Macro cyclic Metal Complexes: Part IV—Electrochemical Studies on Cobalt(III) Macrocyclic Complexes

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Received 13 May 1982; revised and accepted 5 October 1982

Electrochemical studies on fluoro-boro-bridged macrocyclic complexes of cobalt(III), Co[bofamcyclaene(14) B'X] and Co[bofaphyclaene(14) B'X], and on their respective parent non-macrocyclic complexes have been done in aqueous dimethylformamide using tetraethylammonium perchlorate as the supporting electrolyte. Two well defined redox steps corresponding to Co(III)-Co(II) and Co(II)-Co(I) couples have been observed. For all the macrocycles, the redox potentials are more anodic as compared with those observed for their respective parent complexes, the values being ~200-250 mV and ~700 mV respectively for the two steps. The anodic shift of \(E_1\) values for the first stage of reduction is due to decrease in electron density on central cobalt atom due to the presence of electronegative \(\text{BF}_2\) groups at the bridge head of the macrocycles. The relative ease of reduction for Co(II)-Co(I) couple in the macrocycles implies greater stabilization of metal ion in the low oxidation state which is one of the pronounced characteristics of cyclic ligand systems.

Materials and Methods

Dimethylformamide (BDH), perchloric acid (E Merck, AR) and tetraethylammonium hydroxide (25% solution, Fluka) were used for polarographic measurements. Parent complexes, Co(OximeH)\(_2\) B'X[OximeH = monoanion of 1, 2-dimethyl-1, 2-dione dioxime (dimethylglyoxime) or 1, 2-diphenylethane-1, 2-dione dioxime (α-benzildioxime), B' = pyridine, β-picoline or γ-picoline and X = Cl\(^-\), Br\(^-\), or I\(^-\)] were prepared by the literature method\(^5\). Their fluoro-boro-bridged macrocyclic derivatives [Co[bofamcyclaene(14)] B'X] and Co[bofaphyclaene(14)]B'X] were prepared as described earlier by us\(^6\). Polarographic curves were recorded with a recording polarograph LP 7 fitted with a EZ 7 line recorder. A dropping mercury electrode (d.m.e.) was used as an indicator electrode and an external saturated calomel electrode (S.C.E.) was used as the reference electrode.

The aqueous dimethylformamide solution of the complex (1 \(\times\) 10\(^{-3}\) M)(DMF: H\(_2\)O = 80:20) containing 0.1 M tetraethylammonium perchlorate (TEAP) was connected with a saturated calomel electrode (S.C.E.). The capillary of d.m.e. had the characteristics, \(m = 6.6 \text{ mg sec}^{-1}\), \(t = 3.7 \text{ sec for a mercury column of height} 42 \text{ cm. Half-wave potentials were measured at a}

Extensive polarographic studies on metal complexes with π-acceptor ligands have been reported\(^1,2\). Cobalt(II) complexes of bis-2, 6-(2'-quinoliny]pyridine and dicyanobispyridyl complexes of cobalt(III) have been studied\(^3,4\). The heteroligand complex, [Co(CN)\(_2\)(Bipy)]\(^+\) is reduced at dropping mercury electrode (d.m.e.) in DMSO and gives rise to three diffusion waves, each corresponding to the transfer of one electron. Electrochemical studies of macrocyclic complexes have also received considerable attention in recent years\(^5,6\). Polargraphic studies on macrocyclic metal complexes of cobalt(III) of the type, [CoL(NO\(_2\))\(_2\)]\(^+\) where L represents a series of 14-membered macrocyclic ligands, viz., 1, 4, 8, 11-tetraazacyclo-tetradecane(cyclam), 2, 3-dimethylcyclocktetradeca-1, 8, 11-tetraazacyclo-tetradeca-1, 3-diene(DIM) and 2, 3, 9, 10-tetramethyl-1, 8, 11-tetraazacyclotetradeca-1, 3, 8, 10-tetraene(TIM) have been done in methanol\(^7\).

