

598. *Studies on Bond Type in Certain Cobalt Complexes. Part II.**
The Constitution of Cobalt Complexes with Salicylaldehyde Anils.

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Efforts have been made to separate mixtures of bis(salicylidene aniline)-cobalt and cobalt acetate in pyridine solution by chromatography on alumina and similar surfaces and by use of an ion-exchange resin. A break-up of the complex on these surfaces has been demonstrated by the use of the ^{60}Co -labelled complex. A partial separation has been attempted by the use of an electro-diffusion cell but some cobalt from the complex tends to move to the cathode. Measurements of the absorption spectra of the complex and the base in ethyl alcohol-water mixtures have shown that an ionization may occur in the presence of water, as do conductivity measurements taken in pyridine-water mixtures. These results point to the weakness of binding of the cobalt atom in such complexes, all the bonds apparently having considerable ionic character.

IN Part I * some conclusions were drawn as to the type of bonding in a group of cobaltous compounds of the inner complex type, where extremely rapid exchange was observed to occur between cobaltous ions in pyridine solution and the cobalt of the complexes. It had been tacitly assumed in discussing the results presented in that paper that the separation method used (extraction with chloroform and water) had no effect on the exchange observed. Several authors, however (*e.g.*, Garner and Meier, *J. Amer. Chem. Soc.*, 1951, **73**, 1894; Prestwood and Wahl, *ibid.*, 1948, **70**, 880), have shown that an apparent exchange can be induced by the separation procedure used in studying an exchange reaction when precipitation methods of separation are employed. Calvin and Duffield (*J. Amer. Chem. Soc.*, 1946, **68**, 557) have reported that keeping an extraction mixture of bis(salicylaldehyde)ethylenediaminecopper and radioactive copper acetate for 15 minutes did not cause a greater % exchange than was expected for the time at which the exchange was stopped by addition of chloroform and water for the purpose of separation. However, this type of experiment does not show whether or not an induced exchange occurs on the *addition* of the solvents for extraction purposes. In the cobalt exchange results reported in Part I (*loc. cit.*) evidence was obtained for a constant exchange of 6% occurring whenever the solvent extraction process was used for bis-(4 : 4'-dicarboxy-3 : 3' : 5 : 5'-tetramethyldipyrromethene)cobalt(II), a separation made after 40-seconds reaction time always giving a value much higher than the slow rate of exchange would allow, at the end of so short a time interval. This was used to correct all other values for % exchange at other time intervals. For bis(salicylideneaniline)-cobalt and similar compounds where exchange was observed to be complete after times as short as 30 seconds, "standard" exchanges similar to that carried out for the pyrromethene complex were impossible. Consequently, attempts were made to effect a separation of the reaction components by methods other than extraction procedures with a view to determine whether water or chloroform could cause exchange to occur when added to a reaction mixture.

A separation technique involving precipitation of one or other component could not be found, since most normal insoluble cobalt salts such as the phosphate, carbonate, etc., could not be obtained in pyridine solution. Organic metal complexes also would themselves be soluble in pyridine and could not be employed for that reason. There may exist a difficultly soluble compound of cobalt which could be formed in pyridine, but it is almost certain that water would have to be added in the process, and would, of necessity, invalidate the technique. Attention was then turned to physical methods such as diffusion and chromatographic adsorption.

It was decided to use bis(salicylideneaniline)cobalt as the complex in all these investigations, mainly for the reason that no other evidence, such as a magnetic susceptibility measurement, was available to enable a comparison of the bond type determined by that

* Part I, preceding paper.

method and by the exchange method to be made so that a decision as to the effect of the separation procedure on exchange was possibly of more urgent importance with this compound. In order to judge the separation that could be effected by the various procedures tried, a sample of the complex was synthesised containing radioactive cobalt. Activity determinations could then give immediate information as to the distribution of the complex.

