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Effect of Solvent on the Electrochemical Properties of Chromotropic Copper(II) Mixed Chelates

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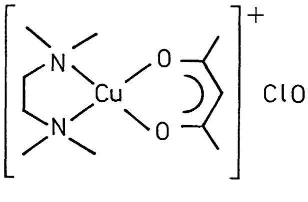
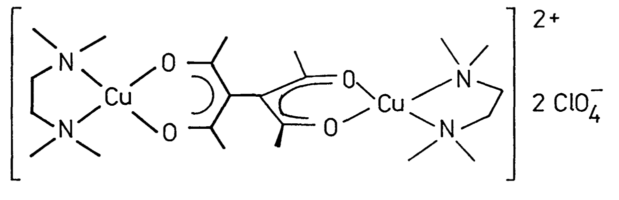
Electrochemical and electronic spectral bahaviors of complexes [Cu(acac)(tmen)]ClO_4 and [Cu_2(taet)(tmen)$_2$](ClO_4)$_2$, where acac=acetylacetonate ion, tmen=*N,N,N′,N′*-tetramethylethylenediamine, taet=1,1,2,2-tetraacetylethanediide ion, were investigated in six solvents by cyclic voltammetry, constant potential coulometry, and visible absorption spectroscopy. Copper(II) undergoes electrolytic reduction to copper(I) coupled with the complex decomposition. The values of reduction potential vs. $\tilde{\nu}_{max}$ of the d-d absorption band show linear correlation in accordance with coordination ability of the solvent.

Many kinds of copper(II) mixed ligand complexes with *N,N′*-polyalkylated ethylenediamine (diam) and a *β*-diketonate ion (dike) have been synthesized; the general formula [Cu(dike)(diam)]ClO_4 which are very soluble in many organic solvents and are solvatochromic.[1–4] Systematic spectroscopic examination of these chelates in many nonaqueous solvents showed a good correlation between their d-d absorption maxima in solutions and the donor strengthes of the solvents used; i.e., the absorption peak of the chelate in an inert solvent like 1,2-dichloroethane shifts much more higher frequencies than that in the strong solvent like DMSO. This solvatochromic behavior has been also examined by ESR measurements, and it was reported that there is a good correlation between ESR parameters ($g_{//}$ values) of the chelate in solutions and the donor abilities of the solvents used.[5]

Besides the spectroscopic properties,[3] it is also very interested to know whether electrochemical parameters, in particular redox potential, of the chelate in various organic solvents correlate with the solvent polarity.[6–9] Then the aim of the present paper is to find the correlation between the electrochemical properties and the spectral ones of the chelates. The complex (**1**) [Cu(acac)(tmen)]ClO_4 (acac=acetylacetonate, tmen= *N,N,N′,N′*-tetramethylethylenediamine) as well as the dinuclear complex (**2**) [Cu_2(taet)(tmen)$_2$](ClO_4)$_2$ (taet=1,1,2,2-tetraacetylethanediide ion) have been chosen for the study, among which the latter complex is newly obtained in this study.



Formula **1**.



Formula **2**.

Experimental

The complex **1**, [Cu(acac)(tmen)]ClO_2, was prepared as described previously,[1] and the dinuclear one **2**, [Cu_2(taet)(tmen)$_2$](ClO_4)$_2$, is prepared as follows: Ligand H_2(taet)[10] 1.00 g (5 mmol) and KOH 0.56 g (10 mmol) in 30 ml of EtOH(ethanol) were added to the solution of Cu(ClO_4)$_2$·6H_2O 3.70 g (10 mmol) in 40 ml of EtOH. To the solution tmen 1.28 g (11 mmol) was added. The color of the solution was changed from blue to bluish violet. Crude dark violet crystals were recrystallized from 1,2-dichloroethane (Yield 80%). Analytical data: C, 33.73, H, 6.06, N, 7.10%. Calcd for [Cu_2(taet)(tmen)$_2$](ClO_4)$_2$·1.5H_2O: C, 33.81, H, 6.06, N, 7.17%. All other chemicals used were extra pure or analytical grade. Solvents were dehydrated by usual methods.

