The Polarography of *N*,*N*'-Ethylenebis(acetylacetoniminato) and *N*,*N*'-Ethylenebis(salicylaldehydeiminato) Complexes of Cobalt(III), Nickel(II), and Copper(II) in an *N*,*N*-Dimethylformamide Solution

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The polarographic behavior of *N*,*N*'-ethylenebis(acetylacetoniminato) (baen) and *N*,*N*'-ethylenebis(salicylaldehydeiminato) (bisaen) complexes of cobalt(III), nickel(II), and copper(II) in DMF solutions was studied thoroughly. At the dropping mercury electrode, these metal complexes give well-defined cathodic waves corresponding to the reduction of metal(II) to metal(I). A careful and systematic study of the polarographic behavior of *β-cis* and *trans* cobalt(III)-baen and -bisaen complexes of the general formulae: $CoZY^{1-a}$ and $CoZX_2^{1-2b}$, and that of nickel(II)- and copper(II)-baen complexes, revealed that the unusual stability of the metal(I)-baen and -bisaen complexes can be ascribed mainly to the stable square-planar nature of baen and bisaen. The effect of the replacement of the ligand by the halogen atom was also investigated.

Recently, Olson, and Vasilevskis[1-3] reported, in their polarographic investigation of cyclic amine complexes of nickel(II), copper(II), and cobalt(II), that these complexes give single well-defined polarographic steps corresponding to the reduction of metal(II) to metal(I), and that the unusual stability of cyclic amine complexes containing the metal formally in the +1 oxidation state can be ascribed to the cyclic nature of ligands. In our laboratory, a series of mixed *β-cis* and *trans* cobalt(III)-*N*,*N*'-ethylenebis(acetylacetoniminato) (baen) and -*N*,*N*'-ethylenebis(salicylaldehydeiminato) (bisaen) complexes containing ammonia, amino acids, acetylacetone, and 2,2'-dipyridyl were prepared by oxidizing the cobalt(II)-baen and -bisaen complexes, which have long been known to be oxygen carriers.[4-6] These baen and bisaen-cobalt(III) complexes and their cobalt(II) complexes in the *N*,*N*-dimethylformamide (DMF) give a reversible cathodic step corresponding to the reduction of cobalt(II) to cobalt(I), as in the cases of metal(II)-cyclic amine complexes. In this paper, we will study systematically the polarographic behavior of the mixed cobalt(III)-baen and -bisaen complexes in DMF and will discuss the nature of baen and bisaen, which can trap the metal ion in an uncommon oxidation state. Some comparisons will also be made between the cabalt and copper and nickel complexes in order to describe the precise nature of baen and bisaen as ligands.

Experimental

Reagents. The *N*,*N*-dimethylformamide (DMF) used for the polarographic work was purified by a procedure described by Fujinaga *et al.*[7] The supporting electrolyte, tetraethylammonium perchlorate (TEAP), was prepared by the method given by Fujinaga, Izutsu, and Takaoka.[8] Baen, bisaen, and their cobalt(II) complexes were prepared by the methods given by Morgan and Smith[9] and by Diehl and Hach.[10] The cobalt(III)-baen and -bisaen complexes used in this study were prepared by oxidizing the cobalt(II)-baen and -bisaen complexes with hydrogen peroxide in solutions containing ammonia, amino acids, acetylacetone, or 2,2'-dipyridyl. The detailed ways of preparing them, the determination of their stereochemical configuration, and the elemental analyses will be described in a future paper. All the other chemicals used were reagent-grade and were used without further purification.

