

# Spectrochemical and Electrochemical Properties of Distorted Pentacoordinate $[\text{Cu}(\text{chel})_2\text{X}]\text{Y}$ Complexes

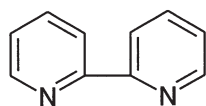
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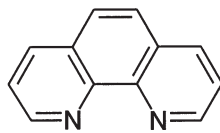
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The trigonal bipyramidal complexes of the general formula  $[\text{Cu}(\text{chel})_2\text{X}]\text{ClO}_4$ , where  $\text{chel} = 2,2'$ -bipyridine (bpy), 1,10-phenanthroline (phen);  $\text{X} = \text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{NCS}^-$ ,  $\text{CN}^-$ , were prepared and their electronic absorption spectra were measured in Nujol mull and nitromethane solution. Using Hathaway's electronic criteria the square-based pyramidal distortion of the trigonal bipyramidal coordination of the complexes in the solid state as well as in nitromethane solutions was analyzed. The electronic spectra indicate that the solid bpy complexes are more distorted than their phen analogues, the greatest difference being found for chloro and the smallest for isothiocyanato complexes. The electronic spectra of some complexes in nitromethane indicate square-based pyramidal distorted trigonal bipyramidal coordinations, while another indicate near trigonal bipyramidal coordinations. The halfwave potentials of complexes in nitromethane, except cyano complexes were in the range  $-0.40\text{ V} - -0.32\text{ V}$  for bpy and  $-0.43\text{ V} - -0.34\text{ V}$  for phen complexes *vs.* ferrocenium/ferrocene couple. A linear correlation between the halfwave potentials and the standard electrode potentials  $E^\circ(\text{X}_2/\text{X}^-)$  was found for both series of bpy and phen  $[\text{Cu}(\text{chel})_2\text{X}]\text{ClO}_4$  complexes in nitromethane indicating that the redox properties of the  $[\text{Cu}(\text{chel})_2\text{X}]\text{ClO}_4$  complexes are predominantly affected by the nature of the ligands X.

Pentacoordinate copper(II) complexes  $[\text{Cu}(\text{chel})_2\text{X}]\text{Y}$  and  $[\text{Cu}(\text{chel})_2\text{L}]\text{Y}_2$ , where  $\text{chel}$  are 2,2'-bipyridine (bpy) or 1,10-phenanthroline (phen) and X and L are anionic and neutral ligands, respectively, and Y are different anions, have been extensively studied by different methods. Crystal and molecular structure of a number of these complexes [1] shows a remarkable distortion of the regular trigonal bipyramidal coordination towards a tetragonal pyramidal stereochemistry, which has been widely studied and correlated especially with electronic and ESR spectra [2–4].



bpy



phen

The trigonal bipyramidal coordination of 2,2'-bipyridine and 1,10-phenanthroline copper(II) complexes  $[\text{Cu}(\text{chel})_2\text{X}]\text{Y}$  and  $[\text{Cu}(\text{chel})_2\text{L}]\text{Y}_2$  showed a redox stabilization of copper(II) relative to copper(I). The preparation and structure of a number of these complexes showed that the equatorial position of the

trigonal bipyramid can be occupied by such reducing ligands X and L like iodide, cyanide, thiocyanate, and thiourea without copper(II) being reduced to copper(I) [5]. It was suggested from ESCA measurements of 2,2'-bipyridine and 1,10-phenanthroline copper(II) complexes  $[\text{Cu}(\text{chel})_2\text{X}]\text{ClO}_4$ , where  $\text{X} = \text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ , and  $\text{NCS}^-$  that the redox stability of the Cu—X bond by electron transfer from X to Cu(II) results from its equatorial position in the trigonal bipyramid. In this position there is a minimum overlap between the ligand X orbitals and  $d_z^2$ -orbital of the copper(II) atom and thus the electron transfer from the ligand X to the  $d_z^2$ -orbital of copper(II) which contains an unpaired electron, becomes impossible [6].