Fluoro-boro-bridged macrocyclic complexes of cobalt(III) of the type, Co(Cy)B'X, where Cy represents macrocyclic ligands, 1, 8-diboro-1, 1, 8, 8-tetrafluoro-2, 7, 9, 14-tetraoxa-3, 6, 10, 13-tetraaza-4, 5, 11, 12-tetramethylcyclocktetradeca-3, 5, 10, 12-tetraene[abbr. bofamcyclaene(14)] and 1, 8-diboro-1, 1, 8, 8-tetrafluoro-2, 7, 9, 14-tetraoxa-3, 6, 10, 13-tetraaza-4, 5, 11, 12-tetraphenylecyclotetradeca-3, 5, 10, 12-tetraene[abbr. bofaphyclaene(14)]; B' represents a pyridine base and X represents a halide ion (B' and X occupying trans-axial positions) have been reported by us\(^8\). Electrochemical studies on these complexes have been carried out with a view to correlating the half-wave potentials with changes in structural parameters and stabilities of the chelates. We have used dimethylformamide (DMF)-water mixture (80:20) as the solvent medium because of the solubility of the complexes in the former solvent and its aprotic nature. Apart from the macrocyclic complexes, their parent compounds, Co(LH\(_2\))B'X, have been also studied polarographically to throw light on the changes that occur on account of the macrocyclic effect.
scanning rate of 100 mV/min. Tetraethylammonium perchlorate (0.1 M), used as the supporting electrolyte, was prepared and dimethylformamide was purified as reported earlier 10.

Results and Discussion

The electrochemical data for the complexes (halo) (pyridine)-bis(1, 2-dimethylethane-1, 2-dione dioximato)cobalt(III) [Co(dmgH)₂B'X] and (halo) (pyridine) bis(1, 2-diphenylethane-1, 2-dione dioximato)cobalt(III) [Co(bdoH)₂B'X], and their macrocyclic derivatives are presented in Tables 1 and 2. A representative plot of $\log(i/i_d - i)$ vs $E$ is shown in Fig. 1. For the 14-membered macrocycles and their parent complexes (for the series containing X and B' as axial ligands) two well defined reduction waves have been observed. These redox waves may correspond to species having the metal ion in the oxidation states +1 and +2 respectively. In the macrocyclic complexes of the type Co[bofaph-cyclaene(14)B'X], a third wave was observed in the potential range -1.13 to -1.30 V. However, no such wave was observed for the macrocycles Co[bofamcyclaene(14)B'X] within the potential range studied i.e. up to -2.0 V. The third wave in the former series of macrocycles has not been fully investigated; it may be either due to the reduction of the macrocyclic ligand or the reduction of the metal ion from oxidation state +1 to 0. The first two polarographic waves of these complexes were found to be diffusion controlled at the dropping mercury electrode as revealed by the linear plots of $i_d$ versus $\sqrt{n_{eff}}$ and $i_d$ versus concentration, which pass through the origin.

The results of the electrochemical studies indicate some salient features concerning the influence of the nature of the ligand on the nature of the electrode reaction. In terms of the first stage of reduction, the electrochemical processes can be broadly divided into two groups. The first stage of reduction for the macrocyclic complexes, Co[bofamcycalene(14) B'X]

| Table 1 — Electrochemical Data of Cobalt(III) Macrocycles of the Type, Co[bofamcycalene(14)B'X] and Their Parent Complexes |
|-----------------|-----------------|-----------------|
| Complex         | $E_{1/2}$ (V)   | Slope (mV)      |
|                 |                | $E_{1/2}$ (V)   | Slope (mV)      |
| CoL₁PyCl        | -0.788         | 68              | -0.99           | 64               |
| CoL₁PyBr        | -0.786         | 60              | -0.988          | 69               |
| CoL₁PyI         | -0.784         | 67              | -0.984          | 86               |
| CoL₁β-PicCl     | -0.823         | 67              | -1.014          | 59               |
| CoL₁β-PicBr     | -0.792         | 54              | -0.968          | 75               |
| CoL₁β-PicI      | -0.807         | 67              | -0.992          | 88               |
| CoL₁γ-PicCl     | -0.820         | 74              | -1.023          | 87               |
| CoL₁γ-PicBr     | -0.794         | 54              | -0.992          | 75               |
| CoL₁γ-PicI      | -0.802         | 69              | -0.989          | 88               |
| Co(dmgH)₂PyCl   | -1.028         | 93              | -1.770          | 80               |
| Co(dmgH)₂PyBr   | -1.013         | 87              | -1.761          | 88               |
| Co(dmgH)₂β-PicCl| -1.055         | 86              | -1.763          | 83               |
| Co(dmgH)₂β-PicBr| -1.026         | 96              | -1.798          | 100              |
| Co(dmgH)₂β-PicI | -1.005         | 120             | -1.778          | 88               |
| Co(dmgH)₂γ-PicCl| -1.128         | 75              | -1.769          | 94               |
| Co(dmgH)₂γ-PicBr| -1.092         | 72              | -1.756          | 67               |
| Co(dmgH)₂γ-PicI | -0.979         | 82              | -1.750          | 71               |

