November, 1975] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48 (11), 3133—3136 (1975) 3133

The Polarography of *trans*-Cobalt(III) Complexes of Tetradentate Schiff Bases and *α*-Methylbenzylamine in *N*,*N*-Dimethylformamide and Methanol Solutions

Mutsuo Kodama

Department of Chemistry, College of General Education, Hirosaki University, Bunkyo, Hirosaki 036

(Received April 21, 1975)

The polarographic behavior of mixed-ligand cobalt(III) complexes of tetradentate Schiff bases and α-methylbenzylamine (pheNH$_2$) of the general formula of [CoZ(pheNH$_2$)$_2$]$^+$ in methanol and *N*,*N*-dimethylformamide solutions was studied. At the dropping mercury electrode, these metal complexes give well-defined, two-step waves corresponding to the reduction of cobalt(III) to cobalt(II) and that of cobalt(II) to cobalt(I). A careful and systematic study of their polarographic behavior revealed that the reaction mechanism in the presence of uncomplexed pheNH$_2$ can be formulated as:

$$[\mathrm{CoZ(pheNH_2)_2}]^+ + \mathrm{e}^- \rightleftarrows [\mathrm{CoZ(pheNH_2)_2}]^0$$

$$[\mathrm{CoZ(pheNH_2)_2}]^0 + \mathrm{e}^- \rightleftarrows [\mathrm{CoZ(pheNH_2)_2}]^-$$

while, in the absence of pheNH$_2$, the reaction mechanism for the second step of the *N*,*N*′-ethylenebis(acetylacetoneiminato) and *N*,*N*′-ethylenebis(benzoylacetoiminate) systems is given by:

$$[\mathrm{CoZ(pheNH_2)_2}]^0 + \mathrm{e}^- \rightleftarrows [\mathrm{CoZ(pheNH_2)}]^- + \mathrm{pheNH_2}$$

This can be ascribed to the labile nature of the axial ligand, pheNH$_2$, in these two complexes. The introduction of halogen atoms on the methyl or methylene carbon of *N*,*N*′-ethylenebis(acetylacetoneiminato) and that of the benzene ring on the framework of the equatorial ligand remarkably shifted the half-wave potential towards more positive potentials. This fact suggests the electron withdrawal from the cobalt atom by these groups. Furthermore, by examining the nature of the half-wave potentials the redox orbitals of *N*,*N*′-ethylenebis(salicylideneaminato) and *o*-phenylenebis(salicylideneaminato) systems were concluded to be essentially different from those of other Schiff-base systems.

Previously,$^{1)}$ the present author studied the polarographic behavior of a series of mixed *β-cis* and *trans*-cobalt(III) complexes of tetradentate Schiff-base dianions, baen and salen,$^{2)}$ in an *N*,*N*-dimethylformamide (DMF) solution. All these complexes gave two well-defined polarographic steps corresponding to the reduction of cobalt(III) to cobalt(II) and that of cobalt(II) to cobalt(I). A thorough investigation of these led to the conclusion that the planar nature of baen and salen plays an important role in trapping the metal ion in an uncommon oxidation state. In order to get a deeper insight into the nature of the Schiff-base as a equatorial ligand, it seemed that it would be worthwhile to investigate the influence of tetradentate Schiff bases on the polarographic behavior of cobalt(III) complexes. In this paper, the present author will describe a polarographic study of *trans* mixed-ligand cobalt(III) complexes of tetradentate Schiff-base dianions (Z^{2-}) and methylbenzylamine (pheNH$_2$) with the general formula of [CoZ(pheNH$_2$)$_2$]$^{+\ 2)}$ in DMF and methanol solutions.

Experimental

Reagents. All the cobalt(III) complexes, [CoZ(pheNH$_2$)$_2$]ClO$_4$, used in this study were obtained from Dr. Y. Fujii (Department of Chemistry, Ibaraki Uiversity, Bunkyo, Mito, Ibaraki). The purification of DMF was described previously.$^{3)}$ The tetraethylammonium perchlorate (TEAP) was prepared by the method given by Fujinaga *et al.*$^{4)}$ The methanol used in this study was purified by employing the method given in a previous paper.$^{5)}$ All the other chemicals used in this study were of a reagent grade and were used without further purification.