Chromatographic Adsorption.—1. *Alumina.* Alumina columns, prepared as described on p. 3127, were used to study the adsorption of cobalt ions and of bis(salicylideneaniline)-cobalt, both from pyridine solution. By using cobalt acetate solutions labelled with ^{60}Co it was found possible to adsorb more than 99.5% of Co on alumina columns at 0.003M. Labelled bis(salicylideneaniline)cobalt, however, showed that the complex, at 0.017M, could only be eluted from similarly constructed columns to a maximum extent of 58.7%. Lower elution percentages were obtained with lower concentrations of complex or with slight increases in the amount of alumina in the column. In chromatography of solutions of the complex, a pink band similarly placed to that obtained with cobalt acetate was noticed which was presumably due to adsorbed $[\text{Co}(\text{py})_x]^{++}$ ions in both cases. Also the colour of the eluate from the complex adsorptions was bright yellow rather than the yellow-orange associated with pyridine solutions of the complex. The free base gives an intensely yellow solution in pyridine (and other organic solvents), so all the evidence points to at least a partial break-down of the complex on the column, leading to the adsorption of a portion of the cobalt and elution of the remainder of the complex together with the excess of free base. Possibly hydrogen ions present in the column may replace the cobalt atoms in the complex molecules, although strict precautions were taken with the alumina used to remove the last traces of acid. On the other hand, water molecules which would still, in all probability, be present in the alumina could react with the complex, giving hydrated cobaltous ions and base ions. The latter possibility seems the more probable in view of the spectroscopic and conductimetric evidence to be mentioned below.

In any case a separation procedure using this technique would not preclude the possibility of an induced exchange occurring on the alumina surface since the complex can break up into its components, at least partly, when passed down such a column.

2. Further attempts using magnesia, silica, and talc gave similar results to those obtained with alumina.

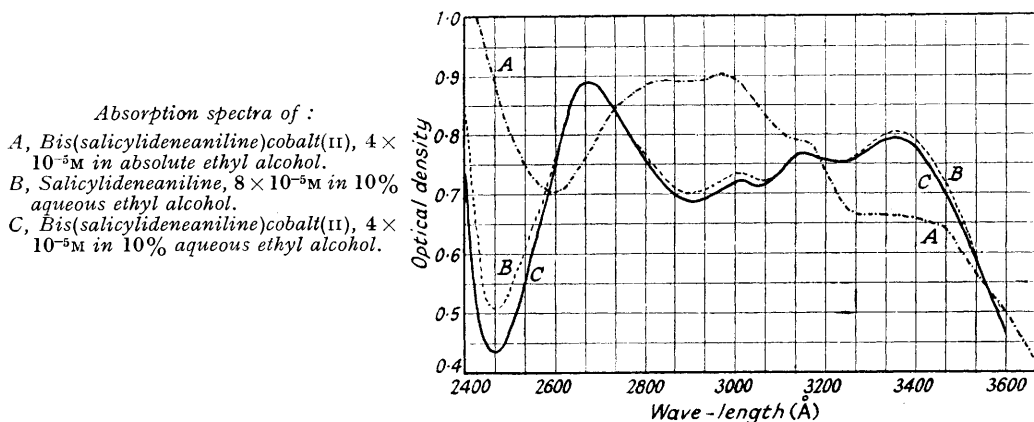
3. *Ion-exchange resin.* A sample of a cationic exchange resin (Amberlite IR-100, Na salt) was then tried, the column technique described below being used. When used directly as obtained, scarcely any separation of the two compounds could be obtained. The complex was 100% eluted at 0.017M, and cobalt acetate at 0.0033M was eluted to the extent of about 91%. The resin was then crushed to a fine powder, in order to increase the surface area, and a hold back of 79% was obtained with a pyridine solution of cobalt acetate. However, the complex could only be eluted to the extent of 57%, and from the bright yellow colour of the eluate it seems probable that, again, break-down of the complex occurs on this column, probably owing to an exchange of the sodium ions on the column for the cobalt of the complex. Consequently, the use of this method suffers from the same difficulty as the alumina column method in that the possibility of a surface exchange is not eliminated.

