597. *Studies on Bond Type in Certain Cobalt Complexes. Part I. Exchange Reactions.*

By B. West.

The exchange reactions with cobaltous ions in pyridine or water solution of nine cobaltous and three cobaltic complexes of the bidentate, chelate type have been examined, radioactive cobalt being used. The cobaltous complexes with salicylaldehyde, salicylideneaniline, salicylidene-*m*-toluidine, salicylidene-*o*-anisidine, acetylacetone, guaiacol, and salicylaldoxime have been shown to undergo very rapid exchange. Cobaltous bis-(4 : 4′-dicarbethoxy-3 : 3′ : 5 : 5′-tetramethyldipyrromethene) exchanges slowly, with $t_{\frac{1}{2}} \overset{\frown}{=} 51{\cdot}5$ hours. Cobaltous phthalocyanine does not show exchange nor does tris-ethylenediaminecobalt trichloride. Tris-α-nitroso-β-naphthol- and tris-acetylacetone-cobalt show evidence for a very slow exchange. The results have been interpreted in terms of bond type between the cobalt atom and its ligands, slow exchange being taken as evidence for partial ionic character, and fast exchange for strong ionic character.

The investigation of the exchange of metal ions between a complex molecule or ion containing the metal and free metal ions in a suitable solvent makes it possible to obtain some evidence as to the types of bonds present in the complex. If the bonding is predominantly ionic, exchange is expected to occur rapidly, probably too fast to be measured. As the bond type changes towards predominantly covalent linking, the rate of exchange is expected to decrease. Where exchange is observed to proceed at a measurable rate, the " mechanism " of exchange must be first established before unequivocal statements as to bond type can be made, *i.e.*, the mechanism must be shown to be that due to (*a*) an ionisation and recombination by the complex, or (*b*) a collision followed by a replacement of the bound metal by the colliding metal ion, or (*c*) the racemization of an optically active complex. Duffield and Calvin (*J. Amer. Chem. Soc.*, 1946, **68**, 557) have shown that a distinction can be drawn between the first and the second mechanism on kinetic grounds. An ionisation–recombination mechanism requires the half-time for the reaction to be independent of the concentrations of the exchanging species, but for a collision mechanism to be operative, the half-time is inversely proportional to concentration; in both cases, concentrations are assumed equal to each other. Chemical considerations should, in general, cover the final case.

At the present stage of knowledge of exchange reactions with chelate-type complexes it seems possible to obtain qualitative evidence as to the strength of bonding by observing whether an exchange is fast, slow, or intermediate in rate without being certain of the exact mechanism of exchange. If strong covalencies exist in a complex, then exchange will be expected to be slow whether it proceeds by an ionisation or a collision mechanism. In the first case, ionisation would be very slight for such a compound. For weak covalent bonds or ionic bonds, rapid exchange could occur by both mechanisms. This procedure has been adopted in the present paper.

Experimental.

Materials.—The pyridine used was of " AnalaR " quality, dried by refluxing over barium oxide followed by fractional distillation whenever required. The fraction of b. p. 115·3° was collected for use.

Chloroform was washed several times with water, dried ($CaCl_2$), and distilled over fresh calcium chloride. Batches were stabilised by the addition of 2% of ethyl alcohol but were never used without fresh treatment if kept longer than two weeks. No trace of carbonyl chloride or hydrogen chloride was detected in any samples used.

Distilled water was used whenever required.

Radioactive Cobalt.—This was supplied by the Isotopes Division of the American A.E.C. as the isotope ^{60}Co in a solution of carrier cobalt sulphate containing small amounts of sulphuric acid and potassium sulphate. It was purified by a double precipitation as sulphide, acetate buffer and ammonium sulphide being used. The product was dissolved in dilute sulphuric acid, and the solution boiled to remove hydrogen sulphide, etc., and evaporated to dryness. The product was then dissolved in water, and small volumes were removed when required for the preparation of solutions. Cobalt sulphate solutions containing the isotope were prepared by weighing out the required amount of the heptahydrate, dissolving it in water, and adding a quantity of the radioactive stock solution. The whole solution was then diluted to the appropriate volume.

Cobalt acetate solutions were prepared by weighing out the quantity of tetrahydrate salt required, adding radioactive stock solution together with a few drops of glacial acetic acid, and evaporating the mixture to dryness with an infra-red lamp. The dry residue was dissolved in pyridine and diluted to the appropriate volume.

