Studies on Bond Type in Certain Cobalt Complex Compounds. Part IV.*
The Exchange Reactions of Quadridentate Complexes.

By B. O. WEST.

[Reprint Order No. 4523.]

Both *NN'*-disalicylidene-ethylenediaminecobalt(II) and *NN'*-disalicylidene-*o*-phenylenediaminecobalt(II) undergo exchange with cobaltous ions in pyridine solution. The mechanism of exchange has been shown for the latter compound to be probably due to a collision process. Some attempt is made to explain the differences between the ease of exchange of these compounds and those of other metals.

IN Part I (*J.*, 1952, 3115) the results of exchange studies on several cobalt complexes were presented. Two complexes of the quadridentate, chelate type have now been examined, *viz.*, *NN'*-disalicylidene-ethylenediaminecobalt and *NN'*-disalicylidene-*o*-phenylenediaminecobalt. Owing to the ability of such compounds to absorb oxygen (Calvin, Bailes, and Wilmarth, *J. Amer. Chem. Soc.*, 1946, **68**, 2254), the investigations were carried out under nitrogen.

NN'-Disalicylidene-ethylenediaminecobalt(II).—The data obtained for this compound are shown in Table 1. Exchange was found to be immeasurably fast at 30° with $1\cdot21 \times 10^{-2}$M-complex and $8\cdot5 \times 10^{-3}$M-cobalt acetate, while a measurable rate was observed at 15° with $9\cdot1 \times 10^{-5}$M-complex and $8\cdot5 \times 10^{-5}$M-cobalt acetate. A plot of log (100 − % exchange) against time (Fig. 1) for the data at 15° shows the expected first-order rate curve for the appearance of activity in the complex.

TABLE 1. *The exchange of cobalt ions with disalicylidene-ethylenediaminecobalt*(II) *in pyridine solution in the absence of oxygen.*

Concns. (M) after mixing :

Complex	Cobalt acetate	Temp.		
$1\cdot21 \times 10^{-2}$	$5\cdot7 \times 10^{-3}$	$30° \pm 0\cdot1°$	Complete exchange in <6 min.	
$9\cdot1 \times 10^{-5}$	$8\cdot5 \times 10^{-5}$	$15 \pm 0\cdot1$	$t_{\frac{1}{2}}$	19·5 ,,

When oxygen was in contact with the deep red solution of this complex a rapid change to brown occurred. When this solution was extracted with chloroform and water the brown colour was removed almost completely into the aqueous layer. The addition of

* Part III, *J.*, 1952, 4727.

aqueous ammonium thiocyanate to the brown pyridine solution failed to produce any precipitate. Treatment of a pyridine solution of cobalt acetate with the reagent, however, precipitated $Co(CNS)_2py_4$ (py = pyridine) quantitatively. This was used to effect a separation of the oxygenated complex and cobalt acetate when one run was performed to discover the exchange capability of this complex. The results are given in Table 2.

TABLE 2. *The exchange of cobalt ions with* NN'-*disalicylidene-ethylenediaminecobalt*(II) *in pyridine in the presence of oxygen at* 15°. [Chelate = 0·0346M; $Co(OAc)_2$ = 0·017M *before mixing.*]

Activity (counts/min.)		Reaction time, min.	Exchange, %	Activity (counts/min.)		Reaction time, hr.	Exchange, %
Chelate	Cobalt			Chelate	Cobalt		
180·7	412·8	6	44·6	315·0	295·7	3·7	75·6
233·2	374·7	32	56·2	334·0	261·6	5·5	82·2

The results show that slow exchange took place, and a plot of log (100 — % exchange) against time (Fig. 2) showed a " zero-time " exchange of 43%. Although a further investigation of this system was not made, it appears that the substance undergoing slow exchange was formed by the interaction of oxygen and disalicylidene-ethylenediamine-

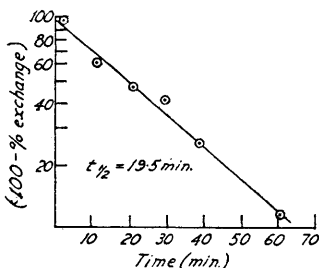FIG. 1. *The exchange of* NN'-*di-salicylidene-ethylenediamine-cobalt at* 15°.

