Redistribution Reactions of Some Transition-metal Chelate Complexes. Part II.[1] Kinetics of Bidentate Ligand Exchange between Chelate Complexes of Nickel(II)

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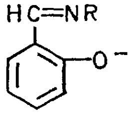
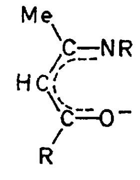
Redistribution reactions between the chelate complexes NiL_2 and ML_2' (M = Co, Ni, Cu, or Zn; L and L′ = bidentate salicylaldiminato- and β-ketoiminato-ligands or two different β-ketoiminato-residues) have been monitored using contact shifts in the ^1H or ^{19}F n.m.r. spectra. Kinetic data for reactions of half-life greater than a few minutes fit a rate law for a reversible reaction with second-order forward and reverse steps. Rate constants and some activation parameters are presented. Activation energies of 64—120 kJ mol^{-1} were observed. The rates of reaction are dependent on the nature of the substituent on the imino-nitrogen atom within any ligand series, α- and γ-substituents on the β-ketoiminato-ligand, aryl ring substituents on the salicylaldiminato-ligand, added pyridine, and the nature of the central metal atom (M = Co, Ni, Cu, or Zn). Reaction probably proceeds through bond interchanges in a preformed oxygen-bridged mixed dimer.

IN Part I,[1] details of equilibria observed in reactions of nickel chelate complexes NiL_2 and NiL_2' containing asymmetric bidentate ligands [equation (1)] were presented. The ligands L and L′ were of the salicylaldiminato-, (I), or β-ketoiminato-type, (II). The



(I); R = Pr^n, Pr, Bu^n, Bu^t, 1-Ethylpropyl, o-MeC_6H_4, and $MeO[CH_2]_3$



(II); R = Pr^i
R′ = Me, CF_3, or Ph

kinetics of these reactions have now been investigated, using as probe contact-shifted ^1H n.m.r. signals of the

$$NiL_2 + NiL_2' \rightleftharpoons 2NiLL' \qquad (1)$$

chelated ligands previously described,[1-4] and are presented in this paper. Very little kinetic information is available concerning the kinetics of such redistribution reactions, except where exchange is rapid enough to affect n.m.r. line-shapes or slow enough for a conventional kinetic analysis.[5] The latter technique could be applied in the systems studied here where L = (I), L′ = (II), or L = L′ = (II). However, when L = L′ = (I) the reactions were too fast for conventional analysis ($t_{\frac{1}{2}}$ *ca.* ≤10 min) but sufficiently slow for separate n.m.r. signals to be observed at all temperatures investigated. These will subsequently be referred to as fast reactions and were described in Table 1 of Part I. Some reactions took a number of hours to reach completion; these will be referred to as slow reactions.

EXPERIMENTAL

The materials were prepared as described in Part I.[1] Solutions for kinetic investigation were prepared in n.m.r. tubes as previously,[1] frozen in solid carbon dioxide, then inserted into the probe of the n.m.r. spectrometer which had previously been thermostatted at the temperature of the run. Spectra were recorded as soon as possible after insertion of the tube and subsequent spectra were recorded at appropriate time intervals until equilibrium was reached. A Bruker 90 MHz spectrometer with a variable temperature unit, calibrated with ethylene glycol, was used. The solvent tetrachloroethylene (liquid range 251—394 K) permitted the use of higher temperatures than did deuteriochloroform (liquid range 209—334 K), although the latter was used for mixtures [equation (1)] in which either NiL_2 and/or NiL_2' was insoluble in the former. Internal references were TMS (^1H) and $CFCl_3$(^{19}F).

Each recorded spectrum showed one signal from one of the reactants and the corresponding signal for the product (*e.g.* the separate α-methyl groups of β-ketoiminato-complexes NiL_2' and NiLL′) (Figure 1). The areas of these signals were obtained using a Dupont 310 electronic curve analyser and were reproducible within ±2%. Typical plots of concentration against time, kinetic analysis, Arrhenius plots, *etc.*, are to be found in Supplementary Publication No. SUP 20636 (21 pp., 1 microfiche).† Typical contact-shift temperature dependence plots also appear in the Supplementary Publication and refs. 2—4. The fast reactions observed in Part I (see also ref. 2) were not amenable to kinetic study since the present technique was inapplicable and the temperature of peak coalescence was not reached. For the mixture of complexes NiL_2 [L = (I); R = Pr^i] and NiL_2' [L′ = (I); R = 1-ethylpropyl] the separations of the signals for the 3-H and 5-H hydrogen atoms of the aryl ring (which appear to have the same chemical shift under most conditions) were δ = 21 Hz for L in the complexes NiL_2 and NiLL′ and δ = 198 Hz for L′ in those of NiLL′ and NiL_2', at 293 K in dry $CHCl_3$ solution.