Apparatus and Experimental Procedures. The DC polarographic waves were measured by using a manual polarograph similar to that of Kolthoff and Lingane[11] or Yanagimoto pen-recording polarograph PA-102. All the AC polarograms were also 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 (4.1 kΩ). For all the measurements, we used three dropping mercury electrodes. They have m values of 0.7396, 0.9153, and 0.5836 mg/sec, and drop times, t_d's, of 4.10, 5.10, and 4.40 sec respectively, in an air-free DMF (0.15 M TEAP) solution at the mercury height of 70.0 cm and with an open circuit. A saturated calomel electrode (SCE) with a large area was used as the reference electrode and was connected to the cell solution through the salt bridge proposed by Takaoka.[12] In the AC polarographic measurements, a 200-μF condenser was used to minimize the effect of cell resistance.[13] All the polarographic studies were carried out at 20°C using sample solutions containing no free ligand. The oxygen dissolved in the sample solutions was removed by bubbling pure nitrogen gas saturated with pure DMF through the solution. All the free ligands, except *N*,*N*'-ethylenebis-(3-bromoacetylacetonimine) (baen-Br_2), used in this study were found to give no reduction wave under the present experimental conditions.

Results and Discussion

As is illustrated by the DC polaragrams in Figs. 1 and 2, the cobalt(III)-baen and -bisaen complexes in

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TABLE 1. THE DEPENDENCE OF LIMITING CURRENT ON THE HEIGHT OF MERCURY COLUMN
The concentration of Co(baen)(acac)^0=1.82 mM, 20°C
The TEAP concentration=0.15 M

h, cm	$h_c^{1/2}$	i_{l_1}, μA (−1.30 V)	i_{l_2}, μA (−2.00 V)	$i_{l_1}/h_c^{1/2}$	$i_{l_2}/h_c^{1/2}$
70.0	8.21	1.90_9	1.74_5	0.232	0.213
75.5	8.65	2.00_0	1.83_6	0.231	0.212
85.0	9.08	2.14_1	1.96_3	0.235	0.216

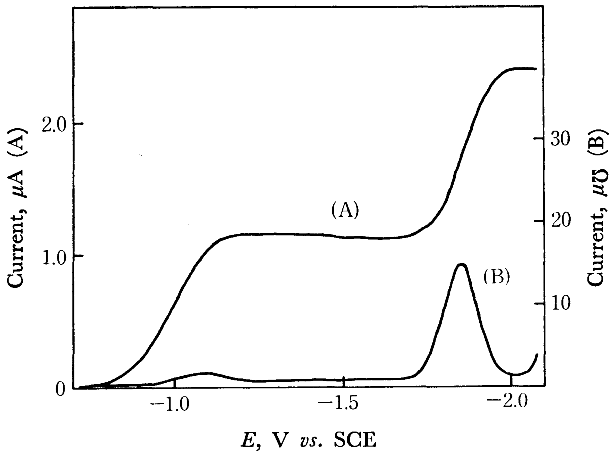

Fig. 1. DC and AC polarograms of K[Co(baen)(ala)$_2$]. 0.15 M TEAP, 20°C
The concentration of K[Co(bean)(ala)$_2$]=1.09 mM
A: DC polarogram, B: AC polarogram

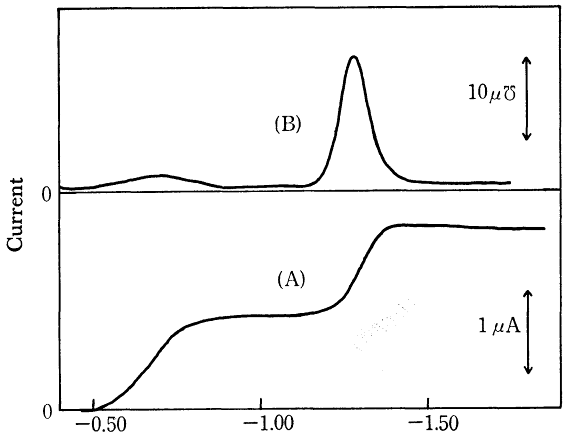

Fig. 2. DC and AC polarograms of K[Co(bisaen)(ala)$_2$]. 0.15 M TEAP, 20°C
The concentration of K[Co(bisaen)(ala)$_2$]=1.09 mM
A: DC polarogram, B: AC polarogram