FIG. 2. *The exchange of* NN'-*di-salicylidene - ethylenediamine - cobalt in the presence of oxygen.*
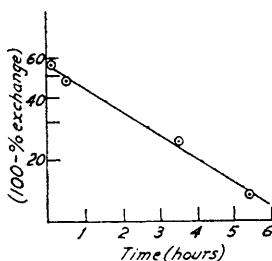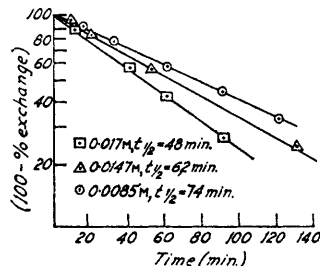
FIG. 3. *The exchange of* NN'-*di-salicylidene - o - phenylenedi - aminecobalt at* 15°.

cobalt since, in the absence of oxygen, exchange should have been very rapid at the concentrations studied (cf. Table 1).

The identity of the substance (or substances) undergoing slow exchange has not been discovered, but it would seem to be either an " oxygenated " molecule of the form (chelate)(O_2) or (chelate)$_2(O_2)$ or a cobaltic complex of salicylidene-ethylenediamine, e.g., $Co[C_{16}H_{14}O_2N_2]^+$; or, indeed, a mixture of all these complexes may exist, each of which undergoes slow exchange. Calvin and Harle (*J. Amer. Chem. Soc.*, 1946, **68**, 2612), from their investigations of oxygen uptake by solutions of cobalt complexes similar to the ethylenediamine compound, suggested that such compounds as those mentioned above may all be formed in the same solution.

To explain the " zero-time " exchange, one can only suggest a " separation-induced " exchange. A more detailed investigation is required for a full understanding of the behaviour of this system.
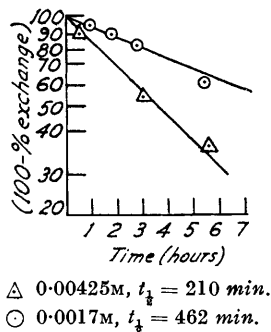
NN'-*Disalicylidene-o-phenylenediaminecobalt*(II).—The results for this compound are shown in Table 3. Runs over a ten-fold range of concentration have been carried out at 15° in order to examine the concentration dependence of the rate of exchange. The appearance of activity in the complex followed the expected first-order law in each case. This is shown by the straight-line plots of log (100 — % exchange) against time (Figs. 3 and 4). The half-times ($t_{\frac{1}{2}}$) of exchange when plotted against 1/concn. also give a straight line (Fig. 5). This indicates that the exchange process proceeds by a second-order reaction. The most probable mechanism involves a collision between a cobalt ion and a molecule of the complex. This mechanism has also been suggested by Calvin and Duffield (*J.*

Amer. Chem. Soc., 1946, **68**, 557) as operating in the exchange of copper ions with analogous copper complexes in pyridine solution. From the runs at 15°, 25°, and 35° an energy of activation of approximately 17 kcal. was found.

TABLE 3.

Concn. (M) of complex and cobalt acetate before mixing	Temp.	$t_{\frac{1}{2}}$, min.	Concn. (M) of complex and cobalt acetate before mixing	Temp.	$t_{\frac{1}{2}}$, min.
0·017	15° ± 0·1°	48	0·0017	15° ± 0·1°	462
0·0147	15 ± 0·1	62	0·017	25 ± 0·1	30
0·0085	15 ± 0·1	74	0·017	35 ± 0·1	6
0·00425	15 ± 0·1	210			

Discussion.—The magnetic susceptibilities measured by Bakelew and Calvin (*ibid.,* p. 2267) show that each of the two cobalt complexes possesses one unpaired electron. This indicates square-bonded, planar structures with the cobalt utilising $3d3sp^2$ hybrid orbitals in bond formation. Since these hybrid orbitals are expected to form strong bonds (Pauling, " Nature of the Chemical Bond," Cornell University Press, New York, 1948, p. 98) one might expect that the complexes would exert considerable resistance to the replacement of their central metal atoms, *i.e.*, that the rate of exchange should be slow, even at relatively high concentrations. This is not at all obvious from the present

FIG. 4. *The exchange of NN'-disalicyl-idene-o-phenylenediaminecobalt at 15°.*

△ 0·00425M, $t_{\frac{1}{2}} = 210$ *min.*
⊙ 0·0017M, $t_{\frac{1}{2}} = 462$ *min.*