In this paper the electronic spectra and the results of voltamperometric study of distorted trigonal bipyramidal  $[\text{Cu}(\text{chel})_2\text{X}]\text{ClO}_4$  complexes, where  $\text{chel} = 2,2'$ -bipyridine and 1,10-phenanthroline and  $\text{X} = \text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{NCS}^-$ , and  $\text{CN}^-$ , are presented and the effects of the ligands on the structure and redox properties of the  $[\text{Cu}(\text{chel})_2\text{X}]\text{ClO}_4$  complexes are discussed.

## EXPERIMENTAL

The  $[\text{Cu}(\text{chel})_2\text{X}]\text{ClO}_4$  complexes, where  $\text{chel} = \text{bpy}$ , phen and  $\text{X} = \text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{NCS}^-$ ,  $\text{CN}^-$ , were

**Table 1.** Elemental Analysis of [Cu(chel)<sub>2</sub>X]ClO<sub>4</sub> Complexes

Complex	$w_i(\text{calc.})/\%$ $w_i(\text{found})/\%$			
	Cu	C	H	N
[Cu(bpy) <sub>2</sub> Cl]ClO <sub>4</sub> (I)	12.44	47.03	3.16	10.19
[Cu(bpy) <sub>2</sub> Br]ClO <sub>4</sub> (II)	12.41	46.88	3.09	10.82
[Cu(bpy) <sub>2</sub> I]ClO <sub>4</sub> (III)	11.44	43.26	2.90	10.09
[Cu(bpy) <sub>2</sub> NCS]ClO <sub>4</sub> (IV)	11.43	43.16	2.86	9.91
[Cu(bpy) <sub>2</sub> CN]ClO <sub>4</sub> (V)	10.55	39.89	2.68	9.30
[Cu(phen) <sub>2</sub> Cl]ClO <sub>4</sub> (I')	10.31	39.44	2.75	9.44
[Cu(phen) <sub>2</sub> Br]ClO <sub>4</sub> (II')	12.67	50.31	3.22	13.97
[Cu(phen) <sub>2</sub> I]ClO <sub>4</sub> (III')	12.59	49.66	3.18	13.53
[Cu(phen) <sub>2</sub> NCS]ClO <sub>4</sub> (IV')	11.91	47.28	3.02	13.13
[Cu(phen) <sub>2</sub> CN]ClO <sub>4</sub> · 0.5H <sub>2</sub> O (V')	11.49	47.33	3.10	13.10
	11.37	51.58	2.89	10.03
	11.28	51.84	2.94	9.87
	10.53	47.78	2.67	9.29
	10.28	48.01	2.76	9.23
	9.77	44.33	2.48	8.62
	9.71	43.75	2.45	8.32
	11.38	53.77	3.07	12.54
	11.46	53.51	2.83	12.02
	10.93	51.64	2.77	12.04
	10.91	51.92	2.77	11.79

prepared using a modified procedure described elsewhere [7] by reaction of 5 mmol Cu(chel)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub> and 5 mmol KX each dissolved in acetone—water ( $\varphi_r = 1:1$ ) solutions at room temperature. Collected crystalline products were washed with acetone—water mixture and dried *in vacuo*. The results of the elemental analysis of the complexes are presented in Table 1. Nitromethane solutions of the complexes were measured immediately after preparation.

Tetrabutylammonium perchlorate (TBAP) was synthesized from perchloric acid and tetrabutylammonium hydroxide. Nitromethane was dried over anhydrous calcium chloride and then twice fractionally distilled.

Electronic absorption spectra of the [Cu(chel)<sub>2</sub>X]ClO<sub>4</sub> complexes were recorded in Nujol mull and nitromethane solutions with a Specord 200 instrument.

Electrochemical measurements were made on a polarographic analyzer PA (Laboratorní přístroje, Prague), utilizing three-electrode geometry consisting of a platinum-wire working electrode, a platinum-foil auxiliary electrode, and an aqueous saturated calomel reference electrode (SCE). The SCE was separated from the test solution by a bridge filled with the nitromethane and the supporting electrolyte.

Voltammograms of the complexes were done in nitromethane solution (0.05 mol dm<sup>-3</sup> TBAP) under an argon atmosphere at room temperature with scan rate 50 mV s<sup>-1</sup>. At the end of the measurements, ferrocene was added to the measured solution as an internal standard, and all measured potentials were referenced to the formal potential of the ferrocene/ferrocenium couple.

