Spectroscopic and electrochemical studies on the chromotropism of ternary copper(II) complexes

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Ternary complexes of copper(II) with β-ketoesters [β-keto = ethyl acetoacetate (HETAA) and ethyl benzoylacetate (HETBA)] and diamines [diam = N,N,N′,N′-tetramethylethylenediamine (Me$_4$en), N,N,N′-trimethylethylene-diamine (Me$_3$en), N,N,N′-triethylethylenediamine (Et$_3$en) and N-methyl-1,4-diazacycloheptane (medach)] of general formula Cu(β-keto)(diam)X, where X$^-$ = ClO$_4$, BPh$_4$, NO$_3$, Cl or Br, have been prepared. Their structure and chromotropicity have been characterized using spectral analyses, electrochemical and magnetic susceptibility measurements. Complexes having perchlorate, tetraphenylborate and nitrate as anions show a remarkable change from reddish violet to green in different solvents and anions with increasing donor strength of the solvent or anion. Complexes having chloride and bromide as anions are highly influenced by the acceptor property rather than the donor property of the solvent. The spectral studies revealed the possibility of using these complexes as Lewis acid–base color indicators for both solvent and anion donor strength. Cyclic voltammetric measurements on the complexes in different solvents showed that the reduction process is mainly diffusion controlled and quasi-reversible or irreversible. Such behavior has been explained according to the ECE mechanism (E = electrochemical step, C = chemical step). The solvent effect has been rationalized in terms of the thermo-dynamics and kinetics of the redox processes. A correlation has been found between the copper(II) reduction potential and the spectral data in different solvents.

Introduction

The ternary complexes of copper(II) with β-diketones and methylated diamines have attracted great interest as color indicators for solvent and anion donor strength.[1–10] However, β-ketoesters have not attracted the same attention as β-diketones in this field. In our previous work spectral and molecular orbital calculations on copper(II) complexes with thenoyltrifluoroacetone and diamine derivatives were reported.[11] As expected from the behaviors of the analogous copper(II)–β-diketone complexes, the ternary complexes of copper(II) with the β-ketoesters ethyl acetoacetate (HETAA) and ethyl benzoylacetate (HETBA) would be expected to be strongly solvato- and anionochromic.

Based on the above, the present work reports the synthesis of seven new ternary complexes: Cu(β-keto)(diam)X (β-keto = ETAA or ETBA; diam = diamine = N,N,N′,N′-tetra-methylethylenediamine (Me$_4$en), N,N,N′-trimethylethylenedi-amine (Me$_3$en), N,N,N′-triethylethylenediamine (Et$_3$en) and N-methyl-1,4-diazacycloheptane (medach); X$^-$ = ClO$_4$, BPh$_4$, NO$_3$, Cl or Br). The effects of anions, solvents and substituents on both β-ketoester and diamine ligands on the structure have been investigated. These effects are correlated with the spectral and electrochemical data of these complexes.

Experimental

Materials and methods

All the reagents and solvents used were from either Merck or Aldrich. β-Ketoester and diamine ligands were used without further purification. The solvents, 1,2-dichloroethane (DCE), nitromethane (MeNO$_2$), acetonitrile (MeCN), acetone (Me$_2$CO), methanol (MeOH), formamide (FA), dimethyl-formamide (DMF), dimethyl sulfoxide (DMSO) and hexa-methylphosphotriamide (HMPA), were purified using standard methods.[12,13] The effect of anions was studied using their tetrabutylammonium salts (Bu$_4$NX) where X$^-$ = ClO$_4$, CF$_3$SO$_3$, I, SCN, Br, N$_3$ or Cl, which were prepared as described earlier,[11,14] except for the CH$_3$CO$_2$$^-$ and CO$_3$$^{2-}$ anions which were ammonium salts.

The visible absorption spectra for Cu(β-keto)(diam)X (5 × 10^{-3} mol dm^{-3}) solutions in various organic solvents, and anions in nitromethane, and for solid complexes in Nujol mulls were recorded with a Hitachi U-2000 spectrophotom-eter using 10 mm quartz cells at 25 °C. The infrared spectra in KBr (400–4000 cm^{-1}) were recorded using a Shimadzu FTIR 8101 spectrometer. Magnetic moments were calculated from the molar susceptibility values measured using the Gouy method and a Johnson Matthey Alfa Products magnetic balance MSB-MK I. Cyclic voltammetric measurements were performed using a standard polarographic and potentiostat–galvanostat system (Princeton Applied Research, Texas) based on a three electrode system as described elsewhere.[15] Cyclic voltammograms were recorded at a potential scan rate of 100 mV s^{-1} for solutions of 0.1 mol dm^{-3} tetrabutylammonium perchlorate as supporting electrolyte. Then 1 × 10^{-3} mol dm^{-3} of the investigated complex and the internal reference were added, respectively. In the current study, two internal references, ferrocene–ferrocenium (Fc–Fc$^+$) and bis(bi-phenyl)chromium(I)/(0)[16] have been employed due to the restrictions on the solubility of both in the solvents used. All potentials were then re-scaled to bis(biphenyl)chrom-ium(I)/(0)[17,18] due to its higher solubility in most solvents used.