TABLE 2. THE DEPENDENCE OF LIMITING CURRENT ON THE CONCENTRATION OF COMPLEX
The TEAP concentration=0.15 M, 20°C

Concentration of K[Co(baen)(ala)$_2$] C, mM	i_{l_1}, μA (−1.30 V)	i_{l_1}/C	i_{l_2}, μA (−2.00 V)	i_{l_2}/C
1.0	1.01_2	1.01	0.93_6	0.93_6
1.5	1.52_0	1.01	1.40_4	0.93_7
2.0	2.02_1	1.01	1.87_6	0.93_6
3.0	3.04_0	1.01	2.80_8	0.93_6

TABLE 3. DIFFUSION CURRENT CONSTANTS OF METAL COMPLEXES
0.15 M TEAP, 20°C

System[c]	I[a]	
	1st wave	2nd wave
Co(acac)$_3$^{0}	1.21_5	—
(Et)$_4$NCoY2H$_2$O	1.24	—
Co(baen)(H$_2$O)$_2$^{0}	—	1.25
K[Co(baen)(ala)$_2$]·7H$_2$O	1.17_5	1.18
K[Co(baen)(val)$_2$]·8H$_2$O	1.20	1.20
K[Co(baen)(isoleu)$_2$]·8H$_2$O	1.17	1.16
K[Co(baen)(leu)$_2$]·8H$_2$O	1.24	1.22
K[Co(baen)(phenala)$_2$]·6H$_2$O	1.28	1.28
[Co(baen)(NH$_3$)$_2$]ClO$_4$	1.24	1.26
Co(baen)(acac)^0	1.21	1.22
Co(baen)(bzacac)^0	1.20	1.20
[Co(baen)(dip)]ClO$_4$	1.22	1.24
Co(baen-Br$_2$)(acac-Br)^0	1.13_5	1.16[b]
Co(bisaen)(H$_2$O)$_2$	—	1.26_3
K[Co(bisaen)(ala)$_2$]·12H$_2$O	1.18	1.19
[Co(bisaen)(NH$_3$)$_2$]ClO$_4$	1.20	1.20
[Co(bisaen)(dip)]ClO$_4$	1.16	1.18
Co(bisaen)(acac)^0	1.24	1.24
Cu(baen)^0	1.33	—
Cu(baen-Cl$_2$)^0	1.31	—
Cu(baen-Br$_2$)^0	1.33	—
Ni(baen)^0	1.22	—
Ni(baen-Cl$_2$)^0	1.21_5	—

a) $I=i_d/Cm^{2/3}t_d^{1/6}$
b) less accurate
c) acac; acetylacetonate anion, Y^{4-}; EDTA anion, ala; alanine, val; valine, leu; leucine, isoleu; isoleucine, phenala; phenylalanine, bzacac; benzylacetone, dip; 2,2-dipyridyl

a DMF solution give two cathodic waves, the limiting currents of which are exactly proportional to their bulk concentration and to the square-root of the effective pressure on the DME (Tables 1 and 2). The peak-heights of the AC polarograms in Figs. 1 and 2 show that the electrode reaction at the first step of these complexes is irreversible, but that at the second wave, reversible in a polarographic sense. Furthermore, the diffusion current constants, I_d's ($=i_d/C\,m^{2/3}\,t_d^{1/6}$), of both steps were found to be nearly identical to that for the reduction wave of the trisacetylacetonatocobalt(III) complex in the DMF solution (Table 3). It was also found that cobalt(II)-baen and -bisaen complexes give a single reversible reduction wave, the reduction potential of which agrees