Compounds.—The salicylideneaniline type complexes were prepared by using the method developed by Bailes and Calvin (*J. Amer. Chem. Soc.*, 1947, **69**, 1886) for preparing cobaltous compounds out of contact with air. The Schiff's base was first prepared by warming equivalent amounts of salicylaldehyde and amine in ethyl alcohol, evacuating, then adding the requisite amount of cobalt acetate dissolved in warm water, shaking, and re-evacuating. The following complexes, precipitated as red crystals, were filtered off and recrystallised several times from absolute alcohol. Solutions were prepared by dissolving weighed amounts in pyridine and making up to the required volume. Bis(salicylideneaniline)cobalt(II) [Found: C, 69·2; H, 4·5. Calc. for $Co(C_{13}H_{10}ON)_2$: C, 69·2; H, 4·5%]; bis(salicylidene-*m*-toluidine)cobalt(II) [Found: C, 69·8; H, 5·04. Calc. for $Co(C_{14}H_{12}ON)_2$: C, 70·1; H, 5·05%]; bis(salicylidene-*o*-anisidine)cobalt(II) [Found: 65·9; H, 4·8. Calc. for $Co(C_{14}H_{12}O_2N)_2$: C, 65·75; H, 4·7%]

Bis(guaiacol)cobalt(II) was prepared by Mellor and Craig's method (*J. Proc. Roy. Soc. N.S.W.*, 1940, **74**, 495) [Found: C, 55·4; H, 5·6. Calc. for $Co(C_7H_7O_2)_2$: C, 56·1; H, 4·6%].

Bis(acetylacetone)cobalt(II) [Found: C, 40·9; H, 6·6. Calc. for $Co(C_5H_7O_2)_2,2H_2O$: C, 40·7; H, 6·8%] and bis(salicylaldehyde)cobalt(II) [Found: C, 48·6; H, 4·5. Calc for $Co(C_7H_5O_2)_2,2{\cdot}5H_2O$: C, 48·6; H, 4·1%] were prepared as hydrates by adding the calculated amount of cobaltous chloride hexahydrate dissolved in water to an alcohol solution of the base, and crystallised from aqueous alcohol.

Bis-(4 : 4′-dicarbethoxy-3 : 3′ : 5 : 5′-tetramethyldipyrromethene)cobalt(II) was prepared by a method analogous to that used by Mellor and Lockwood (*ibid.*, 1940, **74**, 141) for the nickel derivative, and recrystallised from absolute alcohol [Found: C, 61·5; H, 6·4. Calc. for $Co(C_{19}H_{23}O_4N_2)_2$: C, 61·2; H, 6·22%]. Bis(salicylaldoxime)cobalt(II), prepared by the addition of an aqueous solution of the chloride hexahydrate to an alcoholic solution of the base, formed a brown amorphous product which could not be recrystallised [Found: C, 49·4, 49·4; H, 3·72. Calc. for $Co(C_7H_6O_2N)_2$: C, 50·8; H, 3·65%]. This sample was used in the first exchange experiments with this compound. However, in view of later work (see Discussion, p. 3119) it seems probable that the complex prepared in this manner has taken up oxygen, forming a mixed product which could contain an oxygenated derivative together with some bis(salicylaldoxime)cobalt.

Samples of cobaltous phthalocyanine and of the ammonium salt of the tetrasulphonic acid derivative were kindly supplied by Dr. M. Rogers through the courtesy of Imperial Chemical Industries Limited

The tris(ethylenediamine)cobalt(III) chloride complex was prepared as a hexahydrate (*Inorg. Synth.*, **2**, 221) (Found: C, 18·0; H, 8·1; N, 21·5; Co, 15·0. Calc. for $C_6H_{24}N_6Cl_3Co,6H_2O$: C, 18·3; H, 9·2; N, 21·4; Co, 15·0%). Tris-(1-nitroso-2-naphthol)cobalt(III) was prepared as recommended by Vogel ("Text Book of Quantitative Analysis," Longmans, 1948, p. 547) [Found: C, 62·6; H, 3·5. Calc. for $Co(C_{10}H_6O_2N)_3$: C, 62·6; H, 3·15%]. Tris(acetylacetone)-cobalt(III) was prepared by Urbain and Debierne's method (*Compt. rend.*, 1899, **129**, 302) and recrystallised from absolute alcohol. The green, crystalline product had m. p. 196·0° (uncorr.); Urbain and Debierne give 241° [Found: C, 50·2; H, 5·9. Calc. for $Co(C_5H_7O_2)_3$: C, 50·6; H, 5·9%].

