1.81
$[Cu(acac)Me_2en]ClO_4$	dark violet	93	127–129	31.12 (30.86)	5.34 (5.47)	8.20 (8.00)	68	1.86
$[Cu(CN\text{-acac})Me_2en]PF_6$	blue	81	207–208	28.92 (28.54)	4.39 (4.31)	10.12 (9.98)	88	2.21
$[Cu(CN\text{-acac})Me_2en(H_2O)]BF_4$	royal blue	74	165–168	31.76 (31.55)	5.23 (5.30)	10.04 (11.04)	76	2.10
$[Cu(CN\text{-acac})Me_2en(H_2O)]ClO_4$	blue	94	146–148	31.68 (30.54)	5.13 (5.13)	11.75 (10.68)	91	1.86
$[Cu(CN\text{-acac})Me_2en]N_3$	royal blue	74	118–120	37.73 (37.78)	5.86 (5.70)	25.86 (26.44)	5.5	1.80
$[Cu(CN\text{-acac})Me_2en(ONO)]$	blue	85	88d	36.91 (35.34)	5.50 (5.67)	17.80 (17.52)	9.6	1.69
$[Cu(CN\text{-acac})Me_2en(NCO)]$	blue–green	68	105–108	37.73 (37.55)	5.91 (5.70)	17.27 (16.68)	13.5	1.69
$[Cu(CN\text{-acac})Me_2en(NCS)]$	blue–green	62	134–136	41.00 (41.57)	5.87 (5.36)	15.90 (16.58)	15	1.71
$[Cu(CN\text{-acac})Me_2en(NC)]$	dark blue	74	70d	38.88 (39.10)	5.88 (6.01)	18.80 (18.56)	16.5	1.61
$[Cu(CN\text{-acac})Me_2en(F)]$	dark blue	61	101–103	40.63 (40.74)	6.40 (6.15)	13.85 (14.25)	19	1.73
$[Cu(CN\text{-acac})Me_2en(Cl)]$	dark blue	87	131–133	38.48 (38.58)	6.04 (5.83)	13.17 (13.50)	19	2.14
$[Cu(CN\text{-acac})Me_2en(Br)]$	light blue	92	152–153	32.90 (33.76)	4.99 (5.10)	11.54 (11.84)	26	1.89
$[Cu(CN\text{-acac})Me_2en]B(Ph)_4$	blue	64	87d	68.13 (68.58)	6.62 (6.43)	6.92 (7.06)		1.72
$[Cu(NO_2\text{-acac})Me_2en]ClO_4$	grey–blue	90	181–182	27.38 (27.49)	4.68 (4.64)	10.71 (10.68)	98	1.80
$[Cu(NO_2\text{-acac})Me_2en]NO_3$	blue–green	93	187d	29.05 (30.38)	5.04 (5.10)	15.04 (15.75)	81	1.81
$[Cu(CN\text{-acac})_2(Me_2en)_2]$	bleu–mauve	96	164–165	49.82 (49.22)	7.57 (7.43)	18.37 (17.22)	12	2.02
$[Cu(CN\text{-acac})_2(Me_4en)]$	green	98	143–145	50.31 (50.40)	6.27 (6.58)	6.57 (6.53)	19	1.89

Preparation of the cationic chelates

The ternary chelates {Cu(β-dionato)enR(Z)} were prepared by placing a mixture of equimolar quantities of β-ketoenol and N-substituted ethylenediamine, enR, in a separatory funnel containing a small amount of ethanol. Then an equimolar to 1,2-diamine quantity of copper(II) nitrate, perchlorate or chloride was added, followed by sodium carbonate sufficient to neutralize the β-ketoenol. After shaking the mixture vigorously for a while and letting the carbon dioxide out, the solution was left unperturbed for about 15 min and following filtration, it was concentrated either in a water bath or by bubbling through nitrogen. Use of sodium salts of β-dione rendered the addition of sodium carbonate or sodium acetate unnecessary. Details of the isolation and recrystallisation of this class of chelates are given elsewhere [12]. Another method was employed for the preparation of water soluble [Cu(CN-acac)Me$_2$en]Z species. An equimolar quantity of Cu(CN-acac)$_2$ was added to an aqueous solution of [Cu(Me$_2$en)$_2$]Z$_2$ (Z = Cl$^-$, ClO$_4^-$, NO$_3^-$, $\frac{1}{2}$SO$_4^{2-}$). Slow evaporation of the solvent afforded crystals. In the one-batch method, equimolar quantities of the ligands and the sodium salt of the appropriate anion were added to a methanol solution of copper(II) acetate. More rewarding proved the method involving replacement of the ions ClO$_4^-$, NO$_3^-$, SO$_4^{2-}$ by the desirable groups, exploiting differences in solubility. For instance, the chelate [Cu(CN-acac)Me$_2$en(Br)] was obtained by reacting the sulfate with CaBr$_2$. Physicochemical measurements suggest a rather elongated Cu–Br bond and preliminary X-ray structural analysis [16] indicates that the bromide occupies the apex of a distorted square pyramid, the basal plane of which is formed by the atoms of the bidentate ligands bonded to copper(II). The same structure is envisaged for the other mixed-ligand compounds in which copper(II) is bonded to unidentate ligands.



Preparation of [Cu(CN-acac)$_2$(enR)$_x$] adducts

The synthesis of the adducts [Cu(CN-acac)$_2$(enR)$_x$] was achieved by adding the appropriate amount of 1,2-diamine (enR) in a solution of Cu(CN-acac)$_2$ in benzene, acetone, ethanol or CH$_2$Cl$_2$ and allowing the crystals to be formed upon slow evaporation of the solvent [12]. While the reaction of Me$_4$en produced green crystals of the mono adduct, [Cu(CN-acac)$_2$Me$_4$en], addition of either the MeenMe or the asymmetric Me$_2$en invariably afforded the blueish mauve adducts [Cu(CN-acac)$_2$(enR)$_2$], regardless of the copper-to-diamine ratio. To increase the yield, in subsequent preparations a slight excess of the stoichiometric amount of the 1,2-diamine was added.