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Syntheses of Cu(β-keto)(diam)X complexes

These complexes were prepared by adding a mixture of β-ketoester, ethyl benzoylacetate or ethyl acetoacetate (1.78 and 1.30 g, 10 mmol, respectively) in 30 mL ethanol and solid anhydrous Na_2CO_3 (1 g, 10 mmol) to an ethanolic solution of $CuX_2 \cdot nH_2O$ (2.42 and 3.70 g, 10 mmol) for $X = NO_3^-$ and ClO_4^-, respectively) with continuous stirring for about 30 min. A solution of diamine (10 mmol) in 10 mL EtOH was added dropwise with continuous stirring for 25 min. The resulting solution was filtered and left to stand overnight and the complexes obtained were recrystallized from nitromethane.
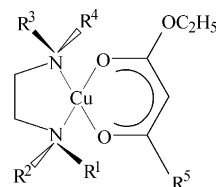
Preparation of Cu(ETAA)(Me₄en)BPh₄

1.85 g (5 mmol) of Cu(ETAA)(Me₄en)NO₃ was dissolved in 25 mL 1,2-dichloroethane and then added, with vigorous stirring, to a suspension of 3.10 g (10 mmol) NaBPh₄ in 20 mL DCE. The resulting mixture was filtered and the solution kept at 60 °C for an hour then filtered. The pale reddish violet precipitate obtained was filtered off then washed with DCE.

Results and discussion

Table 1 lists the colors, analytical data, and magnetic moments of the prepared complexes. Elemental analyses confirm the proposed formulae, Cu(β-keto)(diam)X (Scheme 1). The magnetic moment values are found in the range 1.67–1.98 μ_B, indicating the absence of Cu–Cu interaction,[11] and suggest a square planar geometry similar to that of CuN_2O_2 complexes.[6]

Infrared spectra

The main characteristic IR absorption frequencies of the investigated complexes are given in Table 2. The observed

No.	Complex	R^1	R^2	R^3	R^4	R^5
(1)	Cu(ETBA)(medach)ClO₄	CH_3	—(CH₂)₃—[a]		H	C_6H_5
(2)	Cu(ETBA)(Et₃en)ClO₄	C_2H_5	C_2H_5	C_2H_5	H	C_6H_5
(3)	Cu(ETBA)(Me₃en)ClO₄	CH_3	CH_3	CH_3	H	C_6H_5
(4)	Cu(ETBA)(Me₄en)ClO₄	CH_3	CH_3	CH_3	CH_3	C_6H_5
(5)	Cu(ETAA)(Me₄en)ClO₄	CH_3	CH_3	CH_3	CH_3	CH_3
(6)	Cu(ETAA)(Me₄en)BPh₄	CH_3	CH_3	CH_3	CH_3	CH_3
(7)	Cu(ETAA)(Me₄en)NO₃	CH_3	CH_3	CH_3	CH_3	CH_3

[a] Bridging substituent.

Scheme 1 Position of the substituents on the β-keoester and diamine-ligands in the investigated Cu(β-keto)(diam)X complexes.

bands are assigned in comparison with related copper(II) complexes.[3,11,19,20] The coordination modes of the anions have to be inferred from the IR data.

Perchlorate anion shows two IR stretching vibrational bands at 1100 and 630 cm⁻¹. Weak splitting of the strong broad band $\nu_{ClO_4^-}$ at 1100 cm⁻¹ indicates that the ClO_4^- is partially involved in coordination.[19,20] In the current study weak splitting of this band was observed for Cu(ETBA)(Me₃en)ClO₄ and Cu(ETBA)(medach)ClO₄ complexes which indicates that ClO_4^- is partially contributing to the coordination sphere of copper(II). In contrast, the other perchlorate complexes do not show any splitting, which indicates that the perchlorate anion is mainly ionic.[19]

The nitrate complex Cu(ETAA)(Me₄en)NO₃ shows three vibrational modes at 1464, 1273 and 1024 cm⁻¹ which correspond to $\nu_1(A_1) \rightarrow \nu(N=O)$, $\nu_5(B_2) \rightarrow \nu_{asym}(NO_2)$ and $\nu_2(A_1)$

