Electrochemical behaviour of some *N*-salicylideneaminoalkanoate copper(II) complexes and cuprates(II)

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Using voltammetry on static mercury drop electrode and stationary platinum electrode in aqueous and dimethyl sulfoxide solutions the electrochemical behaviour of a particular group of copper(II) complexes with tridentate Schiff bases of the *N*-salicylideneaminoalkanoates (TSB) type as well as with additional molecular (H_2O) or anionic ligand (NCS^-, NCO^-) was investigated. The TSB ligands in the investigated compounds are derived from L- or D, L-α-amino acids, glycine or β-alanine. The complexes undergo a one-electron reduction localized on the central atom which is quasi-reversible on mercury electrode. The Cu(I) complexes arisen as reduction products are stable only in the voltammetric time scale. The values of half-wave potentials occurring in the interval from -0.165 V to -0.335 V (*vs.* SCE) were determined. They are discussed in respect to the activity of these complexes resembling that of the superoxide dismutase.

The Schiff bases of the *N*-salicylideneaminoalkanoates type are coordinated to central atom most frequently as tridentate dianionic ligands TSB^{2-} through their O,N,O-donor atoms. Thus the complexes with fused chelate rings arise with the metallocycles which are either 5,6-membered (TSB derived from α-amino acids) or 6,6-membered (TSB derived from *N*-salicylidene-β-alanine) [1—3]. In the solid state Cu(II) usually coordinates not only TSB but also another ligand which can be molecular (L) [4, 5] or anionic (A) [6—8]. A schematic representation is given in Fig. 1.

The almost planar coordination of donor atoms in the base of coordination polyhedron, the formed system of bonds and the strength of chelate rings have significant influence on the redox stability of Cu(II) in these complexes. Owing to this fact some reductive additional ligands, such as thiourea and its derivatives or the NCS^- ions [6, 8] can be linked to Cu(II) in these complexes without any change in its oxidation state. A more detailed knowledge of the redox properties of Cu(II) in these complexes is especially important from the viewpoint of biocoordination chemistry. Recently we found that some compounds

of the type mentioned above exhibit a significant activity which is similar to that of superoxide dismutase (SOD) [9, 10]. In general, this activity is also dependent on the redox Cu(II)/Cu(I) changes in the coordination compounds [11, 12] which are used and examined as simple models of the active centre of metalloenzyme Cu/Zn-SOD [13].
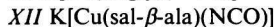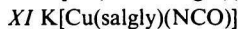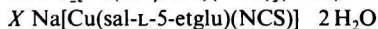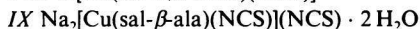

I [Cu(sal-L-gluH)(H$_2$O)$_2$] H$_2$O
II K[Cu(sal-L-glu)(H$_2$O)]
III K[Cu(sal-D,L-glu)(H$_2$O)]
IV [Cu(sal-L-5-etglu)(H$_2$O)] H$_2$O
V [Cu$_2$(sal-β-ala)$_2$(H$_2$O)] H$_2$O
VI K[Cu(salgly)(NCS)] 2 H$_2$O

VII K[Cu(sal-L-α-ala)(NCS)]
$VIII$ K[Cu(sal-D,L-α-ala)(NCS)]
IX Na$_2$[Cu(sal-β-ala)(NCS)](NCS) · 2 H$_2$O
X Na[Cu(sal-L-5-etglu)(NCS)] 2 H$_2$O
XI K[Cu(salgly)(NCO)]
XII K[Cu(sal-β-ala)(NCO)]
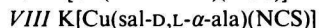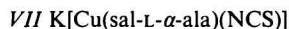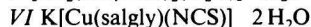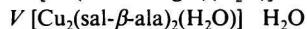
Fig. 1. N-Salicylideneaminoalkanoate copper(II) complex.