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 performed in a series of solutions of analytical grade nitrobenzene and nitromethane and concentrations ranging from 10^{-4} M to 10^{-2} M were employed in order to examine the likelihood of concentration dependence. Molecular mass determinations were accomplished on a Knauer apparatus. Magnetic susceptibility measurements in powdered samples were performed at 25 °C employing the Faraday method on a home-build balance calibrated against Hg[Co(SCN)$_4$]. Diamagnetic corrections were estimated from Pascal's constants and employing the experimental values obtained for Me$_2$en and (RCOCHCOR′)Na. The effective magnetic moments, μ_{eff}, were calculated using the expression

$$\mu_{\mathrm{eff}}\,(\mathrm{m_B}) = 48.98(\chi_{\mathrm{M}}^{\mathrm{corr}})^{1/2} \quad (T = 298\ \mathrm{K})$$

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 new mixed-ligand copper(II) chelates {Cu(β-dionato)enR(Z)} (Z = F$^-$, Cl$^-$, Br$^-$, CN$^-$, N$_3^-$, OCN$^-$, SCN$^-$, ONO$^-$, ClO$_4^-$, NO$_3^-$, BF$_4^-$, PF$_6^-$, B(Ph)$_4^-$) are deeply coloured crystals or crystalline powders and are stable in the air, both in the solid state and in organic solvents. The compounds prepared, their melting points and elemental analyses are listed in Table 1.

Results and discussion

The concurrent reaction of copper(II) with certain β-ketoenols (β-diones) and N-substituted 1,2-diamines (enR) proceeds following an Eigen-Wilkins pathway in which the formation of the metal–ligand bond is sequential, and affords mixed-ligand chelates with the entity [Cu(β-dionato)enR]$^+$ omnipresent [10–12]. The same compounds are obtained exploiting the lability of copper(II) in the interaction of bis(β-dionato)copper(II) chelates with [Cu(enR)$_2$]$^{2+}$ species (Table 1). For example, the entity [Cu(acac)MeenMe]$^+$ was also obtained by adding an equimolar quantity of water-insoluble Cu(acac)$_2$ to an aqueous solution of [Cu(MeenMe)$_2$]$^{2+}$. The mutual ligand exchange and the formation of ternary copper(II) chelates are reaffirmed when 1,2-diamines forming weaker copper–nitrogen bonds than the symmetric *N*,*N*′-dimethyl-1,2-diaminoethane, MeenMe, are employed. For instance, use of the non-symmetric *N*,*N*-dimethylethylenediamine, Me$_2$en, contemporaneously with acacH in reactions with copper(II) 'salts' also affords mixed-ligand chelates although the enthalpy of formation, ΔH_f°, of [Cu(Me$_2$en)]$^{2+}$ is only 41.1 kJ mol^{-1} compared to $\Delta H_f^\circ = 53.4$ kJ mol^{-1} for the [Cu(MeenMe)]$^{2+}$ species [17]. Stoichiometric analyses revealed increased hydrogen content in samples carefully recrystallised from water implying presence of one water molecule, and the indications were augmented by the strong absorptions in the IR spectra at about 3500 cm^{-1} (see Tables 1 and 2).

The absorption of these chelates in the visible is associated with ligand-field excitation, and the small effect of the counterion in the solution spectra in basic solvents suggests preservation of the copper(II) chromophore (Fig. 1). The IR spectra, discussed later on, indicate that in [Cu(β-dionato)enR]$^+$ the 1,2-diamines attain *gauche* conformation. Each ligand coordinates through the atoms possessing a lone pair of electrons and chelate rings are formed with copper(II) as common vertex. The position and the low intensity of the ligand-field absorption of the aforementioned compounds (see Table 3) precludes the tetrahedron as a likely structure of the CuN$_2$O$_2$ chromophore [9]. The stability and the reactivity of the [Cu(β-dionato)enR]$^+$ entity are susceptible to effects instigated by substituents in the bidentate ligands. The charge distribution in the [Cu(β-dionato)enR]$^+$ entity and its physicochemical properties are expected to be additionally influenced by the symmetry properties of the ligands. For instance, in the [Cu(acac)MeenMe]$^+$ species symmetrical electron population pertains and potentially chiral centers and conformers are envisaged with the methyl groups in the five-membered chelate ring occupying either the so-called axial position or the equatorial one, with the energy barrier for interconversion being rather low [5]. The vicinity of the methyl groups in Me$_2$en suggests steric hindrance in [Cu(acac)Me$_2$en]$^+$ and inequality in the copper–nitrogen bonds, inducing an uneven electron distribution. Accumulation of additional substituents in the nitrogens hinders the approach of a second 1,2-diamine molecule to copper(II) in [Cu(enR)]$^{2+}$ but does not impede the coordination of the anion of a β-dione, which is accomplished through the carbonyl oxygens [10, 12].

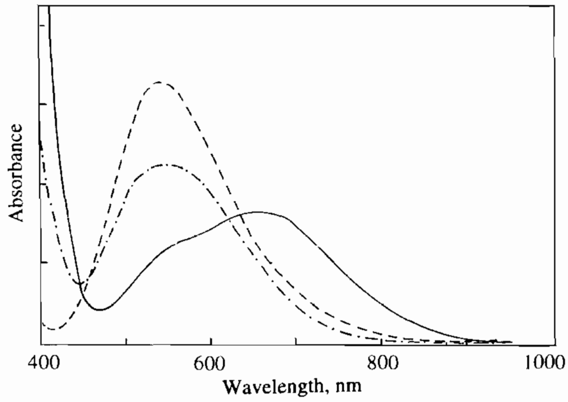


Fig. 1. Electronic excitation spectra of Cu(acac)$_2$ (——), [Cu(acac)Me$_2$en]ClO$_4$ (- - - -), and [Cu(Me$_2$en)$_2$](ClO$_4$)$_2$ (– · –) in nitromethane ($C = 1$ mmol dm^{-3}).

The electron density on the carbonyl oxygens is determined by groups within the β-dionato moiety because of electronic effects. The repercussions of the inductive effect and the consequences on the interactions of the [Cu(β-dionato)enR]$^+$ entity are far reaching. While the dissolution of Cu(acac)$_2$ to an aqueous solution of Cu(Me$_2$en)$_2$(NO$_3$)$_2$ indicated the formation of [Cu(acac)Me$_2$en]$^+$, attempts to isolate the nitrate proved unsuccessful. Irrefutable evidence of the existence of [Cu(acac)Me$_2$en]$^+$ was accrued from the electronic spectra of equimolar mixtures of nitromethane solutions of the above compounds (Fig. 1). The spectrum of the composite solution is distinctly different from the sum of the spectra of the pure components. The hypsochromic shift and the hyperchromic effect (relative to Cu(acac)$_2$) are clear indications of product formation. The inability to isolate the nitrates is in contrast to the behaviour observed when extensive N-substitution in the 1,2-diamine occurs, in which case the preparation of the [Cu(X-acac)enR]NO$_3$ chelates proceeds without undue difficulty [10, 12]. In order to improve our understanding regarding the behaviour of the [Cu(X-acac)Me$_2$en]$^+$ entity, a series of anions as well as a different β-ketoenol were employed concurrently with the present 1,2-diamine, Me$_2$en. Addition of Me$_2$en to a methanolic solution of [Cu(NO$_2$-acac)NO$_3$] afforded the mixed-ligand chelate and highlighted the significance of electronic effects that are engendered by substituents within the β-dionato moiety (Table 1). The importance of the solvent in these reactions is demonstrated by the gradual decomposition of certain mixed-ligand chelates in aqueous solutions.