Table 1 Colors, analytical data, and magnetic moments of Cu(β-keto)(diam)X complexes

	Complex/ Empirical formula	Formula weight	Color	Yield(%)	Found (Calc.)			μ_{eff}/μ_B
					C%	H%	N%	
1	Cu(ETBA)(medach)ClO₄ C₁₆H₂₃N₂O₇ClCu	454.23	Reddish violet	73	41.85 (42.27)	4.86 (5.10)	5.72 (6.16)	1.86
2	Cu(ETBA)(Et₃en)ClO₄ C₁₈H₂₉N₂O₇ClCu	484.40	Reddish violet	58	44.78 (44.59)	5.96 (6.04)	5.56 (5.78)	1.84
3	Cu(ETBA)(Me₃en)ClO₄ C₁₅H₂₃N₂O₇ClCu	442.23	Reddish violet	53	41.06 (40.70)	5.53 (5.24)	6.41 (6.33)	1.69
4	Cu(ETBA)(Me₄en)ClO₄ C₁₆H₂₅N₂O₇ClCu	456.25	Reddish violet	74	41.89 (42.08)	5.65 (5.52)	5.84 (6.14)	1.72
5	Cu(ETAA)(Me₄en)ClO₄ C₁₂H₂₅N₂O₇ClCu	408.55	Reddish violet	79	34.95 (35.25)	5.95 (6.17)	6.73 (6.85)	1.68
6	Cu(ETAA)(Me₄en)BPh₄ C₃₆H₄₆N₂O₃Cu	617.92	Violet	59	70.14 (69.91)	7.19 (7.50)	4.27 (4.53)	1.76
7	Cu(ETAA)(Me₄en)NO₃ C₁₂H₂₅N₃O₆Cu	370.75	Bluish violet	62	39.23 (38.80)	6.39 (6.80)	11.48 (11.30)	1.98

Table 2 Wavenumber/cm⁻¹ of the main absorptions in the infrared spectra of Cu(β-keto)(diam)X complexes; vs = very strong, s = strong, m = medium, w = weak, b = broad

	Complex	ν(NH)	ν(C=O)	ν(C=C)	ν(ClO₄⁻)			ν(Cu–O)
1	Cu(ETBA)(medach)ClO₄	3285 w	1619 s	1527 m	1380 m	1123 s	1091 s	632 s	
2	Cu(ETBA)(Et₃en)ClO₄	3229 m	1613 vs	1528 s	1389 m	1107 vs	—	625 s	559 w
3	Cu(ETBA)(Me₃en)ClO₄	3252 w	1613 vs	1520 s	1369 m	1111 vs	1089 s	625 s	556 w
4	Cu(ETBA)(Me₄en)ClO₄	—	1619 s	1525 m	1377 m	1105 b	—	630 s	
5	Cu(ETAA)(Me₄en)ClO₄	—	1615 vs	1518 s	1385 m	1103 vs	—	625 s	525 m
6	Cu(ETAA)(Me₄en)BPh₄	—	1601 vs	1516 s	1366 m	—	—	—	471 w
7	Cu(ETAA)(Me₄en)NO₃	—	1620	1520	1381	—	—	—	440 w

$\rightarrow v_s(NO_2)$, respectively. The separation of the two highest-frequency bands (191 cm^{-1}) indicates that the nitrate anion might act as a bidentate ligand to the copper(II) in the solid state. Additional evidence was obtained from the separation of the combination bands, $v_1 + v_4$, which appear at 1763 and 1700 cm^{-1}. The separation of 63 cm^{-1} confirms the presence of a bidentate NO$_3^-$ anion.[19]

Moreover, the IR absorptions corresponding to the C=O stretching frequencies of the Cu(ETAA)(diam)X complexes are found at 1601, 1615 and 1620 cm^{-1} for X$^-$ = BPh$_4$, ClO$_4$ and NO$_3$, respectively. This finding indicates that this stretching frequency is influenced by the coordination ability of the anion toward the central copper(II), i.e. the $v_{C=O}$ values are shifted to a higher frequency as the donor strength value of the anion (DN$_X$) increases.[2] This means that coordination of the anion with the central metal ion weakens the Cu–O bond (see Table 2), as expected from the extended donor–acceptor concept.[21] This interpretation is further confirmed by the negative slope of the linear correlation of the Cu–O stretching frequencies with the donor strength of the anions (DN$_{X, NM}$), $v_{Cu-O} = 564 - 6.46$ DN$_{X, NM}$, $r = 0.999$. This negative slope indicates that the strength of the Cu–O bond decreases as the donor strength of the coordinating anion increases.