4. *Electro-diffusion.* An apparatus was constructed for carrying out separations by electro-diffusion (see p. 3127), as the times required to accomplish separations by simple, flow-diffusion were expected to be much greater than the possible completion of exchange with this compound. By using 200 v D.C. across the apparatus, cobalt could be made to pass into the cathode compartment from pyridine solutions of cobalt acetate to the extent of about 3% in 20 minutes. The complex also showed a tendency for activity to enter the cathode, while a distinct yellow colour could be observed on the anode compartment side of the sintered-glass disc separating the anode from the central compartment. Evidently, in this case also, break-down of the complex can occur on passage of an electric current, so the probable ionic type bonds already suggested for this compound may allow migration of the appropriate ions. It did not seem possible, in consequence of this, to use the method as a separation procedure.

In spite of the failure to find a separation technique which did not, of itself, cause the

break-down or ionization of the complex, this especial fact is extremely important in that it shows a pronounced weakness of the bonds in this particular complex compound. Thus, very rapid exchange may be expected to occur in any case, and a technique such as that developed by Barker (reported by Betts *et al.*, *J. Amer. Chem. Soc.*, 1950, **72**, 4978) would seem to be ideally suited for investigating the exchange of compounds of this type.

As a further aid in elucidating the effect of water on the constitution of the complex, the ultra-violet absorption spectra of the complex and base were obtained in absolute ethyl alcohol and in aqueous alcohol at various percentages of water. Ethyl alcohol was used instead of pyridine for the determination of spectra because of the strong tendency of pyridine solutions of the complex to creep over the top of the only cells available for the instrument and to flow down the optical faces, thus causing fluctuations in optical density readings. This occurred even when the cells were covered with the plastic caps supplied by the manufacturer. The concentration of salicylideneaniline used was $8 \times 10^{-5}M$, and that of the cobalt complex formed from the base, $4 \times 10^{-5}M$. If an ionization should occur on the addition of water to the complex solution, then complete ionization would be shown by the similarity of the optical density- λ curves obtained for base and complex solutions of the above concentrations at some particular percentage of water. Since two molecules of salicylideneaniline are present in one molecule of the cobalt complex, the



liberation of these molecules gives a solution of base twice the strength of the complex solution. As is shown in the figure, this has occurred when 10% of water is present. Also in the figure is shown the curve for the complex in absolute alcohol. Salicylideneaniline gives essentially the same curve both in absolute alcohol and in 10% aqueous alcohol.

A weak absorption band for the cobalt ion occurs at much longer wave-lengths (*ca.* 5000 Å); consequently, it is not expected to interfere with the absorption due to the free base ion between 2600 and 3500 Å. Therefore, the disappearance of the band due to the cobalt complex upon the addition of water and the appearance of a curve similar to that of the free base is good evidence that a break-down (presumably due to ionization) of the complex is occurring with the liberation of free base ions. Further, since the curves for complex and base at 10% of water are essentially the same, *i.e.*, each contains the same amount of free base or ion, at this stage complete ionization must have occurred.

Since it was not possible to show directly that a similar state of affairs existed for pyridine-water systems because of the experimental difficulty mentioned above, a series of conductivity measurements were made on pyridine solutions of bis(salicylideneaniline)cobalt containing various percentages of water, and the results compared with similar measurements on similarly prepared pyridine-water mixtures. No claim is made for the absolute accuracy of the results given in Table 1 because the purpose of the measurements was solely to obtain a demonstration of ionization, and this could be gained by a comparison of the two sets of conductivity data. The solutions used in each case were prepared, and their conductivities measured, in exactly the same manner (see p. 3128), but the limitations of the measuring system were too great to allow any but semiquantitative values to be obtained. The

results show quite definitely, however, that a much greater increase in conductivity occurs for pyridine solutions of the complex to which water is added than is found when water is added to pyridine alone. The higher value of κ obtained for the complex solution in pure pyridine than for solvent alone is probably not significant owing to the difficulty of measuring such high resistances accurately with the equipment available; although, in view of the evidence of migration of cobalt obtained in the experiments on electro-diffusion, some ionization may occur, even in the pure solvent.