Interactions of the counterion with the [Cu(β-dionato)enR]$^+$ entity may contribute to its stability. For example, the interaction of chloride with the Cu(acac)enR]$^+$ entity emulates that of the trigonal nitrate, NO_3^-. Insertion of the cyano group in 2,4-pentanedione alters the electron density in the CuN_2O_2 choromophore. The change so induced although inadequate to sustain the [Cu(CN-acac)enR]NO_3 chelate, it suffices to stabilize the mixed-ligand compound [Cu(CN-acac)enR(Cl)] which is obtained upon addition of NaCl to the reaction mixture. The interactions of the [Cu(β-dionato)enR]$^+$ entity with other species depend on their structure, stereochemical and electronic. For instance, the bulky ClO_4^- group interacts electrostatically and invariably affords the expected mixed-ligand chelates (Table 1) while the angular NO_2^- anion coordinates. It transpires that in addition to the solvent, the stability of the Cu(β-dionato)enR(Z) chelates depends on the extent of N-substitution of the 1,2-diamine, the electronic properties of substituents within the β-dionato moiety, and the interactions with the counterion, Z^-.

The exclusion of the tetrahedral as a likely structure of the [Cu(β-dionato)enR]$^+$ entity in these chelates suggests that the copper(II) ion in the CuN_2O_2 chromophore lacks coordination saturation, since when bonded to oxygen or nitrogen atoms it has a tendency to achieve coordination numbers exceeding four. This unsaturation insinuates susceptibility of the CuN_2O_2 chromophore to covalent interactions which is enhanced upon insertion of electron-withdrawing substituents in the β-dionato moiety [1, 7]. The spatial requirements of the groups in the proximity of the coordination sites in [Cu(X-acac)Me_2en]$^+$ and in [Cu(X-acac)MeenMe]$^+$ allow axial interactions, the extent of which depends on the nucleophilicity, the size and the structure of the approaching species. This is substantiated by the appreciable drop in the molar conductivity of the [Cu(X-acac)Me_2en(Z)] chelates. For instance, the bulky perchlorate group interacts electrostatically since the molar conductivity indicates ionic bonding with the molecules dissociating extensively in nitromethane solutions and behaving as 1:1 electrolytes ($\Lambda_M \approx 85$ S cm^2 M^{-1}) [18].

The occurrence of water as ligand demonstrates the coordination unsaturation of copper(II) in the [Cu(CN-acac)Me_2en]$^+$ entity which exhibits enhanced Lewis acidity. The electrostatic interactions revert to covalent ones ($\Lambda_M \approx 18$ S cm^2 M^{-1}) whenever monoatomic, diatomic or linear triatomic anions neutralise the charge of the entity. Nucleophiles that could exist as anions, may coordinate as unidentate or as bridging ligands. In the [Cu(X-acac)Me_2en(Z)] series (Z = anion or unidentate ligand), it is difficult to predict the actual stereochemistry of each individual member. Magnetic susceptibility measurements at room temperature did not reveal any usual magnetic interactions while the effective magnetic moments are consistent with magnetically dilute copper(II) chelates (Table 1). Molecular mass determinations in solution indicated mononuclear species. In the case of [Cu(CN-acac)Me_2en(NCS)] the results are ambiguous.

The electronic excitation spectra ($\tilde{\nu}_{LF} < 1.55$ μm^{-1}) and thermodynamic considerations favour a square-pyramidal structure of the [Cu(X-acac)Me_2en(Z)] chelates with the unidentate ligand coordinated along an axis normal to the plane of the CuN_2O_2 chromophore (*z* axis). Indeed preliminary X-ray structure elucidation of [Cu(CN-acac)Me_2en(Br)] indicated a distorted square pyramid with copper(II) elevated towards bromide which is positioned at the apex of the pyramid at a distance of about 266 pm from copper [16]. It should be noted that this interatomic distance is only slightly longer than the in-plane Cu–Br distance (244 pm) in $CuBr_2$ [19], and is indicative of semi-coordination [9b].

The interactions of the [Cu(CN-acac)Me_2en]$^+$ entity are not limited to monoatomic anions and solvent molecules. Addition of the sodium chelate of the 3-cyano-2,4-pentanedionate anion, CN-acacNa, to [Cu(CN-acac)Me_2en(Cl)] leads to formation of [Cu(CN-acac)$_2$(Me_2en)$_2$] which is obtained as bluish mauve crystals. This compound is also formed when the 1,2-diamine is added to a solution or suspension of Cu(CN-acac)$_2$ in a rather inert and volatile organic solvent. Attempts to prepare the 1:1 adduct invariably resulted in a mixture of Cu(acac)$_2$ and the 1:2 addition compound. The reactivity of [Cu(CN-acac)Me_2en]$^+$ towards CN-acac$^-$ differs appreciably from that exhibited by [Cu(CN-acac)Me_4en]$^+$ since their reaction leads to 1:1 adduct. It is known that the Cu(β-dionato)$_2$ chelates behave as Lewis acids and their tendency for coordination is enhanced upon insertion of electron-attracting substituents in the β-dionato moiety [1]. While unidentate ligands in 1:1 adducts coordinate axially occupying the apex of the resulting distorted square-pyramidal structure [20], in coordination saturated addition compounds involving nitrogenous bases *cis* configuration is preferred. This is particularly true in the case of the 1,2-diamines that behave as bidentate ligands. In the resulting tetragonally distorted octahedral structure inequality of the Cu–O bonds pertains, with the longer and weaker ones in axial position [21]. This structure describes [Cu(CN-acac)$_2$$Me_4$en] adequately and suggests the need for a different explanation to account for the occurrence of [Cu(CN-acac)$_2$(Me_2en)$_2$] since the absence of absorptions at frequencies higher than 3380 cm^{-1} implies that both nitrogens of the diamine (Me_2en) are linked to copper [22].

