

## Substituent Effects on Oxidation Potentials of Co(II) and Cu(II) Complexes with Tetradentate Thioiminate Schiff Base Ligands

A. KOTOČOVÁ, D. VALIGURA, P. FODRAN and J. ŠIMA

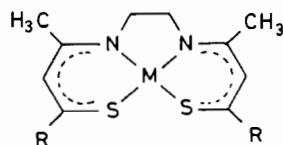
Department of Inorganic Chemistry, Slovak Technical University, 812 37 Bratislava, Jánska 1, Czechoslovakia

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The electrochemical oxidation of the Co(II) and Cu(II) complexes with a series of tetradentate thioiminate ligands,  $N,N'$ -ethylenebis( $R$ -monothioacetimininate) ( $H_2N_2S_2R_2$ ), where  $R = CH_3, CF_3, C_6H_5, p-OCH_3C_6H_4$  and  $p-BrC_6H_4$ , was investigated by cyclic voltammetry in methanol solvent at a platinum electrode. The one-electron oxidation potentials for the cobalt complexes varied linearly with the Hammett substituent constants and those for copper complexes with the Taft ones. Coordination of triphenylphosphine in the axial position of the complexes was also studied.

### Introduction

In the preceding articles [1–4] we discussed the redox properties of the complexes of Co(II) and Cu(II) with  $N,N'$ -ethylenebis(monothioacetylacetoniminate) ligand. Much attention has been paid to axial interactions of the above complexes. In order to complete a systematic study on the redox properties of Co(II) and Cu(II) complexes with extended  $\pi$ -system Schiff base ligands, we report here the electrochemical behaviour of the complexes of the type



$M = Co, Cu$

$R = CH_3, CF_3, C_6H_5, p-OCH_3C_6H_4, p-BrC_6H_4$

further on denoted as  $MN_2S_2R_2$ .

The present paper deals with the changes of the redox properties of these complexes caused by an equatorial modification of the tetradentate ligand with a substituent of various electronic properties.

### Experimental

The complex  $CuN_2S_2(CH_3)_2$  and the ligands  $H_2N_2S_2R_2$ , where  $R = CH_3, C_6H_5, p-OCH_3C_6H_4$  and

$p-BrC_6H_4$  were prepared according to the literature methods [5, 6]. The preparations of the ligand  $H_2N_2S_2(CF_3)_2$  and the other  $CuN_2S_2R_2$  complexes have not yet been reported [7]. Analyses for carbon, hydrogen and nitrogen were in concordance with the calculated values. The cobalt complexes due to their reactivity with oxygen were prepared by synthesis of cobalt(II) acetate with a corresponding ligand directly in an electrolyzed compartment.

Commercially available triphenylphosphine (TPP) was purified by threefold recrystallization from ethanol. Tetrabutylammonium perchlorate (TBAP) was synthesized from perchloric acid and tetrabutylammonium hydroxide. Methanol was purified by the standard procedure.

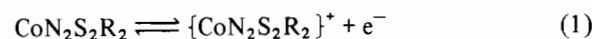
Electrochemical experiments were performed with a polarograph OH 105 (Radelkis, Budapest). A three electrode configuration was used consisting of a platinum-wire working electrode, a platinum-foil auxiliary electrode, and an aqueous saturated calomel reference electrode (SCE). The SCE was separated from the test solution by a bridge filled with the solvent and the supporting electrolyte. Voltammograms of all complexes were recorded on methanol solution (0.05 M TBAP) at room temperature. The scan rate was  $66.6 \text{ mV s}^{-1}$ .

The changes of the redox properties of the cobalt and copper complexes were prepared in all cases with those of the corresponding complexes with substituent  $R = CH_3$ . Triphenylphosphine was added to the system until further addition did not cause any change of the observed redox properties.

### Results and Discussion

#### $CoN_2S_2R_2$

The electrode potentials of the reaction 1 were



reasonably responsive to the inductive properties of the substituents  $R$ , as can be seen by inspection of Table I. The potentials were determined from the sum of the peak potentials  $E_{1/2}' = (E_{pa} + E_{pc}) 2^{-1}$  and

TABLE I. Electrochemical Data for the  $\text{CoN}_2\text{S}_2\text{R}_2$  Complexes.