Apparatus and Experimental Procedures. The DC polaro graphic waves were measured by using a manual polarograph similar to Kolthoff and Lingane's or a Yanagimoto pen-recording polarograph, P-8. All the AC polarograms were recorded automatically by employing the above pen-recording polarograph. The DC polarographic data given in this paper were corrected for the residual current and the ohmic drop of the cell circuit (4.2 kΩ). The characteristics of the dropping mercury electrode (DME) used have been given previously.$^{6)}$ As reference electrodes, a saturated calomel electrode (SCE) and a silver-silver chloride electrode (Ag/AgCl) were used in the DMF and methanol solutions respectively. The Ag/AgCl electrode was prepared by employing the method of Mizuguchi and Ueno.$^{7)}$ TEAP for the DMF system and LiCl for the methanol system were used as supporting electrolytes. All the other experimental procedures employed were described in a previous paper.$^{1)}$

Results and Discussion

As is illustrated by the DC polarogram of [Co(benacen)(pheNH$_2$)$_2$]$^+$ complex in Fig. 1, all the cobalt(III) complexes in DMF and methanol containing an excess of uncomplexed pheNH$_2$ gave two cathodic waves, the limiting currents of which were exactly proportional to their bulk concentration and to the square-root of the effective pressure on the DME. Furthermore, their diffusion-current constants were nearly identical to that of the reduction wave of the tris(acetylacetonate) cobalt(III) complex in the DMF solution, suggesting a one-electron reduction$^{1)}$ for both steps. The plot of log $(I/(I_\mathrm{d}-I))$ against the DC potential, E, invariably gave a straight line with a reciprocal slope falling in the range from −57 mV to −70 mV (20 °C). This indicates that the electrode reactions at both steps proceed reversibly in the polarographic sense. This explanation could be also confirmed AC-polarographically. An AC polarogram with two sharp maximal

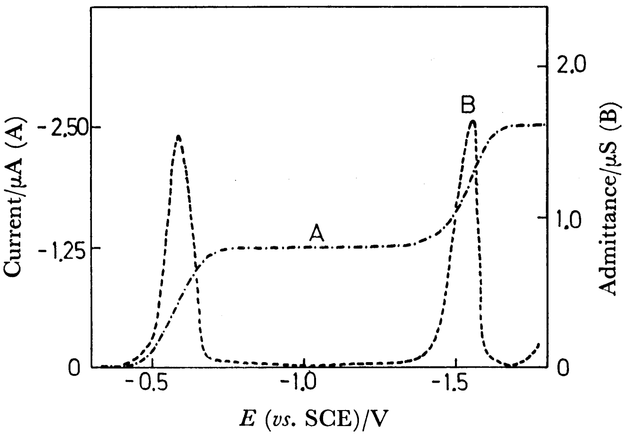

Fig. 1. DC (A) and AC (B) polarograms of 1.20 mM [Co(benacen)(pheNH$_2$)$_2$]$^+$ in DMF solution containing an excess of pheNH$_2$.
[TEAP]=0.20 M, [pheNH$_2$]=0.32 M.

currents corresponding to the DC reduction steps was obtained (Fig. 1). The concentration of the excess pheNH$_2$, when higher than 10 mM*, had no effect on the half-wave potential and the wave-height. These findings clearly suggest that the electron-transfer step is not accompanied by the dissociation of pheNH$_2$ from the complex; hence, the reaction mechanisms for the first and second steps can be expressed by Eqs. (1) and (2) respectively:

$$[\mathrm{CoZ(pheNH_2)_2}]^+ + e^- \rightleftharpoons [\mathrm{CoZ(pheNH_2)_2}]^0 \quad (1)$$

$$[\mathrm{CoZ(pheNH_2)_2}]^0 + e^- \rightleftharpoons [\mathrm{CoZ(pheNH_2)_2}]^- \quad (2)$$

The electrode reaction at the second step in the absence of pheNH$_2$ also proceeded reversibly in the polarographic sense. However, the first step became extended, showing an irreversible nature. The plot of $\log(I/(I_d-I))$ against E gave a straight line with a reciprocal slope falling in the range from -75 mV to -85 mV. Furthermore, a prestep appeared at a less negative potential, and its wave-height increased with the time at the expense of the first wave-height (Fig. 2). This prestep can probably be ascribed to the reduction of the [CoZ(pheNH$_2$)]$^+$ or CoZ$^+$ formed upon the dissociation of the axial ligand, pheNH$_2$, because the transformation of [CoZ(pheNH$_2$)$_2$]$^+$ into [CoZ(pheNH$_2$)]$^+$ or CoZ$^+$ lowers the energy level of the redox orbital,[8] which will then accept the electron in the course of the reduction process. The wave-height of the prestep at a given time was almost parallel with the following order of the rate constants for the dissociation of the axial ligand, pheNH$_2$, from the [CoZ(pheNH$_2$)$_2$]$^+$, lending strong support to the above explanation:

baen > benacen > salen > saloph > tfbaen[9]

