

ELECTROCHEMICAL REDUCTIONS OF Ni²⁺, Cu²⁺ AND Zn²⁺ COMPLEXES OF AZINYL METHYL KETOXIMES ON MERCURY

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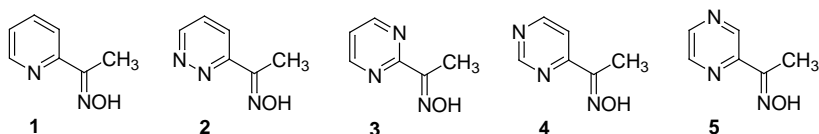
Dedicated to the memory of the late Professor Antonín A. Vlček.

Electroreductions of Ni²⁺, Cu²⁺ and Zn²⁺ complexes of azinyl (pyridin-2-yl, pyridazin-3-yl, pyrimidin-2-yl, pyrimidin-4-yl, pyrazinyl) methyl ketoximes on mercury electrode were studied using dc polarography. Three different types of complex behavior on the mercury electrode were observed: In the Ni²⁺ complexes, the hydroxyimino group of the ligand is reduced, whereas in the Cu²⁺ complexes, the reduction proceeds on the metal ion. With Zn²⁺ complex of methyl pyridin-2-yl ketoxime, only reduction waves of the uncoordinated ligand and metal were observed due to a rapid decomplexation pre-equilibrium. The structure of [Zn(methyl pyridin-2-yl ketoxime)₂(NO₃)₂], isolated from water-ethanolic solution, was determined by X-ray diffraction. The distorted octahedral coordination sphere around the zinc atom, made up of two pyridine and two oxime nitrogen atoms and two nitrate oxygen atoms, was verified.

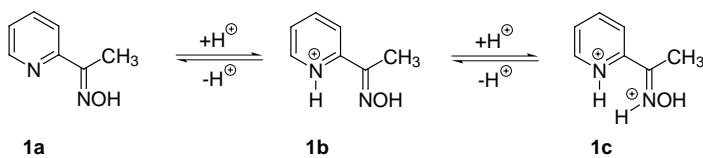
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Azinyl methyl ketoximes 1–5 and their metal chelate complexes are both active as catalysts in hydrolysis of esters¹. In our previous paper², the reducibility of free azinyl methyl ketoximes was studied and correlated with their hydrolytic activity. It was found that the most easily reducible group is the oxime moiety which is reduced in a four-electron process to the corresponding amine. Depending on pH, all the oximes can exist at least in

three forms: double-protonated (**1c**), single-protonated (**1b**) and neutral (**1a**) (as examples, the structures are presented for the pyridin-2-yl derivative **1**; Scheme 1). In diazine derivatives **2–5**, the other heterocyclic nitrogen facilitates the oxime reduction. Moreover, at more negative potentials, the diazine heterocyclic rings are reduced.



The coordination with metals introduces new possibilities of “tuning” the catalytic properties of the studied compounds. The complexes with ligands **1–5** thus represent models of metallomicellar hydrolytic catalysts



SCHEME 1

based on chelates of lipophilic azinyl dodecyl ketoximes (Fig. 1). It has been shown^{1a} that the activity of homogeneous aqueous solutions of azinyl methyl ketoxime complexes (as well as that of micellar solutions of their lipophilic derivatives) in hydrolysis of alkanooates depends strongly not only on the ligand used but also on the coordinated metal: Complexes of Ni^{2+} and Zn^{2+} exhibit a very high hydrolytic activity in comparison with free ligands. On the other hand, the presence of Cu^{2+} or Co^{2+} practically did not accelerate the rate of hydrolysis catalyzed by ligands only. The different activity of the complexes is caused by the contradictory influence of coordination on the acidity of the oxime group and on the nucleophilicity of the

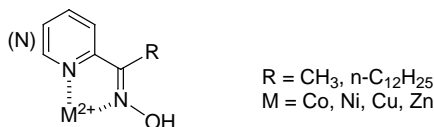


FIG. 1
Coordination of alkyl azinyl ketoximes to transition metal ions

oximate anion (the latter is the nucleophile attacking the ester function of the substrate). Coordination causes higher acidity of the oxime grouping, *i.e.* higher concentration of the corresponding oximate anion; on the other hand, the nucleophilicity of the coordinated oximate is lower.

The aim of this paper is to investigate electrochemically (polarographically) reduction of the above-mentioned complexes under various pH and various metal-to-ligand (M : L) ratios in order to characterize the acid-base and complex equilibria of the catalysts. The interpretation of electroreduction mechanism can give information concerning the electronic properties of studied complexes and might be consequently used for correlation with their catalytic activity.

