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Polarography of some *Trans*-Acidoaminebis(dimethylglyoximato)cobalt(III) Complexes

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A series of neutral cobaloximes of the type Co-(DH)$_2$(B)(X) (where DH$^-$ = dimethylglyoximate anion, B = pyridine, ammonia or aniline, X$^-$ = I$^-$, Br$^-$, Cl$^-$, N$_3^-$, SCN$^-$ and NO$_2^-$) have been studied polarographically. In aqueous neutral solution, two one electron waves which correspond to the redox couple Co(III) → Co(II) and Co(II) → Co(I) are observed. In all the cases, the first wave is irreversible. There is a correlation between the first $E_{1/2}$ and the ligand basicity. The established polarographic stability order of the ligands i.e., *I$^-$ ~ Br$^-$ ~ Cl$^-$, SCN$^-$ < N$_3^-$ < NO$_2^-$, is observed for the* trans-*acidopyridinecobaloximes. At low pH, the first $E_{1/2}$ is shifted towards more positive potentials. This is attributed to the protonation of the complexes. Electrode kinetic data, computed using Koutecky's analysis, are also prevented.*

Introduction

Since the initial report by Maki [1], the reduction of bis(dimethylglyoximato)cobalt(III) complexes, commonly known as cobaloximes, has been investigated polarographically by a number of workers [2–5]. Such studies assume significance for our work on electron transfer reactions of cobaloximes with metal ions and the dropping mercury electrode. In our earlier report [6] on the iron(II) reduction of azidopyridine and azidoamminebis(dimethylglyoximato)cobalt(III) complexes, we reported kinetic evidence for the protonation of the cobaloximes in acid solution. Polarographic studies of the cobaloximes in acid medium would provide significant information on the nature of the species reduced at the electrode. The effect of variation of ligands on the reducibility of the central metal ion could also be determined by a polarographic study of a series of complexes containing various anions and neutral bases as ligands and would usefully complement the data on the homogeneous reduction of these cobaloximes. In this paper we report our studies on the polarography and electrode kinetics of a series of *trans*-acidoaminebis(dimethylglyoximato)cobalt(III) complexes with the axial bases, aniline, pyridine and ammonia and the anionic ligands, I$^-$, Cl$^-$, Br$^-$, N$_3^-$, SCN$^-$ and NO$_2^-$.

Experimental

All the complexes investigated were prepared as reported in the literature [7, 8]. The purity of the complexes was checked by their uv–visible spectra and also by elemental analysis. Reagent grade chemicals were used without further purification. Aqueous solutions were prepared from doubly distilled water. The supporting electrolyte was 0.2 mol dm^{-3} NaClO$_4$ and was adjusted to the desired pH with perchloric acid.

Since the complexes were not soluble in pure water, studies were carried out in 4 vol.% dimethylsulphoxide–water mixture. Solutions of weighed amounts of the complexes were prepared and diluted to the desired concentrations.

Polarograms were obtained with a Radelkis OH-105 model polarograph. A sodium chloride saturated calomel reference electrode (SSCE) was used. Its potential was 5 mV more negative than that of a standard SCE [9]. All measurements were made at 27.0 ± 0.2 °C. The dropping mercury electrode had an open circuit flow rate of 2.47 mg s^{-1} at a mercury column height of 52 cm and a drop time of 3.2 seconds.

Results and Discussion

In aqueous neutral solution, two successive reduction steps are indicated by well resolved polarographic waves corresponding to two one electron processes, Co^{III} → Co^{II} and Co^{II} → Co^{I}, respectively. This two step reduction pattern is a characteristic of the class of cobalt complexes with low valence stabilizing ligands such as dipyridyl, *o*-phenanthroline and Co(CN)$_5^{3-}$ [10]. From the logarithmic analysis

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TABLE I. Reduction Potentials of *trans*-Acidoaminebis(dimethylglyoximato)cobalt(III) complexes[a] in 4 vol.% DMSO–H_2O mixture. Supporting electrolyte = 0.2 mol dm^{-3} $NaClO_4$ and 0.006% gelatin at 27.0 ± 0.2 °C.

