Exchange Reactions and Magnetic Susceptibilities of Complex Salts. Part III. Exchange Reactions of Some Nickel Complex Salts.*

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The synthesis and use in exchange studies of [*carbonyl*-^{14}C]salicylaldehyde is described. In pyridine solutions, rapid and complete exchange of the active ligands of bis-salicylaldoximenickel and bis-*N*-methylsalicylaldiminenickel and bis-salicylaldiminenickel was observed, while zero exchange occurred with bis-salicylaldehyde-ethylenedi-iminenickel and bis-salicylaldehyde-*o*-phenylenedi-iminenickel. The results are correlated with the magnetic susceptibilities.

THE mechanisms of isotopic exchange reactions of complex compounds have recently been discussed by Taube (*Chem. Rev.*, 1952, **50**, 69), Adamson and Wilkins (*J. Amer. Chem. Soc.*, 1954, **76**, 3379), and MacDiarmid and Hall (*ibid.*, p. 4222). For the "outer orbital" type of octahedral complex, where highly polar sp^3d^2 hybrid bonds occur, the exchange mechanism probably involves the dissociation of a ligand grouping, the energy required for such a dissociation being offset by the removal of a relatively unstable $4d$ orbital from hybridisation. Slow exchange will generally be expected for "inner orbital" complexes except where an available low-energy orbital allows the formation of an activated intermediate complex of low energy and higher co-ordination number. Exceptional cases may occur where stereochemical requirements outweigh the effect of electronic structure and bond type and cause large activation energies. Thus fairly slow rates of ligand exchange will generally be expected for quadridentate ligands (Ruben, Kamen, Allen, and Nahinsky, *ibid.*, 1942, **64**, 2297).

Part II (*loc. cit.*) gave the results of magnetic measurements on solutions of several nickel complexes. The present paper contains the results of ligand-exchange studies with these same solutions. Exchange of the central nickel atom of these complexes has been investigated by Johnson and Hall (*ibid.*, 1948, **70**, 2344) and Hall and Willeford (*ibid.*, 1951, **73**, 5419), using radioactive nickel, and it was hoped that this investigation of ligand exchange would remove several anomalous results.

Complex	Time (min.)	Relative activity of complex	Relative activity of ligand	Ratio of rel. act.
Bis-salicylaldoximenickel	5	1192	1095	1·09
	10	1142	1128	1·01
	15	1176	1128	1·04
Bis-salicylaldiminenickel	5	985	935	1·05
	10	960	935	1·02
	60	975	935	1·04
Bis-*N*-methylsalicylaldiminenickel	5	1152	1125	1·02
	10	1170	1125	1·04
	60	1170	1125	1·04
Bis-*N*-methylsalicylaldiminenickel *	1	956	950	1·00
	5	958	908	1·05
	60	960	950	1·00
,, ,, ,, †	5	955	905	1·05
	10	998	965	1·03
Bis-salicylaldehyde-ethylenedi-iminenickel	10	98	2484	0·03
	60	164	2440	0·07
	1440	130	2530	0·02
Bis-salicylaldehyde-*o*-phenylenedi-iminenickel	10	161	2180	0·07
	60	224	2080	0·10
	300	225	2020	0·11
	5400	112	2210	0·05

* In dioxan. † In ethyl alcohol.

Discussion of Results.—Activity determinations were made on infinitely thick samples with the apparatus and procedure described in Part I (*J.*, 1954, 63). The results in the Table

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* Part II, preceding paper.

show the relative activities of complex and free ligands expressed as counts per equiv. of salicylaldehyde per minute. The solvent was pyridine except in the two cases noted.

Discussion.—In pyridine solution bis-salicylaldoximenickel forms a paramagnetic octahedral pyridine adduct (see Part II), presumably using $4s4p^34d^2$ hybrid orbitals. The observed rapid exchange would thus be expected and probably occurs as follows :

(*a*) $[\mathrm{Ni(ligand)_2py_2}] \rightleftharpoons [\mathrm{Ni(ligand)_2}] + 2\mathrm{py}$ (py = pyridine)

(*b*) $[\mathrm{Ni(ligand)_2}] + (\mathrm{ligand})^* \rightleftharpoons [\mathrm{Ni(ligand)_2(ligand)^*}]$

(*c*) $[\mathrm{Ni(ligand)_2(ligand)^*}] \rightleftharpoons [\mathrm{Ni(ligand)(ligand)^*}]' + (\mathrm{ligand})$

(*d*) $[\mathrm{Ni(ligand)(ligand)^*}] + 2\mathrm{py} \rightleftharpoons [\mathrm{Ni(ligand)(ligand)^*py_2}]$

This stepwise mechanism is postulated since reactions (*a*) and (*c*), involving a decrease in the co-ordination number from six to four, would temporarily remove the two high-energy 4*d* orbitals from hybridisation. Hence the activation energy would be small, leading to rapid exchange.