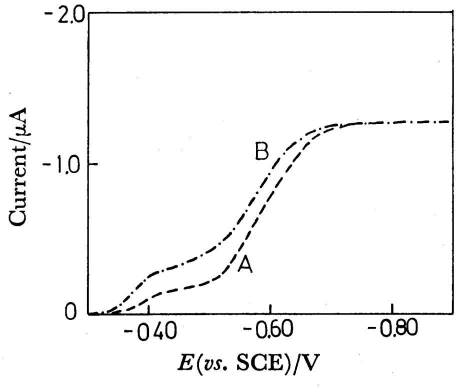

Fig. 2. DC polarogram of 1.20 mM [Co(baen)(pheNH$_2$)$_2$]$^+$ in DMF solution not containing pheNH$_2$. [TEAP]=0.20 M
A) Time, t=10 min. B) t=30 min.

In the light of the above findings, the irreversible nature of the first step in the absence of pheNH$_2$ can probably be ascribed to the slow partial dissociation of the axial ligand in the course of the electron-transfer step. The finding that the second step of the tfbaen complex gave a straight line with a reciprocal slope of -65 mV between $\log(I/(I_d-I))$ and E, while that of the substitution-labile benacen complex gave a linear relationship between $\log(I^2/(I_d-I))$ and E, also supports the above explanation (Fig. 3). The linear relation between $\log(I^2/(I_d-I))$ and E clearly suggests the following reaction mechanism for the second step of the benacen complex:

$$[\mathrm{CoZ(pheNH_2)_2}]^0 + e^- \rightleftharpoons [\mathrm{CoZ(pheNH_2)}]^- + \mathrm{pheNH_2} \quad (3)$$

In the methanol solution, the second step of the baen system merged into the base current. Therefore, no accurate log-plot examination could be achieved under the present experimental conditions. However, in the DMF solution, quite a similar result was obtained by conducting the above log-plot examination. This indicates that the electrode reaction in the second step of the baen system in the absence of pheNH$_2$ can also be given by Eq. (3).

The equatorial ligand will have a profound effect on the physicochemical properties and the reactivity of the ligand at the axial position. With a given axial ligand, the coordination of the equatorial tetradentate ligand,

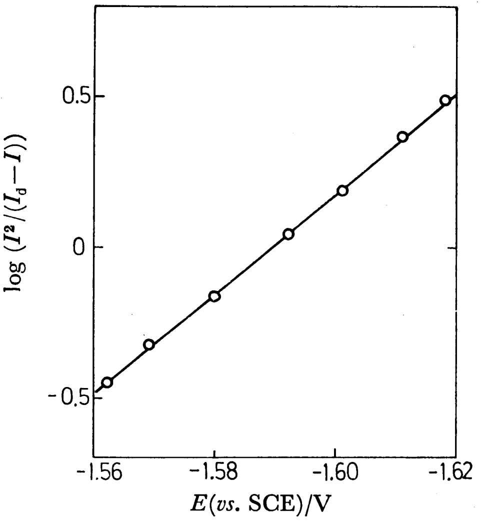

Fig. 3. The linear relation between the log $(I^2/(I_d-I))$ and E for the 2nd step of 1.0 mM [Co(benacen)(pheNH$_2$)$_2$]$^+$.
[TEAP]=0.20 M

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* M is mol dm^{-3}.

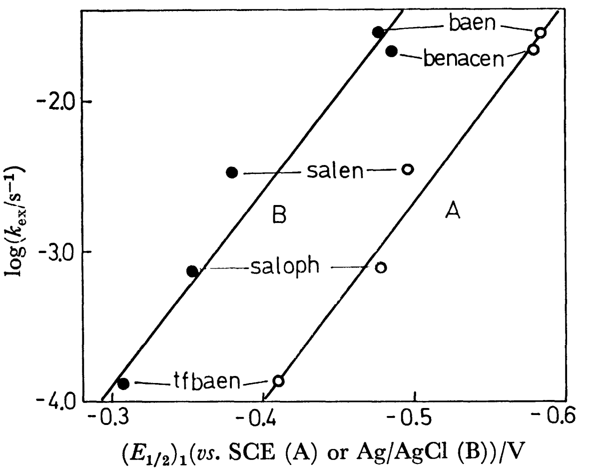

Fig. 4. The relation between the half-wave potential for the 1st step and log (k_{ex}/s^{-1}).
[pheNH$_2$]$=0.32$ M
A) DMF solution; [TEAP]$=0.20$ M
B) Methanol solution; [LiCl]$=0.30$ M