$L₁ = $ bofamcycalene(14)

| Table 2 — Electrochemical Data of Cobalt(III) Macrocycles of the Type, Co[bafaphcycalene(14)B'X] and Their Parent Complexes |
|-----------------|-----------------|-----------------|
| Complex         | $E_{1/2}$ (V)   | Slope (mV)      |
|                 |                | $E_{1/2}$ (V)   | Slope (mV)      |
| CoL₂PyBr        | -0.514         | 80              | -0.842          | 75               |
| CoL₂PyI         | -0.537         | 64              | -0.857          | 78               |
| CoL₂β-PicCl     | -0.532         | 78              | -0.787          | 79               |
| CoL₂β-PicI      | -0.595         | 76              | -0.903          | 88               |
| CoL₂γ-PicCl     | -0.561         | 70              | -0.780          | 80               |
| CoL₂γ-PicBr     | -0.525         | 75              | -0.790          | 70               |
| CoL₂γ-PicI      | -0.559         | 82              | -0.940          | 68               |
| Co(bdoH)₂PyBr   | -0.755         | 71              | -1.495          | 75               |
| Co(bdoH)₂PyI    | -0.776         | 77              | -1.570          | 80               |
| Co(bdoH)₂β-PicBr| -0.750         | 65              | -1.550          | 82               |
| Co(bdoH)₂γ-PicBr| -0.762         | 61              | -1.601          | 69               |
| Co(bdoH)₂γ-PicI | -0.760         | 83              | -1.524          | 83               |

$L₂ = $ boafaphcycalene(14)
appears to be reversible\textsuperscript{11} at the d.m.e. (reciprocal of
the slope lies within 58-68 mV) Table 1, Fig. 1a) while for
the macrocycles, Co[bis(baphycyclanene(G) B\textsuperscript{X})] the
first stage of reduction may be regarded as quasi-
reversible as determined from the reciprocal of
the slope of the plot of \( \log (i/i_{\text{d}} - i) \) versus \( E \) (Table 2). For
other complexes the first and second reduction stages
are either irreversible or quasi-reversible (Fig. 1b).
This type of redox processes occur for cobalt(III)
complexes with bipyridine\textsuperscript{4}, phenanthroline and several
macroyclic ligands\textsuperscript{5}. Bis(1, 2-dimethylthene-1, 2-
dione dioximato) cobalt(III) complexes have been
studied polarographically by Schrauzer \textit{et al.}\textsuperscript{12} A
series of base adducts of different \( pK_a \) values have been
studied by Costa and coworkers\textsuperscript{13}. The latter workers
observed that the first reduction wave is irreversible or
quasi-reversible for the pyridine complex and develops
with half-wave potential, \( E_{1/2} \), between -0.33 and
-0.89 V (vs S.C.E.). For the present series of bis(1, 2-
dimethylthene-1, 2-dione dioximato)cobalt(III)
complexes, the first reduction wave, which develops with
half-wave potential between -0.979 and -1.005 V in
aqueous DMF (Table 1), is more cathodic than the
earlier reported values and is presumed to be
influenced by the solvent molecules and/or nephelauxetic effect (vide infra).