RESULTS

All the reactions in Table 1 were found to obey the rate law for opposed second-order reactions. Equilibrium

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† For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are supplied as full size copies).

[1] Part I, J. C. Lockhart and W. J. Mossop, *J.C.S. Dalton*, 1973, 19; *Chem. Comm.*, 1971, 61.

[2] R. H. Holm, G. W. Everett, jun., and A. Chakravorty, *Progr. Inorg. Chem.*, 1966, **7**, 83.

[3] A. Chakravorty and R. H. Holm, *J. Amer. Chem. Soc.*, 1964, **86**, 3999.

[4] G. W. Everett and R. H. Holm, *J. Amer. Chem. Soc.*, 1965, **87**, 2117.

[5] J. C. Lockhart, 'Redistribution Reactions,' Academic Press, New York, 1970.

was approached only from the foward direction of equation (1), since in no instance was the mixed complex separated.

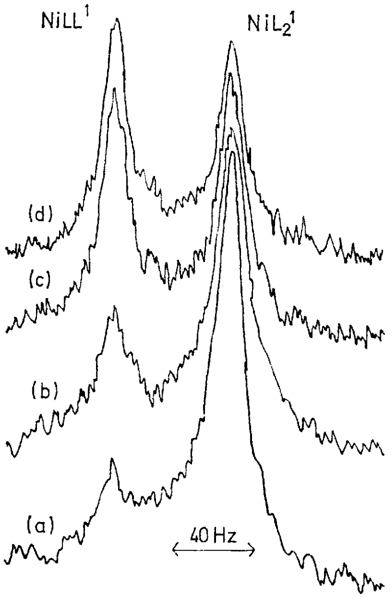
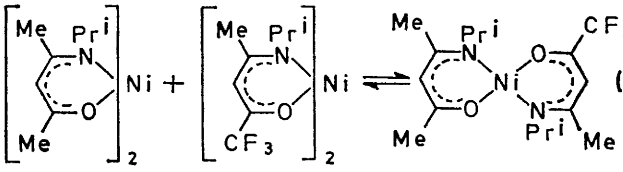


FIGURE 1 ^1H N.m.r. spectra for the α-CH_3 hydrogen atoms of L′ in the reactants and products of equation (1) where the complexes NiLL′ and NiL_2' [L = (I), R = Pr^i; L′ = (II), R = Pr^i] contain one and two α-CH_3 groups respectively. Recorded in C_2Cl_4 at 318·3 K (a), 12; (b), 46; (c), 147; and (d), 242 min after mixing

Usually equimolar quantities of the reactants were employed. The solubility of the substrates in the reaction described by equation (2) enabled us to run the reaction under pseudo-first-order conditions, employing ^{19}F n.m.r. spectra



(2)

to measure the concentrations of the fluorine-containing species. This reaction was shown to be first order in NiL_2' [L′ = (II); R = Pr^i, R′ = CF_3] and second order overall. Arrhenius plots were drawn by the method of least squares and activation parameters calculated.

It was possible to check the effect on the rate constant of the following features: (*a*) the gross variation in ligand from salicylaldimine to (II; R = Pr^i, R′ = Me, CF_3, or Ph); (*b*) lesser variations in the ligand including the bulk of the substituent on the imino-nitrogen atom and aryl ring substitution in the salicylaldiminato ligands; (*c*) added pyridine; and (*d*) change of the central metal atom. Since the effect of these variations on the geometrical and electronic structure of the reactants is well understood,[2-4,6,7] the effect of reactant structure on the rate of reaction can also be determined from the data and such items as (*e*) the stereochemistry of the nickel atom, (*f*) the tendency of the NiL_2 or NiL_2' complex to associate, and (*g*) the alternative tendency for π-bonding to the nickel atom have been considered. Experimental results concerning (*a*)—(*f*) can be found in Table 1 (see also ref. 1).