## RESULTS AND DISCUSSION

In nitromethane solutions the perchlorate anions of the [Cu(bpy)<sub>2</sub>X]ClO<sub>4</sub> and [Cu(phen)<sub>2</sub>X]ClO<sub>4</sub> complexes and nitromethane molecules which are considered to have low coordination ability reduce a possible conversion of the pentacoordination especially to a hexacoordination. The complexes, where X = Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, NCS<sup>-</sup> are uni-uni electrolytes in nitromethane, the dissociation of the complex cations, eventually the hexacoordination have not been observed [7]. However, the pentacoordination of the complexes in the solid state as well as in solutions can vary to a great extent from the trigonal bipyramidal coordination to a square-based pyramidal coordination depending on the nature of X, ClO<sub>4</sub><sup>-</sup> and solvent molecules.

Hathaway *et al.* have characterized the distortion of the complex cations in solid [Cu(bpy)<sub>2</sub>X]Y and [Cu(phen)<sub>2</sub>X]Y complexes [3, 4] by parameter  $\tau$  [8], where  $\tau = 1$  for the regular trigonal bipyramidal and  $\tau = 0$  for a regular square-based pyramidal coordination. For the complexes with known structure presented in Table 2  $\tau$  ranges from 0.95 to 0.62. Significantly square-based pyramidal distorted trigonal bipyramidal coordination is shown by the [Cu(bpy)<sub>2</sub>Cl]ClO<sub>4</sub> complex with  $\tau = 0.62$ , while one of the distortion isomers formulated here as  $\alpha$ -[Cu(phen)<sub>2</sub>Br]ClO<sub>4</sub> complex shows a near regular trigonal bipyramidal coordination with  $\tau = 0.95$ . The  $\tau$  values of 0.81 for [Cu(phen)<sub>2</sub>Cl]ClO<sub>4</sub>, 0.85 for [Cu(bpy)<sub>2</sub>Br]ClO<sub>4</sub>, and 0.86 for [Cu(bpy)<sub>2</sub>I]ClO<sub>4</sub> and  $\beta$ -[Cu(phen)<sub>2</sub>Br]ClO<sub>4</sub> refer to a slightly square-

**Table 2.** Electronic Absorption Spectra of [Cu(chel)<sub>2</sub>X]ClO<sub>4</sub> Complexes in Nujol and Nitromethane (in parentheses are molar absorption coefficients ( $\epsilon/(10^3 \text{ cm}^2 \text{ mol}^{-1})$ ))

Complexes of bpy	$\tau^a$	$\tilde{\nu}_{\text{max}} \cdot 10^{-3}/\text{cm}^{-1}$		Complexes of phen	$\tau$	$\tilde{\nu}_{\text{max}} \cdot 10^{-3}/\text{cm}^{-1}$	
		Nujol	Nitromethane			Nujol	Nitromethane
<i>I</i>	0.62	13.99 10.01	13.57 (212) 10.28 (148)	<i>I'</i>	0.81 <sup>b</sup>	11.76 br –	12.99 (700) ≈ 10.30 sh
<i>II</i>	0.85	12.59 ≈ 10.20 sh	13.40 (404) 10.57 (220)	<i>II'</i>	0.86 <sup>b</sup> 0.95 <sup>c</sup>	11.86 br –	13.44 (328) 10.75 (179)
<i>III</i>	0.86	12.18 ≈ 10.10 sh	13.57 (214) 10.28 (151)	<i>III'</i>	–	11.63 br –	13.01 (784) ≈ 10.30 sh
<i>IV</i>	–	12.94 ≈ 10.60 sh	14.07 (195) 10.57 (122)	<i>IV'</i>	–	12.08 ≈ 10.30 sh	13.99 (182) 10.76 (112)
<i>V</i>	–	15.27 12.15	14.56 (141) ≈ 12.00 sh	<i>V'</i>	–	13.81 ≈ 11.80 sh	14.54 (118) 12.10 sh

a) Ref. [4], b) Ref. [3], c) Ref. [9].