Method.—Several methods were used to follow the exchange. The usual one was to add 5 c.c. of a pyridine solution of the complex compound (0·017M) in a 150-c.c. separating funnel held in a water-thermostat at the required temperature. When the solution reached temperature equilibrium, 5 c.c. of radioactive cobalt acetate (0·017M) were added from a storage vessel kept at bath-temperature. After the required time, a mixture of 14 c.c. of chloroform and 14 c.c. of water was added, and the mixture shaken. Each layer was then re-extracted once with 14 c.c. of the appropriate solvent. The extracts were combined and made up to 50 c.c. with ethyl alcohol in volumetric flasks. Aliquots were then counted in either 10-c.c. or 20-c.c. glass-skirted Geiger counters. For water-soluble complexes, reaction mixtures were prepared as above but separation was effected by the addition of 6 g. of ammonium thiocyanate and 10 c.c.

of an amyl alcohol–ether mixture (4 : 1). Each layer was re-extracted once more with appropriate solvent, the extracts made up to 50 c.c., and aliquots counted.

Bis(guaiacol)cobalt being almost insoluble in all conventional solvents, a weighed sample was shaken for various lengths of time with 5 c.c. of aqueous radioactive cobalt sulphate solution (0·017M) plus 5 c.c. of ethyl alcohol. The weight of complex used contained an equivalent amount of cobalt. The solution was filtered through a sintered-glass funnel, the filtrate made up to 50 c.c., and the residue dissolved in dilute hydrochloric acid (1 : 3) and also made up to 50 c.c. An aliquot of each solution was then counted.

In the second series of experiments with bis(salicylaldoxime)cobalt, the complex was preformed in pyridine solution by dissolving equivalent weighed amounts of cobalt acetate and reagent in 40 c.c. of solvent to give a solution 0·0085M. The solution was prepared under nitrogen and after complete solution of the materials had occurred a further 60 minutes was allowed for completion of chelation. Then 20 c.c. of a 0·017M-pyridine solution of radioactive cobalt acetate were added, and aliquots removed under nitrogen pressure at suitable intervals, and shaken with chloroform and water. The colour of the solution of the complex thus formed was light yellow at this concentration, but on exposure to air a deep brown solution resulted similar to that obtained with the amorphous product used in the first instance.

In each case where a solvent-extraction method was used a standard extraction using 5 c.c. of the radioactive solution plus 5 c.c. of pyridine (or water) was carried out in order to check distribution. This effect has been allowed for in each case. The extraction of most complexes showed that some chelate was held in the aqueous layer even after double extractions. For two cases, bis(salicylideneaniline)cobalt and bis(salicylidene-*m*-toluidine)cobalt, the total cobalt in each layer after extraction was determined in inactive solutions by precipitation of the sulphide and ignition to Co$_3$O$_4$. This allows corrections to be made for uneven distribution of activity. In other cases, constancy of activity in the chloroform solution over long time intervals when almost equal to that expected for complete exchange has been taken to imply that complete exchange has occurred. Since the object of this research was not primarily accurate kinetic measurements, but rather the surveying of groups of compounds, the above procedure has proved sufficient for the purpose. Measurements of activity were carried out with an Austronic (Australian) scale of 100 units and liquid-type Alltool counters. Corrections for background were applied in all cases, but no corrections were needed for radioactive decay (^{60}Co half-life = 5·3 years; Livingwood and Seaborg, *Phys. Review*, 1941, **60**, 913) nor were any applied for possible coincidence loss or density effects. Trials, however, showed that the latter effect was negligible at the activities used in the work.

Results. (A preliminary note dealing with the results obtained with a few of these compounds has been published: West, *Nature*, 1950, **165**, 122.)—The results obtained for twelve compounds are summarised in Table 1. Only one set of results has been presented for each substance, although, in general, at least two separate runs were made. Since the separation fractions were made up to definite volumes in all cases (25 or 50 c.c.) the activities listed under the headings " complex " and " Co^{++} " are those of aliquot samples, either 10 c.c. or 20 c.c. In the calculation of % exchange, where necessary, allowance has been made for incomplete extraction of cobalt salt. This has been determined by standard extractions using only a sample of the radioactive cobalt salt, and the results are given under the activity heading, enclosed in parentheses thus (1 200). The smaller figure represents always the activity left in the solvent layer which normally would contain the complex after extraction, and the larger is that of the bulk of the cobalt activity. The activity expected in the complex after complete exchange is obtained by dividing the total standard activity in the ratio of the concentrations of reacting species. In most cases here, since both concentrations are 0·017M, the " complete-exchange " activity is taken as one half of the total standard activity. For bis(salicylideneaniline)cobalt and bis(salicylidene-*m*-toluidine)cobalt, allowance has been made for incomplete extraction of the complex. The amounts of complex in the chloroform extracts (determined as above with an accuracy of about 5%) for the two compounds are given below :