Generally, the reduction of a complex can proceed either through the central metal ion or through the ligand³. The first case is more frequent since most ligands are electron-rich, thus non-reducible. Here, the coordination causes increase of electron density on the central metal ion whose reduction potential is then shifted to more negative values. In addition, substitution on the ligand can further affect the reducibility of the central metal ion. In the other case when the ligand is more easily reducible, the coordination causes a decrease in electron density on the ligand and thus its reduction potential is more positive as compared with the free ligand.

The electrochemical (polarographic) approach is useful also for the determination of stability and stoichiometry of complexes⁴.

EXPERIMENTAL

Apparatus

Elemental analysis was performed on a Perkin-Elmer 240 analyzer (C, H, N) and Varian Spectra AA 880 absorption spectrophotometer (Ni). pH Measurements were performed on a Jenway 3020 pH meter. Polarographic measurements were carried out with a PA4 polarographic analyzer (Laboratorní přístroje Praha) in phosphate (pH 1.6–9.3) and acetate (pH 4.0) buffers ($c = 0.1 \text{ mol l}^{-1}$) under pure argon (Linde) atmosphere with an aqueous saturated calomel electrode (SCE) as a reference electrode, a Smoler dropping mercury electrode (capillary with benched tip to 45°, *cf. ref.*⁵; Hg column height 36 cm) as a working electrode and mercury pool as an auxiliary electrode.

Chemicals and Solutions

Buffers were prepared from analytical grade chemicals obtained from Lachema Brno, Czech Republic (phosphoric acid, sodium hydrogenphosphate, sodium dihydrogenphosphate, acetic acid and sodium acetate) with ionic strength 0.1. Nickel, copper and zinc nitrates of analytical grade were obtained from Lachema. Synthesis of methyl pyridin-2-yl (1), methyl pyridazin-3-yl (2), methyl pyrimidin-2-yl (3), methyl pyrimidin-4-yl (4) and methyl

pyrazinyl (**5**) ketoximes were described in previous paper^{1a}. Ketoximes were characterized by ¹H and ¹³C NMR spectra and by elemental analysis^{1a}.

Solutions of azinyl methyl ketoximes and metal ions in various ratios were prepared in electrochemical cell by addition of a stock solution of the ketoxime ($c = 1 \cdot 10^{-2}$ mol l⁻¹) and metal ion nitrate ($c = 5 \cdot 10^{-3}$ or $5 \cdot 10^{-2}$ mol l⁻¹) to 5 ml of the buffer. Solution of [Ni(methyl pyridin-2-yl ketoxime)₂(NO₃)₂] was prepared in electrochemical cell by addition of a stock solution of the complex ($c = 5 \cdot 10^{-3}$ mol l⁻¹) to 5 ml of the buffer. Solutions were deaerated with argon before measurements.

Preparation of [Ni(Methyl Pyridin-2-yl Ketoxime)₂(NO₃)₂]

Water solution of nickel nitrate (1.48 ml, $c = 0.46$ mol l⁻¹) was added to a solution of 0.20 g (0.0015 mol) of oxime **1** in 3 ml of ethanol. The mixture was heated at 60 °C for 1 h. After evaporation of solvents and washing the residue with ethanol, 0.32 g of blue crystalline product were obtained. For NiC₁₄H₁₆N₆O₈ (455.0) calculated: 36.96% C, 3.54% H, 18.47% N, 12.90% Ni; found: 36.30% C, 3.76% H, 18.25% N, 12.32% Ni.

Preparation of [Zn(Methyl Pyridin-2-yl Ketoxime)₂(NO₃)₂]

Water solution of zinc nitrate (1.48 ml, $c = 0.50$ mol l⁻¹) was added to a solution of 0.20 g (0.0015 mol) of oxime **1** in 3 ml of ethanol. The mixture was heated under reflux for 3 h. After evaporation of solvents and after crystallization of crude product from a mixture ethanol–hexane, 0.25 g of white crystals were obtained, m.p. 173–175 °C. Crystals for X-ray measurement were prepared by crystallization from ethanol–hexane system.

Crystal Structure Determination

The selected crystal of bis(methyl pyridin-2-yl ketoxime)dinitratozinc(2+) was mounted on glass fibres with epoxy glue. Diffraction intensities were measured on a Nonius KappaCCD diffractometer with graphite monochromatized MoK α radiation ($\lambda = 0.71073$ Å) and ω scans mode. An Oxford Cryostream low-temperature device was used to cool crystal at 150 K.