Recourse to investigations on the thermodynamics of bond formation in reactions of Cu(β-dionato)$_2$ chelates with 1,2-diamines revealed [23] that the Cu–N bonds are stronger than the equatorial (strong) Cu–O bonds since they differ in the enthalpy of formation by 38 kJ mol^{-1}. In cases in which electronic effects and steric hindrance are inadequate to prevent formation of the CuN_4 chromophore, rapture of the two equatorial Cu–O bonds is envisaged (Scheme 1), as it actually happens in the reaction of bis(hexafluoroacetylacetonato)copper(II), $Cu(hfac)_2$, with Me_2en. In that case the ionic compound $[Cu(hfac)_2(Me_2en)_2]$ is obtained, with hfac$^-$ 'coordinating' as unidentate ligand through one of its oxygens. The molecular plane of hfac$^-$ is normal to the CuN_4 plane and the Cu–O distance 279 pm [22]. Such a mode of interaction of the anion of a β-dione has also been observed in $[Cu(acac)_2(en)_2]$ (Scheme 1) albeit with a different orientation of the molecular plane of acac$^-$, which in that case is slanted against the CuN_4 plane [20]. Distinct differences in the molar conductivity and, more importantly, in the spectra of $[Cu(CN\text{-}acac)_2(Me_2en)_2]$ suggest as unlikely the coordination of CN-acac$^-$ through one of its carbonyl oxygens.

Infrared spectra

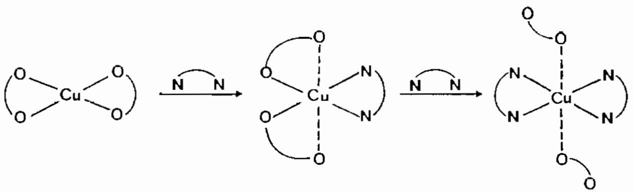
Absorption bands in the IR spectra of the new chelates that are characteristic of the anions divulge information concerning their interactions with the $[Cu(X\text{-}acac)enR]^+$ (enR = Me_2en, MeenMe) entity. The existence of the $[Cu(X\text{-}acac)enR]^+$ entity is revealed by the disappearance of peaks associated with the free ligands and the emergence of bands in specific regions of the spectrum, indicative of the mode of bonding and the conformation of the bidentate ligands [4, 24–26] (Table 2). The understanding of the IR spectra is improved when the spectra of model compounds are also considered and the bands are distinguished into those originating from the counterion and unidentate ligands, and those emanating from the 1,2-diamine and the β-dione.

Spectra of the bidentate ligands

Bonding of the anion of the β-dione, X-acac$^-$, through the carbonyl oxygens and formation of a six-membered chelate ring, comprising the copper(II) and the β-dionato entity, is disclosed by the intense absorptions in the region 1650–1500 cm^{-1}, attributed to perturbed $C\overset{\cdots}{-}O$ and conjugated $C\overset{\cdots}{-}C$ bonds, and the changes in the frequencies of their vibrational modes in the free ligands [4, 24, 26]. Small but discernible shifts are additionally observed, albeit in the opposite direction, when the IR spectra of $Cu(acac)_2$ and the $[Cu(X\text{-}acac)enR]ClO_4$ chelates are compared. Thus, while in $Cu(acac)_2$ the frequency of the perturbed $C\overset{\cdots}{-}O$ is observed at 1575 cm^{-1} the corresponding vibrational mode in the $[Cu(acac)enR]^+$ chelates occurs at 1580 cm^{-1} (Fig. 2). The replacement of hydrogen in the methinic carbon (γ-position) is disclosed by the disappearance of the bands that in $Cu(acac)_2$ occur at 1548 and 1189 cm^{-1}, and are considered to be a combination band between the IR active and the inactive out-of-plane C–H vibrations, γ(C–C–H), the former, and the in-plane deformation, δ(C–C–H), the latter. The insertion of substituents in the β-dionato moiety in the hindmost position from copper(II) induces frequency shifts, attributed to the well documented receptiveness of the perturbed $C\overset{\cdots}{-}C$ and $C\overset{\cdots}{-}O$ bonds to mass and electronic effects [4], and brings about additional bands indicative of the attached groups. Thus, the presence of the cyano group in CN-acacH is divulged by the sharp intense absorption at 2220 cm^{-1}, which upon coordination to copper(II) is shifted to 2212 cm^{-1} [13]. The existence of the nitro group is revealed [27] by the absorptions at 1479 and 1370 cm^{-1} due to the stretching vibrations of the group and the band at 827 cm^{-1} emanating from the out-of-plane deformation.

Coordination of the 1,2-diamines is disclosed by the loss of intensity and the shift of the prominent bands that in the IR spectra of the free bases occur in the 2850 ± 100 cm^{-1} region and are associated with the $N\text{–}CH_2\text{–}C$ group. The bands of medium intensity that in the free Me_2en peak at 3400, 3320 and 3200 cm^{-1} attributed to the N–H stretching vibration are of particular importance [25, 26]. Upon coordination the frequency of these bands is shifted to lower wavenumbers. In $Cu(Me_2en)_2Z_2$ the extent of the shift depends on the anion Z. For example in $[Cu(enR)_2](ClO_4)_2$ it is observed at 3225 cm^{-1} while in $[Cu(enR)_2]Cl_2$, in which the Cu–Cl distance is expected to be longer than that of Cu–O (ClO_4), the band occurs at only 3078 and 3178 cm^{-1}. The region 1650 to 600 cm^{-1} provides information regarding the conformation adopted by the 1,2-diamine. X-ray crystallographic data on the compounds $[Cu(enR)_2]Z_2$ indicated that the copper–diamine ring is in the *gauche* conformation [9a]. Since the IR spectra of this series of copper(II) compounds show the same general band type, it seems reasonable to assume that the five-membered chelate ring has the *gauche* conformation.

In the IR spectra of the addition compounds $[Cu(CN\text{-}acac)_2(Me_2en)_2]$ and $[Cu(CN\text{-}acac)_2(Me_4en)]$, the shifts in the frequencies of the perturbed $C\overset{\cdots}{-}O$ and the



Scheme 1.