FIG. 5. *The relation between half-time and 1/con-centration for the exchange of NN'-disalicyl-idene-o-phenylenediaminecobalt.*
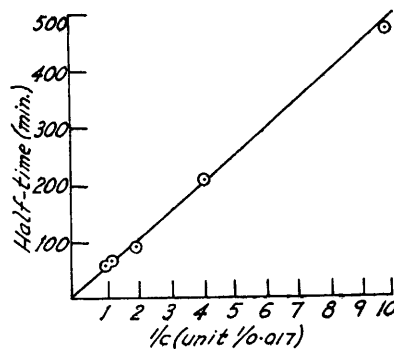
study, both complexes undergoing rapid exchange though the *o*-phenylenediamine compound seems to be the more resistant

This suggests that other factors besides the bonding orbitals used by a metal in complex formation considerably influence the stability of the resulting compounds. A consideration of the analogous copper complexes and of bis-salicylideneaniline copper is of interest in this respect. Each of these three compounds has been shown by Stackelberg (*Z. anorg. Chem.*, 1947, **253**, 136) to have a planar distribution of Cu–O and Cu–N bonds. This implies the use of square-bonding, $3d4sp^2$ hybrid orbitals by the copper ions. Calvin and Duffield (*loc. cit.*) have found considerable differences in the rates of exchange of these three compounds under similar conditions. The aniline complex exchanged immeasurably rapidly, while the ethylenediamine and *o*-phenylenediamine complexes exchanged with half-times of 2·1 hr. and more than 4 hr. respectively.

If we use the ability to exchange as a measure of the stability of these complexes, then one factor which can be related to the increased stability of the quadridentate over the bidentate complexes is the increased number of chelate rings formed by the complexing agents of the former class. This stabilising effect has been amply demonstrated in a quantitative manner by determinations of instability constants, the results being reviewed by Burkin (*Quart. Reviews*, 1951, **5**, 10).

The difference in the ease of exchange of the ethylenediamine and *o*-phenylenediamine complexes for both copper and cobalt must then be related to some property of the chelating molecules themselves in addition to effects due to the metals themselves. A comparison

of the two compounds (I) and (II) shows that ring 2 in the *o*-phenylenediamine complex has a C–C link which is part of an aromatic ring system. Calvin and Wilson (*J. Amer. Chem. Soc.*, 1945, **67**, 2003) have suggested that the stabilities of metal complexes (in
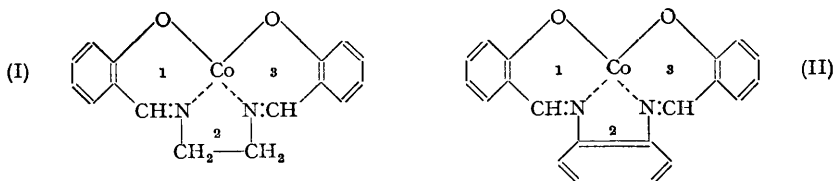
particular cupric complexes) with hydroxy-aldehydes are related to the degree of resonance permitted in the chelate rings formed by such ligands. For (I) and (II) rings 1 and 3 are analogous to those discussed by Calvin and Wilson, but in (II) are connected by the ring system 2 which may be considered as a resonating system because of its aromatic C–C link; *i.e.*, the *o*-phenylenediamine complex can be considered as a conjugated ring system and is expected therefore to be stabilised more than the ethylenediamine complex, where no such conjugation of chelate rings is possible owing to the single C–C linkage in ring 2.

Finally, a comparison of the relative ease of replacement of Cu, Ni, Co, and Zn ions with their disalicylidene-ethylenediamine and -*o*-phenylenediamine complexes is of interest. The copper derivatives have been examined by Calvin and Duffield (*loc. cit.*), the nickel derivatives by Hall and Willeford (*J. Amer. Chem. Soc.*, 1951, **73**, 5419), and the zinc derivatives by Atkins and Garner (*ibid.*, 1952, **74**, 3527), all in pyridine at concentrations and temperatures similar to those used in the present work.