Voltammetric measurements were performed with a Polarographic Analyzer PA 4 (Laboratórní přístroje, Prague). A conventional three-electrode electrochemical cell was used; a platinum microelectrode and a hanging mercury drop electrode, a platinum flag, and a saturated calomel electrode(aqueous 4 mol dm^{-3} LiCl) connected via a salt bridge containing the supporting electrolyte in the corresponding nonaqueous solvent served as the working, counter, and reference electrodes, respectively. Supporting electrolyte was tetrabutylammonium tetrafluoroborate or sodium perchlorate in the concentration of 0.1 mol dm^{-3}. Cyclic voltammograms were recorded at a potential scan rate of 100 mV s^{-1}. Argon was used as an inert gas.

Coulometric measurements were made with a universal OH-404 Coulometric Analyzer (Radelkis, Budapest). The working electrode consisted of a double circular platinum gauze, placed parallel to a frit separating the cathode from the anode compartment in the electrolytic cell. The auxiliary electrode was a platinum coil. The reference electrode was constituted as for voltammetric measurements.

Visible absorption spectra were obtained by a Specord UV-

VIS spectrophotometer Model M 40 (Zeiss, Jena) and a Hitachi 340 spectrophotometer. All measurements were performed at 25 °C.

Results and Discussion

Dinuclear complex containing bridged tetraketonate ion (1,1,2,2,-tetraacetylethanediide=taet) and *N,N,N′,N′*-tetramethylethylenediamine(tmen) was newly synthesized in this study. The analytical data show that the complex is sesquihydrate, dark violet crystal which has 2.69 BM (per mole; 1.90 BM per Cu^{2+}) at room temperature. The complex is very soluble in various solvents and shows characteristic solvatochromism, which are very similar to those of the mononuclear complexes $[Cu(acac)(tmen)]^+$.

Electrochemical properties of the complexes were studied by cyclic voltammetry in six solvents, i.e., pyridine, DMSO, DMF, water, CH_3CN, and acetone, with the stationary platinum microelectrode and the hanging mercury drop electrode. The complexes undergo a reduction which is localized, evidently, on the metal atom. The reduction process is diffusion controlled as it follows from the linearity of the peak current dependence on the square root of the scan rate (the range of $V=0.05$ to $0.50\ V\ s^{-1}$). Ferrocene was used as an internal standard for assignment of potential values as well as evaluation of transfered electron number. On the platinum electrode the ferrocenium/ferrocene redox couple was situated at $E_{1/2}=0.38$ V vs. SCE(CH_3CN) and exhibited the potential separation of $E_p=80$ mV and the i_{pc}/i_{pa} peak current ratio equal to one.

For both copper(II) complexes, **1** and **2**, the potential of the reduction peak (E_{pc}) depends upon the solvent as well as the working electrode used and its values are listed in Tables 1 and 2. The character of the reduction pathway is the same on both working electrodes and the change of the supporting electrolyte (Bu_4NBF_4 to $NaClO_4$) has no influence on the redox characteristics of the complexes. The peak currents at E_{pc} are almost the same for both complexes and near to that of ferrocene oxidation at the same concentration of all complexes. It indicates, at least for the complex **1**, that the reduction involves 1 mol of electron per mol of Cu(II) complex. In the case of the complex **2** such comparison may be non-adequate as the dinuclear complex has probably smaller value of diffusion coefficient than the complex **1**. (Considering the double amount of Cu(II) centers in the complex **2** solution, the peak currents of both complexes will be almost the same if the diffusion coefficient of the complex **2** is four-times smaller than that of the mononuclear complex.) Therefore, the number of electrons transfered in the electrode process was also determined coulometrically. The coulometric reduction was carried out at a fixed potential of −0.75 V.

Table 1. Electrochemical Data for $[Cu(acac)(tmen)]ClO_4$ Reduction and Re-Oxidation Processes in Various Solvents[a)]

Solvent[b)]	Peak potential/V					
	Platinum electrode			Mercury electrode		
	E_{pc}	$E_{pa\,1}$	$E_{pa\,2}$	E_{pc}	$E_{pa\,1}$	$E_{pa\,2}$
Pyridine (33.1)	−0.78, −0.94	—	−0.53	−0.78	−0.60	−0.50
DMSO (29.8)	−0.70, −0.90	−0.10	+0.10, +0.30	−0.57, −0.72	−0.30	+0.05, +0.23
DMF (26.6)	−0.70	−0.05	+0.22	−0.57	−0.22	+0.05, +0.20
Water (18.0)	−0.45	—	—	−0.30	−0.17	+0.02
Acetone (17.0)	−0.60	—	—	−0.35	−0.18	—
CH_3CN (14.1)	−0.63	−0.30	−0.17	−0.46	−0.40	+0.08

a) 0.1 mol dm^{-3} tetrabutylammonium tetrafluoroborate supporting electrolyte, potential in V vs. 4 mol dm^{-3} LiCl SCE, potential scan rate $0.1\ V\ s^{-1}$. b) Solvent donor numbers are shown in parentheses (unit in kcal mol^{-1}).

