

# Comparison of Electrochemical Behaviour of Cu(II), Co(II), Ni(II), and Fe(III) Schiff Base Type Complexes

A. KOTOČOVÁ and J. ŠIMA

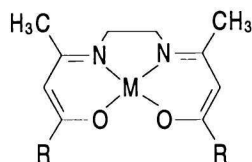
Department of Inorganic Chemistry, Faculty of Chemical Technology,  
Slovak Technical University, SK-812 37 Bratislava

Received 11 June 1993

The electrochemical oxidation of Cu(II), Co(II), and Ni(II) complexes and reduction of Fe(III) complexes with a series of substituted *N,N'*-ethylenebis(monooxo-R-acetoimines)  $H_2N_2O_2R_2$ , where R = 4-OCH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>, 4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>, C<sub>6</sub>H<sub>5</sub>, CH<sub>3</sub>, 4-FC<sub>6</sub>H<sub>4</sub>, 4-ClC<sub>6</sub>H<sub>4</sub>, 4-BrC<sub>6</sub>H<sub>4</sub>, and 4-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>, were investigated by cyclic voltammetry in acetonitrile and methanol solutions at a platinum electrode. The anodic peak potentials for the copper and nickel complexes varied linearly with the Taft resonance substituent constant, whereas for the cobalt and iron complexes such a relationship between the formal potentials and the Taft resonance substituent constant was not observed. The symmetry of redox orbitals is considered.

The present work originated from our previous work for finding the relation between the redox properties of some metal complexes and axial and equatorial electronic properties of the ligand. Till now, we have published some papers concerning this problem for Cu(II), Co(II) [1–4], Ni(II) [5], and Fe(III) [6] complexes of Schiff base ligands with various axial and equatorial interactions.

Here we present a comparison of the redox behaviour of the nearly square-planar complexes (further on denoted as  $MN_2O_2R_2$ ) in which an equatorial plane was modified by the substituent R with different electronic properties.



M = Cu, Co, Ni, Fe  
R = 4-OCH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>, 4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>,  
C<sub>6</sub>H<sub>5</sub>, 4-FC<sub>6</sub>H<sub>4</sub>, 4-ClC<sub>6</sub>H<sub>4</sub>,  
4-BrC<sub>6</sub>H<sub>4</sub>, 4-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>

## EXPERIMENTAL

The complexes  $CuN_2O_2R_2$  and the ligands  $H_2N_2O_2R_2$  were prepared according to a literature method [7]. Analyses for carbon, hydrogen, and nitrogen were in accordance with the calculated values.

The cobalt, nickel, and iron complexes were prepared by reaction of Ni(II) and Co(II) acetates, and Fe(III) chloride with the corresponding ligand directly in an electrolytic cell under an argon atmosphere at room temperature.

Tetrabutylammonium perchlorate (TBAP) was synthesized from perchloric acid and tetrabutylammonium hydroxide. Acetonitrile was of high-purity spectroquality and methanol was purified using a standard procedure.

Electrochemical measurements were performed under an argon atmosphere by using a PA 3 polarographic analyzer (Laboratorní přístroje, Prague). The electrochemical cell employed the standard three-electrode configuration, 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 supporting electrolyte.

Voltammograms of the complexes were recorded in acetonitrile and methanol (only Ni(II) complexes) solutions ( $c(\text{TBAP}) = 0.05 \text{ mol dm}^{-3}$ ;  $c(\text{metal complexes}) = 1.6 \times 10^{-3} \text{ mol dm}^{-3}$ ) at room temperature with scan rates  $v/(\text{mV s}^{-1})$  20, 50, 100, 200, and 500 and are uncorrected for junction contributions.

## RESULTS AND DISCUSSION

### $CuN_2O_2R_2$ and $NiN_2O_2R_2$

The one-electron oxidation potentials of the studied complexes are summarized in Table 1. Cyclic voltammograms were evaluated according to a theory published in the literature [8].