which gives the increase in the effective charge on the cobalt atom, will weaken the coordination bond in the axial positions and will shift the half-wave potential towards more negative potentials. Therefore, a close relationship between the half-wave potential and the magnitude of the exchange-rate constant of the axial ligand, pheNH$_2$, can be expected. As is illustrated in Fig. 4, a linear relation was found between the half-wave potential for the first step and the logarithm of the exchange-rate constant, log (k_{ex}/s^{-1}),[9] measured in the methanol solution by employing an NMR method. The half-wave potential determined in the presence of an excess of pheNH$_2$ was compared with log (k_{ex}/s^{-1}), because, only when the electrode process is rigorously reversible and the chemical reactions, including the dissociation of axial ligands which follows the electron transfer can be kept slow enough to be studied separately, the polarographic half-wave potential can give quantitative information concerning the thermodynamic aspects of the interaction of the axial ligand with the rest of the molecule.[10] As is shown by the results in Fig. 4, the replacement of the methyl group of the baen by the phenyl group (benacen) has no appreciable effect on the half-wave potential or the exchange rate of the axial ligand, pheNH$_2$. However, the replacement of the methyl hydrogen atoms of baen by fluorine (tfbaen) and the introduction of the benzene ring onto the framework of the equatorial ligand (salen and saloph) remarkably shifted the half-wave potential towards more positive potentials and reduced the rate of the exchange reaction of pheNH$_2$. The introduction of a chlorine (baen-Cl) or bromine (baen-Br) atom on the 3-position of baen also gave a positive shift of the half-wave potential (Fig. 5). As has been stated above, the half-wave potential gives a relative measure of the electron density on the cobalt atom.[11,12] Therefore, the above findings suggest that the benzene group on the framework of the equatorial tetradentate ligand and the halogen atom on the methyl or methylene carbon of baen can effectively decrease the electron density on the cobalt atom, hence enhancing the strength of the cobalt-pheNH$_2$ bond.

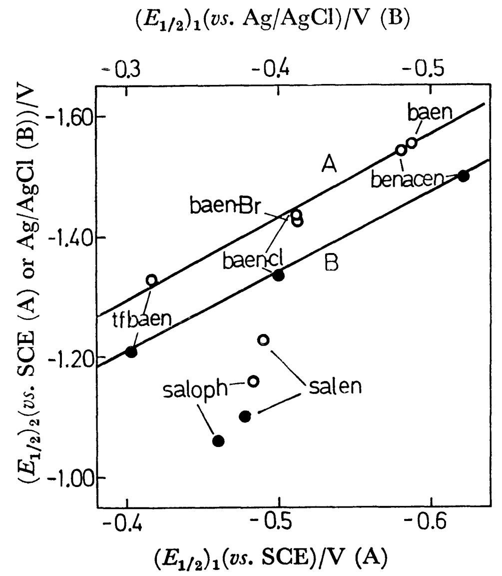

Fig. 5. The relation between the half-wave potentials for the 1st, $(E_{1/2})_1$ and 2nd steps, $(E_{1/2})_2$.
[pheNH$_2$]$=0.32$ M
A) DMF solution; [TEAP]$=0.20$ M
B) Methanol solution; [LiCl]$=0.30$ M

Finally, the present author wants to mention the following fact. As is shown by the results in Fig. 5, a linear relation holds in the DMF solution between the half-wave potentials of the first and second waves for all the tetradentate Schiff-base systems other than the salen and saloph systems. In the methanol solution, a similar linear relation also roughly holds. This probably indicates that the redox orbitals of the salen and saloph systems are essentially different from those of the other Schiff-base systems investigated. In order to describe precisely the nature of the redox orbital, though, further systematic investigation is required.

The author wishes to express his heartfelt thanks to Dr. Yuki Fujii of the Department of Chemistry, Faculty of Sciences, Ibaraki University, for his kind gift of the pure cobalt(III) complexes used in this study.

References

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2) The following abbreviations are used throughout: baen *N,N′*-ethylenebis(acetylacetoneiminato) dianion; baen-X, *N,N′*-ethylenebis(3-halogenoacetylacetoiminato) dianion; tfbaen, *N,N′*-ethylenebis(trifluoroacetylacetoniminato) dianion; benacen, *N,N′*-ethylenebis(benzoylacetoiminato) dianion; salen, *N,N′*-ethylenebis(salicylideneaminato) dianion; saloph, *o*-phenylenebis(salicylideneaminato) dianion.

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