Studies on Bond Type in Certain Cobalt Complexes. Part V. The Exchange Reactions of Cobaltous* 1 : 10-*Phenanthroline and Tripyridyl Complexes.*

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The exchange of cobalt ions with [tris-(1 : 10-phenanthroline)cobalt(II)]$^{++}$, [tris-(5-methyl-1 : 10-phenanthroline)cobalt(II)]$^{++}$, and [tris-(5-nitro-1 : 10-phenanthroline)cobalt(II)]$^{++}$ is very rapid at 15° and 0·005M-concentrations. With [bistripyridylcobalt(II)]$^{++}$, however, under analogous conditions slow exchange ($t_{\frac{1}{2}}$ = 2·8 hr.) is observed.

The exchange of cobaltous ions with several cobalt–1 : 10-phenanthroline complexes and bis-αα′α″-tripyridylcobalt(II) dibromide has been investigated in aqueous solution at 15°, the results being presented in the Table. It can be seen that the exchange of phenanthroline complexes is much more rapid than that of the tripyridyl complex under comparable conditions.

The exchange of cobalt ions with cobaltous complexes of several o-*phenanthrolines and tripyridyl at* 15°.

Complex	Concn., M Complex	 $CoSO_4$	$t_{\frac{1}{2}}$
[Co(1 : 10-phenanthroline)$_3$]$^{++}$	0·005	0·005	<28 sec.
[Co(5-methyl-1 : 10-phenanthroline)$_3$]$^{++}$	,,	,,	<36 sec.
[Co(5-nitro-1 : 10-phenanthroline)$_3$]$^{++}$	,,	,,	<25 sec.
[Co(tripyridyl)$_2$]$^{++}$	,,	,,	2·8 hr.

With regard to the 1 : 10-phenanthroline complexes, Brandt and Gullstrom (*J. Amer. Chem. Soc.*, 1952, **74**, 3532) have shown that the stabilities of the corresponding ferrous derivatives increase in the order $NO_2 < H < CH_3$, *i.e.*, that of the dissociation constants of the free bases. On the assumption that the stabilities of the cobalt compounds would follow the same order, it had been hoped to discover differences in the ease of exchange of the cobalt *o*-phenanthroline complexes also in the same order. However, although the upper limits for the $t_{\frac{1}{2}}$ values of these compounds do lie in this order, exchange proceeded too rapidly for accurate measurements of $t_{\frac{1}{2}}$ to be made, and the order may be fortuitous.

This rapid exchange, however, leads to the conclusion that ionic or weakly covalent bonds are present in the three cobalt–phenanthroline complexes. This view is supported by magnetic evidence. Cambi and Cagnasso (*Atti R. Accad. Lincei*, 1934, **19**, 458) give the value of 5·1 B.M. for the magnetic moment of the corresponding dibromide of the unsubstituted *o*-phenanthroline complex, which implies " ionic-type " bonds in this compound. One may expect that similar moments would be found for the two substituted phenanthroline complexes.

The tris-(1 : 10-phenanthroline)ferrous compound has been shown to undergo extremely slow exchange (Ruben, Kamen, *et al.*, *J. Amer. Chem. Soc.*, 1942, **64**, 2297), which may be reconciled with the strong covalent bonding indicated by its diamagnetism (Biltz, *Z. anorg. Chem.*, 1928, **170**, 161).

The magnetic moment of the tripyridyl–cobalt complex has not been determined, so no direct evidence as to the bonds existing in this complex is available. One may suggest covalent $3d^24sp^3$ bonding on the basis of the slow exchange rate, bearing in mind the *o*-phenanthroline ferrous complex where slow exchange and strong covalent bonding apparently are complementary. However, in view of the pronounced stabilising effect brought about by an increase in the number of chelate rings per molecule of base (Burkin, *Quart. Reviews*, 1951, **5**, 10), this factor may be causing the increased stability of the tripyridyl over the

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formally analogous phenanthroline derivatives. Nevertheless, Morgan and Burstall (*J.*, 1937, 1649) have shown that the complex may be oxidised to the cobaltic state by fairly powerful oxidisers such as chlorine, which could mean that the complex did have covalent bonds of the $3d^24s4p^3$ hybrid type and one $3d$ electron had been promoted to the more energetic $5s$ orbital, whence it could be more easily removed by oxidising agents.

It is significant that Pfeiffer and Werdelmann (*Z. anorg. Chem.*, 1950, **261**, 197) have observed that the tris-1 : 10-phenanthroline complex is extremely resistant to oxidation—a situation to be expected if all unpaired electrons lay in $3d$ orbitals as in the free ion. The measured moment shows that such a configuration is certainly present in this complex.

EXPERIMENTAL

Exchange Procedure.—Equal volumes (2 c.c.) of solutions of the complex and cobalt sulphate, the latter labelled with ^{60}Co, at appropriate concentrations were mixed in small flasks in a thermostat. After the required time interval excess of an aqueous solution of $K_2[CdI_4]$ was added, which precipitated each complex studied as the $[CdI_4]^{2-}$ salt. This was filtered off and dissolved in hot concentrated nitric acid. The resulting solution and the filtrate containing cobalt sulphate were each made up to a standard volume, and aliquot portions were counted in a liquid-type counter.

Radioactive ^{60}Co.—This was obtained from the American Atomic Energy Commission through the courtesy of C.S.I.R.O.

Phenanthroline Complexes.—These were all prepared by Pfeiffer and Werdelmann's method (*loc. cit.*) for the unsubstituted complex. The composition of tris-(1 : 10-phenanthroline)-cobalt(II) dichloride septahydrate was verified [Found: C, 54·6; H, 4·7. Calc. for $(C_{12}H_8N_2)_3CoCl_2,7H_2O$: C, 54·3; H, 4·8%].

*Tris-5-methyl-*1 : 10-*phenanthrolinecobalt*(II) *dichloride hexahydrate.* Cobalt chloride hexahydrate (0·24 g., 1 mol.) was dissolved in the minimum quantity of hot water, and the solution added to a warm suspension of 5-methyl-1 : 10-phenanthroline (0·65 g., 3 mols.) in water (10 c.c.). The base rapidly dissolved, and the solution darkened and was filtered and set aside. A light yellow powder was soon precipitated. This was filtered off and redissolved in warm water. The light yellow powder was reprecipitated as soon as the source of heat was removed, and was filtered off and dried in the air [Found : C, 56·9; H, 5·6; Co, 6·7. $(C_{13}H_{10}N_2)_3CoCl_2,6H_2O$ requires C, 57·1; H, 5·2; Co, 7·0%].

*Tris-5-nitro-*1 : 10-*phenanthrolinecobalt*(II) *dichloride nonahydrate.* Cobalt chloride hexahydrate (0·24 g., 1 mol.) in water was added to a suspension of 5-nitro-1 : 10-phenanthroline (0·75 g., 3·3 mols.) in water. When no more base would dissolve the solution was filtered and evaporated to crystallization. Yellow-brown prisms were obtained which were recrystallized from water and air-dried [Found : C, 44·7; H, 4·0; Co, 6·0. $(C_{12}H_7N_3O_2)_3CoCl_2,9H_2O$ requires C, 44·7; H, 4·01; Co, 6·1%].

Bis-αα′α″-tripyridylcobalt(II) *dibromide.* This was prepared by Morgan and Burstall's method (*loc. cit.*) as a hydrate [Found : C, 47·9; H, 4·0; N, 11·2. Calc. for $(C_{15}H_{11}N_3)_2CoBr_2,3·5H_2O$: C, 48·1; H, 3·9; N, 11·2%].

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