Further evidence supporting the view mentioned above (effect of the anion on the strength of the Cu–O bond) was obtained by correlating the stretching frequencies v_{Cu-O} with the d–d visible absorption band of the Nujol mull of these complexes; a linear correlation was obtained (vide infra).

Electronic spectra

Fig. 1 shows the visible absorption spectra of the Cu(ETAA)(Me$_4$en)ClO$_4$ complex in a number of organic solvents. As was the case for the well-known [Cu(acac)(diam)]$^+$ complexes,[1] the d–d band observed exhibits a red shift with the increase of the solvent's donor number (DN).[21] Similar spectral changes are found for the complexes in the present work. The changes in their d–d visible absorption spectral data in different solvents are given in Table 3. In general, the λ_{max} values of the tetraphenylborate complex in different solvent solutions are lower than those of the corresponding perchlorate and nitrate complexes. On the other hand, in the weak or intermediate donor solvents the d–d visible absorption band of the nitrate complex was shifted to higher wavelengths than those of the corresponding perchlorate complexes. These observations are consistent with the coordination ability of anion toward the central metal ion as concluded from the IR studies.

Moreover, the d–d visible absorption bands of Nujol mulls of Cu(ETAA)(Me$_4$en)X (X$^-$ = BPh$_4$, ClO$_4$ or NO$_3$) complexes are found at 569, 580 and 619 nm, respectively. These data
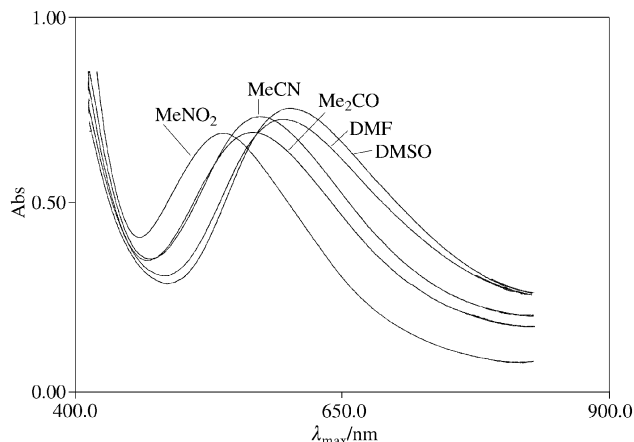
Fig. 1 Electronic absorption spectra of Cu(ETAA)(Me$_4$en)ClO$_4$ (5×10^{-3} mol dm^{-3}) in MeNO$_2$, MeCN, Me$_2$CO, DMF and DMSO solutions at 25 °C.

yield linear relationships with both of the stretching frequencies of Cu–O (v_{Cu-O}) of these complexes and DN$_{X, NM}$ of the anions, $v_{max} = 10966 - 11.835 v_{Cu-O}$, $r = 0.997$ and $v_{max} = 17854 - 76.30$ DN$_{X, NM}$, $r = 0.99$, respectively. This linearity reflects the extent of the anion's coordination toward the central metal ion and its effects on the Cu–O bond strength.

In contrast, the d–d visible absorption bands of the bromide and chloride complexes, Cu(β-keto)(Me$_4$en)X (prepared by adding Bu$_4$NBr or Bu$_4$NCl to a nitromethane solution of the corresponding perchlorate complex in the molar ratio 2 : 1), are weakly affected by the donor strength of the solvent interaction, indicating that the bromide and chloride anions coordinate more strongly with the central metal ion than most of the solvents used in the current study.

The λ_{max} values of the d–d visible absorption band of the present complexes in DCE (DN = 0) are remarkably higher than those in MeNO$_2$ (DN 2.7). This trend was observed for similar complexes and ascribed to the formation of ion pairs in DCE.[5,6,11] This conclusion is further supported by the linear correlation of the v_{max} values of perchlorate complexes in DCE solution vs. their IR Cu–O (v_{Cu-O}) stretching frequencies in the solid state, $v_{max} = 25048 - 14.27 v_{Cu-O}$, $r = 0.97$. It was also found that the λ_{max} values in Me$_2$CO (DN 17.0) are slightly lower than in MeCN (DN 14.1) solution. This might be attributed to steric and π-bonding effects in acetone and acetonitrile, respectively, since they are acting in opposite directions.[11]

Table 4 shows that the anion effect on the d–d visible absorption bands of perchlorate complexes in nitromethane solution is similar to that found for the solvent effect, i.e. the same red-shift was observed as the donor strength of the