Formula ZnC₁₄H₁₆N₆O₈ (M_r 461.707), monoclinic system, space group *Cc* (No. 9), $a = 16.9721(4)$ Å, $b = 15.1261(4)$ Å, $c = 8.1577(2)$ Å, $\beta = 117.992(2)^\circ$, $V = 1\,849.25(8)$ Å³, $Z = 4$, $D_{\text{calc}} = 1.658$ g cm⁻³, $\mu(\text{MoK}\alpha) = 1.39$ mm⁻¹, $F(000) = 944$.

The structure was solved by direct methods and subsequent Fourier techniques. All non-H atoms were refined anisotropically by full-matrix least-squares based on F^2 values. The positions of H atoms were found from the expected geometry and their isotropic thermal parameters were fixed at the 1.2 multiple of the value of those of matter atoms. The position and thermal parameters of hydrogen atoms from O–H groups were refined isotropically. The absolute configuration was determined by refinement of the Flack enantiopole parameter^{6a} to the final value 0.004. Data collection and refinement parameters are listed in Table I. Drawing of the complex is shown in Fig. 5. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC-154961. Copies of the data can be obtained free of charge on application to CCDC, e-mail: deposit@ccdc.cam.ac.uk.

RESULTS AND DISCUSSION

Reduction of complexes of azinyl methyl ketoximes **1–5** was studied by dc polarography with a dropping mercury electrode in aqueous buffered media (phosphate and acetate buffers, pH 1.6–9.3). The complexes were freshly prepared before each experiment directly in the cell by mixing solutions of the metal ion and the ligand in various ratios. The complexes are formed instantaneously after mixing^{1a}.

Ni²⁺ Complexes

The buffer solution of pH 3.6 containing oxime **1** and Ni²⁺ ions (and also the complex), exhibits three reduction waves (Figs 2a, 2b). The most posi-

TABLE I
Data collection and refinement parameters

Crystal dimensions	0.4 × 0.3 × 0.1
Crystal color	colorless
Diffractometer and radiation used	Nonius KappaCCD, λ(MoKα) = 0.71073 Å
Temperature, K	150
Range of <i>h</i> , <i>k</i> and <i>l</i>	-22→20, -19→19, -8→10
Total number of reflections measured	10 115
θ range, °	1–27.48
No. of unique reflections	3 758
No. of unique observed reflections	3 571
Criterion for observed reflections	$F_o > 4\sigma(F_o)$
Function minimized	$\sum w(F_o^2 - F_c^2)^2$
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0539P)^2 + 1.14P]$ $P = (\text{Max}(F_o^2, 0) + 2(F_c^2)/3)$
Parameters refined	189
Value of <i>R</i> , <i>wR</i> and <i>S</i>	0.0360, 0.1008, 1.215
Ratio of max. least-squares shift to e.s.d. in the last cycle	0
Max. and min. heights in final Δρ map, eÅ ⁻³	0.67, -1.06
Source of atomic scattering factors	International Tables for X-Ray Crystallography (ref. ^{6b})
Programs used	SHELXL97 (ref. ^{6c}), SHELXS97 (ref. ^{6c})

tive wave (A) corresponds to reduction of the double-protonated free ligand (**1c**) (checked in an experiment without the metal – Fig. 2a, curve 1). The second wave (B) represents reduction of the formed chelate and the third one (C) at -1.05 V vs SCE is the reduction wave of solvated Ni^{2+} ions