In order to determine the reduction potential of Cu(II) and to characterize the influence of the coordination sphere consisting of different TSB and additional ligands, we investigated the electrochemical properties of a selected group of complexes of the above type. The measurements were carried out under different conditions because the redox parameters were also dependent on solvent and working electrode used [14].
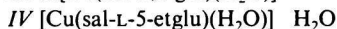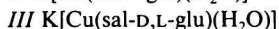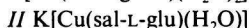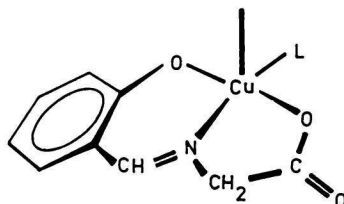
Experimental

N-Salicylideneaminoalkanoates (TSB^{2-}) coordinated in the investigated copper(II) complexes or complex cuprates(II) were derivatives of glycine (salgly)$^{2-}$, L-α-alanine (sal-L-α-ala)$^{2-}$, D,L-α-alanine (sal-D,L-α-ala)$^{2-}$, β-alanine (sal-β-ala)$^{2-}$, L-glutamic acid (sal-L-gluH)$^{2-}$, L-glutamate (sal-L-glu)$^{3-}$, D,L-glutamate (sal-D,L-glu)$^{3-}$ or 5-ethyl ester of L-glutamic acid (sal-L-5-etglu)$^{2-}$ The chemical formulae of compounds and the numerical denotation used in this paper are given in the text to Fig. 1.

Complex I was obtained according to [1] and complex II was prepared by neutralization of the terminal carboxyl group of complex I by using equivalent amount of KOH in ethanolic solution. Complex III was prepared like complex II, the only difference being that Cu(sal-D,L-gluH)(H$_2$O) 2 H$_2$O obtained after racemization of complex I according

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to [7] was used as starting substance. Complex *IV* was prepared in the same way as complex *I* by using 5-ethyl ester of L-glutamic acid. Complex *V* was obtained according to [4]. The reactions of the corresponding aqua-(*N*-salicylideneaminoalkanoate)copper(II) complexes with NaSCN, KSCN or KOCN as described in papers [6, 7] were used for preparing complexes *VI—XII*. The purity of these preparations was tested by elemental analysis.

The electrochemical measurements were carried out with a polarographic analyzer PA 4 equipped with a unit comprising static mercury drop electrode SMDE and X—Y recorder (Laboratorní přístroje, Prague). The three-electrode arrangement comprising a mercury drop electrode or platinum electrode as working electrode, a large-surface auxiliary platinum electrode and a saturated calomel reference electrode (SCE) standardized for the redox couple ferricinium/ferrocene in DMSO ($E_{1/2} = 0.400$ V) was applied. The measurements were performed at 25 °C in argon atmosphere, at the scan rate of $100 \, \text{mV s}^{-1}$ A solution containing 0.1 M-KNO$_3$ and 0.002 % Triton X 100 was used as a supporting electrolyte.

Results and discussion

All the investigated compounds undergo a one-electron diffusion-controlled reduction localized on the central atom. Typical voltammograms are represented in Figs. 2 and 3. The electrochemical picture contains several cathodic and
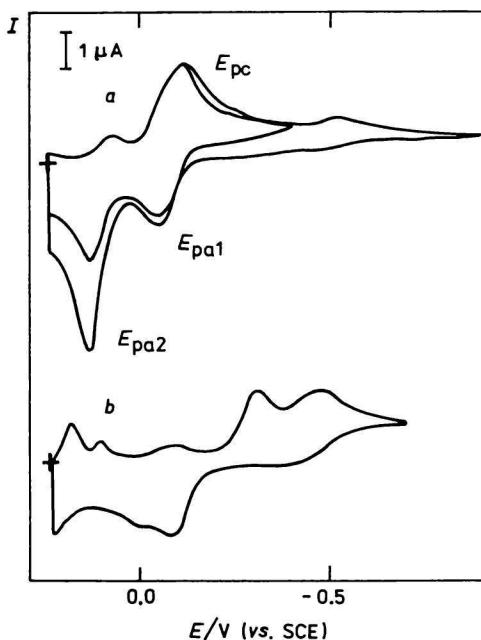

Fig. 2. Cyclic voltammograms for compound *I* ($c = 1 \times 10^{-3} \, \text{mol dm}^{-3}$) at pH 4.1 (*a*) and pH 9.9 (*b*) recorded with a static mercury drop electrode in 0.1 M-KNO$_3$ (scan rate 0.1 V s^{-1}).

anodic peaks of different form dependent on potential scan rate which indicates that the electrochemical reaction is complicated by other physical and chemical processes.