based pyramidal distorted trigonal bipyramidal coordination. However, the  $\tau$  values must be applied to structural considerations carefully, since [Cu(chel)<sub>2</sub>X]Y complexes of the same composition prepared by different procedures may have different  $\tau$  values. This can be demonstrated by the two independent distortion isomers  $\alpha$  and  $\beta$  of the [Cu(phen)<sub>2</sub>Br]ClO<sub>4</sub> complex with  $\tau = 0.95$  [9] and 0.86 [3], respectively. From known structures of isothiocyanato [Cu(bpy)<sub>2</sub>NCS]NO<sub>3</sub> · H<sub>2</sub>O and [Cu(bpy)<sub>2</sub>NCS][BF<sub>4</sub>] complexes [1] the respective  $\tau$  values 0.88 and 0.61 can be calculated. For cyano complexes with known structure [1] [Cu(bpy)<sub>2</sub>CN]NO<sub>3</sub> · 2H<sub>2</sub>O, [Cu(phen)<sub>2</sub>CN]NO<sub>3</sub> · H<sub>2</sub>O, and [Cu(phen)<sub>2</sub>CN]cnmet · 2H<sub>2</sub>O (cnmet = tricyanomethanide)  $\tau = 0.54$ , 0.69, and 0.63 have been calculated, respectively, showing a significant square-based pyramidal distorted trigonal bipyramidal coordination of these complexes.

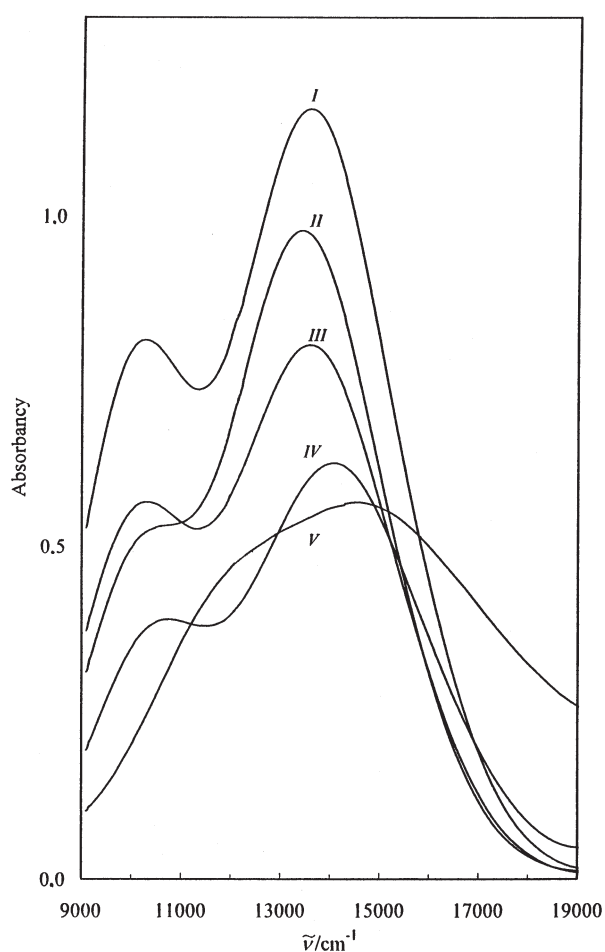
Hathaway *et al.* also analyzed the relations between the structure and electronic reflectance spectra of the bpy and phen [Cu(chel)<sub>2</sub>X]Y complexes with X = Cl<sup>–</sup>, Br<sup>–</sup> and a great number of Y. They drew electronic criteria of stereochemistries for these complexes [3, 4]. The complexes with the regular trigonal bipyramidal coordination show a single band at ≈ 12000 cm<sup>–1</sup>. A broad asymmetric band at ≈ 12000 cm<sup>–1</sup> found for [Cu(bpy)<sub>2</sub>Cl]Y, Y = PF<sub>6</sub><sup>–</sup> · H<sub>2</sub>O, Cl<sup>–</sup> · 6H<sub>2</sub>O complexes indicates almost regular trigonal bipyramidal coordination. A broad asymmetric band at ≈ 12000 cm<sup>–1</sup> with some evidence for a possible low-energy shoulder at ≈ 11100 cm<sup>–1</sup> found for [Cu(phen)<sub>2</sub>Br]Y, Y = Br<sup>–</sup> · H<sub>2</sub>O, ClO<sub>4</sub><sup>–</sup>, PF<sub>6</sub><sup>–</sup>, complexes is consistent with near trigonal bipyramidal stereochemistries. A square-based pyramidal distorted trigonal bipyramidal stereochemistry shows two clearly resolved bands in the regions 13400–14100 cm<sup>–1</sup> and 10100–10300 cm<sup>–1</sup> found for [Cu(bpy)<sub>2</sub>Cl]Y, Y = BF<sub>4</sub><sup>–</sup>, CF<sub>3</sub>SO<sub>3</sub><sup>–</sup> · H<sub>2</sub>O, ClO<sub>4</sub><sup>–</sup>, CF<sub>3</sub>(CF<sub>2</sub>)<sub>3</sub>SO<sub>3</sub><sup>–</sup>, complexes. Near square-based