TABLE 2. Wavenumber of the main absorptions in the IR spectra of Cu(CN-acac)Me_2en(Z) and allied chelates

Compound	ν (cm^{-1})								
	Z				C⩦O[a]	CH_3	C⩦N	N–H	H_2O
[Cu(acac)MeenMe]ClO_4	1120	1100	1080	625	1575	1413		3290, 3243	
[Cu(acac)Me_2en]ClO_4	1120	1100	1080	625	1575	1392		3310, 3260	
[Cu(CN-acac)Me_2en]PF_6	878	835	556		1612	1393	2228	3365, 3310	
[Cu(CN-acac)Me_2en(H_2O)]BF_4	1130	1059	1023	1002	1608	1393	2225	3340, 3285	
[Cu(CN-acac)Me_2en(H_2O)]ClO_4	1120	1100	1080	625	1607	1395	2223, 2205	3305, 3260	3515
[Cu(CN-acac)Me_2en]N_3	2053	1370	640		1618	1392	2198	3310, 3240	3425
[Cu(CN-acac)Me_2en(ONO)]	1465	1340	1110	835	1620	1390	2200	3295, 3242	
[Cu(CN-acac)Me_2en(NCO)]	2168	1358	612		1620	1380	2203	3230, 3120	
[Cu(CN-acac)Me_2en(NCS)]	2135	2080	810w	445m	1590	1400	2188	3300, 3222	
[Cu(CN-acac)Me_2en(CN)]	2178	618	328		1612	1388	2200	3315, 3240	
[Cu(CN-acac)Me_2en(F)]					1610	1400	2190	3190, 3120	
[Cu(CN-acac)Me_2en(Cl)]					1597	1408	2198	3205, 3117	
[Cu(CN-acac)Me_2en(Br)]					1610	1398	2203	3285, 3240	
[Cu(CN-acac)Me_2en]B$(Ph)_4$	1573	735	708		1610	1382	2214	3290, 3245	
[Cu(NO_2-acac)Me_2en]ClO_4	1130	1105	1070	625	1598	1385		3335, 3275	
[Cu(NO_2-acac)Me_2en]NO_3	1415	1340	1317	825	1595	1381		3285, 3230	
[Cu$(CN\text{-}acac)_2(Me_2en)_2$]					1623	1380	2173	3225, 3123	
[Cu$(CN\text{-}acac)_2$(Me_4en)]					1630, 1615	1383	2182		

[a] It is actually a C⩦O and C⩦C combination band.

conjugated C⩦C bonds and the stretching vibration ν(CN) exceed those of any other chelate (Table 2). In the 1:1 adduct the higher frequency band is split peaking at 1630 and 1615 cm^{-1} (Fig. 3) insinuating disparate Cu–O bonds, in accordance with the proposition of *cis* (equatorial) coordination of Me_4en and tetragonal distortion of the resulting octahedral structure. The elongation of the axial Cu–O would enhance the elcctron density in the neighbouring C–C bond causing the observed shift to higher frequencies. Absence of splitting and a smaller shift to higher frequencies of the vibrations associated with the perturbed double bonds is observed in [Cu$(CN\text{-}acac)_2(Me_2en)_2$]. However, the stretching vibration ν(CN) is shifted to lower frequencies suggesting interaction of the cyano group with copper. Such a possibility exists since CN-$acac^-$ may act as a chelating bidentate and a bridging ligand [12]. The spectra rather suggest that the ligand exists in a different mode from that found in Cu$(CN\text{-}acac)_2$ and the mixed-ligand chelates. The availability of an electron lone pair makes the nitrogen of the cyano group a likely coordination site.

Counterion spectra

The presence of the counterions is indicated by absorptions in specific regions of the IR spectrum [26]. The bands associated with the counterion are also listed in Table 2. The broad intense band with a poorly defined maximum at about 1090 cm^{-1} that appears in the spectra of the [Cu(X-acac)enR]ClO_4 chelates, notwithstanding other groups that also absorb in the same region (Table 2), indicates that the tetrahedral ClO_4^- group may not be considered to be even semi-coordinated [28]. The molar conductivity values of the [Cu(CN-acac)Me_2en]PF_6 and the [Cu(CN-acac)Me_2en]BF_4 chelates indicate that the existence of the PF_6^- and the BF_4^- groups is purely ionic. The absence of splittings in the broad strong band at 835 cm^{-1} enhances the indications of the existence of the PF_6^- group as anion [29]. In the IR spectra of [Cu(CN-acac)Me_2en]BF_4 the occurrence of the BF_4^- ion is revealed by the broad band at *c*. 1060 cm^{-1}, attributed to the ν_3 vibrational mode [30]. The absence of splittings of the band at 518 cm^{-1} (ν_4 mode) indicates absence of coordination and so does the inability to observe either the ν_2 or the ν_1 mode, which when activated by coordination are expected to be present at *c*. 355 and 765 cm^{-1}, respectively. The presence of the $B(Ph_4)^-$ in the corresponding compound is disclosed by the split band with peaks at 735 and 708 cm^{-1}.

The electrostatic interactions of the aforementioned counterions confer to the $[Cu(CN\text{-}acac)Me_2en]^+$ entity stability that the trigonal nitrate ion, NO_3^-, fails to provide. However [Cu(NO_2-acac)Me_2en]NO_3 is stable enough as the shifts in the bands emanating from the bidentate ligands indicate. The presence of the NO_3^- group is divulged [31] by absorptions such as the band at 1469 cm^{-1} and the increase in intensity of the band at 1340 cm^{-1}, that is attributed to the C–O stretching vibration of the coordinated β-dionato ligand. The assignments for the nitrate group are more difficult because the characteristic bands are coincident with the richer parts of the spectrum of the β-dionato ligand [27] (Fig. 2). Taking into consideration the absence of

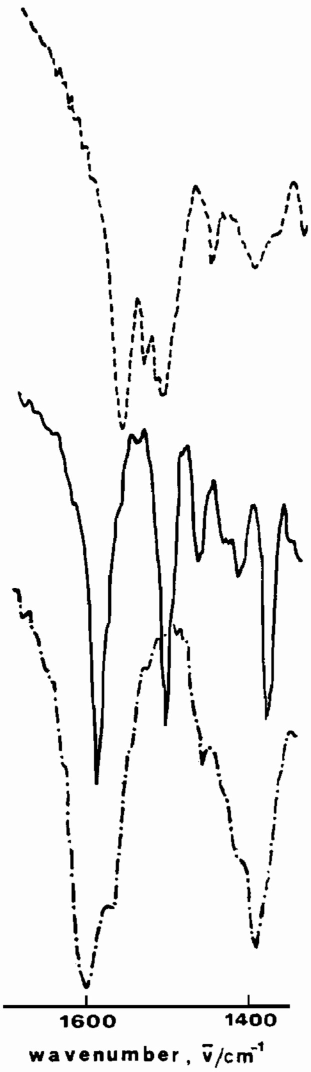


Fig. 2. Absorption bands in region 1700–1350 cm^{-1} in the IR spectra of [Cu(acac)Me$_2$en]ClO$_4$ (- - - -), [Cu(NO$_2$-acac)$_2$Me$_2$en]ClO$_4$ (——) and [Cu(CN-acac)$_2$Me$_2$en]ClO$_4$ (– · –).