(*a*) Reactions between a complex containing β-ketoiminato-ligands and those containing salicylaldiminato- or other β-ketoiminato-ligands were usually of measurable rate, while reactions between two complexes containing salicylaldiminato-ligands were usually fast. Certain exceptions to these generalities must be made where no apparent reaction occurred and hence no rate constant was available for comparison (Table 2). (*b*) The substituent on the imino-nitrogen atom was varied within the salicylaldiminato-series and the reaction was faster when R was a secondary rather than a tertiary alkyl group. This may be a steric effect.[3] Reactions in which R = Ph or *o*-tolyl appeared to provide an example of steric hindrance to reaction, since substituted aniline complexes reacted very rapidly but no reaction of substituted *o*-toluidine complexes was found. We cannot say whether this is a kinetic or a thermodynamic effect. 5-Methyl substitution on the salicylaldehyde aromatic ring did not have a marked effect. (*c*) The rate constant and activation parameters were effected when the reaction [equation (2)] was carried out in the presence of pyridine (see Table 1). (*d*) The

TABLE 1

Summary of kinetic data

	Reactant											
	NiL_2			NiL_2'								
Solvent	L	R	R′	L′	R	R′	E_a [a] kJ mol⁻¹	E_a' [a] kJ mol⁻¹	$\Delta S_{298}^{\ddagger}$ [b] J K⁻¹ mol⁻¹	$\Delta S_{298}'^{\ddagger}$ [b] J K⁻¹ mol⁻¹	k_{303} * l mol⁻¹ s⁻¹	k_{303}' * l mol⁻¹ s⁻¹
C_2Cl_4	(I)	Bu^t	*c*	(II)	Pr^i	Me	100	101	+8·8	+4·1	$4{\cdot}8 \times 10^{-4}$	$1{\cdot}14 \times 10^{-4}$
C_2Cl_4	(I)	Bu^t		(II)	Pr^i	Me	106	115	+28	+38	$2{\cdot}7 \times 10^{-4}$	$2{\cdot}4 \times 10^{-5}$
C_2Cl_4	(II)	Pr^i	CF_3	(II)	Pr^i	Me	64		−95		$1{\cdot}71 \times 10^{-3}$	
C_2Cl_4	(II)	Pr^i	CF_3	(II)	Pr^i	Me [d]	89	79	−8·8	−53	$2{\cdot}7 \times 10^{-3}$	$6{\cdot}8 \times 10^{-4}$
$CDCl_3$	(II)	Pr^i	Ph	(I)	1-Ethylpropyl		118	117	+59	+46	$9{\cdot}9 \times 10^{-5}$	$3{\cdot}1 \times 10^{-5}$
$CDCl_3$	(II)	Pr^i	Ph	(I)	Bu		226	209	+437	+361	$1{\cdot}17 \times 10^{-3}$	$1{\cdot}13 \times 10^{-4}$
$CDCl_3$	(II)	Pr^i	Ph	(II)	Pr^i	CF_3 [e]					$4{\cdot}3 \times 10^{-4}$	$8{\cdot}4 \times 10^{-5}$
C_2Cl_4	(II)	Pr^i	Me	(I)	1-Ethylpropyl						$3{\cdot}7 \times 10^{-3}$	$3{\cdot}8 \times 10^{-3}$
C_2Cl_4	(II)	Pr^i	Me	(I)	Pr^i						$6{\cdot}0 \times 10^{-3}$	$6{\cdot}3 \times 10^{-3}$

* The rate constants k_{303} and k_{303}', and their associated activation parameters, correspond to the forward and reverse reactions, respectively, in equation (1).

[a] ±10 kJ mol⁻¹. [b] ±30 J K⁻¹ mol⁻¹. [c] Me substituted at the 5-position of the aryl ring. [d] Pyridine added. [e] *k* and *k*′ at 322 K.