pyramidal stereochemistry of the [Cu(phen)<sub>2</sub>Br]BPh<sub>4</sub> complex is indicated by a high-energy band at 14400 cm<sup>–1</sup> and a low-energy shoulder at 10700 cm<sup>–1</sup>.

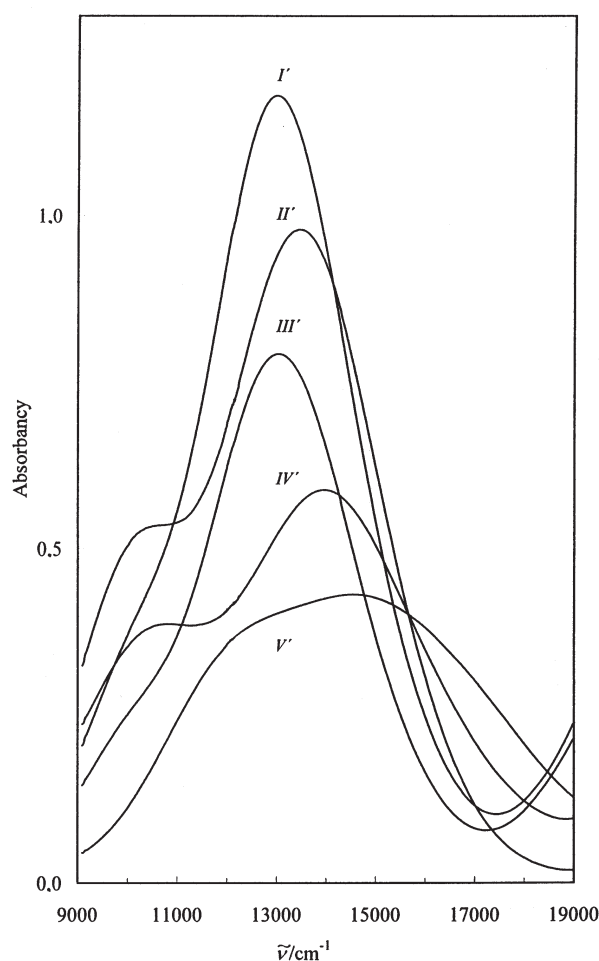
The electronic criteria presented above have been applied to electronic Nujol mull spectra of the [Cu(bpy)<sub>2</sub>X]ClO<sub>4</sub> *I*–*V* and [Cu(phen)<sub>2</sub>X]ClO<sub>4</sub> *I'*–*V'* complexes summarized in Table 2. The single broad symmetric band of *III'* at 11630 cm<sup>–1</sup> and single broad almost symmetric bands of *I'* and *II'* at 11760 cm<sup>–1</sup> and 11860 cm<sup>–1</sup>, respectively, are consistent with the regular trigonal bipyramidal coordination. The complexes *IV'*, *II*, *III*, and *IV* show broad asymmetric bands at 12080 cm<sup>–1</sup>, 12590 cm<sup>–1</sup>, 12180 cm<sup>–1</sup>, and 12940 cm<sup>–1</sup> with shoulders at ≈ 10300 cm<sup>–1</sup>, ≈ 10200 cm<sup>–1</sup>, ≈ 10100 cm<sup>–1</sup>, and ≈ 10600 cm<sup>–1</sup>, respectively, indicating near trigonal bipyramidal coordinations. Clearly resolved bands of *I* at 13990 cm<sup>–1</sup> and 10010 cm<sup>–1</sup> indicate a square-based pyramidal distorted trigonal bipyramidal coordination.