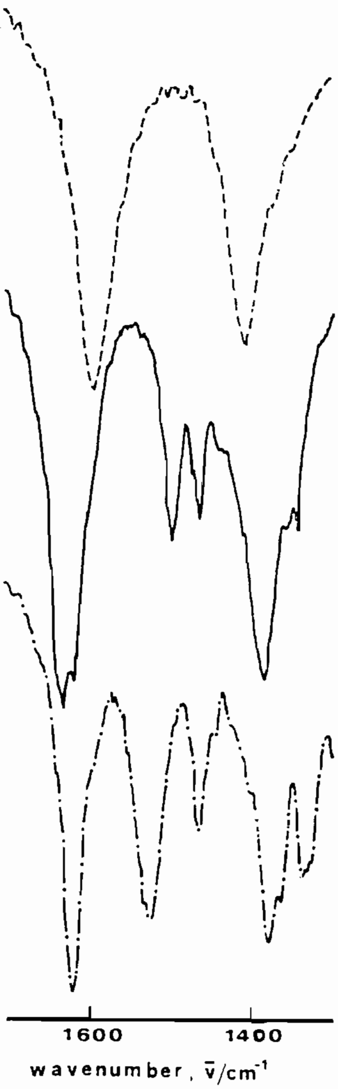


Fig. 3. Absorption bands in region 1700–1300 cm^{-1} in the IR spectra of Cu(CN-acac)$_2$ (- - - -), [Cu(CN-acac)$_2$(Me$_4$en)] (——) and [Cu(CN-acac)$_2$(Me$_2$en)$_2$] (– · –).

splitting in the weak absorption at 1750 cm^{-1}, which constitutes Lever's criterion [32], the nitrate appears to exist as anion in agreement with the indications of the conductivity of [Cu(NO$_2$-acac)enR]NO$_3$ solutions in nitromethane.

The angular NO$_2$$^-$, the linear N$_3$$^-$, the halides and the pseudohalides CN$^-$, OCN$^-$, SCN$^-$, may interact electrostatically or covalently, since these anions are capable of coordinating as unidentate or polydentate ligands, as bridging groups or even as chelating agents, and the IR spectra assist to discern their mode of interaction. For instance, the NCO$^-$ ion may coordinate as cyanato, isocyanato or even fulminato moiety. In the IR spectra of [Cu(CN-acac)Me$_2$en(NCO)] the additional band observed at 2190 cm^{-1}, a frequency associated with the cyano group, precludes coordination through carbon [26]. The band at 622 cm^{-1}, associated with the deformation of the group, δ(NCO), is more informative since it also rules out existence of NCO$^-$ as fulminato and insinuates coordination through either the nitrogen or the oxygen atoms. The intense absorption at 1316 cm^{-1} rather suggests coordination through nitrogen since this absorption in cyanates occurs at lower frequencies [26]. In the IR spectra of the azido chelate a band at 2050 cm^{-1} of equal intensity to the absorption due to ν(N=N) uncovers the presence of this pseudohalide. The CN$^-$ and the NCS$^-$ groups in the corresponding chelates also exhibit absorptions in the same region (Table 2). Actually, in the spectra of [Cu(CN-acac)enR(NCS)] the band due to ν(CN) is split with peaks at 2135 and 2080 cm^{-1} of almost equal intensity. In the same spectra the weak absorption at 810 cm^{-1} is associated with the C–S stretch, while the

TABLE 3. Wavenumber ($\tilde{\nu}$ (μm^{-1})) of the maximum absorption of the ligand field excitation of Cu(CN-acac)Me$_2$en(Z) and allied chelates in a series of solvents

Compound	$C_2H_4Cl_2$	CH_3NO_2	CH_3CN	H_2O	C_2H_5OH	DMSO
[Cu(acac)MeenMe]ClO$_4$	1.754	1.808	1.784	1.714	1.688	1.656
[Cu(acac)Me$_2$en]ClO$_4$	1.776	1.880	1.727	1.720	1.681	1.626
[Cu(CN-acac)Me$_2$en]PF$_6$	1.709	1.771	1.681	1.762	1.639	1.590
[Cu(CN-acac)Me$_2$en(H$_2$O)]BF$_4$	1.619	1.721	1.675	1.736	1.645	1.590
[Cu(CN-acac)Me$_2$en(H$_2$O)]ClO$_4$	1.709	1.791	1.689	1.658	1.665	1.629
[Cu(CN-acac)Me$_2$en]N$_3$	1.426	1.492	1.448	1.634	1.552	1.515
[Cu(CN-acac)Me$_2$en(ONO)]	1.437	1.498	1.452	1.718	1.647	1.565
[Cu(CN-acac)Me$_2$en(NCO)]	1.441	1.489	1.500	1.704	1.570	1.594
[Cu(CN-acac)Me$_2$en(NCS)]	1.511	1.594	1.585	1.543	1.502	1.458
[Cu(CN-acac)Me$_2$en(CN)]	1.429	1.485	1.450	1.674	1.567	1.520
[Cu(CN-acac)Me$_2$en(F)]	1.460	1.491	1.491	1.696	1.597	1.560
[Cu(CN-acac)Me$_2$en(Cl)]	1.436	1.426	1.395	1.540	1.502	1.458
[Cu(CN-acac)Me$_2$en(Br)]	1.391	1.458	1.449	1.658	1.605	1.553
[Cu(CN-acac)Me$_2$en]B(Ph)$_4$	1.513	1.642	1.691	insoluble	1.647	1.590
[Cu(NO$_2$-acac)Me$_2$en]ClO$_4$	1.718	1.779	1.676	1.637	1.649	1.597
[Cu(NO$_2$-acac)Me$_2$en]NO$_3$	1.616	1.672	1.661	1.652	1.652	1.590
[Cu(CN-acac)$_2$(Me$_2$en)$_2$]	1.455	1.534	1.558	1.762	1.675	1.745
[Cu(CN-acac)$_2$(Me$_4$en)]	1.385	1.477	1.653	1.654	1.588	1.582

medium intensity band at 445 cm^{-1} may be due to the NCS$^-$ bend. The shape, intensity and frequency of all these bands have been suggested as criteria for the determination, with a reasonable degree of certainty, of the mode of bonding of the NCS$^-$ group [33]. While the frequency of the δ(NCS) vibrations suggests S-bonded or a bridging thiocyanato group [34], the C–S stretch is indicative of N-bonding since in isothiocyanato compounds this vibration occurs [33] at frequencies higher than 790 cm^{-1}.