Table 4. The polarographic data

System	1st wave			2nd wave			
	Log-plot slope $\left(\log\frac{i}{i_d-i}\right)$, mV	$E_{1/2}$ (V *vs.* SCE)	R[a]	Log-plot slope, mV $\left(\log\frac{i^n}{i_d-i}\right)$ $n=1$	$n=2$	$E_{1/2}$ or E_f[b] (V *vs.* SCE)	R[a]
$Co(acac)_3{}^0$	92	−0.410	0.51	—	—	—	—
$Et_4NCoY\cdot 2H_2O$	120	−0.518	0.75	—	—	—	—
$Co(baen)(H_2O)_2{}^0$	—	—	—	—	—	−1.845	7.20
$K[Co(baen)(ala)_2]\cdot 7H_2O$	107	−1.020	0.51	70	—	−1.845	7.20
$K[Co(baen)(val)_2]\cdot 8H_2O$	102	−0.972	0.37	70	—	−1.834	9.00
$[Co(baen)(NH_3)_2]ClO_4$	108	−0.750	0.68	72	—	−1.852	7.16
$Co(baen)(acac)^0$	119	−0.945	0.49	—	66	−1.826	8.56
$[Co(baen)(dip)]ClO_4$	125	−0.452	0.65	—	60	−1.832	7.70
$Co(bisaen)(H_2O)_2{}^0$	—	—	—	75	—	−1.280	5.77
$K[Co(bisaen)(ala)_2]\cdot 12H_2O$	115	−0.665	0.70	68	—	−1.279	7.50
$[Co(bisaen)(NH_3)_2]ClO_4$	114	−0.590	0.52	65	—	−1.287	6.00
$Co(bisaen)(acac)^0$	125	−0.400	0.90	—	64	−1.315	6.00
$[Co(bisaen)(dip)]ClO_4$	132	−0.104	0.92	—	56	−1.315	7.55
$Cu(baen)^0$	80	−1.541	2.55	—	—	—	—
$Cu(baen\text{-}Cl_2)^0$	68	−1.306	4.70	—	—	—	—
$Cu(baen\text{-}Br_2)^0$	70	−1.289	3.92	—	—	—	—
$Ni(baen)^0$	75	−2.004	7.10	—	—	—	—
$Ni(baen\text{-}Cl_2)^0$	80	−1.760	6.11	—	—	—	—

a) R: R is defined as $I_p/ni_dt_d{}^{1/2}$, where I_p is the peak-height of AC polarogram.
b) E_f: The potential where $\log(i^2/(i_d-i))$ is equal to zero.

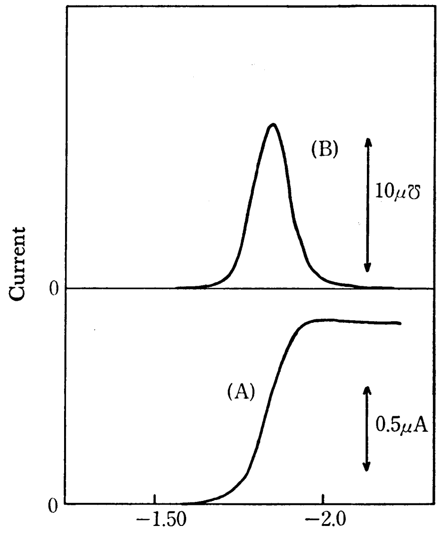

Fig. 3. DC and AC polarograms of $Co(bean)(H_2O)_2{}^0$. 0.15 M TEAP, 20°C
The concentration of $Co(baen)(H_2O)_2{}^0=1.10$ mM
A: DC polarogram, B: AC polarogram

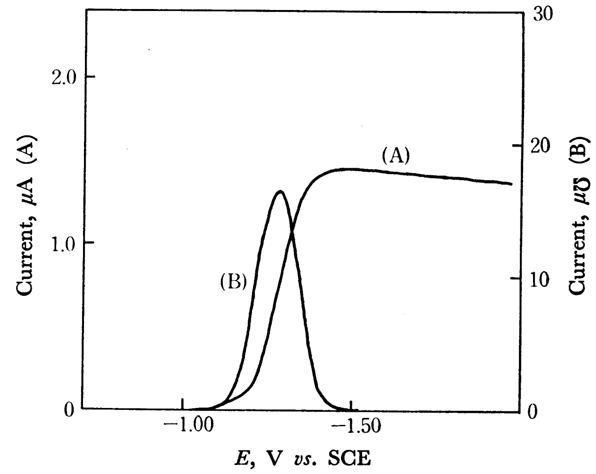

Fig. 4. DC and AC polarograms of $Co(bisaen)(H_2O)_2{}^0$. 0.15 M TEAP, 20°C
The concentration of $Co(bisaen)(H_2O)_2{}^0=1.40$ mM
A: DC polarogram, B: AC polarogram