TABLE 1

H ₂ O, %	0	2	5	10	15	20	30
10 ⁶ κ { Complex solution	0.085	0.47	0.98	1.7	4.2	7.5 *	8.1
{ Solvent only	0.042	0.085	0.22	0.47	0.89	1.7	3.0

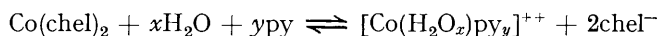
Complex concentration = $8.5 \times 10^{-3}M$.

* 20% or more of water causes precipitation of the complex from solution.

DISCUSSION

It appears, therefore, from these experimental results that the introduction of water to a pyridine solution of bis(salicylideneaniline)cobalt can bring about the formation of "dissociated" ionic species. The word "dissociated" has been used because the adsorption of cobalt by alumina from pyridine solutions of the complex seems to imply that in pure pyridine the complex molecules may be formulated as undissociated, neutral, ion triplets, the conductivity of the complex in pure pyridine being so small that it is extremely doubtful whether any free ions are present in solution, *i.e.*, the bonding of the cobalt to the two ligands may be considered as being essentially ionic. With such a weak binding, cobalt is expected to be easily removed by the active alumina. Probably at least two pyridine molecules are co-ordinated to the cobalt ion in each complex molecule, making up the total possible co-ordination number of 6 for bivalent cobalt (see also p. 3127).

When water is added to the solution, the increase in conductivity observed may be accounted for by assuming that replacement of the chelating ligands can take place by water and pyridine molecules, leading to the production of various ionic species, *e.g.*



The presence of water may also exert a dielectric effect and aid in dissociation, whereas in pure pyridine, although the formation of $[\text{Co py}_4]^{++}$ ions is possible, the low dielectric constant of the medium may prevent actual dissociation of the molecule, *i.e.*, an ion-triplet formulation could be expected, as mentioned previously.

Thus the observation of rapid exchange with compounds of this type in pyridine (Part I, *loc. cit.*) when a separation procedure involving water is used would probably also be noticed if a separation method not involving the use of water could be devised. The bonds in the complex must presumably be regarded as possessing considerable ionic character and therefore not presenting a strong barrier to replacement by other cobalt ions present in solution. If one regards a free cobalt ion in pyridine as being $[\text{Co py}_4]^{++}$ then easy replacement is to be expected by collision with the postulated ion triplet whether this be $\text{Co py}_2 \text{chel}_2$ or $[\text{Co py}_4]^{++}(\text{chel})_2$.

It is noteworthy in this regard that a series of unpublished experiments on the chromatography of benzene, nitrobenzene, and ethyl alcohol solutions of bis(salicylideneaniline)-cobalt on alumina have shown analogous effects to those obtained with pyridine solutions, *i.e.*, some cobalt is adsorbed and free base plus complex is eluted. In each case the conductivities of the solutions used are not detectably different from those of the pure solvents. For these solutions, and especially for benzene, no "solvation" is expected similar to that possible with pyridine. This seems to strengthen the view that the complex must be regarded as having cobalt-ligand bonds with strong ionic character.

With regard to the spectroscopic data obtained in ethyl alcohol-water solutions for the salicylideneaniline complex, although the change in spectrum may be interpreted as being due to an ionization of the complex in the presence of water, an alternative explanation might be possible in view of the work of Mellor and his co-workers (*J. Proc. Roy. Soc. N.S.W.*, 1944, 78, 70). In an investigation of the spectra of nickel complexes of the chelate

type, he has shown that complexes possessing paramagnetic susceptibilities, and hence tetrahedral ionic structures, show absorption spectra similar to those of the bases from which they are obtained. Square complexes with presumed covalent bonding have spectra somewhat different from those of the free bases. The spectrum of the complex being investigated here is quite different from that of the free base, and it is only on the addition of water that a change to the base spectrum occurs. Consequently, if Mellor's conclusions are of wide application, they may point to the change from a square, coplanar configuration of bis(salicylideneaniline)cobalt when in absolute alcohol to a tetrahedral configuration in the presence of water. The former configuration would allow the compound to form covalent type bonds between the metal and the surrounding ligands, while the latter would imply the formation of bonds, mainly ionic in character, giving the complex in aqueous media the form of a neutral ion triplet. The bonds in the square form would necessarily be weak in order to allow the change in bond type to occur easily.