The cyano complexes *V* and *V'* show somewhat different electronic spectra compared with those of other related [Cu(chel)<sub>2</sub>X]ClO<sub>4</sub> complexes. The complex *V* exhibits two resolved bands at 15270 cm<sup>–1</sup> and 12150 cm<sup>–1</sup>, while *V'* shows a very broad band at 13810 cm<sup>–1</sup> with an unresolved shoulder at ≈ 11800 cm<sup>–1</sup>. The energies of these bands indicate two superimposed effects: a strong ligand field of the cyano ligand and a significant square-based pyramidal distortion of the trigonal bipyramidal coordination, which is stronger for bpy (*V*) than for phen (*V'*) complex.

The electronic spectra of the solid *I*–*V* and *I'*–*V'* complexes indicate that the trigonal bipyramidal coordination of bpy complexes is more distorted than that of corresponding phen complexes. This may be associated with the differing rigidity of the bpy and phen ligands [4]. In general, the energy of the high-energy bands follows the spectrochemical series of the ligands X. The exceptions are the complexes showing



**Fig. 1.** Electronic spectra of  $[\text{Cu}(\text{bpy})_2\text{X}]\text{ClO}_4$  complexes in nitromethane. For X: *I* –  $\text{Cl}^-$ , *II* –  $\text{Br}^-$ , *III* –  $\text{I}^-$ , *IV* –  $\text{NCS}^-$ , *V* –  $\text{CN}^-$ .



**Fig. 2.** Electronic spectra of  $[\text{Cu}(\text{phen})_2\text{X}]\text{ClO}_4$  complexes in nitromethane. For X: *I'* –  $\text{Cl}^-$ , *II'* –  $\text{Br}^-$ , *III'* –  $\text{I}^-$ , *IV'* –  $\text{NCS}^-$ , *V'* –  $\text{CN}^-$ .

a clear departure from the trigonal bipyramidal coordination.

The solid and nitromethane solution electronic spectra of *I–V* and *I'–V'* are similar. The nitromethane solutions show better resolved bands compared with those of solids. This may indicate a stronger square-based pyramidal distortion of the trigonal bipyramidal coordination of the complexes in nitromethane, although the resolution of the bands can also be affected by the state of matter. The similarity of the solid and nitromethane solution electronic spectra enables us to apply the electronic criteria to the complexes *I–V* and *I'–V'* dissolved in nitromethane.

The electronic spectra of *I–V* and *I'–V'* in nitromethane are presented in Figs. 1 and 2. The energy of the bands and the molar absorption coefficients of the resolved bands referred to zero lines are summarized in Table 2. The bpy complexes *I*, *III*, and *IV* in nitromethane show two clearly resolved bands, *I* at  $13570\text{ cm}^{-1}$  and  $10280\text{ cm}^{-1}$ , *III* at  $13570\text{ cm}^{-1}$  and  $10280\text{ cm}^{-1}$ , and *IV* at  $14070\text{ cm}^{-1}$  and  $10570\text{ cm}^{-1}$ .

Two resolved bands are shown in nitromethane only by the phen complexes *II'* at  $13440\text{ cm}^{-1}$  and  $10750\text{ cm}^{-1}$  and *IV'* at  $13990\text{ cm}^{-1}$  and  $10760\text{ cm}^{-1}$ . The resolved bands could indicate square-based pyramidal distorted trigonal bipyramidal coordinations of these complexes in nitromethane. The bpy complex *II* with a band at  $13400\text{ cm}^{-1}$  and an expressive shoulder at  $10570\text{ cm}^{-1}$  can also be arranged in this group of the complexes. However, the phen complexes *I'* and *III'* show a band and a weak low-energy shoulder, *I'* at  $12990\text{ cm}^{-1}$  and  $\approx 10300\text{ cm}^{-1}$  and *III'* at  $13010\text{ cm}^{-1}$  and  $\approx 10300\text{ cm}^{-1}$  suggesting near trigonal bipyramidal coordinations of these complexes in nitromethane. The suggested one-electron ground state configuration [10] for the trigonal bipyramidal coordination is  $d_{z^2} > d_{xy} \approx d_{x^2-y^2} > d_{xz} \approx d_{yz}$ . The high-energy band may be assigned as a  $d_{xz} \approx d_{yz} \rightarrow d_{z^2}$  transition and the low-energy band or shoulder as a  $d_{xy} \approx d_{x^2-y^2} \rightarrow d_{z^2}$  transition. The cyano complexes *V* and *V'*, unlike other complexes, exhibit in nitromethane very similar electronic spectra showing broad bands at  $14560\text{ cm}^{-1}$  and  $14540\text{ cm}^{-1}$  with massive low-energy shoul-