Table 3 Absorption maxima λ_{max}/nm (absorption coefficients are in the range 100–120 dm^3 mol^{-1} cm^{-1}) for the Cu(β-keto)(diam)X complexes in various organic solutions at 25 °C

	Complex	HMPA	DMSO	DMF	FA	MeOH	Me$_2$CO	MeCN	MeNO$_2$	DCE
1	Cu(ETBA)(medach)ClO$_4$	655	622	611	609	596	581	585	577	585
2	Cu(ETBA)(Et$_3$en)ClO$_4$	699	663	647	630	617	602	611	572	588
3	Cu(ETBA)(Me$_3$en)ClO$_4$	657	633	627	609	608	599	601	570	584
4	Cu(ETBA)(Me$_4$en)ClO$_4$	659	646	649	625	610	593	604	568	580
5	Cu(ETAA)(Me$_4$en)ClO$_4$	665	644	633	633	624	609	600	551	570
6	Cu(ETAA)(Me$_4$en)BPh$_4$	656	624	619	609	601	583	593	551	565
7	Cu(ETAA)(Me$_4$en)NO$_3$	667	642	634	626	610	610	602	568	575
8[a]	Cu(ETAA)(Me$_4$en)Br	645	645	665	625	621	664	672	680	718
9	Cu(ETBA)(Me$_3$en)Br	690	665	690	613	624	703	708	697	702
10	Cu(ETBA)(Et$_3$en)Br	721	696	723	646	645	733	748	737	740
11	Cu(ETBA)(medach)Cl	725	719	744	641	639	712	701	710	736

[a] Bromide and chloride complexes are formed in solution by mixing Bu$_4$NX and the complex in a 2 : 1 ratio in nitromethane solution.

Table 4 Absorption maxima λ_{max}/nm (absorption coefficients are in the range 110–130 $dm^3\ mol^{-1}\ cm^{-1}$) of Cu(β-keto)(diam)X complexes with various anions in nitromethane solutions at 25 °C

Complex[a]	ClO_4^-	NO_3^-	OAc^-	CO_3^{2-}	I^-	Br^-	SCN^-	N_3^-	Cl^-
1	577	615	623	617	631	669	698	696	710
2	572	617	639	586	676	737	700	715	729
3	570	599	604	581	654	697	657	680	694
4	568	630	644	608	669	712	683	685	721
5	551	613	648	620	646	680	681	669	721

[a] Numbers as in Table 1.

solvent or anion increases. Therefore, these complexes are highly solvato- and aniono-chromic, respectively.[4]

The chromotropicity of the present complexes could quantitatively be expressed by linear regression analysis, using the equation $v^c = v^0 + a$ (DN), where, v^c = the measured wavenumber, v^0 = the extrapolated wavenumber and a = the slope (chromotropicity).[11] Linearity indicates stabilization of the ground state of these complexes achieved by coordination with solvent molecules or anions.[11] The chromotropic data given in Table 5 reveal that the relative stability of the four-coordinate species of the Cu(ETBA)(diam)ClO_4 complexes according to the v_s^0 or v_x^0 values follow the order: Me_4en > Et_3en > Me_3en > medach. This order is opposite to the ability to form Cu(II)···ClO_4 ion-pair attractions perpendicular to the CuN_2O_2 complex plane. This interpretation is further confirmed by the weak splitting of the $v_{ClO_4^-}$ IR stretching bands at 1100 cm^{-1} which was found for Cu(ETBA)(medach)ClO_4 and Cu(ETBA)(Me_3en)ClO_4 complexes (see Table 2).

Likewise, the order of chromotropicity, a, is found to be: Et_3en ⩾ Me_4en ≫ Me_3en > medach. This reveals that increasing the relative stability of the square planar species will make the environment of Cu(II) more planar such that the coordinated solvent or anion can easily attack the square-planar species in the same order.[5]

It is now known that these spectral changes are mainly due to the changes in the degree of axial solvation or anation of the complex. This solvation, which tends to shift the d–d band to the red, increases with the donor strength (DN) of the solvent, but is reduced according to the steric hindrance of the diamine ligand as indicated from the low values of a_s and a_x for Cu(ETBA)(medach)ClO_4, where the medach ligand provides steric hindrance due to its cyclic structure.[3,11]

Comparison of the chromotropic data of the present complexes with those of analogous β-diketonate complexes, Cu(acac)(Me_4en)ClO_4 and Cu(bzac)(Me_4en)ClO_4 (acac = acetylacetonate and bzac = benzoylacetonate), is interesting in this connection. v_s^0 values were found to be in the order: acac > bzac > ETAA > ETBA. This indicates that the relative stability of the square planar β-keto complexes is lower

than that of the corresponding β-diketonate complexes. This could be ascribed to the electron attracting properties of the OR group on the β-keto ligand which weakens the coordination ability of the carbonyl group toward Cu(II) compared with the alkyl group on the corresponding β-diketonate ligand (electron-donating properties). This explanation is further supported by the linearity of the v_s^0 values with Taft's σ parameter, $v_s^0/10^3 = 18.80 - 0.35\ σ$, $R = 0.98$.