Table 2. Electrochemical Data for $[Cu_2(taet)(tmen)_2](ClO_4)_2$ Reduction and Re-Oxidation Processes in Various Solvents[a)]

Solvent[b)]	Peak potential/V					
	Platinum electrode			Mercury electrode		
	E_{pc}	$E_{pa\,1}$	$E_{pa\,2}$	E_{pc}	$E_{pa\,1}$	$E_{pa\,2}$
Pyridine (33.1)	−0.75, −0.98	—	−0.55	−0.80, −0.95	−0.55	−0.40
DMSO (29.8)	−0.69	−0.05	+0.12, +0.30	−0.55, −0.68	−0.23	+0.06, +0.25
DMF (26.6)	−0.68	−0.15	+0.22	−0.51, −0.70	−0.30	+0.10
Water (18.0)	−0.59	—	—	−0.34	−0.07	+0.11
Acetone (17.0)	−0.60	—	—	−0.31, −0.46	0.00	—
CH_3CN (14.1)	−0.64	−0.25	−0.18	−0.38, −0.47	−0.31	+0.12

a, b) Notes as under the Table 1.

The results showed the consumption of one electron for the complex **1** species and two electrons for the species of the complex **2**. The voltammetric cathodic peak currents as well as the results of coulometry may be also influenced by partial reduction of Cu^+ (see below).

Cyclic voltammograms of the complexes are rather complicated showing quasi-reversible or irreversible Cu(II) reduction (See Fig. 1). On the anodic part of the voltammograms there are at least two peaks (in Tables 1 and 2 denoted as E_{pa1} and E_{pa2}) which indicate the Cu(I) species being less stable. Change of the potential scan rate in the above mentioned range had no significant influence on the shape of the anodic branch. The first peak, E_{pa1}, represents oxidation of the electrogenerated Cu(I) complex and the second one, E_{pa2}, belongs to re-dissolution of the deposited copper metal. This assignment is based on the fact that the second anodic peak has a shape of the stripping type and markedly grows when the working electrode is polarized at the E_{pc} potential for several seconds. The potential situation of Cu^0 stripping peak was confirmed by the cyclic voltammograms of the Cu(II) perchlorate. In DMSO and DMF the third anodic peak in the region +0.2 to +0.3 V takes place due to the oxidation of Cu^+(solvated) resulted from the decomposition of unstable Cu(I) complex.

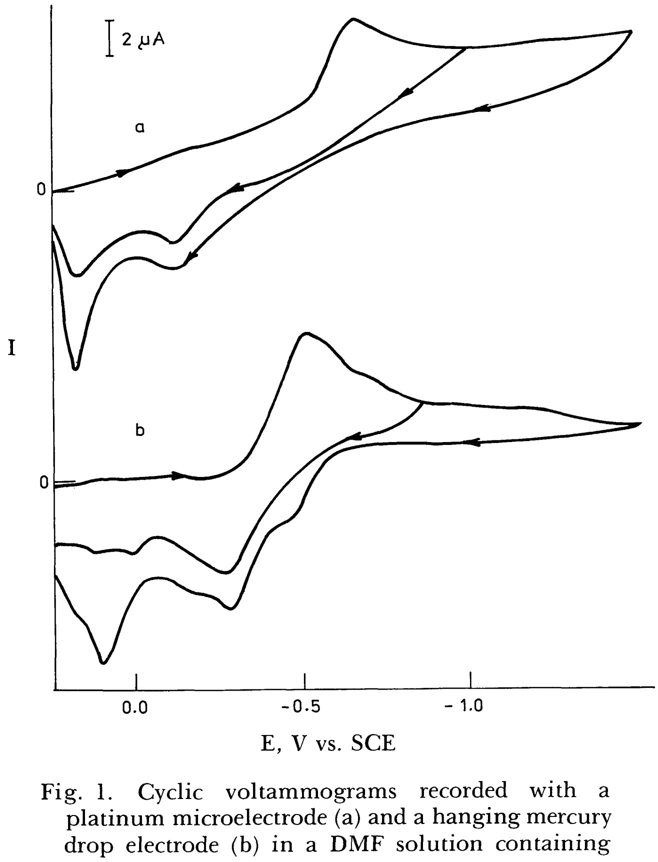


Fig. 1. Cyclic voltammograms recorded with a platinum microelectrode (a) and a hanging mercury drop electrode (b) in a DMF solution containing complex **2** (1.2×10^{-3} mol dm^{-3}) and $NaClO_4$ (0.1 mol dm^{-3}). Scan rate: 0.1 V s^{-1}.