**Table 3.** Halfwave Potentials<sup>a</sup> and Reversibility of [Cu(chel)<sub>2</sub>X]ClO<sub>4</sub> Complexes in Nitromethane

Complexes of bpy	$\Delta E_{1/2}/V^a$	Rev/mV	Complexes of phen	$\Delta E_{1/2}/V^a$	Rev/mV
<i>I</i>	-0.40	220—240	<i>I'</i>	-0.43	200
<i>II</i>	-0.33	155	<i>II'</i>	-0.36	210
<i>III</i>	-0.31	180	<i>III'</i>	-0.31	300
<i>IV</i>	-0.32	125	<i>IV'</i>	-0.34	230
<i>V</i>	- <sup>b</sup>	- <sup>b</sup>	<i>V'</i>	-0.37	240

a) Vs. ferrocene/ferrocenium couple. b) Not detected.

ders at  $\approx 12000\text{ cm}^{-1}$  and  $\approx 12100\text{ cm}^{-1}$ , respectively. These bands, unlike absorptions of other presented complexes could be attributed to a trigonal bipyramidal distorted square-based pyramidal coordination with the suggested one-electron ground state configuration  $d_{x^2-y^2} > d_{z^2} > d_{xy} > d_{xz} \approx d_{yz}$  and the transitions  $d_{xz} \approx d_{yz} \rightarrow d_{x^2-y^2}$  for the high-energy bands and  $d_{z^2} \rightarrow d_{x^2-y^2}$  for the low-energy shoulder.

The bpy and phen ligands are considered to be good electron donors. It could be expected that the donation of electrons by bpy and phen in the trigonal bipyramidal [Cu(bpy)<sub>2</sub>X]ClO<sub>4</sub> and [Cu(phen)<sub>2</sub>X]ClO<sub>4</sub> complexes will increase an electron density on the copper(II) atoms. The ESCA measurements revealed [6] practically the same values of the Cu2p<sub>3/2</sub> binding energy for [Cu(bpy)<sub>2</sub>X]ClO<sub>4</sub> and [Cu(phen)<sub>2</sub>X]ClO<sub>4</sub> complexes which are at the same time close to the related binding energies of simple copper(II) salts. However, the equatorial ligands X = Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, and NCS<sup>-</sup> possess higher electron density than in simple copper(II) and copper(I) salts indicating the electron density transfer from the bpy and phen ligands *via* the copper(II) atoms to the ligands X. Obviously, the extent of the electron density transfer on the paths bpy(phen)—Cu(II)—X will depend on more factors of which the distortion of the trigonal bipyramidal coordination,  $\pi$ -bonding, and nature of the ligands X can be considered as the most important.

Analysis [11] of  $\pi$ -bonding of the chelating bpy and phen ligands occupying two apical positions in the trigonal bipyramidal coordination of copper(II) showed that these ligands have full  $\pi$ -function and fully accept electrons from the copper(II)  $d_{xz}$  and  $d_{yz}$  orbitals, while in two equatorial positions they have reduced  $\pi$ -function and only partly accept electrons from the partly antibonding copper(II)  $d_{xy}$  and  $d_{x^2-y^2}$  orbitals. There is no interligand  $\pi$ -conjugation. These  $\pi$ -functions contribute to the shortening of the Cu—N(apical) bonds compared with those of the Cu—N(equatorial). In the square pyramidal coordination equatorial bpy and phen ligands have full  $\pi$ -function and four chelating *N*-donor atoms fully accept electrons from the copper(II)  $d_{xz}$  and  $d_{yz}$  orbitals. As a result the equatorial Cu—N bonds are shorter than the apical Cu—X bond. Consideration of  $\pi$ -bonding tends therefore to stabilize a regular square pyramid.