However, the chromotropicity, a_s values, are found to be in the order ETAA > ETBA ⩾ acac > bzac complexes which is opposite to the order of the relative stability of the square planar species. This indicates that, as the electron density around the central metal ion increases, the chromotropicity of the complex decreases which is contrary to the effect of diamine ligand.

Chromotropic data, v^0 and a, in Table 5, indicate that the relative stability and chromotropicity of the perchlorate complexes are more highly affected by the anion than the solvent.

Once again, the perchlorate and tetraphenylborate complexes in most solvents exhibit lower λ_{max} values than do the corresponding halide complexes (see Table 3). This indicates that the former complexes in non- or very weak coordinating solvents (DCE or $MeNO_2$) retain their four-coordinate geometry since the coordinating ability of tetraphenylborate and perchlorate anion to the central metal ion is very weak as expected from their donor number (DN_X).[2] The d–d band of the latter complexes is shifted strongly to higher wavelengths, at about 700 nm, which could be a result of distorted square-pyramidal geometry.[3,12,22]

The effect of solvents on the halide complexes Cu(β-dik)(diam)X (X = Br or Cl) is rather complicated as it depends upon both the donor and acceptor properties of the solvent. Therefore, a multiple linear regression analysis was employed to analyze the spectral data of these complexes in different solvents (see Table 3) which resulted in the following relationships: $v_{max}/10^3\ cm^{-1} = 13.58 + 40.20\ AN + 38.7\ DN$, $r = 0.91$; $12.91 + 67.9\ AN + 22.1\ DN$, $r = 0.95$; $12.19 + 67.4\ AN + 24.7\ DN$, $r = 0.94$ and $12.58 + 69.5\ AN + 9.48\ DN$, $r = 0.93$, for Cu(ETAA)(Me_4en)Br, Cu(ETBA)(Me_3en)Br, Cu(ETBA)(Et_3en)Br and Cu(ETBA)(medach)Cl, respectively.

Table 5 Chromotropicity parameters of the Cu(β-keto)(diam)X complexes, according to the equation $v^c = v^0 + a$(DN)

Complex	10^{-3} Intercept/cm^{-1}		Slope/cm^{-1}		r[a]	
	v_s^0	v_x^0	a_s	a_x	Solvent	Anion
1 Cu(ETBA)(medach)ClO_4	17.80	18.52	61.73	119.0	0.99	0.93
2 Cu(ETBA)(Et_3en)ClO_4	17.86	18.70	91.60	146.0	0.99	0.96
3 Cu(ETBA)(Me_3en)ClO_4	17.71	18.57	64.14	122.0	0.97	0.94
4 Cu(ETBA)(Me_4en)ClO_4	17.74	18.80	69.87	139.0	0.99	0.93
5 Cu(ETAA)(Me_4en)ClO_4	17.70	18.74	70.58	128.0	0.98	0.95
6 Cu(ETAA)(Me_4en)BPh_4	18.25	—	77.66	—	0.97	—
7 Cu(ETAA)(Me_4en)NO_3	17.73	—	73.4	—	0.99	—
Cu(bzac)(Me_4en)ClO_4[b]	18.61		78.8	—	0.99	—
Cu(acac)(Me_4en)ClO_4[b]	18.75	—	83.11	—	0.98	—

[a] r = Correlation coefficient. [b] Data taken from ref. 20.

These relationships indicate that the solution of the halide complex is mainly affected by the acceptor properties (AN) rather than the donor properties (DN) of the solvent.

The d–d transition band in the visible region of the electronic absorption spectrum of the current complexes is completely resolved, which allows an accurate determination of the band's oscillator strength (f). The expression $f = 4.6 \times 10^{-9} \, \varepsilon_{max} \nu_{1/2}$, where ε_{max} is the absorption coefficient at the maximum band height in $dm^3 \, mol^{-1} \, cm^{-1}$ and $\nu_{1/2}$ the bandwidth at half band height, was used to calculate f values.[23] The oscillator strength, f, is a dimensionless quantity that is used to express the electronic transition probability.[11,24] Table 6 collects the f values of the present complexes, in several solvents. These values indicate that the d–d visible transition probability for these complexes decreases as the donor strength of the solvent interaction increases. The Et$_3$en complex is the most sensitive of the series towards solvent.