However, this mechanism would require the two pyridine molecules to occupy *cis*-positions to allow the entry of the third ligand. Hence the ligand molecules must be rearranged as the complex enters solution or during the exchange process since the solid complex has a planar structure. Such a rearrangement is possible since Dwyer and Mellor (*J. Amer. Chem. Soc.*, 1941, **63**, 81) showed that the dipyridine derivative of bisdiazoaminobenzenenickel has two pyridine molecules occupying *cis*-positions. Bis-*N*-methylsalicylaldiminenickel in pyridine solution also formed an octahedral dipyridine compound. In agreement with observation, rapid exchange proceeding by the above mechanism would also be expected here.

In ethyl alcohol, dioxan, chloroform, and methylbenzene solutions, temperature-dependent equilibria occurred. In chloroform and methylbenzene solutions the paramagnetic form is probably tetrahedral, while in ethyl alcohol and dioxan, either an octahedral or a tetrahedral form is consistent with the observed exchange rates. Unfortunately, no exchange studies could be made in chloroform or methylbenzene solutions, owing to the lack of a suitable separation procedure.

As a solid, bis-salicylaldehyde-ethylenedi-iminenickel is diamagnetic and hence planar. In pyridine solution it is diamagnetic and may be planar or may form a dipyridine-octahedral complex with a $3d^24s4p^3$ hybrid bond system involving the promotion and pairing of two electrons in the 5*s* orbital as suggested by Burstall and Nyholm (*J.*, 1952, 3570). Both of these structures would result in the observed diamagnetism and a negigible substitution rate. (For this and the following complex, the observed complex activities were probably due to contamination caused by incomplete separation.)

The observed zero exchange of bis-salicylaldehyde-*o*-phenylenedi-iminenickel in pyridine solution was unexpected in view of the magnetic measurements, although Hall and Willeford had also observed a slow rate of substitution of the central nickel atom. Attempts to formulate an exchange mechanism explain to some extent this inertness. As the ligand is quadridentate and planar, the paramagnetic form observed in pyridine solution is unlikely to have a tetrahedral structure but instead is probably octahedral with two pyridine molecules occupying *trans*- rather than *cis*-positions. Two substitution mechanisms can be suggested, the first involving the dissociation of the complex by the simultaneous breaking of all four bonds between the nickel atom and the ligand, *i.e.*, a simple collision mechanism. This would require considerable energy and the activation energy would probably be so high as to prohibit substitution of either ligand or metal.

The second possible mechanism would involve the formation of an activated intermediate complex with the nickel atom increasing its co-ordination number from six to eight so as to hold two ligand molecules simultaneously. Since there are no suitable low-energy orbitals for such an increase, and since it would be extremely difficult to arrange two such planar ligands around one nickel atom, the activation energy would again be high, causing very slow substitution rates. Stereochemical requirements also prohibit the formation of an activated intermediate containing two ligand groupings, each bound by, say, two bonds to the nickel atom.

In contrast to the zero exchange of the nickel complex, West (*J.*, 1954, 395) has ascribed the slow exchange of the corresponding cobalt complex and the very rapid exchange of the zinc complex (Atkins and Garner, *J. Amer. Chem. Soc.*, 1952, **74**, 3527) to differences in solvation, but the different electronic structures of these metals and hence the widely differing stabilities of the planar, tetrahedral, and octahedral configurations will also influence the exchange rates.

So the observed rates of ligand substitution can all be correlated with the magnetic susceptibilities and hence with the electronic structure of the central nickel atom, except where the large activation energy, arising from stereochemical considerations, outweighs the influence of the electronic structure.

EXPERIMENTAL

Preparation of [carbonyl-^{14}C]*Salicylaldehyde.*—This synthesis was carried out in three stages: (*a*) carboxylation of *o*-methoxyphenylmagnesium bromide to *o*-anisic acid by use of $^{14}CO_2$; (*b*) reduction of *o*-anisoyl chloride to *o*-methoxybenzaldehyde; and (*c*) demethylation of the aldehyde to [*carbonyl*-^{14}C]salicylaldehyde.