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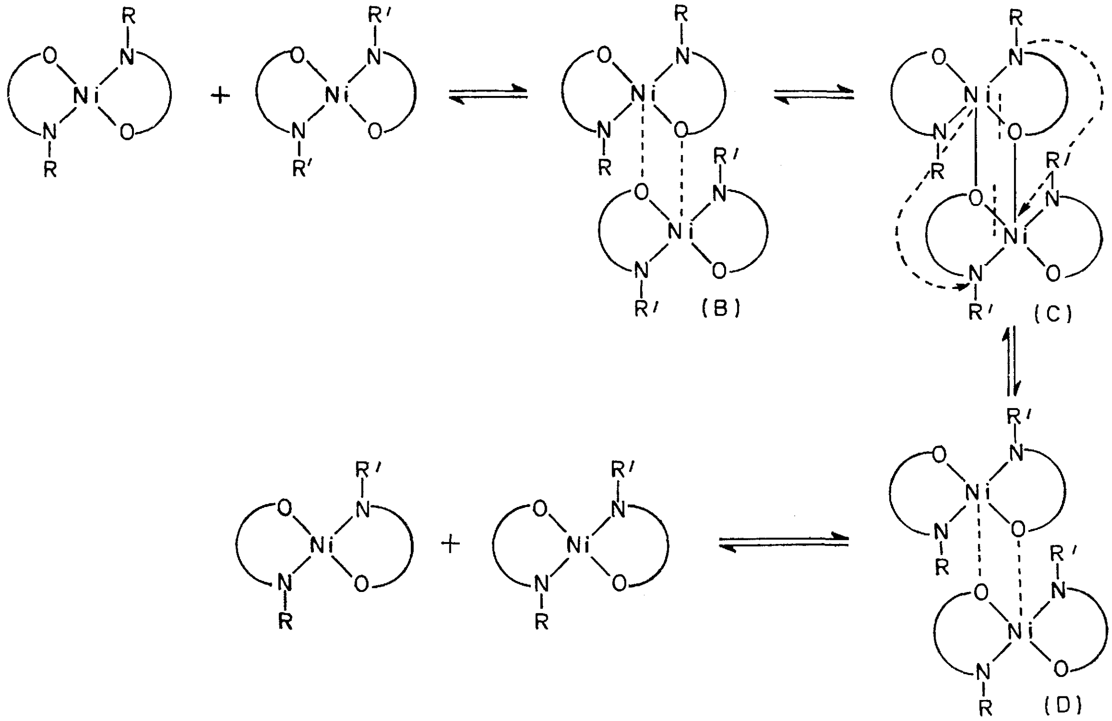
[6] R. H. Holm and T. L. McKinney, *J. Amer. Chem. Soc.*, 1960, **82**, 5506.

[7] R. H. Holm, *J. Amer. Chem. Soc.*, 1961, **83**, 4683.

order of the tate of reaction between salicyclaldiminato-complexes of two different metals [Ni and M = Co, Ni, Cu, or Zn, equation (3)] was Co, Ni > Cu ~ Zn.

$$NiL_2 + ML_2' \rightleftharpoons NiLL' + MLL' \qquad (3)$$



SCHEME

Measurably slow reactions involved at least one β-keto-iminato-complex which was fully tetrahedral.* Amongst the reactions which did not proceed (Table 2) were confrontations between a fully square-planar and a fully tetrahedral system [(i), (ii), (v), (ix), and (x)]. At least one of these reactions (see Part I) does not proceed for thermodynamic reasons.[1,3] The lack of reactivity of the fully tetrahedral or associated systems [(iii), and (vi)—(viii)] may be different in origin. Relevant structural differences between the salicylaldiminato- and β-ketoiminato-ligands appear to be (*f*) for the former and (*g*) for the latter, which do not associate.[2-4] The slow reactions involve at least one complex for which negligible self-association occurs, thus the extent of association to give an aggregate containing both complexes may be important in the mechanism. Alternatively the N–Ni π-bonding in the β-keto-iminato-complexes is *ca.* 3/2 times stronger than that in the salicylaldiminato-complexes,[4] so that Ni–N bond-fission may be a decisive feature of the mechanism. Both these factors must feature in any logical sequence proceeding from reactants to products. The extent of aggregate formation for several salicylaldiminato-complexes has been measured by magnetic and u.v. measurements, and molecular-weight determinations in a variety of solvents and conditions.[2-4,6,7] However it is the extent of mixed-dimer formation (B or D in the Scheme) which is relevant to the proposed mechanism and we were unable to devise any technique for measuring this, since the mixed complex NiLL′ could not be isolated.

DISCUSSION

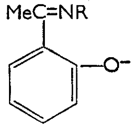
Two Ni–O and two Ni–N bonds must be broken and four similar bonds formed to produce the mixed complex

TABLE 2

Mixtures in which no reaction (1) was observed after several days at room temperature. Complexes NiL_2 and NiL_2' have a pseudo-tetrahedral structure in solution unless otherwise stated