	Co as Co$_3$O$_4$	
Salicylideneaniline	5·5 mg. (mean of 3)	Maximum for complete extraction in each case, 6·8 mg.
Salicylidene-*m*-toluidine	5·6 mg. ,,	

The complex activities in both cases were increased in the ratio maximum/amount found.

In other cases, although the extraction of a complex was never quite complete, the results at a series of time intervals clearly indicated whether exchange had occurred in less than 50 seconds, did not occur at all, or was proceeding slowly. Consequently, since only qualitative

TABLE 1. *The exchange of cobalt ions with cobalt complexes.*

Compound	Solvent	Temp.	Activity in complex	Activity in Co^{++}	Reaction time	Exchange, %
			(counts/min.)			
Cobaltous						
Bis-salicylaldehyde	A	20° ± 0·1°	123	122·0	40 secs.	103
			(0·0	238·1)		
Bis-salicylideneaniline	B	20 ± 0·1	65·8	87·9	50 secs.	102
			66·3	90·4	6 mins.	103
			63·4	88·1	68 mins.	99
			(0·0	159·3)		
Bis-salicylidene-*m*-toluidine	B	20 ± 0·1	86·6	137·0	45 secs.	95
			88·1	137·8	2 mins.	97
			85·6	131·2	3 mins.	94
			(0·0	222·2)		
Bis-salicylidene-*o*-anisidine	B	20 ± 0·1	73·7	134·0	40 secs.	74 [d]
			70·0	137·7	2 mins.	70 [d]
			76·7	129·3	29 mins.	76 [d]
			(3·9	188·4)		
Bisacetylacetone ($2H_2O$)	B	20 ± 0·1	90·3	104·2	50 secs.	92 [d]
			91·2	108·9	1·5 mins.	93 [d]
			94·6	100·1	2 mins.	96 [d]
			(0·0	196·6)		
Bisguaiacol	C	~20	25·7	215·0	5 mins.	19
			107·9	135·6	1 hr.	80
			(	269·4)		
Bis-salicylaldoxime (brown amorphous product)	A	20 ± 0·1	20·0	228·7	3 mins.	15
			19·9	223·0	6 mins.	15
			18·3	232·0	60 mins.	14
			(0·0	258·0)		
		45 ± 0·1	29·8	220·7	10 mins.	23
			32·7	224·9	90 mins.	25
			35·4	220·5	240 mins.	27
			(0·0	259·3)		
(Preformed complex)	B	20 ± 0·1	186·8	191·1	18 mins.	99 [e]
			179·7	181·1	40 mins.	99·6
			196·2	190·9	60 mins.	102 [e]
			199·0	184·7	120 mins.	104 [e]
			191·5	183·9	180 mins.	102 [e]
Phthalocyanine [a]	B	30 ± 0·1	8·9	530·7	17 hrs.	0·4
			10·3	534·1	109 hrs.	0·8
			(8·0	532·9)		
Phthalocyaninetetrasulphonic acid derivative [b] (ammonium salt)	D	30 ± 0·1	3·6	1748·4	13 days	—0·4
			(7·3	1799·9)		
Pyrromethene complex	B	30 ± 0·1	111·9	1105·6	62 mins.	—2
			138·0	1091·5	3·2 hrs.	4
			203·0	1026·0	11·2 hrs.	16
			349·1	885·3	37·4 hrs.	40
			463·5	769·4	68·2 hrs.	61
			529·3	712·2	93·5 hrs.	72
			(79·0)	1146·2)		
			56·2	503·5	50 secs.	6
			165·8	410·9	43·5 hrs.	42
			(39·3	519·4)		
Cobaltic						
Trisethylenediamine chloride ($6H_2O$)	D	20 ± 0·1	2·0	241·4	10 mins.	1·6
			—1·1	239·7	1 hr.	—0·92
			—2·0	234·0	5 hrs.	—1·6
			—1·3	241·0	24 hrs.	—1·7
			(0·0	238·1)		
Tris-1-nitroso-2-naphthol [c]	B	25 ± 0·1	1·0	392·3	35 secs.	—0·98
			8·7	386·2	113 mins.	4·9
			20·3	352·4	90 hrs.	13·7
			(2·3	397·2)		
			15·4	178·6	221 hrs.	23·8
			22·4	171·7	26 days	34·6
			(0·0	194·0)		
Trisacetylacetone	B	30 ± 0·1	122·8	1362·7	3 days	3
			139·1	1383·2	6 days	5
			153·4	1383·6	9 days	7
			185·4	1364·1	18 days	12
			203·3	1338·3	21 days	14
			(101·2	1383·2)		