Anodic peak potentials,  $E_{pa}$ , were dependent on the inductive properties of the substituent R as shown in Table 1. From the values it is evident that with increasing Taft resonance substituent constants,  $\sigma_R$ ,  $E_{pa}$  values also increase, *i.e.* the electron density on the reaction centre of the complex was influenced by the electronic properties of the substituent R. The magnitude of the substituent interaction with the reaction centre, *i.e.* the influence of the electron-donating or electron-withdrawing character of the substituent, was quantified by a linear free energy relationship [9]

$$E_{pa} = \rho \sum \sigma_R \quad (1)$$

**Table 1.** Redox Properties of the  $\text{CuN}_2\text{O}_2\text{R}_2$  and  $\text{NiN}_2\text{O}_2\text{R}_2$  Complexes Dependent on the Substituent R

R	$E_{\text{pa}}(\text{Cu})/\text{V}$	$E_{\text{pa}}(\text{Ni})/\text{V}$	$\sigma_{\text{R}}^{\text{a}}$
4- $\text{OCH}_3\text{C}_6\text{H}_4$	0.73	0.62(5)	- 0.21
4- $\text{CH}_3\text{C}_6\text{H}_4$	0.77(5)	0.64(8)	- 0.15
$\text{C}_6\text{H}_5$	0.79(8)	0.67	- 0.13
$\text{CH}_3$	-	0.67(5)	- 0.13
4- $\text{FC}_6\text{H}_4$	0.81(3)	-	- 0.11
4- $\text{ClC}_6\text{H}_4$	0.82(5)	-	- 0.06
4- $\text{BrC}_6\text{H}_4$	0.84(5)	0.70(2)	- 0.06
4- $\text{NO}_2\text{C}_6\text{H}_4$	0.92(5)	-	0.00

a) Taft resonance substituent constant ( $\sigma_{\text{R}} \equiv R$ ) [9].

$\sum \sigma_{\text{R}}$  is the total of substituent constants characteristic of the electronic properties of the substituent R ( $\sum \sigma_{\text{R}} = 2 \sigma_{\text{R}}$ ) and  $\rho$  is the reaction constant, characteristic of the reaction centre as well as expressing the reaction sensitivity to the substituent influence.

According to eqn (1) a close relation was found ( $r = 0.97$ ) with a  $\rho$  value of 0.43 V between  $E_{\text{pa}}(\text{Cu})$  and the sum of Taft resonance substituent constant  $\sigma_{\text{R}}$ . For Ni(II) complexes  $r = 0.98$  and  $\rho = 0.26$  V was found according to eqn (1).

The linear relationship  $E_{\text{pa}}$  vs.  $\sum \sigma_{\text{R}}$  confirms an identical mechanism for the electrode process in the investigated complexes. The value of the reaction constant for the Ni(II) complexes,  $\rho = 0.26$  V, indicates that the oxidation of the nickel(II) complexes is less sensitive to resonance effects in comparison with the corresponding Cu(II) complexes ( $\rho = 0.43$  V). It further shows that the orbital from which the electron is extracted has in both types of complexes the same symmetry (the  $d_{xy}$  orbital) [10] and is localized in the plane of the complexes.

### $\text{CoN}_2\text{O}_2\text{R}_2$ and $\text{FeN}_2\text{O}_2\text{R}_2^{\dagger}$

The redox properties of the  $\text{CoN}_2\text{O}_2\text{R}_2$  and  $\text{FeN}_2\text{O}_2\text{R}_2^{\dagger}$  complexes were investigated similarly to the above case. The formal potentials ( $E_{\text{f}}$ ) were calculated as the average of the cathodic ( $E_{\text{pc}}$ ) and anodic ( $E_{\text{pa}}$ ) peak potentials. The available cyclic voltammetric data show the lack of reversibility (the quasi-reversible behaviour) for the cobalt and iron complexes. The peak-to-peak separation ( $\Delta E_{\text{p}} = E_{\text{pa}} - E_{\text{pc}}$ ) at a scan rate of  $50 \text{ mV s}^{-1}$  is 100 mV and 125 mV, respectively. Under our experimental conditions the reversible couple ferrocenium/ferrocene ( $\text{Fc}/\text{Fc}^+$ ,  $E_{\text{f}} = 0.40$  V vs. SCE) has a  $\Delta E_{\text{p}}$  value of 80 mV, which was used as the criterion for electrochemical reversibility. Also, the ratio of cathodic to anodic peak currents ( $i_{\text{pd}}/i_{\text{pa}}$ ) or *vice versa* is 0.92 and 0.84 (the average values at a scan rate of  $50 \text{ mV s}^{-1}$ ), respectively.