The difficulties encountered in the IR spectra of [Cu(NO$_2$-acac)Me$_2$en]NO$_3$ did not diminish when assigning the bands in the spectra of [Cu(CN-acac)enR(NO$_2$)] emanating from the NO$_2{}^-$ group because they occur in a region dominated by absorptions originating from the bidentate ligands. The bands at 1460, 1370, 1128 and 835 cm^{-1} that are not present in control compounds, i.e. the [Cu(CN-acac)enR(Cl)] and [Cu(CN-acac)enR(Br) chelates, probably originate from the NO$_2{}^-$ group. The band at 835 cm^{-1} may unambiguously be assigned to the deformation vibration of the group, regardless of its mode of existence [35]. The simultaneous occurrence of the other three bands is perplexing considering that the conductivity of the solutions in nitromethane indicate coordination. Assigning the bands at 1460 and 1370 cm^{-1} to the asymmetric and symmetric stretching vibrations of the nitro group, respectively, the band at 1128 cm^{-1} is left unaccountable. Alternatively, assigning the band at 1460 cm^{-1} to the ν(N=O) stretching vibration of the nitrito group then the absorption at 1370 cm^{-1} is inexplicable because the N–O stretch of the coordinated oxygen is unlikely to occur at frequencies higher than 1220 cm^{-1} [26]. Coordination through nitrogen is inferred from the ligand field absorption spectra.

Electronic excitation spectra

The plethora of colours exhibited by the copper(II) chelates under investigation (Table 1) suggest that the ligands influence appreciably the energy levels of the new compounds and in particular the separation of d orbitals of the metal ion since the absorption at long wavelengths, in the visible (Table 3), is due to ligand field excitation. The reflectance spectra of [Cu(X-acac)enR]ClO$_4$ are characterised by a broad structureless band (envelope) in the visible, and a similar envelope of low intensity appears when the spectrum is obtained employing 1,2-dichloroethane solutions and shows similarities with the spectra of [Cu(enR)$_2$]$^{2+}$ chelates in which the copper ion effectively exists in a square-planar environment with a $^2B_{1g}$ ground state [36] (Fig. 1). Some dependence of the position of the extremum of the envelope on the 1,2-diamine and the substituent within the β-dionato moiety becomes evident but it is very small compared to the shifts induced in certain cases by the solvent (Fig. 4) and, more importantly, by the species that neutralise the charge of the [Cu(X-acac)enR]$^+$ entity interacting covalently (Table 3). Bulky, non-coordinating anions induce imperceptible shifts that are noticeable in the reflectance spectra or in solvents of low permittivity that are also poor electron pair donors. Employment of more basic solvents causes the aforementioned red shift (Table 3) and renders the spectra virtually indistinguishable.

These suggest that the absorption is due to the same chromophore, CuN_2O_2, which is formed upon coordination of the bidentate ligands. The square-planar CuN_2O_2 chromophore retains sufficient Lewis acidity and, considering that copper(II) when bonded to nitrogen or oxygen has a tendency to achieve coordination numbers higher than four, is susceptible to nucleophilic attack. Coordination of the halides and pseudohalides, which demonstrates the affinity to nucleophiles, induces a change in geometry with repercussions on the energies of the d orbitals, as the red shift indicates (Table 3). Even so, copper(II) still lacks coordination saturation and solvents that are strong electron pair donors may interact with copper(II) altering the environment in which it exists.

In a square-planar field the d orbitals are no longer degenerate and the d^9 configuration of copper(II) leads to expectation of more than one band, the existence of which is inferred by the broad envelope (width at half-height $\sim 0.65\ \mu m^{-1}$). Upon coordination of a unidentate ligand, as the X-ray structure elucidation of [Cu(X-acac)Me_2en(Br)] revealed, the geometry around the copper(II) ion is altered to distorted square-pyramidal. The interactions of the CuN_2O_2 chromophore are not limited to charged species and the solvent shifts indicate that polar or polarisable species may also interact [37–39]. The solvent interactions are such that in strongly basic solvents, for instance DMSO, dissociation of the unidentate ligand takes place with the [Cu(X-acac)Me_2en(Z)] chelates behaving as 1:1 electrolytes. Under these circumstances upon dissolution of the chelate the solvent molecules (S) induce tetragonal distortion so that the ligand field in the $CuN_2O_2S_2$ chromophore may be approximated to octahedral, with the excitation energy corresponding to the ligand field parameter 10*Dq*. Figure 5 illustrates the changes in the energy of the d orbitals upon change of coordination number and symmetry of the ligand field [40]. The interpretation of the spectra is facilitated by categorising the present series of chelates in two classes, according to the interactions with the counterion and the apparent coordination number of copper(II) with the addition compounds [Cu(CN-acac)$_2$(Me_2en)$_x$] constituting a class of their own.

The solvent shifts are more pronounced in chelates in which electrostatic interactions with the bulky counterions predominate. In solution spectra, shifts in the frequency of maximum absorption are also induced by solvents (Table 3) and in many cases these shifts are more significant than those effected by the electrostatically interacting counterions, suggesting extensive solute–solvent interactions [37–39]. The affinity of the [Cu(X-acac)enR]$^+$ entity towards Lewis bases makes it susceptible to nucleophilic attack. The solvent molecules approach the chelates along the *z* axis and since they are repelled by the two electrons in the d_{z^2} orbital, only the stronger electron pair donors may force their way in and alter the symmetry of the field imposed on copper(II). The bathochromic shifts suggest that the solvent–solute encounters lead to electron pair donor/electron pair acceptor (EPD/EPA) interactions. Solvent induced shifts have been successfully employed for the delineation of solvent properties, and Gutmann [38] propounded the concept of donor number (or donicity), *DN*, to quantify the coordinating ability of solvents. Among the coordination compounds proposed as indicators of solvent properties [41], the [Cu(X-acac)enR]$^+$ entity is included, because the frequency of the ligand field excitation maximum was found to correlate linearly with the donor number of a series of organic solvents. Dependence of the ligand field (LF) excitation maxima of the [Cu(X-acac)enR]$^+$ series on the donicity of a wide variety of solvents (including pyridine and piperidine) is readily obtained and better correlation pertains when a similar parameter *Ds* is

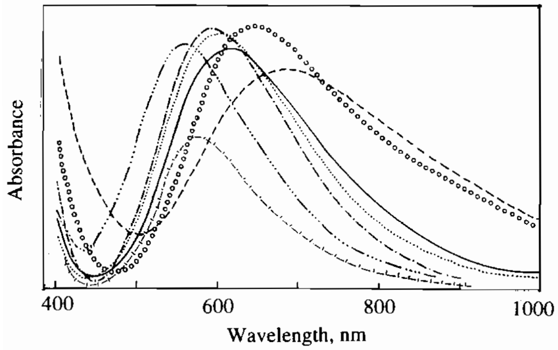


Fig. 4. Solvent shifts in the ligand field excitation band of [Cu(CN-acac)Me_2en]ClO_4. Solvents: 1,2-dichloroethane (-'-'-'), nitromethane (-····-), acetonitrile (–·–), water (·····), DMSO (——), pyridine (- - - -), piperidine (○).