Complex	I Wave, $E_{1/2}$ (Volt *vs.* SSCE)		II Wave, $E_{1/2}$ (Volt *vs.* SSCE)	
	Neutral	Acidic	Neutral	Acidic
$Co(DH)_2(py)I$	+ve	+ve	−0.880	−0.645
$Co(DH)_2(py)Br$	+ve	+ve	−0.900	−0.700
$Co(DH)_2(py)Cl$	−0.095	+ve	−0.900	−0.690
$Co(DH)_2(py)SCN$	−0.075	+ve	−0.850	−0.640
$Co(DH)_2(py)NO_2$	−0.350	−0.060	−0.820	−0.650
$Co(DH)_2(py)N_3$	−0.185	+0.088	−0.900	−0.690
$Co(DH)_2(An)N_3$	−0.160	+ve	−0.880	−0.675
$Co(DH)_2(NH_3)N_3$	−0.225	−0.038	−0.900	−0.650

[a] [Complex] = ~4.8 × 10^{-4} mol dm^{-3}.

TABLE II. Reduction Potentials and Transfer Coefficients of *trans*-Azidopyridinebis(dimethylglyoximato)cobalt(III) Complex[a] as a Function of $[H^+]$ in 4 vol.% DMSO–H_2O Mixture (supporting electrolyte = 1.0 mol dm^{-3} ($NaClO_4$) and 0.006% gelatin at 27.0 ± 0.2 °C).

$[H^+]$, mol dm^{-3}	$E_{1/2}$ (Volt *vs.* SSCE)	α
0.002	+0.005	0.60
0.005	+0.012	0.62
0.010	+0.017	0.63
0.020	+0.028	0.68
0.050	+0.060	0.79
0.100	+0.083	0.79

[a] [complex] = ~4.8 × 10^{-4} mol dm^{-3}.

of the first wave of the complexes, an irreversible electrode process is inferred, consistent with the previous report [11]. The effect of variation of the coordinated groups on the value of $E_{1/2}$ may be seen from Table 1. Among the pyridinecobaloximes containing various anionic ligands the usual polarographic stability order of the ligands is noticed, *viz.*, $I^- \sim Br^- \sim Cl^-$, $SCN^- < N_3^- < NO_2^-$ [10]. For the azidoaminecobaloximes (amine = aniline, pyridine or ammonia), there is a clear correlation between the first half-wave potential and the basicity of the ligands. This is consistent with the raising in energy of the lowest antibonding acceptor orbital with increasing σ-donor strength of the ligands and is in agreement with the results of Prince and Segal [5], besides our homogeneous electron transfer kinetic data wherein we observed the trend $Co(DH)_2(py)N_3$ > $Co(DH)_2(NH_3)N_3$ for the rate of the iron(II) reduction [6].

The near constancy of the Co(II) → Co(I) potential (Table I) suggests that the species being reduced is the same in all the cases and may be $Co^{II}(DH)_2(OH_2)_2$, formed by the hydrolysis of the reduction product. The wave corresponding to Co(I) → Co(0) is not observed in our experiments and Schrauzer [2] has produced convincing spectroscopic evidence for the presence of 5-coordinate cobaloxime (I) in solution.

In 0.1 *M* $HClO_4$–water solution, the first half-wave potential of the complexes is shifted towards more positive potential (Table I) in agreement with previous report [11]. This may be attributed to the protonation of the complexes at low pH. This supports our previous report [6] in which we have observed kinetic evidence for the protonation of the complexes in acid solution as suggested by a decrease in rate of the iron(II) reduction to a limiting value with increasing $[H^+]$. The presence of a single wave without split suggests that the protonation is faster than electron transfer. Also, the wave approaches reversible characteristics with decrease in pH as observed from the change in the values of α for the complex $Co(DH)_2(py)N_3$ (where DH^- = dimethylglyoximate anion, py = pyridine) at various $[H^+]$ (Table II).