(*a*) A solution of *o*-methoxyphenylmagnesium bromide in ether–benzene (1 : 1) was prepared under nitrogen from *o*-bromoanisole (4 g.) and magnesium (0·58 g.). The concentration of the resulting solution was found by titration to be 0·268M, corresponding to a 91% yield of the Grignard reagent.

The carboxylation of 25-ml. samples of this solution was carried out in a vacuum-apparatus similar to that described by Dauben, Reid, and Yankwich (*Analyt. Chem.*, 1947, **19**, 828), the carbon dioxide being generated from active barium carbonate (25 μc). For efficient stirring during carboxylation, a modification of the stirrer described by Joseph (*Ind. Eng. Chem. Anal.*, 1937, **9**, 212) was used. Carboxylation was complete within 20—30 min. The mixture was then hydrolysed with dilute hydrochloric acid and ice, and the ethereal layer extracted six times with 5% sodium hydrogen carbonate solution. On acidification white crystals of *o*-anisic acid were obtained in 60% yield based on barium carbonate.

(*b*) The acid chloride was then prepared by refluxing the *o*-anisic acid with purified thionyl chloride for 5 hr., the excess of thionyl chloride being removed under reduced pressure. The acid chloride was reduced to the aldehyde by means of the apparatus and procedure described by Reid and Jones (*J. Biol. Chem.*, 1948, **174**, 427), the reaction being followed by the evolution of hydrogen chloride, which was passed through standard alkali. The yield of aldehyde obtained in the active preparation was 71% of the theoretical.

(*c*) The active *o*-methoxybenzaldehyde was demethylated by Prey's method (*Ber.*, 1942, **75**, 445) : it was refluxed at 200° for 45 min. with dry pyridine hydrochloride (1·3 g.), and the hot solution then poured with rapid stirring into 2N-hydrochloric acid (40 ml.). The resultant solution was extracted with ether, and the ethereal layer extracted with aqueous potassium hydroxide solution. The final active product was obtained in ethereal solution by acidification of the alkaline extract and extraction with ether. The yield of salicylaldehyde in pilot runs was 30—45% as estimated by formation of the 2 : 4-dinitrophenylhydrazone. Thus the overall yield was approximately 18% based on barium carbonate. All other methods of demethylation resulted only in resin.

The solution for use in exchange experiments was obtained by the addition of 3 g. of pure non-active salicylaldehyde to the final ethereal extract.

Preparation of the Active Ligands.—The active Schiff's bases of salicylaldehyde with ethylenediamine and *o*-phenylenediamine were prepared in 95% yield from concentrated alcoholic solutions of the aldehyde and the corresponding diamine. The other Schiff's bases were not isolated, but were prepared in solution in the required solvent by the addition of the estimated quantities of the various amines to the aldehyde solution.

Separation Procedures.—Four slightly different procedures were employed.

(*a*) From the pyridine solution of bis-salicylaldoximenickel and active salicylaldoxime, the complex was precipitated by addition of excess of water, filtered off, and washed with alcohol. The free salicylaldoxime was then precipitated with nickel acetate solution.

(*b*) Bis-salicylaldiminenickel and bis-*N*-methylsalicylaldiminenickel were separated from their respective free ligands by dilution with sodium chloride solution. The filtrate was acidified, and the free ligands were precipitated as the 2 : 4-dinitrophenylhydrazone, which was filtered off and washed.

(*c*) Salicylaldehyde-ethylenedi-imine was separated from the nickel complex by addition of a limited amount of water. After the free Schiff's base had been filtered off, excess of water was added to the filtrate, precipitating the complex, which was washed with alcohol to remove any remaining traces of free ligand.

(*d*) Bis-salicylaldehyde-*o*-phenylenedi-iminenickel was precipitated from the pyridine solution (15 ml.) on the addition of a small volume of water (7·5 ml.). This precipitation was incomplete but sufficient to provide infinitely thick counting samples. On the addition of excess of water to the filtrate, a mixture of the free ligand and complex was precipitated, this being filtered off and discarded. The final filtrate was acidified, and the 2 : 4-dinitrophenylhydrazone of the free ligand precipitated.

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