Such behavior is quite common to many mononuclear and dinuclear Cu(II) complexes,[11,12] and it has been explained according to the ECE mechanism. In our case the electrochemical reduction of Cu(II) complex at E_{pc} (step E_1) is followed by the chemical step C—a decomposition of the electrogenerated Cu(I) complex under the formation of Cu^+(solvated) which is electroactive at the potential positive of E_{pc}. Thus, for the thermodynamic reasons the liberation of Cu^+ is followed by the reduction to Cu metal (step E_2):

$$\mathrm{Cu(II)} \underset{-e^-,\ E_{pa1}}{\overset{+e^-,\ E_{pc}}{\rightleftharpoons}} \mathrm{Cu(I)} \longrightarrow \mathrm{Cu^+} \xrightarrow{+e^-} \mathrm{Cu^0}$$

This process is accompanied with a partial loss of solution color and the deposition of copper metal on the working electrode during the bulk-phase constant potential electrolysis of the complexes.

In some cases the reduction of complex **1** and **2** in the E_{pc} region consists of two peaks with a small potential separation (see Tables 1 and 2). The second peak represents a shoulder on the decreasing part of the voltammetric curve (Fig. 1) which seems to be a typical complication due to the adsorption of the electroactive particle. At more negative potentials there are also some other small cathodic current maxima (Fig. 1). The investigation of some similar mono- and di-nuclear Cu(II) compounds which is in progress now, shows that this picture is influenced by the type of β-diketonate ligand and the rate of the decomposition of Cu(I) complexes. These factors, however, do not play any important role in the examination of effect of solvent on the redox parameters of the complexes studied in this paper.

The solvent influences both the thermodynamics and the kinetics of the redox processes of the complexes under study. It is clear that there is a relationship between the Cu(II) reduction potential and the coordination ability of the solvent, which is conveniently expressed by the Gutmann's donor number (DN).[13] The differences between the E_{pc} values going from pyridine to CH_3CN are greater when compared to those observed for planar Cu(II) complex with tetraaza macrocyclic ligand (TAAB).[8]

The voltammetric behavior of the complexes **1** and **2** can be explained on the basis of the assumption that the complex ions are solvated. The solvent molecules attack the axial sites of the Cu(II) complexes. The voltammetric properties of the complexes correspond very good to the date about the effect of solvents on their visible absorption spectra. An exception represents water medium. A relationships between the redox potential and $\tilde{\nu}_{max}$ value of d-d absorption band for mono- and dinuclear complexes are depicted on the Figs. 2 and 3. The dependences are linear, characterized by a correlation coefficient r=0.96—0.97.

From the ESR data of the mononuclear complex, [Cu(dike)(tmen)]$^+$, reported previously,[5] the highest, positive hole orbital(LUMO) is the d orbital of Cu(II) ion directed to the equatorial chelate ligands (d_{xz} orbital in C_{2v} symmetry proposed in Ref. 5), and the $g_{/\!/}$ values of the complex in an inert solvent shifts to the higher values in the solvent with more strong coordinating ability, i.e., the $g_{/\!/}$ value increases with the increase of the DN of the solvent used. The absorption maxima of the complex in solutions shift to the lower frequencies with the increase of the coordinating abilities of the solvents(DN). In this study, we could get a fairly good correlation between E_{pc} of the complexes and their $\tilde{\nu}_{max}$ values. Therefore, especially for the mononuclear complex, the ESR parameter ($g_{/\!/}$) of the complex in various solvents should correlate with the reduction potential of the complex studied here.

This result was confirmed also by an examination of the effect of SCN^- ions on the electrochemical and spectroscopic behavior of the complexes. The addition of small excess of NH_4SCN to the complex solution changes both the reduction potential as well as the $\tilde{\nu}_{max}$ value (see Table 3). Although the interaction of NCS^- with the Cu(II) complex is different in various solvents,[3] the nature of axial attack on the Cu(II) center remains the same. The examination of electrochemical properties of 5-coordinated mixed ligand complexes are now in the progress.

