922. *Studies on Bond Type in Certain Cobalt Complexes. Part III.* The Polarographic Reduction of Some Cobalt Inner-complex Compounds.*

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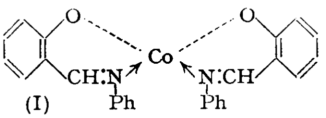
The polarographic reduction of some cobalt complexes with various salicylideneanilines has been attempted. Two-step irreversible curves have been obtained in all curves but the mechanism of reduction has not been clarified.

THE polarographic reduction of a group of cobaltous compounds of the non-electrolyte, inner complex type has been attempted, the object being to discover whether the method provided a measure of the relative stabilities of these compounds. Eight compounds have been examined, all being of the bis(salicylideneaniline)cobalt type (I), with various substituents in the aniline ring. It had been hoped to carry out these investigations in aqueous pyridine in order to facilitate comparisons with the work of Bailes and Calvin (*J. Amer. Chem. Soc.*, 1946, **68**, 949) and the exchange work being carried out by West (Part I, *J.*, 1952, 3115), but this proved impossible since pyridine is reduced at a potential lower than any of the complexes examined.


(I)

After considerable trial, the reductions were finally carried out in 80% ethylene glycol–water solution with potassium chloride or lithium chloride as the supporting electrolyte. For each compound, when the chloride-ion concentration was greater than 0·01N, two-step waves were obtained on reduction, their definition increasing with increasing chloride-ion content. Since comparative results were required, all substances were examined in solutions containing 0·1N-chloride ion. The figure shows some examples of curve obtained.

The reductions all appear to be irreversible, the values of $E_{\frac{3}{4}} - E_{\frac{1}{4}}$ for the lower curves being shown in the table. These values are all much greater than should correspond to a two-electron step, *viz.*, —0·029v, but in several cases values close to —0·058v, the value for a one-electron step, have been obtained. This may imply that the first step in the

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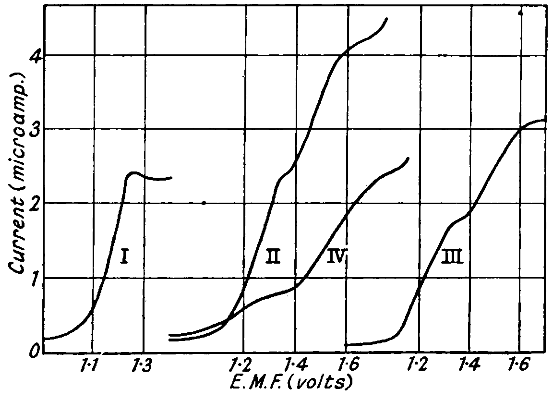
* Part II, *J.*, 1952, 3123.

Polarographic reduction of cobalt chelate complexes at 25°.

R in complex $Co(NR{:}CH{\cdot}C_6H_4{\cdot}OH\text{-}o)$	First wave, $E_{\frac{1}{2}}$ (v)	$E_{\frac{3}{4}} - E_{\frac{1}{4}}$	Second wave $E_{\frac{1}{2}}$ (v)	Supporting electrolyte	p*K* of amine
($CoSO_4$)	−1·156	−0·061	—	0·1N-KCl	—
m-$Cl{\cdot}C_6H_4$	−1·211	−0·09	−1·45	,,	3·52
Ph	−1·238	−0·10	−1·49	,,	4·58
,,	−1·220	−0·064	−1·44	Sat. LiCl	—
m-C_6H_4Me	−1·225	−0·11	−1·47	0·1N-KCl	4·69
p-C_6H_4Me	−1·237	−0·12	−1·47	,,	5·07
cyclo-C_6H_{11}	−1·34	−0·065	[b]	,,	10·61
p-$Cl{\cdot}C_6H_4$	−1·260	−0·11	−1·46	,,	4·00
,,	−1·190	−0·070	−1·43	Sat. LiCl	—
o-$C_6H_4{\cdot}OMe$	−1·280	−0·14	−1·48	0·1N-KCl	4·49
,,	−1·240	−0·11	−1·46	Sat. LiCl	—
p-$C_6H_4{\cdot}OMe$	−1·299	−0·15	−1·50	0·1N-KCl	5·29
,,	−1·250	−0·10	−1·49	Sat. LiCl	—
(Salicylideneaniline)	−1·58 [c]	−0·15	—	0·1N-KCl	—

[a] Values taken from Hall and Sprinkle, *J. Amer. Chem. Soc.*, 1932, **54**, 3469, determined in aqueous solution. [b] Second wave was very large and its finish was not determined. [c] Wave commences at −1·35 v.

reduction of these compounds is that of the central cobalt ion to the univalent state. Calvin and Bailes (*loc. cit.*) have shown that reduction of the analogous cupric complexes presumably involves a reduction to the cuprous state (first wave) and then (second wave) reduction of a simple cuprous ion, the cuprous complexes apparently dissociating upon formation to liberate free cuprous ions. The reduction of cobaltous ions under similar conditions to the complexes gave only one wave showing a pronounced maximum which could not be completely inhibited by the use of gelatin. This wave appears also to be irreversible as calculated from the $E_{\frac{3}{4}} - E_{\frac{1}{4}}$ formula, although the value found, —0·061v, is very close to that required for a one-electron step. There appears to be no evidence for the reversible reduction of simple cobalt ions in aqueous solutions; in fact, Brdicka (*Coll. Czech. Chem. Comm.*, 1930, **2**, 489, 545; 1931, **3**, 396) has shown that large amounts of chloride ions must be present in solution in order to make the normal reduction of cobalt *approach* reversibility. Presumably, it is the chloro-complex ions in aqueous solution which tend to reduce reversibly rather than hydrated cobaltous ions.



