Electron Transfer Reactions involving Alkyl Group Transfer between Cobalt Ions

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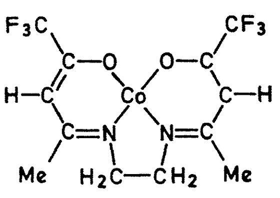
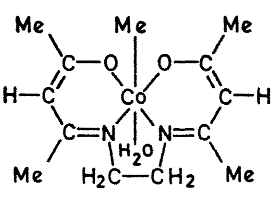
Summary Electron transfer reactions have been observed between a cobalt(II) complex and organometallic cobalt(III) derivatives; the reactions are accompanied by alkyl group transfer between the metal ions.

IT has been reported[1] that Ag^{I} or Hg^{II} ions can aid the replacement of various carbanions co-ordinated in certain cobalt(III) corrinoids, by water molecules. We have now observed rapid electron transfer reactions between a cobalt(II) complex and cobalt(III) organometallic complexes of various tetradentate Schiff-base ligands, accompanied by the transfer of alkyl groups bonded to the original Co^{III} ions to the "new" Co^{III} ion formed upon electron transfer.



(1)



(2)

Thus, *NN'*-ethylenebis-(4,4,4-trifluoro-1-methyl-3-oxobutylideneiminato)cobalt(II), Co(tfen) (**1**) reacts readily in dimethyl sulphoxide ($t_{\frac{1}{2}} < 2$ min) with *NN'*-ethylenebis-(1-methyl-3-oxobutylideneiminato)methylaquocobalt(III),[2] MeCo(acen) (**2**), according to equation (1). The reverse reaction with Co(acen) + MeCo(tfen)[†] has also been carried out and comes to equilibrium very rapidly.

$$\mathrm{Co^{II}(tfen) + MeCo^{III}(acen) \rightleftarrows Co^{II}(acen) + MeCo^{III}(tfen)} \quad (1)$$

A similar rapid reaction occurs between Co(tfen) and EtCo(acen) in which EtCo(tfen)[†] and Co(acen) are formed. These reactions are thus to be considered as electron transfer reactions accompanied by the transfer of an alkyl group between metal atoms. Although group exchange accompanying electron transfer reactions in metal complexes is a well-characterized process, previous observations of the phenomenon have been limited to simple inorganic ions and organic carboxylic acid groups.[3]

The reaction has been followed by examining the ^{19}F n.m.r. spectra of mixtures of the reactants. The resonance due to the CF_3 fluorine atoms in Co(tfen) has experienced a contact shift due to the paramagnetism of the compound ($\mu = 2{\cdot}3$ B.M.) and absorption occurs at δ 56 p.p.m., while in the diamagnetic compound MeCo(tfen) the resonance is at δ 71 p.p.m.

Thus, the presence of the "new" organo-cobalt(III)

[†] Authentic samples of $MeCo(tfen){\cdot}H_2O$, $EtCo(tfen){\cdot}H_2O$, and $C_2F_5Co(acen){\cdot}H_2O$ were prepared by reducing Co(tfen) or Co(acen) with sodium amalgam in tetrahydrofuran,[2] treatment of the product with MeI, EtI, or C_2F_5I, respectively, and precipitation of the complexes with water.

derivative can be readily detected in the presence of unchanged Co(tfen) and integration of the respective spectra gives a measure of the relative proportions of each species in solution. For the forward reaction at 44°, $K_{\mathrm{Me}} = 23$ and for the reverse $1/K_{\mathrm{Me}} = 21$, in reasonable agreement, while $K_{\mathrm{Et}} = 5{\cdot}8$.

It is possible that such a ready movement of alkyl groups between metal ions in different oxidation states is relevant to the biochemical behaviour of species such as the cobalamins.

No reaction has been detected under similar conditions in Me_2SO between Co(tfen) and C_2F_5Co(acen)† after three days at room temperature, indicating the relative inertness of the C_2F_5–Co bond.

The fluoroalkyl-cobalt(III) compounds are demonstrably more resistant to photochemical breakdown than their alkyl counterparts but experiments on the Co(tfen)–MeCo(acen) exchange carried out in the dark have shown that exchange occurs just as readily as in daylight.

An alkyl group can, however, readily exchange with a fluorocarbon group since Co(salen)Me·H_2O [*NN'*-ethylenebis(salicylideneiminato)methylaquocobalt(III)] reacts with C_3F_7I in *ca.* 3 days at room temperature and in 30 min on being heated in ethylene glycol dimethyl ether under reflux to yield Co(salen)C_3F_7 in almost quantitative yield.

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[1] H. A. O. Hill, J. M. Pratt, S. Ridsdale, F. R. Williams, and R. J. P. Williams, *Chem. Comm.*, 1970, 341.

[2] G. Costa and G. Mestroni, *J. Organometallic Chem.*, 1968, **11**, 328.

[3] F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions," Wiley, New York, 2nd edn., 1967, p. 466.