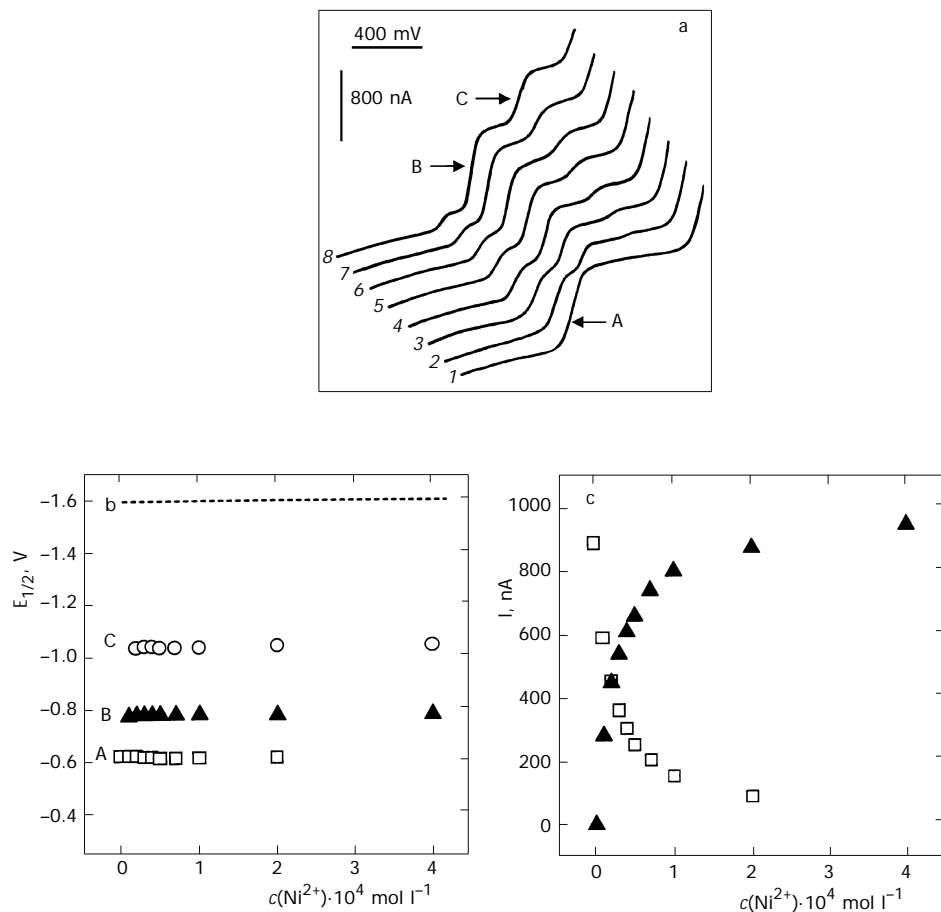


FIG. 2

Polarograms (a), $E_{1/2}$ vs $c(\text{Ni}^{2+})$ (b) and I vs $c(\text{Ni}^{2+})$ (c) plots representing titration of oxime **1** with Ni^{2+} at pH 3.6. All polarographic curves (a) start at the potential 0 V. $c(\text{oxime}) = 5 \cdot 10^{-5} \text{ mol l}^{-1}$ in the case of all curves; $c(\text{Ni}^{2+})$ in mol l^{-1} : 0 (1), $1 \cdot 10^{-5}$ (2), $2 \cdot 10^{-5}$ (3), $3 \cdot 10^{-5}$ (4), $4 \cdot 10^{-5}$ (5), $5 \cdot 10^{-5}$ (6), $7 \cdot 10^{-5}$ (7), $1 \cdot 10^{-4}$ (8). Different symbols (b, c) indicate reduction of double-protonated form of uncoordinated oxime **1c** (\square , wave A), coordinated oxime (\blacktriangle , wave B) and free metal (\circ , wave C). The dash line shows hypothetical reduction potential (pH-independent²) of neutral form **1a** of the ketoxime at pH 3.6; $c(\text{oxime}) = 5 \cdot 10^{-5} \text{ mol l}^{-1}$

(checked in an independent experiment without ligand). A stepwise addition of Ni^{2+} to the ligand solution causes a decrease in the reduction wave of the free ligand and simultaneously an increase in the wave of the new complex (the sum of both limiting currents remains constant – Figs 2a, 2c). It can be concluded that the Ni^{2+} complex of methyl pyridin-2-yl ketoxime (**1**) is reduced through ligand, *i.e.* by a four-electron reduction of the oxime grouping (*cf.* ref.²). According to the general rule mentioned above, the coordinated ligand should be reduced at more positive potential than the free ligand. Here it is necessary to take into account the fact that the observed reduction wave of free ligand at pH 3.6 represents the reduction of the ligand protonated on both heterocyclic and oxime nitrogens (**1c**). For a comparison of reduction potentials, the potential of unprotonated ligand (**1a**) should be considered. This was estimated by polarographic measurement at $\text{pH} > 10$ ($E_{1/2} = -1.58$ V vs SCE, ref.²). Since this reduction potential is pH-independent, it can be used for considerations of the influence of coordination on the reducibility of oxime **1** even at pH 3.6 (Fig. 2b). The difference between the half-wave potential of the coordinated oxime (wave B) and that of the double-protonated oxime **1c** (wave A) reflects the change in electron density on the ligand passing from the “coordination” to two protons to the coordination to Ni^{2+} .