well within several milivolts with that of the second step of the corresponding cobalt(III) complex, and that their I_d values are nearly identical to that of the cobalt(III) complex (Figs. 3 and 4). All the above polarographic evidence indicates that the first and second steps of cobalt(III) complexes correspond, respectively, to the one-electron reduction of cobalt(III) to cobalt(II) and that of cobalt(II) to cobalt(I). The polarographic data on cobalt(III)-baen and -bisaen complexes studied in this paper are summarized in Table 4, together with those on nickel(II) and copper(II)-bean complexes.

As is shown by the data in Table 4, the first waves of the *β-cis* complexes with the general formula $CoZY^{1-a}$ give log-plot (E *vs.* $\log(i/(i_d-i))$) slopes larger than those of *trans* complexes, $CoZX_2{}^{1-2b}$. Although the details of the determination of the configuration have not been described in this paper, the NMR study confirmed that all the cobalt(III) complexes of the general formula $CoZY^{1-a}$ have the *β-cis* configuration, and the $CoZX_2{}^{1-2b}$ complexes the *trans* configuration.

An electrode reaction accompanied by a change in the configuration of the reactant is generally believed to be slow.[14] Therefore, the above finding may imply that the electrode reaction at the first step of the *β-cis* complex is accompanied by a change in its configuration or by a loosening of its structure. This would also explain well the reversible property of the second reduction step of the *β-cis* complex. However, in the case of the irreversible polarographic reduction, from the theoretical point of view the log-plot examination can not be expected to provide many useful information on the electrode reaction mechanism or on the formula of the reduction product. Therefore, we can not describe more precisely the nature of the first wave on the basis of the log-plot examination. On the other hand, in the case of the second step, because of its perfect reversible nature, we can determine exactly the electrode reaction mechanism and, hence, formulate the reduction product by performing a careful log-plot examination (E *vs.* $\log(i^n/(i_d-i))$ plot). The polarographic data gives in Table 4 also indicate that the second waves of the mixed cobalt(III) complexes of baen and bisaen containing bidentate ligands give exclusively straight lines, with reciprocal slopes of about 65 mV, close to the theoretical value of 58 mV for the reversible one-electron reduction in the plot of the DC potential, E, against $\log(i^2/(i_d-i))$ (Fig. 5). As has been stated previously, the sample solutions used in this study contained no free ligand. Therefore, the above linear relation between E and $\log(i^2/(i_d-i))$ implies that one molecule of the ligand will be liberated in the course of the reduction of the complex. Considering the polarographic evidence that the second wave appears at the potential nearly identical to the reduction potential of the corresponding cobalt(II) complex, the ligand liberated in the course of the reduction may be concluded to be the bidentate one. Consequently, the electrode reactions for the reduction of the *β-cis* cobalt(III)-baen and -bisaen complexes at the DME can be formulated as:

$$\mathrm{CoZY}^{1-a} + e^- \rightleftharpoons \mathrm{CoZY}^{a-}$$

$$\mathrm{CoZY}^{a-} + e^- \rightleftharpoons \mathrm{CoZ}^- + \mathrm{Y}^{a-}$$

On the other hand, in the polarography of a series of mixed cobalt(III)-baen and -bisaen complexes involving amino acids or ammonia (the general formula is $\mathrm{CoZX_2}^{1-2b}$), which have the *trans* configuration, the plot of E against $\log(i/(i_d-i))$ for the second step gave straight lines, with slopes falling in the range from 60 to 70 mV, corresponding to the reversible one-electron reduction (Fig. 6). By the addition of lithium(I) perchlorate to the sample solution, the reduction step was shifted remarkably to less negative potentials, and the plot of E against $\log(i^3/(i_d-i))$ in place of $\log(i/(i_d-i))$ gave a straight line with a slope of 57 mV. A typical result is shown in Fig. 7. The above positive shift of the reduction potential and the linear relation between the E and $\log(i^3/(i_d-i))$ can be reasonably explained in terms of the interaction of a lithium(I) ion with the reduction product, the cobalt(I) complex, that is, the coordinative relaxation of the amino acid anion from the cobalt(I)-baen or -bisaen complex.[15] Although the dependence of the potential shift on the concentration of the lithium(I) ion was examined in only a qualitative way, because of the lack of an association constant in the DMF solu-