Mellor and Maley (*Nature*, 1948, **161**, 436) and Irving and Williams (*ibid.*, 1948, **162**, 746) have established, independently, that the stabilities of many chelate complexes of metals of the first transition series increase in the order Co < Ni < Cu > Zn, zinc complexes being somewhat less stable than those of cobalt. If the occurrence of exchange were directly reconcilable with stability, one would expect that the nickel complexes should exchange with nickel ions at rates intermediate between those of copper and cobalt with their respective ions while zinc complexes would exchange at rates faster than any of these metals. A comparison of the half-times for exchange of the various compounds studied (Table 4) shows that although the Cu, Co, and Zn compounds appear to fit into the expected order, the nickel compounds show no evidence of exchange under any of the

TABLE 4. *The exchange of metal ions with metal–chelate complexes of NN′-disalicylidene-ethylenediamine and NN′-disalicylidene-o-phenylenediamine.*

NN′-Disalicylidene-ethylenediamine.

Metal	Cu [1]	Ni [2]	Co [3]	Zn [4]
Concn., M ...	0·015	0·01	0·017	0·01
Temp.	25°	room	30°	25°
$t_{\frac{1}{2}}$	2·1 hr.	No exchange after 48 hr.	Complete in 6 min.	Complete in 0·5 min.

NN′-Disalicylidene-*o*-phenylenediamine.

Metal	Cu [1]	Ni [2]	Co [3]	Zn [4]
Concn., M ...	0·015	0·01	0·017	0·001
Temp.	25°	room	25°	25°
$t_{\frac{1}{2}}$	>4 hr.	No exchange after 48 hr.	30 Min.	99% in 0·5 min.

[1] Calvin and Duffield, *loc. cit.* [2] Hall and Willeford, *loc. cit.* [3] Present work. [4] Atkins and Garner, *loc. cit.*

conditions so far studied. Similar non-exchange was observed by Hall and Willeford for nickel complexes in " methyl-cellosolve." There seems to be no *a priori* reason why nickel should form more stable complexes of the type under discussion than copper. In fact, Glaser, Pfeiffer, and Thielert (*J. pr. Chem.*, 1939, **152**, 145) have found that copper ions will readily exchange with *NN′*-disalicylidene-ethylenediamine in pyridine solution. A possible explanation of this anomaly may lie in differences in solvation among the metal ions in pyridine solution (cf. Atkins and Garner, *loc. cit.*).

Unfortunately, no direct experimental determination of the formation constants of the various metal–pyridine complexes appears to have been made, although Mellor and Maley (*Nature*, 1947, **159**, 370) have quoted overall stability constants for " hexaco-ordinate " pyridine complexes of copper and nickel which indicate that copper forms the more stable complex. Bjerrum (" Metal Ammine Formation in Aqueous Solution," Haase, Copenhagen, 1941, p. 109) has, however, observed that a maximum of four ammonia molecules can be attached strongly to a copper ion, a fifth group being attached but weakly. Nickel (*idem, op. cit.*, p. 189) can attach six ammonia groups with almost equal strength. It seems probable therefore that only four pyridine molecules would be attached firmly to a copper ion, a fifth and a sixth group being attached very weakly. Nickel, on the other hand, may be supposed by analogy to bind six pyridine molecules equally strongly. The cobaltous ion appears to attach a sixth ammonia group much less strongly than the other five (*idem, op. cit.*, p. 189) even when the formation constants are recalculated to allow for the statistical effect of ligand attachment. Zinc ions appear to attach four groups only, with equal facility (*idem, op. cit.*, p. 160).

Thus, exchange of the complexed nickel ions may be prevented by pyridine molecules, surrounding the " free " nickel ions in solution and preventing direct collision between the two species. For the other ions having a smaller number of solvent molecules attached or having some of the attached molecules more weakly bound than others, the appropriate collisions may occur with greater ease.