In addition, it was found that the limiting current of the ligand wave and that of the wave of the complex (both in excess of the free ligand as well as of the complex) follow linear dependences on $h^{1/2}$ (h , height of the mercury reservoir) proving the diffusion character of both waves. It does mean³ that the limiting currents correspond to equilibrium concentrations of the species present in the solution, which enables the estimation of stability constants of the Ni^{2+} complexes by a polarographically followed titration⁷.

The pH dependence of $E_{1/2}$ of the Ni^{2+} complex of oxime **1** in the pH region 1.6–9.3 is shown in Fig. 3. At lower pH values, no wave corresponding to reduction of the Ni^{2+} complex was observed (at $c_M : c_L$ ratio 1 : 2), most probably due to strong protonation of the ligand. In the pH region between 2.7 and 7.5, the three above-mentioned reduction waves (double-protonated form of the free ligand **1c**, the complex and the free metal ion) appear. Around pH 5.0, the pH dependences intersect and the first two waves merge. Due to this fact, their precise evaluation is difficult. At pH higher than 7.5, a new more negative wave appears corresponding to the reduction of single-protonated ligand **1b** (*cf.* Fig. 1a from ref.²). The same electroreduction curves were found for the solution prepared by dissolving the isolated complex $[\text{Ni}(\text{methyl pyridin-2-yl ketoxime})_2(\text{NO}_3)_2]$.

The complexes of azinyl methyl ketoximes **2–5** exhibit analogous behavior. Their reduction proceeds also through the oxime group of the ligand. The half-wave potential of the reduction wave is also pH-dependent, indicating protonation equilibria of the complex. In addition to the reduction of oxime grouping, the voltammograms of the Ni^{2+} complexes show also reduction waves of the diazine heterocycle. This is the reason why the waves of coordinated ligands cannot be evaluated at certain pH values. The half-wave potentials of Ni^{2+} complexes of ligands **1–5** at pH 4.0 are shown in Table II.

In the case of ligands **1–4**, the formation of a Ni^{2+} complex with metal-to-ligand (M : L) ratio 1 : 1 was observed in slightly acidic media (Table II). According to expectations, these compounds are reduced at more positive potentials than chelates with the M : L ratio 1 : 2 since the decrease in the electron density on the ligand in complexes with the M : L ratio 1 : 1 should be more pronounced.

Cu^{2+} Complexes

Polarographic investigation of the Cu^{2+} complexes was performed in the pH region from 2.7 to 7.5. The most informative experiment was that based on stepwise addition of a solution of the respective oxime (**1–5**) to a solution

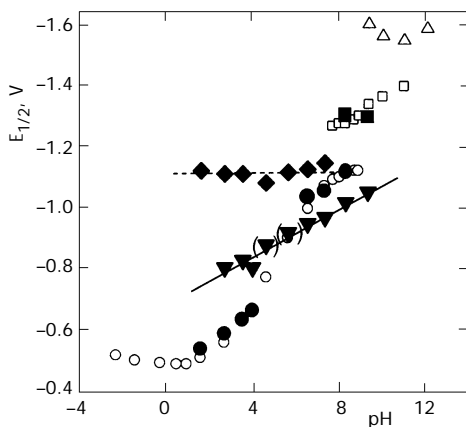


FIG. 3

pH Dependences of half-wave potentials of the reduction of oxime **1–Ni}^{2+} system: $c(\text{oxime}) : c(\text{Ni}^{2+}) = 2 : 1$; uncoordinated ligand – form **1c** (●), uncoordinated ligand – form **1b** (■), coordinated ligand (▼) and free Ni^{2+} ions (◆). Reduction of oxime **1**: double-protonated form **1c** (○), single-protonated form **1b** (□) and unprotonated form **1a** (Δ); ref.²**

of Cu^{2+} ions. Typical evolution of the reduction waves is shown in Figs 4a and 4b. In the above-mentioned pH region, the reduction proceeds in three steps: The most positive wave represents the two-electron reduction of uncoordinated metal ions. The number of electrons involved was checked by comparison of the limiting current with that of four-electron oxime reduction. The second wave appears after the first addition of the ligand. It increases with increasing ligand-to-metal ratio and simultaneously replaces

TABLE II
Half-wave potentials of reduction of oximes 1–5 and their Ni^{2+} complexes at pH 4.0 in acetate buffer