(See references on following page.)

information was required, corrections for incomplete extraction of complex were not applied, the only correction made being that for incomplete cobalt salt removal. For the salicylaldehyde, salicylidene-*o*-anisidine, and acetylacetone complexes, where incomplete extraction might be expected to be considerable, the high, constant activities of the complex extracts show that complete exchange has occurred in less than 40 seconds. The low, constant values for the first salicylaldoxime runs may be regarded as evidence for the existence of a small amount of an exchangeable compound.

An apparent " separation-induced " exchange of 6% has been observed for the pyrromethene complex by a series of runs at times of about 30 seconds. This factor has been allowed for in calculating % exchange.

DISCUSSION

Bis(salicylaldehyde)cobalt(II).—Under the conditions of exchange used in this work complete exchange is observed with this compound in times as small as 50 seconds. This points to the existence of ionic bonds between the metal and surrounding ligands when in pyridine solution. The magnetic data available support this conclusion ($\mu = 4{\cdot}5$; Tyson and Adams, *J. Amer. Chem. Soc.*, 1940, **62**, 1228).

Bis(acetylacetone)cobalt(II).—Similarly, complete exchange has been observed to occur for this compound in less than 1 minute, and hence the existence of ionic bonds may be inferred here also. A susceptibility of 4·3 μ given by Mellor and Goldacre (*J. Proc. Roy. Soc. N.S.W.*, 1939, **73**, 233) supports this view.

Bis(guiacol)cobalt(II).—The slower rate of exchange observed here has been related in a preliminary communication (West, *loc. cit.*) to the experimental procedure adopted. Exchange proceeding between a solid and a solution will perforce be slow because of the necessity for the exchanging ions to diffuse into the crystal structure of the solid. Again, the magnetic evidence supports the conclusion that ionic type bonds exist in this compound, Mellor and Craig obtaining a value of 4·5 μ for this substance (*ibid.*, 1940, **74**, 495).

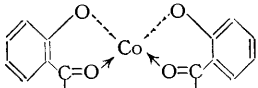
TABLE 2. *The exchange of metal ions with metal complexes.*

Exchanging species	Solvent	Result	Ref.
Mn^{++} bisacetylacetone	Methanol*	Rapid exchange	*a*
Zn^{++} bisacetylacetone	Pyridine	Complete in 30 secs.	*b*
Cu^{++} bisacetylacetone	Chloroform	Complete in 2 mins.	*c*
Cu^{++} bis-salicylaldehyde	Pyridine	,, 15 secs.	*d*
bis-salicylideneaniline	,,	,, 15 secs.	*d*
bis-salicylidenemethylamine	,,	,, 15 secs.	*d*
Ni^{++} bis-salicylaldehyde	Methyl cellosolve	,, 5 mins.	*e*
bis-salicylaldoxime	,,	,, 5 mins.	*e*

a, Drehman, *Z. physikal. Chem.*, 1943, **53**, 227. *b*, Leventhal and Garner, *J. Amer. Chem. Soc.*, 1949, **71**, 371. *c*, Ruben, Seaborg, and Kennedy, *J. Appl. Physics*, 1941, **12**, 308. *d*, Duffield and Calvin, *loc. cit.* *e*, Johnson and Hall, *J. Amer. Chem. Soc.*, 1948, **70**, 2344.

Bis(salicylideneaniline)cobalt(II).—This substance, together with the *o*-anisidine and the *m*-toluidine derivative, also undergoes complete exchange in reaction times of less than 1 minute, showing that ionic-type bonds are present in these compounds. No magnetic susceptibilities are available for these three compounds.