The cyclic voltammograms obtained with mercury electrode exhibit the course typical of quasi-reversible electrochemical reaction. The values of potential of the reduction peak (E_{pc}) and of the peak of anodic oxidation following after the scan reversion (E_{pa1}) as well as the values of half-wave potential ($E_{1/2} = (E_{pc} + E_{pa1})/2$) are listed in Table 1. In most cases, the ratio of the current of the first anodic counterpeak to that of the cathodic peak approaches one and potential peaks separation is near to 200 mV. The double form of the peak at E_{pa1} (Figs. 2b, 3a, 3b) suggests the presence of two forms of Cu(I) at least.

In the region of more negative potentials than E_{pc} the voltammograms are complicated by adsorption of the investigated compounds on mercury. The presence of Triton X 100 significantly suppresses this phenomenon. However, for some complexes (*VI—XII*) the voltammograms indicate the fixation of a
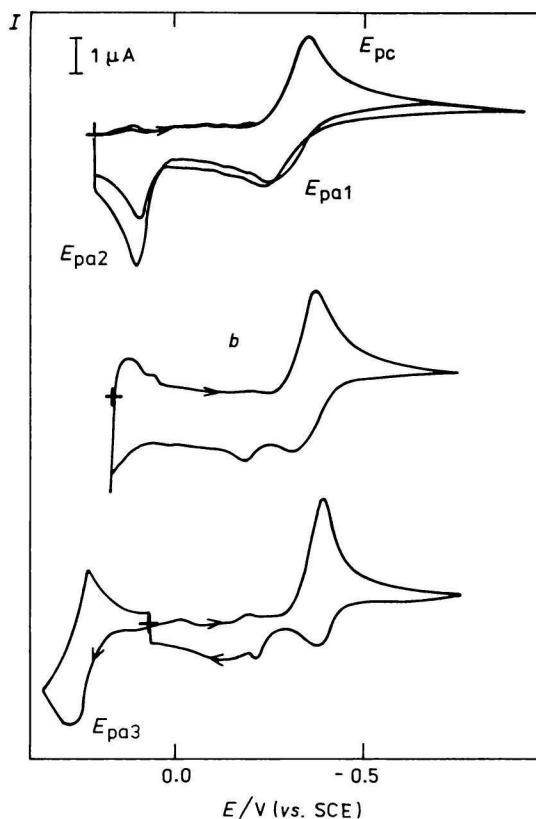

Fig. 3. Cyclic voltammograms for compound *IV* ($c = 1 \times 10^{-3}$ mol dm^{-3}) at pH 6.3 (*a*) and pH 10.0 (*b*) and for *X* ($c = 1 \times 10^{-3}$ mol dm^{-3}) at pH 7.4 (*c*) recorded with a static mercury drop electrode in 0.1 M-KNO$_3$ (scan rate 0.1 V s^{-1}).

part of depolarizer on the surface of electrode also in this medium — a higher cathodic peak and small anodic counterpeak near to it (Fig. 3c). In this case, the assignment of peaks was verified by the record of Cu^{2+} in the presence of SCN^- The peak E_{pa1} is significantly more positive than E_{pc}.