Oxime	$E_{1/2}(\text{ML}_2)$, V	$E_{1/2}(\text{ML})$, V	$E_{1/2}(\text{H}_2\text{L}^{2+})$, V	$E_{1/2}(\text{L})^a$, V
1	-0.780	-0.810 ^b	-0.620	-1.580
2	-0.790	-0.605	-0.560	-1.550
3	-0.840	-0.750	-0.690	-1.350
4	-0.770	-0.660	-0.465	-1.450
5	-0.685	–	-0.490	-1.360

^a At pH 11.6–12.0 (ref.²). ^b At pH 6.5; at pH 4.0, formation of another complex was not observed

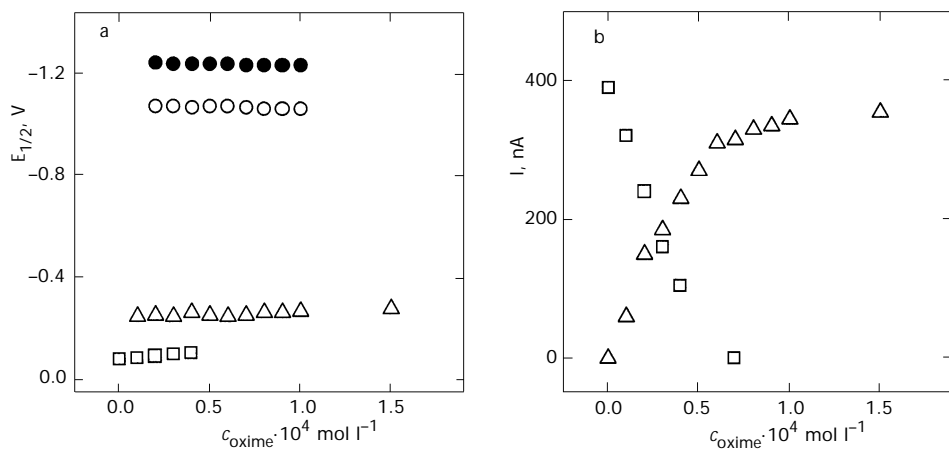


FIG. 4

Titration of Cu^{2+} with oxime 1 at pH 7.5. Reduction of uncoordinated metal (□), coordinated metal (△), free oxime double-protonated form 1c (○) and single-protonated form 1b (●); $c(\text{Cu}^{2+}) = 5 \cdot 10^{-5} \text{ mol l}^{-1}$

the first wave (Fig. 4b). This second reduction wave involving also two electrons is pH-dependent. It corresponds to reduction of the complex, in fact to reduction of coordinated metal, since the reduction potential is shifted to more negative values in comparison with free metal ions³. The most negative reduction step belongs to the reduction of free ligand (namely to the reduction of the oxime grouping) liberated in the course of the second reduction wave. At pH < 7.5, the third reduction step proceeds in one wave corresponding to the reduction of double-protonated ligand **1c**. At pH > 7.5, the reduction of the ligand manifests itself by two waves: the more positive one corresponding to the reduction of double-protonated oxime **1c** and the more negative one representing the reduction of single-protonated ligand **1b** (Fig. 4a). The sum of their limiting currents corresponds to the amount of added ligand. In the case of complexes containing diazine ligands, the reduction of the heterocycle follows at more negative potentials.

With excess of ligand **1**, **3** or **5**, a new reduction wave appears on the voltammogram. The wave is slightly more negative than the above mentioned wave of the complex (Table III). Most probably, this new wave corresponds to the reduction of a complex with more ligands, namely to the complex with the M : L ratio 1 : 2, whereas the more positive wave is caused by reduction of the complex with the M : L ratio 1 : 1. A Cu²⁺ complex of analogous ligands with the M : L ratio 1 : 3 has not been referred yet⁸.

The negative shifts of the reduction potential going from the free metal to the 1 : 1 complex and from the 1 : 1 to 1 : 2 complex are caused by increasing extent of electron donation from the ligand to the metal. The most

TABLE III
Half-wave potentials of reduction of Cu²⁺ complexes of oximes **1-5** at pH 6.3

Oxime	$E_{1/2}(\text{ML}), \text{V}$	$E_{1/2}(\text{M})^a - E_{1/2}(\text{ML}), \text{V}$	$E_{1/2}(\text{ML}_2)^b, \text{V}$
1	-0.225	0.175	-0.280
2	-0.210	0.160	-
3	-0.150	0.100	-0.250
4	-0.150	0.100	-
5	-0.145	0.095	-0.200