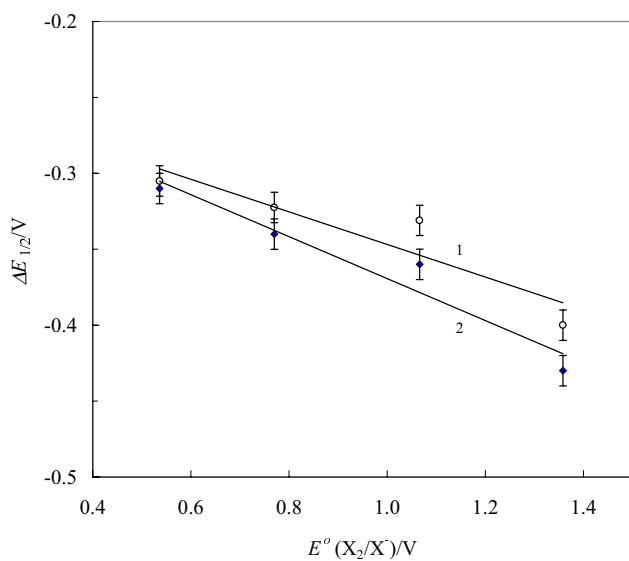
However, there is a loss of  $\pi$ -bond order for configuration other than square pyramidal.

Halfwave potentials measured for bpy and phen [Cu(chel)<sub>2</sub>X]ClO<sub>4</sub> complexes in nitromethane solution (Table 3) show very small, but evident difference between the bpy and phen complexes. Since there is a small difference in  $\pi$ -bonding between the bpy and phen ligands the main contribution to the difference may consist of different distorted trigonal bipyramidal coordinations. As seen from the solution electronic spectra the complexes of bpy *I* and *III* are evidently more distorted than the corresponding complexes of phen *I'* and *III'*. The former complexes *I* and *III* show higher values of halfwave potentials and easier reduction than the latter *I'* and *III'*. The isothiocyanato complexes *IV* and *IV'* show approximately the same distortion and thus close values of halfwave potential. The complexes with more square-based pyramidal distorted trigonal bipyramidal stereochemistry showed higher values of the halfwave potentials than their less distorted analogues. The bromo complexes *II* and *II'* unlike solid electronic spectra exhibit almost identical electronic spectra in nitromethane, however, their halfwave potentials are different.

The value of the halfwave potential  $-0.37\text{ V}$  found for the cyano complex *V'*, which does not fit with the series of the trigonal bipyramidal complexes could refer to the square-based pyramidal coordinations. It is not clear, why the cyano complexes *V* and *V'* showing almost identical electronic spectra in nitromethane solution behave themselves electrochemically quite differently. The reactivity of cyano [Cu(chel)<sub>2</sub>X]ClO<sub>4</sub> complexes which tend to associate through a cyano bridge between the two copper(II) atoms [7] may be the reason that the voltammogram for the complex *V* has not been detected.

There is a linear correlation between the halfwave potentials of both bpy and phen complexes and the standard electrode potentials of the couples X<sub>2</sub>/X<sup>-</sup> in water [12], as shown in Fig. 3. These linear correlations indicate that the effect of the equatorial ligands X on reduction of the [Cu(chel)<sub>2</sub>X]ClO<sub>4</sub> complexes dominates over all other effects. The lower  $E^\circ(\text{X}_2/\text{X}^-)$  value, the easier reduction of the [Cu(chel)<sub>2</sub>X]ClO<sub>4</sub> complex.

Using above linear correlations the halfwave po-



**Fig. 3.** Plot of halfwave potentials vs.  $E^\circ(X_2/X^-)$ . 1 – [Cu(bpy)<sub>2</sub>X]ClO<sub>4</sub> and 2 – [Cu(phen)<sub>2</sub>X]ClO<sub>4</sub> complexes.

tentials (vs. ferrocenium/ferrocene couple) for hypothetical trigonal bipyramidal hydrido and fluoro [Cu(chel)<sub>2</sub>X]ClO<sub>4</sub> complexes were calculated, being 0.05 V and –0.60 V for bpy and 0.08 V and –0.63 V for phen complexes, respectively.

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