Similar results to these have been reported by a number of workers with Mn, Cu, Ni, and Zn complexes (see Table 2).


(I)

For each of these six compounds the conventional valency bond structure would indicate that each organic residue was joined by one co-ordinate linkage and one ionic linkage, as, *i.e.*, bis(salicylaldehyde)cobalt(II) (I). However, Syrkin and Dyatkina ("Structure of Molecules and the Chemical Bond," Butterworths, London, 1950, p. 389) have shown that the structure of the somewhat analogous glycine copper compound is best represented by

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A, Complex in pyridine, $CoSO_4$ in water. B, Complex in pyridine, cobalt acetate in pyridine. C, Solid compound shaken with aqueous $CoSO_4$ and EtOH. D, Complex in water, $CoSO_4$ in water.

a, Solutions in pyridine; complex 0·00425M, cobalt acetate 0·0085M. *b*, Complex 0·001M, cobalt sulphate 0·017M in 0·1M-H_2SO_4. *c*, Complex 0·00425M; 10 c.c. of this solution mixed with 5 c.c. of 0·0085M-cobalt acetate. *d*, 100% exchange assumed since allowance not made for incomplete extraction of complex. *e*, Standard was not obtained; results are calculated on the basis of expected activity at 100% exchange = $\frac{1}{2}$ × (sum of chloroform + water activities). *f*, This value for induced exchange has been used to correct every other % exchange value for this compound.

resonance between a number of structures with the result that no difference is to be observed between either the Cu–O or the Cu–N bonds. Hence each bond must be associated with partial ionic character. Hückel (" Structural Chemistry of Inorganic Compounds," Vol. I, transl. Long, Elsevier, Amsterdam, p. 141), on the other hand, allows a fixed covalent linkage for the Cu–N bond but assumes that the Cu–O linkage represents a transition to a covalent linkage from a simple ionic bond with the probability, however, that this Cu–O linkage can dissociate in water.

For the cobalt complexes Syrkin and Dyatkina's resonance treatment seems the better of the two because the high electronegativity of O and N leads to considerable ionic character in the Co–N or Co–O co-ordinate linkages and some covalent character in the Co–O links between Co and the phenolic OH groups. Thus one may explain the easy exchange of the central metal atom by another without the necessity of postulating the rupture of what one might expect, *a priori*, to be a strong Co–N or Co–O co-ordinate linkage, since these bonds must now be considered to possess considerable ionic character.

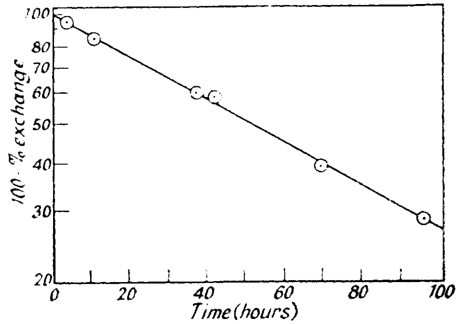
The magnetic susceptibilities of the first three complexes have pointed to a tetrahedral configuration for each compound, and since this is expected with ionic type bonding it is probable that the salicylideneaniline-type complexes have a tetrahedral configuration also.

Bis(salicylaldoxime)cobalt(II).—In the work on the brown, amorphous sample of this complex a small, constant amount of exchange was observed during 60 minutes at 20°, but a slightly higher % exchange was observed at 45° with only a slight further increase in 4 hours. Mellor and Craig (*loc. cit.*) have shown by magnetic measurements that a square, coplanar configuration is to be expected for this compound, with expected strong covalent bonding. These authors also showed that a similar configuration existed in the corresponding nickel derivative (*ibid.*, 1940, **74**, 475). Hence, if exchange were observed, it would be expected to be slow. Johnson and Hall (*loc. cit.*), however, showed that the nickel complex exchanged completely within 5 minutes in 2-methoxyethanol—a fact which points rather to bonds with considerable ionic character. In view of the tendency of many cobaltous salicylideneamine derivatives to absorb oxygen (Calvin *et al.*, *J. Amer. Chem. Soc.*, 1946, **68**, 2254, 2257, 2263, 2267, 2273, 2612), a second run was carried out in which the cobalt complex was pre-formed in pyridine solution under an atmosphere of nitrogen to avoid possible oxygen contamination, and complete exchange was observed within 18 minutes.