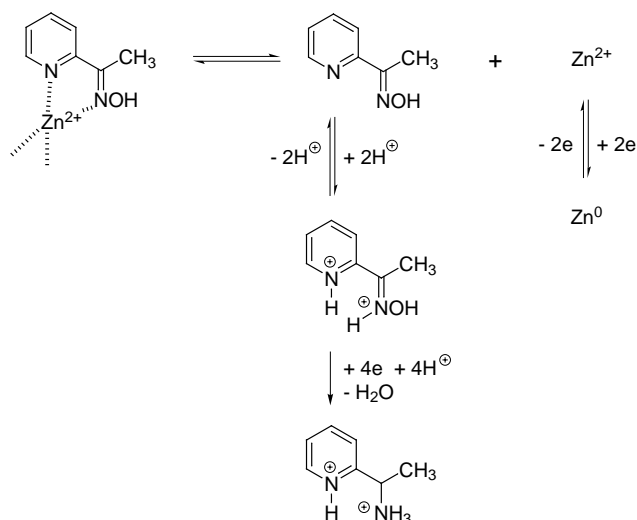
^a Free Cu²⁺ is reduced at -0.050 V. ^b Excess of the oxime.

pronounced difference between $E_{1/2}$ of the free and coordinated Cu^{2+} ion was observed in the case of oxime **1**. This indicates the strongest electron donation and thus the highest stability of its Cu^{2+} complex (Table III).

Zn^{2+} Complexes

The properties of Zn^{2+} complexes have been studied in detail with methyl pyridin-2-yl ketoxime (**1**). In the pH region from 3.6 to 7.2, both titration of a solution of the ligand with Zn^{2+} and additions of the ligand to a solution of the metal ion were electrochemically investigated. In all cases (under all the metal-to-ligand ratios), no new waves corresponding to the complex were observed and no shifts of the half-wave potentials of the metal or ligand caused by addition of the other component were found. A mixture of the oxime and the metal ion solutions exhibited the same behavior on the mercury electrode in the acetate as well in phosphate buffer.

The reason for such a behavior is, most probably, the low stability of the Zn^{2+} complex. This is consistent by the UV-VIS spectrophotometric data^{1a}. During the titration of oxime **1** by Zn^{2+} ions, the new absorption band of the complex appears only in the presence of a high excess of the metal. The first reduction wave corresponds to the reduction of the double-protonated form of the free ligand (**1a**) liberated in rapid complex equilibria (Scheme 2) since it is the most easily reducible species in the system. The



SCHEME 2

expected more negative wave of the complex is absent because the decomposition of the complex is more rapid than its diffusion to the electrode surface. In the close vicinity of the electrode, there are – except the ligand being reduced – only the liberated metal ions, which are reduced in the most negative wave (Scheme 2).

X-Ray Structure of Zn²⁺ Complex of Oxime 1

As mentioned above, the existence of the Zn²⁺ complex could not be proved electrochemically. Its formation was observed in UV-VIS spectra^{1a} and its presence in solution is responsible for the enhancement of hydrolytic efficiency in hydrolysis of alkanooates^{1a,9}. In order to have an unambiguous proof of this coordination species, the complex was isolated and its crystal structure determined by X-ray analysis.

In the solid state, the zinc coordination species is a distorted octahedron, involving two oxime and two pyridine nitrogens (from methyl pyridin-2-yl ketoximes (**1**)) and two nitrate anions in *cis* position (Fig. 5). The structure

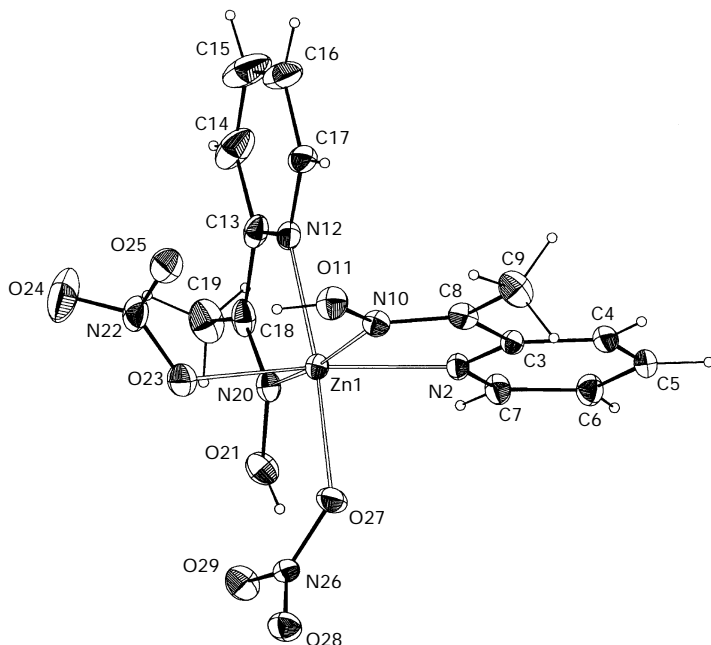


FIG. 5
The ORTEP drawing of $[\text{Zn}(\text{methyl pyridin-2-yl ketoxime})_2(\text{NO}_3)_2]$ with the atom numbering

is similar to that referred¹⁰ for [Ni(methyl pyridin-2-yl ketoxime)₂Br₂] where also both oxime groups remained undissociated.