EXPERIMENTAL

Exchange Technique.—In order to carry out the investigations in the absence of oxygen, a simple apparatus was constructed which consisted of a reaction flask, fitted with a ground-glass head bearing an inlet for nitrogen and an outlet connected to a burette. Samples of the reaction mixture could be forced into the burette by nitrogen pressure when required, and from there could be removed directly into a separating funnel containing 14 c.c. of oxygen-free chloroform and 14 c.c. of oxygen-free water. The funnel was then stoppered, and the contents vigorously shaken. Each layer was removed and made up to 50 c.c. with ethanol. Aliquot portions of these solutions were counted in solution-counters. The reaction mixture was prepared as follows : a measured volume of pyridine was placed in the reaction flask, and nitrogen passed through the solution for 30 min. A weighed sample of the complex in a small glass tube, sufficient to give the appropriate concentration, was then dropped into the pyridine. When the solid had dissolved, an appropriate volume of ^{60}Co-labelled cobalt acetate solution in pyridine was added. The time of addition of half the cobalt solution was taken as zero time, and aliquot parts of the reaction mixture were removed at intervals. For the runs with disalicylidene-ethylenediaminecobalt conducted in the presence of oxygen the same apparatus and technique were used except that oxygen was bubbled through the solutions instead of nitrogen. Aliquot portions were removed by oxygen pressure and allowed to run directly into 10 c.c. of 20% aqueous ammonium thiocyanate, and the mixture stirred to aid flocculation. The pink precipitate was collected on a fine-glass filter, washed with 2 c.c. of cold water, and dissolved in the funnel with acetone. The filtrate containing the oxygenated product was made up to 50 c.c. with acetone for counting.

Radioactive Cobalt.—Solutions containing ^{60}Co-labelled cobalt acetate were prepared as described in Part I (*loc. cit.*).

Determination of Cobalt.—In order to allow for incomplete separation of the reaction components the total cobalt in each layer was determined after extraction. The nitroso-R salt colorimetric procedure (Dewey and Marston, personal communication) was used, 10-c.c. portions of the extracts being evaporated to dryness and ignited, and the residues converted into cobalt sulphate ready for treatment with the complexing agent. A standard extraction was performed with each solution of cobalt acetate used in order to determine the amount of cobalt removed into the chloroform layer. The latter determinations, together with the overall distribution of cobalt obtained by analysis of the extracts from each run, enabled corrected activities to be calculated.

NN′-*Disalicylidene-ethylenediaminecobalt*(II) (cf. Calvin and Bailes, *J. Amer. Chem. Soc.*, 1947, **69**, 1886).—Disalicylidene-ethylenediamine (1·3 g., 1 mol.) was dissolved in ethyl alcohol (30 c.c.) kept just below its b. p., and nitrogen bubbled through the solution continuously. Cobalt acetate tetrahydrate (1·2 g., 1 mol.) was boiled with ethyl alcohol until all the crystalline

solid had been converted into a pink amorphous powder, and the mixture swept out with nitrogen and added to the solution of base. The solid rapidly dissolved, giving a deep red solution which was heated for a further 15 min. with continuous passage of nitrogen. On cooling, the solution deposited small violet-brown prisms (1·2 g.) which were filtered off and dried in a vacuum-desiccator. The substance did not gain in weight on exposure to the atmosphere for 3 months, showing that it did not absorb oxygen when prepared in this manner. It was analysed without recrystallisation, since oxygen was absorbed rapidly by its solutions in all solvents [Found : C, 58·7; H, 4·4; Co, 18·3 (colorimetrically). Calc. for $C_{16}H_{14}O_2N_2Co$: C, 59·1; H, 4·3; Co, 18·1%].

NN'-*Disalicylidene*-o-*phenylenediaminecobalt*(II).—The method used was that described above, with the base (1·6 g., 1 mol.) in ethanol (80 c.c.) and cobalt acetate tetrahydrate (1·25 g., 1 mol.) in ethanol. On mixing, the cobalt salt dissolved, and after several minutes' heating of the deep red solution on the water-bath a feathery, violet-coloured precipitate appeared. The mixture was heated for a further 15 min. and then allowed to cool. The product was filtered off; when kept at room temperature it slowly lost weight, the colour changing to reddish-violet, and the odour of ethyl alcohol being noticeable. A freshly prepared sample, heated *in vacuo* at 70° for 8 hr., became brick-red in colour and lost 10·2% in weight ($C_{20}H_{14}O_2N_2Co,C_2H_6O$ requires loss, 11·0%). Better concordance of weight loss could not be obtained since alcohol was lost as soon as the mother-liquor was removed from the crystals. For the exchange work the red form was prepared from the violet by heating it at 70° over paraffin in a vacuum [Found : C, 64·0; H, 3·95; Co, 15·7 (colorimetrically). $C_{20}H_{14}O_2N_2Co$ requires C, 64·3; H, 3·8; Co, 15·8%]. The *compound* showed no tendency to absorb oxygen on exposure to air.

JOHNSON CHEMICAL LABORATORIES, UNIVERSITY OF ADELAIDE,
          SOUTH AUSTRALIA.

[Present address :
    UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE.]