The results summarized in Table 2 show that the measured one-electron formal potentials for  $\text{CoN}_2\text{O}_2\text{R}_2$  complexes are independent upon the

**Table 2.** Redox Properties of the  $\text{CoN}_2\text{O}_2\text{R}_2$  and  $\text{FeN}_2\text{O}_2\text{R}_2^{\dagger}$  Complexes Dependent on the Substituent R

R	$E_{\text{f}}(\text{Co})/\text{V}$	$E_{\text{f}}(\text{Fe})/\text{V}$	$\sigma_{\text{R}}^{\text{a}}$
4- $\text{OCH}_3\text{C}_6\text{H}_4$	0.08(8)	- 0.28(5)	- 0.21
4- $\text{CH}_3\text{C}_6\text{H}_4$	0.08(3)	- 0.27(3)	- 0.15
$\text{C}_6\text{H}_5$	0.05(3)	- 0.27(4)	- 0.13
4- $\text{ClC}_6\text{H}_4$	0.09(9)	- 0.27(3)	- 0.06
4- $\text{BrC}_6\text{H}_4$	0.08(8)	- 0.25(4)	- 0.06

a) Taft resonance substituent constant ( $\sigma_{\text{R}} \equiv R$ ) [9].

electronic properties of the substituent in the equatorial plane of the complex. The correlation coefficient and the reaction constant have the values of 0.25 and 0.034 V, respectively.

MO calculations [10] showed that the unpaired electron is mainly localized out of the complex plane (the  $d_{yz}$  or  $d_{z^2}$  orbitals) and the equatorial modification of the complex has not an influence on the redox properties of these complexes ( $r^2 = 0.062$ ).

The formal potentials of the one-electron reduction for the iron complexes shift only slightly upon changing the substituent R (Table 2). Calculated  $r = 0.77$  and  $\rho = 0.069$  V. The values of  $E_{\text{f}}$  depend on the substituent R to some extent ( $r^2 = 0.62$ ).

The small substituent effect may be explained by the fact that the electron is added to the  $d_{zx}$  or  $d_{yz}$  orbitals which are influenced by the substituent R only slightly.

The observed electrochemical behaviour of the series of Cu(II), Co(II), Ni(II), and Fe(III) complexes with the same modification of the equatorial plane illustrates the importance of the redox orbital from which the electron is extracted or to which the electron is added.

The above results indicate that the symmetry of the molecular orbitals which are involved in the redox processes seems to be in the studied case decisive for the observed redox behaviour of the complexes.

## REFERENCES

- Kotočová, A. and Šima, J., *Inorg. Chim. Acta* 40, 115 (1981).
- Kotočová, A. and Šima, J., *Chem. Zvesti* 35, 793 (1981).
- Kotočová, A., Valigura, D., Fodran, P., and Šima, J., *Inorg. Chim. Acta* 88, 135 (1984).
- Kotočová, A., Valigura, D., Fodran, P., and Šima, J., *Chem. Zvesti* 38, 67 (1984).
- Kotočová, A., Valigura, D., and Šima, J., *J. Coord. Chem.* 24, 363 (1991).
- Kotočová, A. and Šima, J., *Monatsh. Chem.*, in press.
- Valigura, D., Holubíková, V., Kalužik, J., Fodran, P., Šima, J., and Golier, I., *Abstract of Papers, Vol. II*, p. 837, XXII International Conference of Coordination Chemistry, Budapest, 1982.
- Nicholson, R. S. and Shain, I., *Anal. Chem.* 36, 706 (1964).
- Hansch, C., Leo, A., and Taft, R. W., *Chem. Rev.* 91, 165 (1991).
- Boča, R., *Chem. Zvesti* 36, 45 (1982).

Translated by A. Kotočová