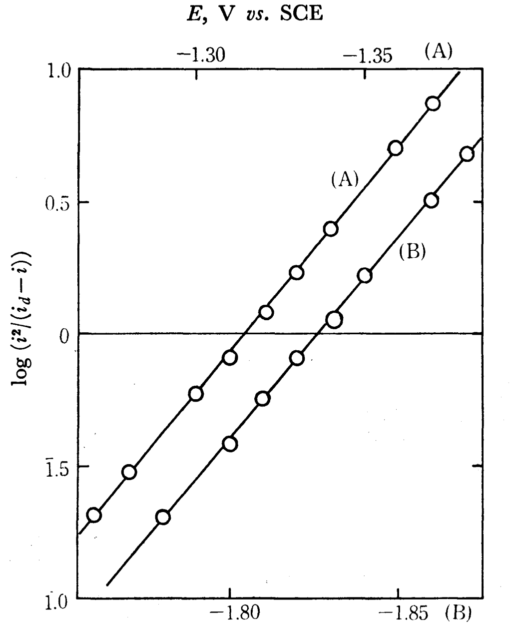

Fig. 5. The log-plot examination of the second wave. 0.15 M TEAP, 20°C
A: Co(bisaen)(acac)°, B: Co(bean)(acac)°

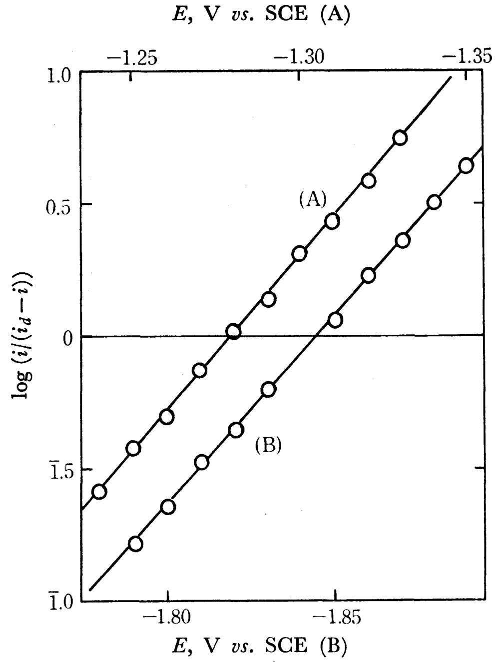

Fig. 6. The log-plot examination of the second wave. 0.15 M TEAP, 20°C
A: K[Co(bisaen)(ala)$_2$], B: K[Co(baen)(ala)$_2$]

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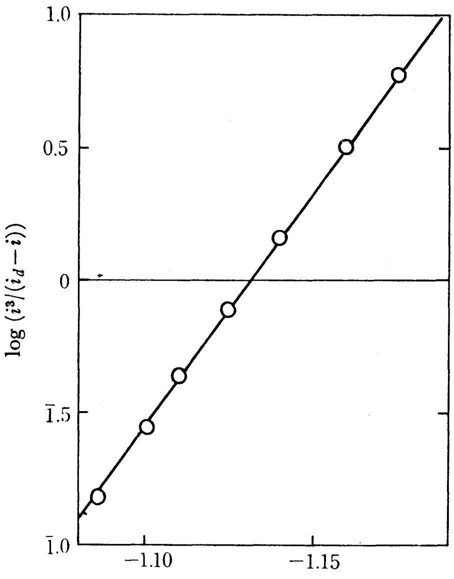