I, $CoSO_4$.
II, *Bis(salicylideneaniline)cobalt.*
III, *Bis(salicylidene-*m*-toluidine)cobalt.*
IV, *Salicylideneaniline.*

(*All solutions are* 0·001M *in* 20% *aqueous ethylene glycol and contain* 0·1N-KCl *as supporting electrolyte.*)

Chloride-ion concentration appears to play a considerable part in the reductions of the cobalt complexes reported here. It has been stated (p. 4727) that the separation of two waves commenced at 0·01N-potassium chloride or above; below this concentration only one curve could be obtained. Increasing the chloride-ion concentration by using 80% ethylene glycol–water solutions saturated with lithium chloride (*ca.* 1—2N) caused a numerical decrease of about 0·04 unit in the values of $E_{\frac{3}{4}} - E_{\frac{1}{4}}$ for several compounds (see table), *i.e.*, the values changed towards the one-electron step value of —0·058v.

The second wave present in the reduction curves of the cobalt complexes cannot be reconciled immediately with the reduction of a lower valency state of cobalt, *i.e.*, univalent cobalt. It may be due to the reduction of the CH:N linkage present in all the complexing molecules examined. Salicylideneaniline itself has a reduction potential of —1·35v, the same as that for the second wave obtained on reduction of bis(salicylideneaniline)cobalt, while the substance prepared by Raney nickel hydrogenation of salicylideneaniline, *i.e.*, containing a $CH_2{\cdot}NH$ linkage, shows no sign of reduction below —1·8v, at which potential a catalytic hydrogen wave is observed similar to that obtained when doing a " blank " reduction on the solvent plus supporting electrolyte (0·1N).

Although the work has had to be suspended, the results are believed to imply that elucidation of these mechanisms cannot be accomplished solely by conventional polarographic methods. No solvent has yet been found for the complexes which will also dissolve considerable amounts of a supporting electrolyte and yet not undergo reduction at potentials below that of the complexes being examined. In spite of the foregoing partial failure, an attempt has been made to correlate the half-wave potentials of the first waves obtained with each compound with the p*K*'s of the amines present in the various salicylidene derivatives used in preparing the complexes.

It has been assumed by analogy with Calvin and Bailes's results (*loc. cit.*) that the first wave found is connected with the reduction of the complex molecule probably involving the cobalt ion present in the complex. Therefore the higher the half-wave potential, *i.e.*, the more difficult it is to reduce the complex, the more stable should the complex be. Further, since the p*K* value of a substituted aniline will be a relative measure of the electron density on the nitrogen atom, it should provide some measure of the " availability " of the unshared electron pair on the nitrogen atom for the formation of a co-ordinate linkage, *i.e.*, some measure of the strength of the Co–N bond. Values of $E_{\frac{1}{2}}$ for the first wave are given in the table together with the appropriate p*K* values of the amines in water.

The small number of compounds examined has limited the attempted correlation. In view of the marked dependence of half-wave potential upon chloride-ion concentration, it is not at all obvious that all cobalt complexes of this type would form a single stability series dependent upon p*K*.

EXPERIMENTAL

The polarograph used was a manually operated instrument of conventional design. An H-type cell was used for the reductions, one arm containing the reference electrode (saturated calomel), and the other the dropping cell. The two arms were connected by an agar–saturated potassium chloride bridge, which was separated from the dropping cell by a sintered-glass plate. The complete unit was kept at 25° ± 0·1°. Characteristics of the capillary were: $m^{\frac{2}{3}} \times t^{\frac{1}{6}} = 1{\cdot}77$. Nitrogen, purified by passage through vanadyl sulphate solutions, was bubbled through the solutions to remove oxygen. Corrections for *ir* drop across galvanometer shunts were allowed for on all $E_{\frac{1}{2}}$ values determined.

All solutions used were 0·001M and were prepared by dissolving the required weight of the compound in ethylene glycol, then making the solution up to the requisite volume by addition of aqueous potassium chloride solution and further glycol. The strength of the chloride solution was such as to give a concentration of 0·1N in the final solution. For reductions employing lithium chloride, a stock solution of 20% aqueous glycol previously saturated with lithium chloride by shaking the mixture with solid for 1 hour at 25° was used to dissolve the compound being examined.

Ethylene glycol was purified by vacuum-distillation and gave no evidence of any reducible impurities when " blank " reductions were carried out in the absence of any complex.

Cobalt sulphate heptahydrate was of " AnalaR " grade and was used without further purification. The complexes used were prepared by the method outlined in Part 1 (*loc. cit.*) for salicylideneaniline-type complexes.

Hydrogenation of Salicylideneaniline.—8 G. of the Schiff's base and 3 g. of W.6 Raney nickel in 20 c.c. of absolute ethanol were shaken with hydrogen at 1 atm. until the yellow colour had completely disappeared (6 hours). The solution was then filtered and crystallised. An almost theoretical yield of N-o-*hydroxybenzylaniline* was obtained as colourless needles, m. p. 105° (Found : C, 78·4; H, 6·6; N, 7·3. $C_{13}H_{13}ON$ requires C, 78·4; H, 6·6; N, 7·0%).

The authors are indebted to Dr. S. W. Pennycuick for his interest in this work.

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