The combination of electrochemical and spectroscopic study allowed us to investigate the axial ligation of the chromotropic chelates in more details. Both electrochemical as well as spectroscopic properties of the Cu(II) complexes **1** and **2** can be utilized to characterize the solvent coordination ability.

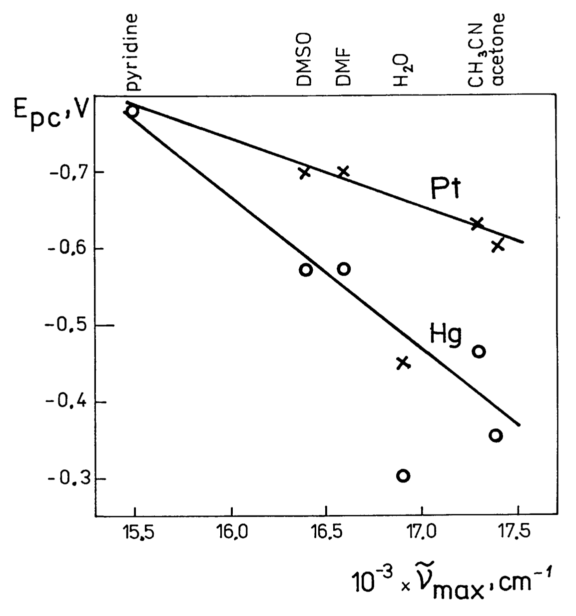


Fig. 2. Relationship between the reduction potential and $\tilde{\nu}_{max}$ value for [Cu(acac)(tmen)]ClO_4 in various solvents.

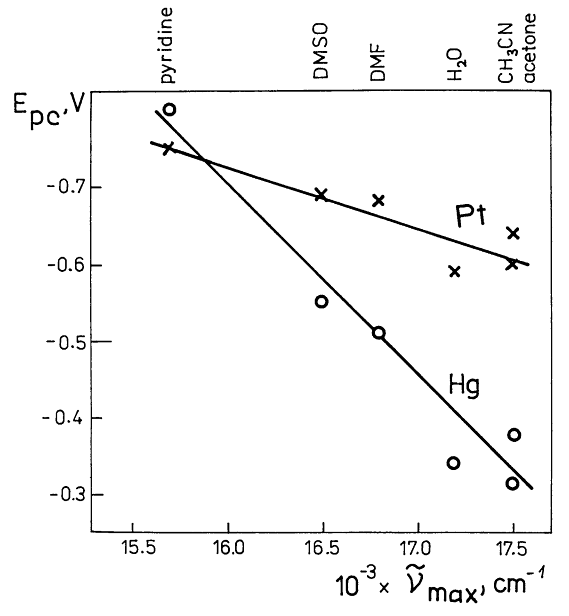


Fig. 3. Relationship between the reduction potential and $\tilde{\nu}_{max}$ value for [Cu_2(taet)(tmen)$_2$](ClO_4)$_2$ in various solvents.

Table 3. Effect of NH_4SCN Addition on the Reduction Potential and d-d Absorption Band of Cu(II) Complexes[a)]

Solvent	NH_4SCN	[Cu(acac)(tmen)]ClO_4		[Cu_2(taet)(tmen)$_2$](ClO_4)$_2$	
		E_{pc} V vs. SCE	$\tilde{\nu}_{max}\times10^{-3}$ cm^{-1}	E_{pc} V vs. SCE	$\tilde{\nu}_{max}\times10^{-3}$ cm^{-1}
DMSO	No	−0.57	16.4	−0.55	16.5
	Yes	−0.65	16.2	−0.65	16.1
DMF	No	−0.57	16.6	−0.51	16.8
	Yes	−0.65	16.3	−0.58	16.7
CH_3CN	No	−0.46	17.3	−0.38	17.5
	Yes	−0.61	15.5[b)]	−0.52	15.4[b)]

a) Reduction on the mercury electrode, NH_4SCN in excess. b) CH_3CN is the weakest donor solvent among the three used and the acceptor properties of the solvent is comparable in these three. So, the axial interaction of NCS^- with the Cu(II) center in this solvent is stronger than those in the other two solvents (see in the text).

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