The structure of coordinated methyl pyridin-2-yl ketoximes is planar (Table IV). The complex is further stabilized by hydrogen bonds between =N-OH group and nitrate oxygen (Table V). The most important bond lengths and angles of the complex are given in Table VI.

TABLE IV

Deviations (in Å) from least-squares planes in methyl pyridin-2-yl ketoxime (1) ligands calculated with SHELXL97 (ref.^{6c})

N2	-0.0077	N12	-0.0242
C3	0.0010	C13	-0.0061
C4	-0.0019	C14	0.0193
C5	0.0034	C15	0.0008
C6	0.0174	C16	0.0292
C7	-0.0065	C17	-0.0131
C8	-0.0252	C18	-0.0190
C9	0.0028	C19	-0.0197
N10	-0.0080	N20	-0.0127
O11	0.0247	O21	0.0456

TABLE V

The list of hydrogen bonds (D-H...A) in [Zn(methyl pyridin-2-yl ketoxime)₂(NO₃)₂]

D	H	A	D...A, Å	D-H...A, Å	D-H...A, °
O11	H37	O25	2.689	1.963	147
O21	H45	O29	2.694	1.993	143

TABLE VI
Selected bond lengths (in Å) and angles (in °) in [Zn(methyl pyridin-2-yl ketoxime)₂(NO₃)₂]

Atoms	Bond lengths	Atoms	Bond lengths
Zn1-N2	2.108(3)	Zn1-N20	2.128(3)
Zn1-N10	2.161(3)	Zn1-O23	2.109(3)
Zn1-N12	2.118(3)	Zn1-O27	2.097(3)
Atoms	Bond angles	Atoms	Bond angles
N2-Zn1-N10	75.50(8)	N12-Zn1-N20	75.56(8)
N2-Zn1-N12	97.60(9)	N12-Zn1-O23	90.75(8)
N2-Zn1-N20	99.55(9)	N12-Zn1-O27	174.45(8)
N2-Zn1-O23	169.33(9)	N20-Zn1-O23	88.93(8)
N2-Zn1-O27	87.28(8)	N20-Zn1-O27	101.10(8)
N10-Zn1-N12	95.18(8)	O23-Zn1-O27	84.72(8)
N10-Zn1-N20	169.01(8)		
N10-Zn1-O23	97.21(8)		
N10-Zn1-O27	88.58(8)		

CONCLUSIONS

Chelates of azinyl methyl ketoxime ligands with divalent metal ions were prepared in solution as well as in the solid state and polarographically investigated in the pH region 1.6–9.3. Three various possibilities of electrochemical reduction have been found for Ni²⁺, Cu²⁺ and Zn²⁺ complexes. While the reduction centre, *i.e.* LUMO, of the Cu²⁺ complexes is located on the coordinated metal, in the case of Ni²⁺ complexes the LUMO is located on the coordinated ligand. This rarely occurring reduction mechanism of Ni²⁺ complexes is caused by the presence of easily reducible oxime grouping on the ligand which is reduced after coordination as first. As for Zn²⁺ complexes, their stability is not high enough and due to the fast decomplexation equilibria no reduction wave corresponding to the complex was observed. Only reduction waves of both components, (the free ligand and

the free metal ion) were present in the polarograms. Half-wave potentials of both Ni^{2+} and Cu^{2+} complexes depend on pH. This fact indicates that protonation/deprotonation equilibria are involved, most probably dissociation of coordinated oxime group under the formation of nucleophilic oximate anion.

The different mechanisms of reduction of the studied complex catalysts did not allow direct correlation between the measured reduction potentials and the observed hydrolytic activity^{1a}. However, they are a good basis for the future determination of stability constants⁷.

The structure of the labile complex – $[\text{Zn}(\text{methyl pyridin-2-yl ketoxime})_2(\text{NO}_3)_2]$ was determined by X-ray structure analysis.

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