Table 1

Redox potentials (in V *vs.* SCE) measured by cyclic voltammetry on a static mercury drop electrode in aqueous solution of 0.1 M-KNO_3 at pH 7.2—7.8

Compound	E_{pc}	E_{pa1}	$E_{1/2}$	E_{pa2}	E_{pa3}
I	−0.270	−0.050	−0.160	0.115	
II	−0.320	−0.050	−0.190	0.145	
III	−0.360	−0.120	−0.240	0.140	
IV	−0.380	−0.220	−0.295	0.120	
V	−0.260	−0.160	−0.220	0.140	
VI	−0.390	−0.180	−0.285		0.290
VII	−0.440	−0.230	−0.335		0.280
VIII	−0.385	−0.160	−0.270		0.280
IX	−0.390	−0.210	·−0.300		0.290
X	−0.380	−0.170	−0.275		0.280
XI	−0.330	−0.220	−0.275		0.330
XII	−0.280	−0.180	−0.230		0.330

The cyclic voltammograms of complexes *I—V* contain another anodic peak at E_{pa2} (Table 1). Its height increases if the potential is held at E_{pc} or the electrode is polarized to rather more negative potentials than E_{pc} (Figs. 2a, 3a). The peak at E_{pa2} represents stripping process and belongs to re-dissolution of Cu^0 This fact points out a partial decomposition of the complexes of Cu(I) (step C) to Cu^+(aq) which is subsequently reduced in the potential region of E_{pc} (step E) to Cu^0 (the so-called ECE mechanism [15]). The presence of pseudohalide hinders the reduction of Cu(I) to Cu^0 and that is why the peak at E_{pa2} was either not observed for complexes *VI—XII* or observed only after acidification of the solution to pH 4. The complexes of Cu(I) as reduction products of the Cu(II) compounds investigated in this study thus persist in solution only for a relatively short period of voltammetric time scale.

Complex cuprates(II), *i.e.* complexes *VI—XII* which have been subjected to direct anodic oxidation or to cathoanodic cyclic voltammetry on ˙mercury electrode (Fig. 3c) exhibit another anodic peak E_{pa3} at about 0.280 V for compounds with NCS ligand and at about 0.330 V *vs.* SCE for compounds with NCO ligand. These peaks are evidently related with the electrochemical oxidation of electrode material (Hg^0) in the presence of complex-forming agent (free

pseudohalide ions). The corresponding cathodic counterpeak representing reduction of the formed Hg(II) compound is separated from the peak at E_{pa3} by 55—75 mV with the unit ratio of peak currents. In the case of complex compound *IX* which contains two SCN⁻ particles (one of them is coordinated) per one copper atom the current of peak at E_{pa3} is evidently higher. These facts give evidence of bond lability of the pseudohalide ions in the Cu(II) complexes which results in their presence in the aqueous solution. Thus it is confirmed that the bridging function of pseudohalides in dimeric units of the investigated compounds, typical of solid state [16—18], is impaired by the transition into solution. The aquation of apical position as well as of equatorial pseudohalide ligand may be described by the following equation

$$[Cu_2(TSB)_2(NCS)_2]^{2-} + 2\,H_2O \;\rightleftharpoons\; 2\,[Cu(TSB)(H_2O)_2] + 2\,SCN^-$$
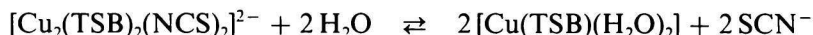
The electrochemical properties of the Cu(II) complexes as a function of pH were also investigated. The solutions of complexes *I—III* are weakly acidic (pH 4.1—5.5), which is due to protolysis of the H_2O molecule strongly coordinated in plane. In the course of reduction on mercury electrode these compounds exhibit several cathodic peaks (Table 2). By increasing the pH value by means of KOH addition the peaks corresponding to more negative potential E_{pc} (Fig. 2b) become dominant, which is caused by the presence and reduction of the anionic Cu(TSB) hydroxo complexes. The potentials of the anodic peaks E_{pa1} and E_{pa2} do not depend on pH of solution. The peak at E_{pa1} is a counterpeak already to the first of the series of cathodic peaks. If the electrode is polarized to more negative potentials (cathodic peaks of the anionic Cu(II) complexes), only an increase in current of the peak at E_{pa1} can be observed.