Plotting the f values *vs.* the donor number of solvent (DN) displays a linear relationship $f = f_0 + b$ DN and the linear regression data are collected in Table 6. The intercept (f_0) represents the extrapolated oscillator strength, which was found to be in the order: Et$_3$en > Me$_4$en > Me$_3$en > medach. This trend is similar to that found for the chromotropicity (*a*). For the same complex cation, Cu(ETAA)(Me$_4$en)$^+$, as the coordination ability of the anion increases the f_0 value decreases. The negative slope, b (see Table 6), indicates that the d–d absorption band becomes broader as the donor strength of the solvent or anion increases.

Electrochemical studies

Electrochemical properties of some of the present complexes were investigated by cyclic voltammetry in five solvents, *i.e.* MeNO$_2$, MeCN, FA, DMF and DMSO, with a stationary platinum microelectrode. The complexes undergo a reduction localized, evidently, on the metal atom. The reduction process is mainly diffusion controlled as was concluded from the linear dependence of the peak current on the square root of the scan rate (the range of $V = 50$ to 100 mV s^{-1}).[23] Ferrocene–ferrocenium (Fc–Fc$^+$) and bis(biphenyl)-chromium(I)/(0) were used as internal standards for assignment of the potential values as well as evaluation of the number of transferred electrons. The character of the reduction pathway and the peak currents at E_{pc} are almost the same for the studied complexes.

Fig. 2 shows the cyclic voltammetric response, obtained at a platinum microelectrode from a DMSO solution of Cu(ETBA)(medach)ClO$_4$ as a typical example for the present complexes. At a scan rate of 100 mV s^{-1} a rather complicated quasi-reversible or irreversible copper(II) reduction is observed, the cathodic peak A being accompanied, in the reverse scan, by the directly associated re-oxidation anodic peak C. A more cathodic peak B and other anodic peaks D and E were observed. At decreasing scan rates C tended to disappear. This finding is clearly due to the re-oxidation of some electrodeposited copper metal. Indeed this voltammetric picture is quite common to many copper(II) complexes,[25–27]
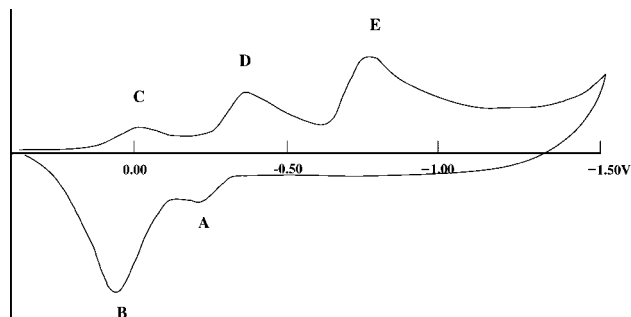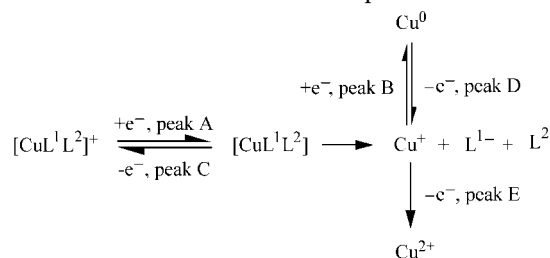

Fig. 2 Cyclic voltammogram recorded with a platinum microelectrode from a DMSO solution for Cu(ETBA)(medach)ClO$_4$ (1.0×10^{-3} mol dm^{-3}), 0.1 mol dm^{-3} Bu$_4$NClO$_4$ as supporting electrolyte and a scan rate of 100 mV s^{-1}.

and has been explained according to the ECE mechanism (E = electrochemical step, C = chemical step) (Scheme 2).

It must be taken into account that the expulsion of copper(I) ions from the complex at the potential of peak A is thermodynamically followed by reduction to copper metal at the potential of peak B. No anodic peak is observed in MeCN for Cu(ETBA)(medach)ClO$_4$ or Cu(ETBA)(Me$_4$en)ClO$_4$ in the first reduction process. In contrast, in the other solvents the anodic peak is always observed even at a slow scan rate. This process is accompanied by a partial loss of the complex solution color and the deposition of copper metal on the working electrode during the bulk-phase constant potential electrolysis of the complexes.