It is striking to note that \( E_{1/2} \) values for Co(III)-
Co(II) couple for the non-macro cyclic parent
complexes are more cathodic than those for their
respective macro cyclic derivatives and the waves are
irreversible as evident from the magnitude of the slopes
(Tables 1 and 2). The \( E_{1/2} \) values for the cobalt(II)-
cobalt(I) couple for the macrocyclic complexes are
found to be more anodic than those for their respective
parent complexes indicating greater stabilization of
Co(I) in the cyclic ligand system. Such behaviour has
been observed for a series of iron(II), nickel(II) and
cobalt(II) complexes\textsuperscript{7}. It has been reported that for the
bis(1, 2-diphenylethane-1, 2-dione dioximato)
cobalt(III) complexes, the \( E_{1/2} \) values for the first and
second stages of reduction are more anodic relative to
those for the bis(1, 2-dimethylthene-1, 2-dione
dioximato) cobalt(III) series of complexes reflecting
higher degree of ligand unsaturated in the former
series. But polarographic studies on a series of
cobalt(III) complexes of the type \([\text{Co(MAC)}
(CH_3CN)_2]^{3+}\), where MAC represents a series of 14-
membered macrocycles varying in their degree and
position of ligand unsaturation and substitution\textsuperscript{5},
show some striking variations from the present
findings. For the MAC series of complexes, the half-
wave potentials for the Co(II)/Co(I) couple vary in a
predictable manner, related to ligand unsaturation,
while the Co(III)/Co(II) couple is insensitive to these
structural variations.

Electrochemical reduction represents an electron
transfer to the lowest unoccupied molecular orbital.
The value of \( E_{1/2} \) represents a thermodynamic
quantity and provides a measure of the energy level of
this orbital in the complex. It is striking to note that
variation of \( E_{1/2} \) values for the first and second stages
of reduction for each series spans a very small range,
~40 mV. The small range implies that the transferred
electron is delocalized embracing a common
unoccupied molecular orbital which is most likely
dominated by planar ligand orbital which is most likely
influenced by the solvent molecules and/or nephelauxetic effect (vide infra).

Half-wave potentials provide a measure of the
electron density on the metal ion\textsuperscript{14}. The anodic shift of
half-wave potential for Co(III)-Co(II) couple reflects a
decrease in electron density on the cobalt ion due to the
presence of highly electronegative \( >\text{F}_2 \) groups at the
bridge head of the macrocycles which decrease the
electron density in the chelate ring and the drift of the
electrons takes place both in the \( \pi \)-electron system and the
\( \sigma \)-frame work.

Another significant aspect of the present electro-
chemical studies is the difference in magnitudes of the
\( E_{1/2} \) values for the first and second stages of reduction
for the macrocyclic complexes and their respective
parent compounds. The second stage of reduction is
substantially easier in the macrocyclic complexes
\((~200 \text{ mV})\) than in their respective non-macro cyclic
parent complexes \((~700 \text{ mV})\) as reflected from the
positions of the cathodic waves. The results show
greater metal-ligand interactions in the equatorial
plane in the macrocycles, further implying a higher
stabilization of the metal ion in the lower oxidation
state. A formal +1 oxidation state of cobalt in the
product and the ligand field strength in the equatorial
plane would indicate a planar structural arrangement,
a very favourable structure with a low spin \( d^8 \) electron
configuration.

Comparison of the present polarographic data with the
available \( E_{1/2} \) values of some macrocycles
illuminates a self consistent pattern. The \( E_{1/2} \) values of
macro cyclic complexes of Co(III) with cyclam, DMC,
DIM and TIM in methanol, for the first step, are found
to range from \(-0.450 \text{ V} \) to \(-0.217 \text{ V} \) and the \( E_{1/2} \)
values for the second stage of reduction are \(-0.841 \text{ V} \)
and \(-0.474 \text{ V} \) for DIM and TIM complexes
respectively. The results show that an increase in
ligand unsaturation leads to an anodic shift of \( E_{1/2} \)
which has been attributed to greater nephelauxetic
effect of the unsaturated ligand. The Racah parameter
\( B \) reflects the measure of nephelauxetic effect. The \( B \)
values lie in the range 350-450 cm\(^{-1}\) for the present
series of complexes\textsuperscript{8} while they are about 600 cm\(^{-1}\) for
the cyclam, TIM, DIM and DMC complexes of
cobalt(III). Relatively higher cathodic \( E_{1/2} \) values for
the present series of complexes are consistent with lower $B$ values arising due to more electrophilic $\textit{BF}_2$ bridges.

Acknowledgement
The authors are thankful to the UGC, New Delhi, for the award of a Teacher Fellowship to J Chakraborty, and to the CSIR, New Delhi for a Fellowship to Kunja B. Naik.

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