Fig. 7. The log-plot examination of the second wave of $K[Co(bisaen)(ala)_2]$ in the presence of 0.10 M lithium(I) salt.
0.15 M TEAP, 20°C

tion, the finding that the reduction potential is shifted to less negative potentials with an increase in the lithium(I) ion concentration also supports the present authors' explanation. Thus, the above linear relation between E and $\log(i^3/(i_d-i))$ suggests the following reaction mechanism for the relaxation process:

$$CoZX_2^{2-} + e^- + 2Li^+ \rightleftharpoons CoZ^- + 2LiX$$

where Z^{2-} and X^- mean the baen or bisaen anion and the amino acid anion. Therefore, the reduction process of *trans* cobalt(III)-baen and -bisaen complexes involving amino acids or ammonia in solutions not containing lithium(I) salt can be formulated as:

$$CoZX_2^- + e^- \rightleftharpoons CoZX_2^{2-} \quad \text{irreversible}$$

$$CoZX_2^{2-} + e^- \rightleftharpoons CoZX_2^{3-} \quad \text{reversible}$$

The addition of calcium(II) salt to the trans cobalt(III)-baen and -bisaen complex solutions also caused a similar coordinative relaxation. That is, in the presence of the calcium(II) ion, the second wave gave a straight line with a slope of 60 mV between E and $\log(i^2/(i_d-i))$. Those results are not shown here.

We have mentioned earlier that a series of *trans* cobalt(III)-baen and -bisaen complexes with the general formula of $CoZX_2^{1-2b}$ all give the reduction product $CoZX_2^{-(1+2b)}$, which has an atomic configuration similar to that of $CoZX_2^{1-2b}$, in their polarographic reduction at the DME. On the other hand, a series of *β-cis* cobalt(III) complexes with the general formula of $CoZY^{1-a}$ are reduced to the cobalt(I) to give the CoZ^-, thus, liberating the bidentate ligand, Y^{a-}. The coordination of a bidentate ligand such as the acetylacetonate anion and 2,2′-dipyridyl to the metal ion force the baen and bisaen to take a *β-cis* configuration in the octahedral complex. Therefore, the dissociation of bidentate Y^{a-} from the metal will allow the baen and bisaen to be in a *trans* configuration, which has less strain than the *β-cis* configuration.

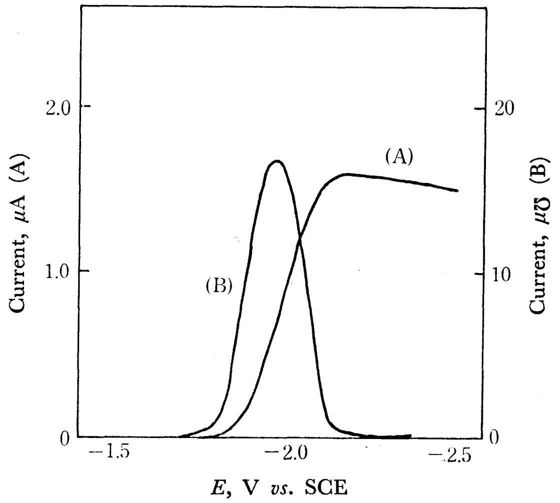

Fig. 8. DC and AC polarograms of $Ni(baen)^0$.
0.15 M TEAP, 20°C
The concentration of $Ni(baen)^0$ = 1.70 mM

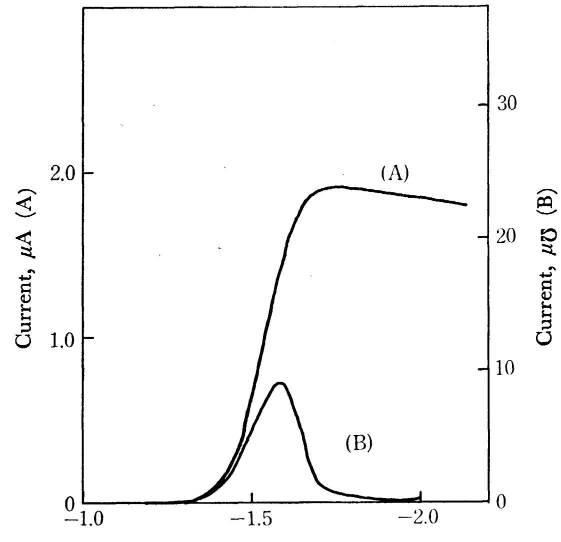

Fig. 9. DC and AC polarograms of $Cu(baen)^0$.
0.15 M TEAP, 20°C
The concentration of $Cu(baen)^0$ = 1.74 mM