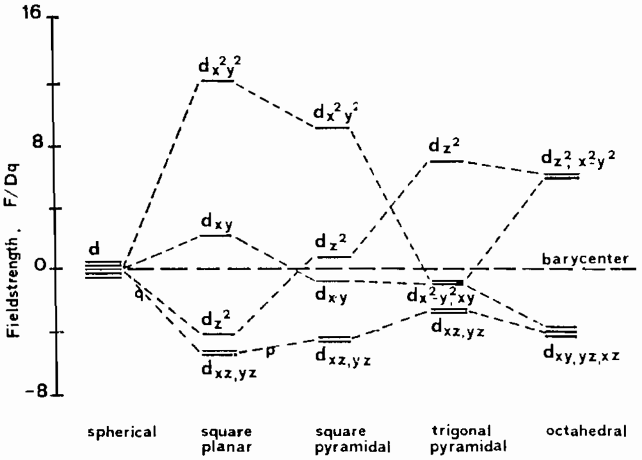


Fig. 5. Energies of the d orbitals in fields of various symmetries as a function of the parameter *Dq*.

employed [42]. Actually the wavenumber of the LF excitation maximum, $\tilde{\nu}_{max}$, is related to Ds by the equation

$$\tilde{\nu}_{max} = 1.824 + 0.00744Ds \ (\mu m^{-1})$$

In the solid state spectra of the [Cu(X-acac)Me_2en(Z)] chelates the position of the extremum of the envelope, $\tilde{\nu}_{max}$, depends on the halogen or the pseudohalogen present and it is of interest to consider the origin of this variation. It is generally accepted [43, 44] that the perturbing power of a ligand on the metal d orbitals is a function of the central ion and its oxidation state and at least four additional effects: (1) purely electrostatic perturbations, (2) influence of ligand lone pairs, (3) metal-to-ligand π-bonding, (4) ligand-to-metal π-bonding. The contemporaneous presence of other ligands makes it more difficult to assess the contribution of each and every effect. In the absence of steric hindrance, the perturbation induced by a ligand is proportional to its spectrochemical factor f_L, provided the relative importance of the previously mentioned effects remains unchanged [43, 44]. In the [Cu(X-acac)enR(Z)] chelates, the bidentate ligands are much the same and none of the ligands is unduly sterically hindered. Dependence of $\tilde{\nu}_{max}$ on f_L is sporadic and deviates appreciably from linearity suggesting that metal-to-ligand π-bonding, inferred by the small shift in the vibrational frequency of the cyano group, may be responsible for the observed deviation. The electron lone pairs endow the halide and pseudohalide ions with electron pair donor (EPD) properties which are quantified by the donor number, *DN* [38]. Although the donor number of these ions is not an invariable quantity [38], some dependence of the excitation maxima on the *DN* is indicated. Solvent shifts accompany the dissolution of the [Cu(X-acac)enR(Z)] chelates. The nucleophilic attack and the attendant electron pair donor/electron pair acceptor (EPD/EPA) interactions may result in ionisation of the [Cu(X-acac)enR(Z)] chelates in cases in which the dielectric constant of the solvent is adequately high, as observed upon dissolution of several chelates in DMSO ($DN = 28.9$, permitivity, $\epsilon_r = 46.45$). Under these circumstances, the convergence of the ligand field excitation maxima suggest that the environment in which copper(II) exists is virtually unaffected by the anion Z^-.

The adducts [Cu(CN-acac)$_2$(enR)$_x$] are a separate class of chelates. Regarding the frequency of the excitation maximum in the solid state spectra of [Cu(CN-acac)$_2$(Me_4en)], it is in line with the notion of a tetragonally distorted pseudooctahedral structure with two elongated Cu–O bonds along the axis normal to the CuN_2O_2 plane [43] and solvent shifts indicative of dissociation and equilibria in solution. There is an uncanny difference in the wavenumber of maximum absorption of [Cu(CN-acad)$_2$(Me_2en)$_2$] relative to that of other [Cu(β-dionato)$_2$(enR)$_2$] adducts indicating digression in the reactivity of CN-acac$^-$. Since the ligand field induced by β-ketoenolates is impervious to electronic effects engendered by substituents within the β-dionato moiety [15], it is not surprising that the ligand field excitation maxima of [Cu(acac)$_2$(en)$_2$]·$2H_2O$ and [Cu(hfac)$_2$(Me_2en)$_2$] at 1.89 and 1.86 μm^{-1}, respectively, are very much the same, with the small shift ascribed to the different orientation adopted by the planes of the β-ketoenolato anions. The addition compound [Cu(CN-acac)$_2$(Me_2en)$_2$] has an excitation maximum at a frequency incompatible with the CuN_4O_2 chromophore of the [Cu(β-dionato)$_2$(Me_2en)$_2$] adducts but in line with a tetragonally distorted $CuN_4N'_2$ chromophore [36]. This implies that the reaction rather proceeds along the path postulated for other Cu(β-dionato)$_2$ chelates; rupture of the weak elongated Cu–O bond precedes the rearrangement of the 3-cyano-2,4-pentanedionato anion which coordinates as nitrile.

In order to test this hypothesis, X-ray elucidation of the crystal structure was undertaken and the results [16] confirm the existence of a centrosymmetric tetragonally distorted $CuN_4N'_2$ chromophore with the Me_2en molecules adopting a *gauche* conformation. The anion of the β-dione assumes *E,Z trans* configuration (S, diketo). The Cu–O distances at 430 pm dispel any notion of direct electronic interaction. From the information available to us (see ref. 3) this mode of existence and coordination of a β-dione has no precedence.

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