While the pentaammine and ethylenediamine complexes of cobalt(III) were reduced in a bielectronic process from Co(II) to Co(0) [12], the cobaloximes reported here exhibit a second wave of unusually large value of i_d in acid medium, possibly due to the reduction of the released ligand dimethylglyoxime. Costa *et al.* [11] have reported that the constant potential reduction of $Co(DH)_2LL^1$ (where L-amine and L^1 = anionic ligands) at the more cathodic potentials corresponding to the second polarographic process in acid solution yielded the products 2,3-diaminobutane and $Co^{2+}_{(aq)}$. Also, this reduction was previously observed for free dimethylglyoxime in acid solution [13, 14]. We therefore conclude that the second wave for the present complexes in acid solu-

TABLE III. Apparent Transfer Coefficients and Rate Constants for the Reduction of Some *trans*-Acidoaminebis(dimethylglyoximato)cobalt(III) Complexes[a] at Dropping Mercury Electrode (DME) in 4 vol.% DMSO–H_2O Mixture (supporting electrolyte = 0.2 mol dm^{-3} $NaClO_4$ and 0.006% gelatin at 27.0 ± 0.2 °C).

Complex	α_{app}	$-\log k_{app}$ at -0.240 V
$Co(DH)_2(py)Cl$	0.49	1.46
$Co(DH)_2(py)SCN$	0.61	1.32
$Co(DH)_2(py)NO_2$	1.00	4.64
$Co(DH)_2(py)N_3$	0.40	2.46
$Co(DH)_2(An)N_3$	0.42	2.30
$Co(DH)_2(NH_3)N_3$	0.22	2.90

[a] [Complex] = ~4.8×10^{-4} mol dm^{-3}.

tion is due to the reduction of the liberated dimethylglyoxime to 2,3-diaminobutane.

Anson and coworkers [15, 16] have made a comparison of rate constants at a common potential where all complexes have measurable rates of reduction so that comparison among rate constants is confined to a discussion of reactivity trend alone. A comparison among the apparent rate constants calculated using Koutecky's analysis and shown [17] in Table III shows the following trend $Co(DH)_2(py)SCN \sim Co(DH)_2(py)Cl > Co(DH)_2(py)N_3 > Co(DH)_2(py)NO_2$. Among the various azidoaminecobaloximes, the expected trend, aniline > pyridine > ammonia is observed. We also studied the effect of the double layer on the rate of electrochemical reduction by varying the ionic strength and the Tafel plots for the various ionic strengths give almost the same slope for the reduction of the complex $Co(DH)_2(py)N_3$. We conclude therefore that the double layer effect is not predominant in these cases.

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References

1 N. Maki, *Nature, 188,* 227 (1960).
2 G. N. Schrauzer, R. J. Windgassen and J. Kohnle, *Chem. Ber., 98,* 3324 (1965).
3 G. N. Schrauzer and R. J. Windgassen, *J. Amer. Chem. Soc., 88,* 3738 (1966).
4 Y. Hohakabe and N. Yamazaki, *Bull. Chem. Soc. Japan, 44,* 1563 (1971).
5 R. H. Prince and M. G. Segal, *Inorg. Chim. Acta, 11,* L35 (1974).
6 P. N. Balasubramanian and V. R. Vijayaraghavan, *Inorg. Chim. Acta, 38,* 49 (1980).
7 V. R. Vijayaraghavan, N. Thillaichidambaram, A. Raghavan and M. Santappa, *J. Indian Chem. Soc., 55,* 532 (1978).
8 (i) A. V. Ablov and M. Filippov, *Russ. J. Inorg. Chem., 4,* 1004 (1959).
(ii) *Inorganic Syntheses,* Ed. by William L. Jolly, McGraw–Hill, New York, *11,* 62 (1968).
9 M. J. Weaver and F. C. Anson, *J. Electroanal. Chem., 65,* 711 (1975).
10 N. Maki, J. Fujita and R. Tsuchida, *Nature, 183,* 458 (1959).
11 G. Costa, A. Puxeddu and G. Tauzher, *Inorg. Nucl. Chem. Letters, 4,* 319 (1968).
12 N. Maki, Y. Shimura and R. Tsuchida, *Bull. Chem. Soc. Japan, 32,* 23 and 150 (1959).
13 K. Burger, G. Syrek and G. Farsang, *Açta Chim. Ac. Scient. Hungaricae, 49,* 113 (1966).
14 M. Spritzer and L. Meites, *Anal. Chim. Acta, 26,* 58 (1962).
15 M. J. Weaver and F. C. Anson, *Inorg. Chem., 15,* 1871 (1976).
16 F. C. Anson, M. G. Finn and A. Yamada, *Inorg. Chem., 16,* 2124 (1977).
17 J. Koutecky, *Chem. Listy, 47,* 323 (1953).