Table 2

Influence of pH of aqueous solution on the reduction potential of coordination compounds *I—III* (the pH value of original solution was adapted by addition of KOH, other conditions as given in Table 1)

Compound	pH	Reduction potential		E_{pc}/V
I	4.1	−0.140	—	−0.520
	6.8	—	−0.270	−0.500
	9.6	—	−0.285	−0.500
II	5.4	−0.100	−0.310	−0.570
	7.5	—	−0.320	−0.570
	9.4	—	−0.330	−0.570
III	5.5	−0.130	−0.320	−0.570
	8.3	—	−0.370	−0.580
	10.1	—	—	−0.590

The solution of complex *IV* in which the noncoordinated carboxyl group is esterified is less acidic (pH 6.2) while the solutions of complexes *V—XII* exhibit pH values in the range 7.2—7.8. The voltammograms of complexes *IV—XII* do not depend on pH of solution in the range pH 4 to 11. The stability of the Cu(I) complexes corresponding to all 12 investigated compounds is greater in weak alkaline medium (the pH range 10—11), owing to which no Cu^+(aq) ions arise and the stripping peak of Cu^0 (E_{pa2}) either does not at all appear or is only very small (Figs. 2*b*, 3*b*).

In principle, the voltammetric bearing of the complexes in dimethyl sulfoxide is similar to their behaviour in aqueous solutions. The position of the Cu(II)/Cu(I) change is by a few hundreds of millivolts more negative than it is in aqueous solution, which confirms the entry of a molecule of solvent as a strong donor into the coordination sphere of copper [14].

The voltammetric reduction of the complex compounds performed on platinum electrode is irreversible in both solvents and the cathodic peaks at E_{pc} are by about 200 mV more negative than they are on mercury electrode. However, if a platinum electrode is used, none of the investigated compounds possesses an anodic peak in the potential region up to 0.7 V, which confirms the interpretation of the peak at E_{pa3} given above.

If we compare the measured potentials of the redox couples Cu(II)/Cu(I) with each other, we can state that the differences in composition of the investigated compounds only insignificantly influence the redox change of Cu(II). Less negative values of half-wave potentials were observed only if TSB^{2-} was represented by $(sal-L-gluH)^{2-}$, $(sal-L-glu)^{3-}$ or $(sal-D,L-glu)^{3-}$ (Table 1) in compounds *I—III*. That may be due to a reduced stability of the Cu(II) atom coordinating as TSB the derivatives of dicarboxylic amino acids [19]. This effect is eliminated in compounds *IV* and *X* owing to esterification of the terminal carboxyl group of the glutamate part of TSB, which manifests itself by a shift in values of the redox potentials into the region characteristic of other investigated substances.

On the basis of negative values of reduction potential we can conclude that Cu(II) state in these compounds is considerably stable with respect to the redox change. This fact is in good agreement with the formation and properties of the redox-stable *N*-salicylideneaminoalkanoatethiourea copper(II) complexes [3] coordinating thiourea as a *S*-ligand of significantly reductive properties [20].

If we search for the relationships between parameters of electrochemical behaviour and significant SOD activity, found for several representatives of the investigated series [9, 10], we must take into consideration that $E_{1/2}$ values are more negative (by 185—355 mV) than the Cu(II)/Cu(I) redox potential characteristic of the active centre of metalloenzyme (EC 1.15.1.1) Cu/Zn-SOD which is equal to 0.020 V *vs.* SCE [21]. The potential calculated from thermodynamic

data for the Cu(II) compounds able to catalyze the dismutation of O_2^- under physiologic conditions [12] depends on the concentration of O_2^- and exhibits slightly positive or slightly negative value *vs.* SCE. A small value of potential (-0.01 V *vs.* SCE [22]) is also displayed by the tetraaza macrocyclic complex $Cu(TAAB)^{2+}$ which is frequently presented as a model of the active centre of metalloenzyme Cu/Zn-SOD [23]. On the other hand, the SOD activity has also been observed in the case of the bis(*o*-phenanthroline)-copper(II) cation [24] the redox potential of which (-0.13 V *vs.* SCE) is already less different from the values determined in this work.

The above discussion on the composition of coordination sphere of the investigated complexes in solution also conduces to the interpretation of their significant SOD activity on the basis of the presence of an apical weakly coordinated water molecule which has appeared to be a place of substrate entry in the active centre of the natural Cu/Zn-SOD enzyme [13].

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