This suggestion could be related to the situation in pyridine if one were to assume that complexes of the type $\text{Co py}_2 \text{chel}_2$ existed in solution. The pyridine molecules could then be regarded as being attached to the cobalt above and below the plane of the ordinary molecule. In this connection Tyson and Adams (*J. Amer. Chem. Soc.*, 1940, **62**, 1228) have mentioned the difficulty of deciding between the two alternative configurations for bis(salicylaldehyde)cobalt even though their magnetic data may be interpreted perhaps more reasonably in terms of the tetrahedral structure. Certainly, the X-ray examination of many copper and nickel derivatives of similar type shows the widespread occurrence of planar forms (Stackelberg, *Z. anorg. Chem.*, 1947, **253**, 136; Cox *et al.*, *J.*, 1935, 731; 1936, 129, 1775). An X-ray crystallographic study of cobalt complexes of the chelate type seems necessary to provide the final explanation. The fact, however, that no isomers have been reported for cobalt complexes of the type under discussion seems to point to the tetrahedral structure being more probable. It is hoped later to present some chemical evidence to support a projected tetrahedral structure.

EXPERIMENTAL

1. The alumina used in the experiments was "B.D.H. Chromatographic Alumina" which was washed in running distilled water for 24 hours or more before use and dried at 250°. Columns were prepared by slurring the oxide with pyridine and pouring it into a glass Buchner funnel, 4 cm. wide and 10 cm. deep, having a perforated, porcelain plate covered with filter-paper of appropriate diameter on the bottom. The height of the column used varied with the experiment, but was in general 2—3 cm. Some of the results obtained are given below, and suffice to illustrate the results obtained with the various materials. Columns of this nature were prepared with each of the other adsorbents tried. Gentle suction was applied to aid the movement of the solutions, and in each case elution of the column was carried out with the aid of pyridine or chloroform. The removal of adsorbed Co^{++} was carried out with warm, dilute nitric acid in all cases, a few c.c. being poured through the column until no further evidence of pink Co^{++} could be seen. A check of the total activity recovered against a standard activity previously prepared guarded against any loss. All counting was carried out in 20-c.c. glass-skirted Geiger counters, with a scale-of-100 counting unit, and corrections for background were applied in each case.

2. Magnesia and silica were both pure reagent-grade samples, washed as above and activated at 300°.

3. The Amberlite IR-100 was treated in bulk with 10% sodium chloride solution, washed thoroughly with distilled water, then boiled with pyridine and kept in pyridine for at least 12 hours before use.

4. *Electro-diffusion*.—The apparatus consisted of a right-angled U-tube of 2.0 cm. internal diameter with two sintered-glass plates of pore size 3, fused parallel to each other inside the base of the U enclosing a volume of 20 c.c. between them. A capillary tap was attached to the bottom of this central compartment, and a filling tube of 1 cm. diameter to the top. So that pressure differences between the side arms and the central compartment could be equalized, this filling tube was made to project to the same height as each side arm. In operation, the side arms were filled to a definite mark with 1% potassium chloride solution, the central compartment meanwhile being stoppered to prevent flow through the glass membranes. The stopper was