Table 7 shows the potential values *vs.* bis(biphenyl)-chromium(I)/(0) of the redox peaks (E_{pc} and E_{pa}) for Cu(ETBA)(medach)ClO$_4$, Cu(ETBA)(Me$_4$en)ClO$_4$ and Cu(ETAA)(Me$_4$en)ClO$_4$ complexes. These potentials depend upon the donor properties of the solvent similar to what is observed for Cu(CF$_3$SO$_3$)$_2$ in different solvents.[18] The solvent influences both the thermodynamics and kinetics of the redox processes of the complexes under study.[26] It is clear that there is a relationship between the copper(II) reduction potential and the solvent donor number (DN). This might be explained on the basis of the assumption that the complex ions are solvated, *i.e.* the solvent molecules attack the axial sites of the copper(II), complexes as concluded from the electronic spectral studies.

The voltammetric properties of the complexes are consistent with their visible absorption spectra as indicated by the linear correlation between the redox potential and the ν_{max}

$$[CuL^1L^2]^+ \underset{-e^-, \text{ peak C}}{\overset{+e^-, \text{ peak A}}{\rightleftharpoons}} [CuL^1L^2] \longrightarrow Cu^+ + L^{1-} + L^2$$

Scheme 2 Suggested mechanism of the reduction and re-oxidation processes for Cu(β-keto)(diam)ClO$_4$ complexes.

Table 6 Oscillator strength (f) of the d–d transition absorption bands of the Cu(β-keto)(diam)X complexes

| Complex | $f \times 10^3$ | | | | | | $f = f_0 + b$ DN | | |
	DMSO	DMF	MeOH	Me$_2$CO	MeCN	MeNO$_2$	$f_0 \times 10^3$	$b \times 10^5$	r
1 Cu(ETBA)(medach)ClO$_4$	6.38	6.49	6.51	6.87	6.73	7.05	7.12	2.45	0.92
2 Cu(ETBA)(Et$_3$en)ClO$_4$	7.89	8.16	8.65	8.93	8.63	9.75	9.85	6.51	0.97
3 Cu(ETBA)(Me$_3$en)ClO$_4$	6.24	6.31	6.49	7.01	6.71	7.33	7.35	4.0	0.98
4 Cu(ETBA)(Me$_4$en)ClO$_4$	6.34	6.59	6.92	7.12	7.05	7.48	7.68	4.15	0.97
5 Cu(ETAA)(Me$_4$en)ClO$_4$	5.94	6.22	6.63	6.97	6.60	8.82	8.93	10.60	0.98
6 Cu(ETAA)(Me$_4$en)BPh$_4$	8.54	8.65	9.01	9.24	9.06	10.2	10.30	6.23	0.99
7 Cu(ETAA)(Me$_4$en)NO$_3$	5.23	6.40	6.57	6.73	6.56	8.28	8.48	10.90	0.95

Table 7 Electrochemical data for the reduction and re-oxidation processes of $Cu(\beta\text{-keto})(diam)ClO_4$ complexes in various solvents; potentials E/V *vs.* bis(biphenyl)chromium(I)/(0) reference electrode

Solvent	**1** $Cu(ETBA)(medach)ClO_4$			**4** $Cu(ETBA)(Me_4en)ClO_4$			**5** $Cu(ETAA)(Me_4en)ClO_4$		
	E_{pc}/V	E_{pa1}/V	E_{pa2}/V	E_{pc}/V	E_{pa1}/V	E_{pa2}/V	E_{pc}/V	E_{pa1}/V	E_{pa2}/V
MeNO$_2$	0.55	0.18		0.89	0.26		0.41	0.22	
	0.93						0.93		
MeCN	0.56	0.10	—	0.67	—		0.64		0.006
FA	0.64	0.75		0.55	−0.31	−0.06	0.65	0.24	0.11
	0.82	0.68		1.00			1.02		
DMF	0.87	0.29	0.02	0.83	0.24	0.07	0.89	0.59	0.10
DMSO	0.79	0.34	−0.04	0.73		0.06	0.81	0.40	−0.06
	0.91	0.58		0.91			0.51		

values of the d–d absorption band of $Cu(ETAA)(Me_4en)ClO_4$ in various solvents, $E_{pc} = 3.36 - 170\,v_{max}$, $r = 0.97$.

The combination of electrochemical and spectroscopic studies enables one to investigate the axial ligation of the chromotropic complexes in detail and can be utilized to characterize the solvent coordination ability. In the absence of X-ray single crystal data for the current complexes, the proposed structures in Scheme 1, based on the above physicochemical studies, are tentative.

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