Square-planar nickel(II) and copper(II)-baen complexes also gave single cathodic waves corresponding to the one-electron reduction of the metal(II) complex (see the I_d values in Table 3). Typical polarograms are reproduced in Figs. 8 and 9. The plot of E against $\log(i/(i_d-i))$ also gave linear relations, with slopes of about 70 mV, corresponding to the following reversible one-electron reduction:

$$MZ^0 + e^- \rightleftharpoons MZ^- \quad \text{reversible}$$

From the above experimental results and the discussion of them, it can be stated that the unusual stability of baen and bisaen complexes containing the metal ion formally in the +1 oxidation state is ascribable to the stable planar configuration of the ligands. The possibility of the formation of cobalt, nickel, and copper metals in the course of the reductions of baen, and bisaen complexes was disproved by the α-nitroso-β-naphthol, dimethylglyoxime, and ammonia tests of aqueous solutions obtained by treating the mercury metal used in the polarographic study with concentrated hydrochloric acid and by then neutralizing the resulted solutions.

The influence of the replacement of the ligand by the halogen atom on the polarographic behavior of baen complexes was also studied. As is shown by the data in Tables 3 and 4, the introduction of the halogen atom on the ligand causes a remarkable positive shift of polarographic waves. However, *N,N'*-ethylenebis(3-halogenoacetylacetoniminato) (baen-X_2) complexes also gave well-defined polarographic steps which correspond to the reversible reduction of M(II) to M(I). Although the influence of such a substitution on the coordinated ligand can be discussed from various points of view, as a first approximation the introduction of a halogen atom may be considered to have a remarkable effect on the delocalized π system of the ligand. In considering that the cobalt(III) ethylenediaminetetraacetate complex gives only one reduction step, corresponding to the reduction from Co(III) to Co(II) under the present experimental conditions (Table 4), we can not completely neglect the possibility that the delocalized π system of the baen or bisaen contributes to some extent to the stabilization of the M(I) oxidation state. Therefore, the finding that the metal(II)- baen-X_2 complexes also give polarographic steps which correspond to the reduction of M(II) to M(I) seems to indicate that the delocalized π system of the acetylacetone segment in the baen and bisaen plays only a minor role in the stabilization of the M(I) oxidation state. Furthermore, we can mention the following two facts (Table 4):

1) The first step of the *β-cis* cobalt(III)-baen or -bisaen complex appears at less negative potentials than that of the *trans* complex, $CoZX_2$[1-2b].

2) The reduction steps of the bisaen complexes appear at less negative potentials than those of corresponding baen complexes.

The former can be ascribed to the asymmetric structure of the *β-cis* complex and to the coordination of the bisentate ligand with a delocalized π system.[14] The latter fact, that the reduction wave of bisaen complex is located at a less negative potential than that of the baen complex, is ascribable to the benzene ring of bisaen.[14]

Olson and Vasilevskis[1-3] stated in their electrochemical and synthetic studies of cyclic amine complexes of nickel(II), copper(II), and cobalt(II) that probably the major factor responsible for the unusual stability of the cyclic amine complexes containing the metal ion in the +1 oxidation state is the cyclic nature of the ligands. However, all the experimental evidence obtained in this polarographic study of the metal complexes of noncyclic Schiff bases, baen and bisaen, leads to the conclusion that the unusual stability of metal(I) complexes can be attributed to the rigid and stable square-planar nature of tetradentate ligands. Here, we can not disregard the role played by the stable environment provided by the inert aprotic solvent, DMF.