As mentioned on p. 3117, the yellowish solution of complex, prepared in the absence of oxygen, became deep brown on exposure to air or on oxygen being bubbled through the solution. It seems probable therefore that the brown amorphous complex used in the first experiments was an oxygenated derivative containing a small amount of pure bis(salicylaldoxime)cobalt, the latter substance being able to exchange quickly with cobalt ions while the former substance was not. If the analytical figures are recalculated for a molecule of bis(salicylaldoxime)cobalt containing half an atom of oxygen, much better agreement is obtained with the carbon value for the amorphous product than previously; thus, Found: C, 49·4, 49·4; H, 3·7. Calc. for $Co(C_7H_6O_2N)_2\frac{1}{2}O$: C, 49·6; H, 3·6%. In the first run, the higher temperature could be causing slight removal of oxygen from the complex, leading to an increase in the amount of "free" bis(salicylaldoxime)cobalt. This explanation seems more in agreement with the existing facts than that given in the first instance (West, *loc. cit.*). It thus appears necessary to presume that both the nickel and the cobalt derivatives contain bonds with considerable ionic character when in solutions of methoxyethanol and pyridine respectively.

Bis-(4 : 4′-*dicarbethoxy*-3 : 3′-5 : 5′-*tetramethyldipyrromethene*)*cobalt*(II).—This compound shows slow exchange proceeding during many hours. A conventional plot of log (100 − % exchange) against time (see Fig.) shows that the appearance of activity is following the expected first-order law with $t_{\frac{1}{2}} \simeq 51{\cdot}5$ hours. There exists no direct evidence about the configuration of this compound, although Mellor (*J. Proc. Roy. Soc. N.S.W.*, 1940, **74**, 138) has suggested that it should be allotted a square, coplanar configuration. Because of the steric interaction of the α-methyl groups, metal complexes of this type will not be completely planar but the metal–nitrogen bonds will be distorted from the coplanar position with a consequent change in bond type from the expected covalent dsp^2 planar type to bonds with considerable ionic character. This has been shown to occur with the nickel derivative, which has a moment of 3·2 Bohr magnetons (Mellor and Lockwood, *ibid.*, 1940, **74**, 141). It is probable, in view of this result, that a tetrahedral configuration may be applicable here in spite of the *X*-ray evidence for the planarity of the four pyrrole nitrogen–Ni bonds in nickel phthalocyanine (Robertson, *J.*, 1937, 219). However, the occurrence of slow exchange for the cobalt complex seems to imply that the bonds between cobalt and the pyrrole nitrogens have considerable covalent character, and this would agree with an essentially square planar structure for the complex with methyl group interaction causing "out of plane" distortion of the Co–N bonds leading to a configuration somewhere between planar and tetrahedral and containing Co–N bonds with partial ionic character. Further exploratory results not given in this paper seem to show that $t_{\frac{1}{2}}$ is not independent of concentration, so the collision mechanism of exchange is probably operating here rather than an ionisation and recombination.

Cobaltous Phthalocyanine.—Klem and Klem (*J. pr. Chem.*, 1935, **143**, 82) have found a value of 2·16 μ for the magnetic moment of this compound, leading to the assumption of a square, coplanar formulation with strong dsp^2 covalent bonds. No evidence for exchange has been obtained for either the simple complex in pyridine or the water-soluble sulphonic acid derivative in aqueous 0·1M-sulphuric acid. The bond here may, therefore, be classified as strong covalent. However, these bonds may not necessarily be as strong as, say, the Co–N linkages in cobaltic ethylenediamine complexes (see below) in spite of the observed lack of exchange. Ruben and his co-workers (*J. Amer. Chem. Soc.*, 1942, **64**, 2297) have shown that ferric ions do not exchange with ferrihaem in which the iron is presumably bound by ionic bonds according to magnetic measurements (Pauling and Coryell, *Proc. Nat. Acad. Sci.*, 1936, **22**, 159). These workers suggest that the fused-ring system present in such compounds would in some way prevent exchange even when bond considerations should permit it. Probably the occurrence of such a strongly resonating structure as the phthalocyanine or porphyrin ring can help to stabilise any metal compounds formed to a greater extent than is possible with other complex-forming molecules.



Cobalt pyrromethene exchange at 30° *in pyridine solutions*, 0·017M.