R	$\Delta E_{1/2}'^a$ (mV)	$\Delta E_{1/2}'^{\text{TPP}^b}$	$\sigma_{\text{R}}^{+c}$ $\sigma_{\text{R}}$
p- $\text{OCH}_3\text{C}_6\text{H}_4$	-112	-155	-0.67 -0.21
$\text{CH}_3$	0	-180	-0.07 -0.07
$\text{C}_6\text{H}_5$	10	-205	0.11 0.06
p- $\text{BrC}_6\text{H}_4$	55	-225	0.26 0.29
$\text{CF}_3$	97	-252	0.52 0.415

<sup>a</sup> $\Delta E_{1/2}' = E_{1/2}'(\text{CoN}_2\text{S}_2\text{R}_2) - E_{1/2}'(\text{CoN}_2\text{S}_2(\text{CH}_3)_2)$ .  
<sup>b</sup> $\Delta E_{1/2}'^{\text{TPP}} = E_{1/2}'(\text{CoN}_2\text{S}_2\text{R}_2 + \text{TPP}) - E_{1/2}'(\text{CoN}_2\text{S}_2(\text{CH}_3)_2)$ .  
<sup>c</sup>Reference [8].

were shifted along the potential axis in concordance with the electron-donating or electron-withdrawing character of the substituent.

In order to quantify the observed variations, *i.e.* the effects of electron-donating and electron-withdrawing substituents attached to the equatorial ligand, a Hammett linear free energy relationship was used [8]:

$$\Delta E_{1/2}' = \rho \Sigma \sigma_{\text{R}} \quad (2)$$

$\Delta E_{1/2}'$  is the difference in  $E_{1/2}'$  oxidation potentials between the  $\text{CoN}_2\text{S}_2\text{R}_2$  and  $\text{CoN}_2\text{S}_2(\text{CH}_3)_2$  complex,  $\rho$  is a constant characteristic of the reaction involved and  $\sigma_{\text{R}}$  is a constant characteristic of the substituent R. In the present study the  $\Sigma \sigma_{\text{R}}$  equals to  $2\sigma_{\text{R}}$  due to additive effects of two substituents R on the equatorial ligand.

There was a close correlation ( $r = 0.94$ ) between the  $\Delta E_{1/2}'$  values of the  $\text{CoN}_2\text{S}_2\text{R}_2$  complex oxidation and the  $\sigma_{\text{R}}$  Hammett substituent parameters. A better correlation was obtained ( $r = 0.99$ ), however, when  $\pi$  resonance conjugation of some substituents ( $\sigma_{\text{R}}^+$ ) was considered. In this case, the Hammett relationship 2 gives a  $\rho$  value of 0.087 V.

The  $\text{CoN}_2\text{S}_2\text{R}_2$  complexes were also investigated in the presence of the triphenylphosphine. Table I summarizes the data obtained in this study. The dependence of  $\Delta E_{1/2}'^{\text{TPP}}$  versus  $2\sigma_{\text{R}}$  gives a  $\rho$  value of  $-0.067$  V indicating a different electrode mechanism when compared with that for  $\text{CoN}_2\text{S}_2\text{R}_2$  complexes without TPP. TPP as a known  $\pi$ -acid is reducing the electron density on the cobalt atom by coordination in the axial position of the complexes. The more electron-donating properties the substituent R has, the more electron density TPP accepts,

TABLE II. Electrochemical Data for the  $\text{CuN}_2\text{S}_2\text{R}_2$  Complexes.

R	$\Delta E_{\text{pa}}^a$ (mV)	$\Delta E_{\text{pa}}^{\text{TPP}^b}$	$\sigma_{\text{R}}^{oc}$
$\text{CF}_3$	390	-110	2.5
p- $\text{BrC}_6\text{H}_4$	320	- <sup>d</sup>	0.83
$\text{C}_6\text{H}_5$	290	-100	0.60
p- $\text{CH}_3\text{OC}_6\text{H}_4$	260	- <sup>d</sup>	0.33
$\text{CH}_3$	0	-110	0.0

<sup>a</sup> $\Delta E_{\text{pa}} = E_{\text{pa}}(\text{CuN}_2\text{S}_2\text{R}_2) - E_{\text{pa}}(\text{CuN}_2\text{S}_2(\text{CH}_3)_2)$ .  
<sup>b</sup> $\Delta E_{\text{pa}}^{\text{TPP}} = E_{\text{pa}}(\text{CuN}_2\text{S}_2\text{R}_2 + \text{TPP}) - E_{\text{pa}}(\text{CuN}_2\text{S}_2(\text{CH}_3)_2)$ .  
<sup>c</sup>Reference [8].  
<sup>d</sup>Value could not be obtained from the experiment.

*i.e.* the harder the oxidation of the complex. These results are also connected with bonding properties observed for the complexes in dependence on the substituent R. Comparison of d-orbital energies of the cobalt(II) complexes [9, 10] with an orbital energy of TPP free electron pair localized on the phosphorus atom [11], which come into interaction with complex orbitals, supports the conclusion that TPP is a stronger  $\pi$ -acceptor toward the cobalt complexes with increased electron-donating properties of substituent R.