Run	Solution used	Column	Eluate activity (counts/min.)	Eluting solvent	Hold back activity (counts/min.)	Standard (counts/min.)	Remarks
1	Cobalt acetate in pyridine (0.0033M), 5 c.c., +5 c.c. of pyridine	Al ₂ O ₃ , 2 cm. high	8.7	CHCl ₃ , 10 c.c.	526.8	529.0	99.5% Hold back
7	Complex in pyridine (0.017M), 5 c.c., +5 c.c. of pyridine	"	123.9	"	100.5	223.1	45% Hold back
8	" "	"	127.7	"	89.7	217.5	58.7% Eluted
11	" "	IR-100 resin, uncrushed, 2 cm. high	227.0	Pyridine, 8 c.c.	0.0	223.8	100% Eluted
12	Cobalt acetate in pyridine (0.0033M), 5 c.c., +5 c.c. of pyridine	"	356.2	"	(Not counted)	385.2	92% Eluted
15	Cobalt acetate in pyridine (0.0033M), 5 c.c., +5 c.c. of pyridine	IR-100 resin crushed	23.7	Pyridine, 10 c.c.	517.6	529.0	4.4% Eluted
16	Complex in pyridine, as for 7	"	66.5	"	(Not counted)	223.8	30% Eluted
22	" "	MgO, 3-cm. column	221.8	"	"	307.4	72% Eluted

then removed, and 20 c.c. of the appropriate solution were run in to the central compartment until the level in the filling tube corresponded with that in the side arms. A bright platinum electrode was then immersed in each side arm, and connection made to the current supply. After the time allowed for diffusion had elapsed, each section of the vessel was emptied, the solutions were made up to similar volumes, and aliquots counted. The entrance of cobalt ions to the cathode compartment was accompanied by the formation of long tendrils of blue Co(OH)₂, due to the hydroxyl ions produced by electrolysis in the cathode compartment. This was dissolved in dilute hydrochloric acid when making up the solution from this compartment, preparatory to counting. It was found extremely difficult to prevent streaming occurring from the solutions in the side arms into the central compartment. However, the method of filling mentioned above seemed to give the best results possible with the apparatus. Runs carried out with low voltages (10 v) gave little evidence for diffusion except after periods of the order of 1½—2 hours. The final runs, therefore, were carried on for 20 minutes at an applied voltage of 200 v D.C. The results are given in Table 2.

TABLE 2.

Run	Solution used	Anode Central Cathode			Time, mins.	Voltage, v	Remarks
		(counts/min.)					
5	0.017M-Cobalt acetate, 10 c.c., +10 c.c. of pyridine	10.4	2772.5	87.4	20	200	3% in cathode
3	0.017M-Cobalt complex, 10 c.c., +10 c.c. of pyridine	0.0	442.6	2.1	20	200	0.5% passing to anode
2	0.017M-Cobalt acetate, 20 c.c., +10 c.c. of pyridine	0.0	2701.5	76.1	90	10	2.8% in cathode
1	0.017M-Complex, 10 c.c., +10 c.c. of pyridine	No activity detected	Not counted	No activity detected	90	10	—

Labelled Complex.—Bis(salicylideneaniline)cobalt containing ⁶⁰Co was synthesised by the method outlined in Part I for the inactive complex. In this case a quantity of the stock radioactive ⁶⁰Co solution, also prepared by the method outlined in Part I, was added to the cobalt acetate solution used in the preparation so that the crystalline material obtained was labelled in a simple manner. Solutions were prepared by dissolving the correct weight of complex in the appropriate solvent.

Spectra.—The spectra were taken with the aid of a Hilger Uvispek spectrophotometer with 1-cm. quartz cells.

Conductivity Measurements.—The cell used was similar in design to that used by Pennycuik (*J.*, 1927, 2600) and was kept in a thermostat at 25°. The cell constant was 0.0085. The

solutions used were prepared by diluting 4 c.c. of a 0.1063M-solution of bis(salicylideneaniline)-cobalt in pyridine to 50 c.c. with further pyridine, sufficient water being added to give the appropriate percentage of water. Pyridine-water mixtures were prepared in the same way. The solutions were kept in the bath until temperature equilibrium had been reached, then the resistance was measured with a Pye and Sons manganin-coil resistance bridge, using an A.W.A. oscillator with variable signal strength, and a pair of headphones. With this equipment it was not possible to obtain greater than 2- or 3-figure accuracy when measuring resistances. Conductivity water (0.9 gemmho) was used whenever necessary.

Solvents.—All solvents were of reagent grade, purified before use by appropriate procedures. British absolute alcohol "for spectroscopy" was used after refluxing with potassium hydroxide and distillation for the absorption spectra determinations.

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