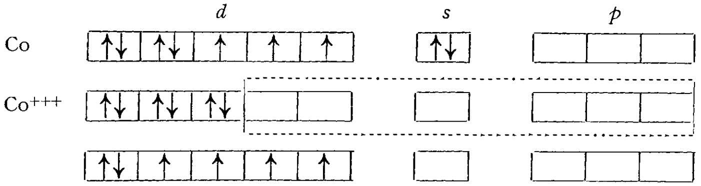
Tris(ethylenediamine)cobalt(III) *Chloride.*—No exchange was observed with this compound in water during 24 hours, in agreement with Lewis and Coryell (*J.*, 1949, S 386), and this fact points to strong covalent bonding. Flagg (*J. Amer. Chem. Soc.*, 1941, **63**, 557) and McCallum, Hoshowsky, and Holmes (*Canadian J. Res.*, 1949, **27**, *B*, 258) have shown that other cobaltic complexes of this type do not exchange with cobaltous ions over long periods.

Tris-(1-*nitroso-*2-*naphthol*)*cobalt*(III).—The occurrence of exchange, even though slight, is doubly interesting in the case of this compound because, first, we have a very stable cobaltic compound undergoing exchange with cobaltous ions, and secondly, in the process an electron transfer must occur between the free cobaltous and the complexed cobaltic ions. It is, no doubt, more correct to speak in every case dealt with in this paper, not of free cobaltous ions but rather $[Co(py)_4]^{++}$, or some similar entities. The very slow rate observed is to be expected if covalent bonding with some ionic character is present in this complex, it being borne in mind that exchange in this case is a two-stage process. With the

1 : 2-naphthaquinone 1-oxime formula given by Hückel (*loc. cit.*, p. 145) for the complex, a definite contribution of ionic valency bond structures to the resonance stabilisation of the complex must be expected because of the high electronegativity of oxygen. Consequently, the assumption of partial ionic character for the Co–O bonds in this complex seems justified in view of the evidence for exchange.

Tris(acetylacetone)cobalt(III).—Cambi and Szego (*Ber.*, 1931, **64**, 2591) quote a value for the magnetic susceptibility of this compound determined by Ishiwara (*Rep. Tohoku Univ.*, 1916, **5**, 53; not available to the author). The value of 4·6 Weiss magnetons is 0·93 Bohr magneton in the more usual modern interpretation, and this has been taken by Cambi and Szego to indicate diamagnetism for the compound. Sugden (*J.*, 1943, 328) has quoted a value of 0·00 μ for this substance without reference to its source. The author has been unable to trace any further reference to a magnetic measurement. In view of the evidence for exchange it appears that the cobalt–ligand bonds must possess some ionic character and are not, therefore, as strongly covalent as would be implied by the assumption of diamagnetism for this substance. Syrkin and Dyatkina (*op. cit.*, p. 391) have accounted for the properties of diamagnetic tris(acetylacetone)aluminium and of the paramagnetic ferric compound by assuming that sp^2 hybridization occurs with the formation of three ordinary electron-pair bonds by the replacement of the acidic hydrogen of the hydroxyl group present in the tautomeric reactive form of acetylacetone.

On the other hand, conventional d^2sp^3 octahedral bonds would cause the cobalt complex to be diamagnetic, as also would the use of the three unpaired electrons of a cobalt atom:



However, if three d orbitals of the cobaltic ion are utilised for covalent bond formation, giving a d^3 hybridization, the constitution of the complex is again similar to the postulate of Syrkin and Dyatkina, leaving one unpaired electron, which should give the complex a magnetic susceptibility of 1·73 μ (Pauling, "Nature of the Chemical Bond," Cornell, 2nd edn., 1940, p. 113). If the value determined by Ishiwara is significant, and several other instances of low paramagnetic susceptibilities have been reported (Cambi, Ferrara, and Colla, *Gazzetta*, 1936, **65**, 1162) for compounds where the value 0·00 μ was expected, then it may point to a state of bonding similar to that suggested. Since d^3 would tend to be weaker than sp^2 bonds, the occurrence of exchange is possibly explained.

On the other hand, the high electronegativity of oxygen could be expected to lead to some ionic character for each Co–O bond; consequently, the exchange seems not incompatible with a conventional octahedral complex. Further information obtained after investigation of other cobaltic complexes seems highly desirable in order to clarify this problem and also that of the 1-nitroso-2-napthol complex.

Microanalyses were carried out by Mr. R. T. Howard and by the C.S.I.R.O., Microanalytical Laboratory, Melbourne.

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