#### $\text{CuN}_2\text{S}_2\text{R}_2$

The redox properties of the  $\text{CuN}_2\text{S}_2\text{R}_2$  complexes were investigated similarly as in the above case. For all the copper complexes, except  $\text{CuN}_2\text{S}_2(\text{CH}_3)_2$ ,  $\{\text{CuN}_2\text{S}_2\text{R}_2\}^+$  ion was not detected during the cathodic sweep in the voltammogram. Evidently, this ion undergoes a rapid irreversible reaction to produce an electrode-inactive species.

Nevertheless, the relative order of the oxidation potentials can be determined from the anodic peak voltages. The data in Table II show that substituents have a marked effect on the oxidation potential which correlates well with the  $\sigma_{\text{R}}^o$  Taft substituent parameters. The  $\sigma_{\text{R}}^o$  values are for non-conjugating reaction centres insulated by a  $\text{CH}_2$  group. In plotting  $\Delta E_{\text{pa}}$  for the oxidation versus  $2\sigma_{\text{R}}^o$ , a linear correlation was obtained ( $r = 0.97$ ) for all substituents R except  $\text{CH}_3$  with a  $\rho$  value of 0.028 V. Thus,  $\text{CuN}_2\text{S}_2(\text{CH}_3)_2$  complex did not fall in the correlation with polar parameters, which ostensibly exclude resonance effects. This fact has also been observed by investigation of the kinetics of central atom exchange reactions between the Schiff base thioiminato-complexes of  $\text{Zn(II)}$  and  $\text{Ni}^{2+}$  ion [12].

From the results obtained it can be assumed that some square-planar geometry deformation in the studied complexes occurs [13] and consequently, the 'pseudoaromaticity' of the rings in the equatorial position is destroyed. The replacement of  $\text{CH}_3$  groups

for substituents R in the equatorial ligand of the copper complexes leads probably to a change in the oxidation site. For  $\text{CuN}_2\text{S}_2(\text{CH}_3)_2$ , the latter is predominantly redox orbital metal in character [14], and we propose that for the other complexes it is the orbital mainly ligand in character.

The redox properties of the  $\text{CuN}_2\text{S}_2\text{R}_2$  complexes were affected to the same degree in the presence of TPP (see Table II). The  $E_{\text{pa}}$  potentials were shifted to the lower values without an evident dependence on the electronic properties of the substituent R. This implies that in this case the substituent R has a negligible effect on the electrode process.

In summary, this paper presents correlations between oxidation electrode potentials and the Hammett  $\sigma_{\text{R}}$  and Taft  $\sigma_{\text{R}}^{\circ}$  parameters. It is shown that the site of oxidation for  $\text{CoN}_2\text{S}_2\text{R}_2$  is different from that found for  $\text{CuN}_2\text{S}_2\text{R}_2$ . As was observed in our previous study of the Co(II) and Cu(II) complexes with  $\text{H}_2\text{N}_2\text{S}_2(\text{CH}_3)_2$  ligand the site of one-electron oxidation was the orbital mostly metal in character. By a substitution of the equatorial ligand the oxidation site of the copper complexes is changed, as was observed for the redox orbital mostly ligand in character.

## References

- 1 A. Kotočová and J. Šima, *Inorg. Chim. Acta*, **40**, 115 (1980).
- 2 A. Kotočová and J. Šima, *Chem. Zvesti*, **35**, 793 (1981).
- 3 A. Kotočová, D. Valigura, P. Fodran and J. Šima, Abstracts of Papers, Vol. II, XXII ICCS, Budapest, 838 (1982).
- 4 A. Kotočová, D. Valigura, P. Fodran and J. Šima, *Chem. Zvesti*, **38**, 67 (1984).
- 5 P. R. Blum, R. M. C. Wei and S. C. Cummings, *Inorg. Chem.*, **13**, 450 (1974).
- 6 L. S. Chen and S. C. Cummings, *Inorg. Chem.*, **17**, 2358 (1978).
- 7 D. Valigura *et al.*, Abstracts of Papers, Vol. II, XXII ICCS, Budapest, 837 (1982); *Chem. Zvesti*, to be published.
- 8 P. Zuman, 'Substituent Effects in Organic Polarography', Alfa, Bratislava (1970).
- 9 C. Cauletti and J. Šima, *J. Electron. Spectrosc.*, **19**, 1 (1980).
- 10 C. Furlani and C. Cauletti, *Str. Bond.*, **35**, 119 (1978).
- 11 M. A. Weiner and M. Lattman, *J. Org. Chem.*, **40**, 1292 (1975).
- 12 J. Šima, P. Fodran, J. Hledík, A. Kotočová and D. Valigura, *Inorg. Chim. Acta*, **81**, 143 (1984).
- 13 R. Cini, A. Cinquantini and P. Orioli, *Cryst. Struct. Comm.*, **9**, 865 (1980).
- 14 R. Boča, P. Pelikán and J. Šima, *Chem. Zvesti*, **34**, 302 (1980).