	NiL_2			NiL_2'		
Mixture	L	R	R′	L′	R	R′
(i)	(I)	Pr^n	*a*	(II)	Pr^i	Me
(ii)	(I)	Pr^n	*a*	(II)	Pr^i	CF_3 [b]
(iii)	(II)	Pr^i	Me	(II)	Pr^i	Ph
(iv)	(I)	Bu^t		(II)	Pr^i	CF_3 [c]
(v)	(I)	Bu^n	*a*	(I)	Bu^t	
(vi)	(I)	Bu^t		(I)	$MeO[CH_2]_3$	*d*
(vii)	(I)	Bu^t		(III)	Pr^n	*a*
(viii)	(II)	Pr^i	Me	(III)	Pr^n	*a*
(ix)	(I)	*o*-MeC_6H_4		(II)	Pr^i	Me
(x)	(I)	*o*-MeC_6H_4		(I)	Bu^t	

[a] Complex is square planar. [b] Addition of pyridine (which changes the geometry of the nickel complexes) caused this reaction to proceed rapidly. [c] Addition of free ligand causes the reaction to proceed. [d] Complex is associated.



(III)

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* The variation of the contact shift with temperature (shown in the Supplementary Publication for some of the complexes) indicates the essentially tetrahedral character of complexes of the β-ketoiminato-series in C_2Cl_4, as previously established by Everett and Holm [4] for the solid state and $CDCl_3$ solutions.

[equation (1)], so it is probable that more than one step is required in the mechanism. However the kinetics appear simple and to require only one rate-determining step. Since the activation energy is high, this step is likely to be a bond fission, probably concerted. Activation entropies are not very helpful, ranging from positive to negative values (Table 1) which suggests a multistep mechanism with different emphases on the different steps for each reaction. From the rate law, we expect an associated species to form in both forward and reverse directions. This species could be the activated complex A) (Figure 2), or there could be two similar intermediates [(B) and (D)] one to the left and one to the right of the reaction co-ordinate. Rate-determining association to give (A) should result in an unfavourable entropy (neglecting solvation which is not expected to be strong in C_2Cl_4). The observed entropies are thus probably composite and suggest pre-equilibria. No intermediate was detected in the n.m.r. spectra.* We thus suggest an intermediate of low stability, formed in a very fast pre-equilibrium, which proceeds slowly to the product. Associated salicylaldiminato-nickel species are known, in both dimeric [2,7] and axially distorted octahedral polymeric forms, with the donor oxygen atoms acting as bridges between the nickel atoms. In solution, even at low temperatures, the reversible formation of such aggregates from monomeric complexes is extremely rapid, since no separate n.m.r. signals can be seen for different aggregates.[3,4] Aggregation in itself is then a rapid process and hence Ni–O bridge-bond formation and fission are also fast.

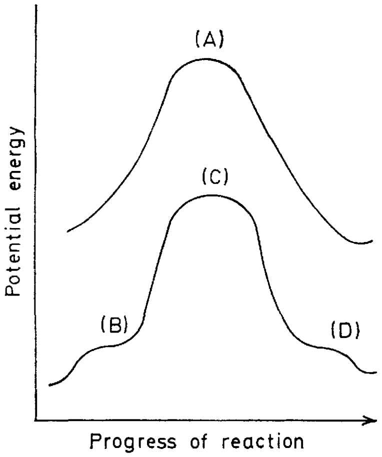

FIGURE 2 Possible reaction paths: lower curve involving O-bonded dimeric intermediates (B) and (D); upper curve for one-step reaction with the activated complex (A)

While the formation of an intermediate of the type proposed is a feasible first step, it does not provide a sufficient route for ligand exchange (see Scheme). The intermediate may hold the reactants in position for the rate-determining step, which probably involves fission (again possibly concerted) of a Ni–N bond. This mechanism provides two explanations for the slow reactions of β-ketoiminato-complexes: (i) the thermodynamic reluctance to form the intermediate (B); and (ii) the kinetic reluctance to break the Ni–N bond. A reaction scheme similar in outline has recently been proposed for the exchange of dithiolato-ligands on nickel and other metals, in one case purely as speculation [8] and in the other with kinetic and structural evidence.[9] We have not considered any mechanism in which one-ended dissociation of the ligand occurs. This possibility seems very remote in such an inert solvent as C_2Cl_4 and would involve the unknown co-ordination number of three for Ni^{II}, so that any dissociative step is considered to be concerted.

Pyridine accelerated the reaction and as the activation parameter E_a increased, an increase in ΔS must have occurred. Clearly pyridine must have a strong effect on association, which it effectively prevents by complexing with the reactant. It was noteworthy that one reactant was always a stronger Lewis acid for pyridine, so that added pyridine in small quantities was always preferentially complexed to one of the three entities present (in this case NiL_2 rather than $NiLL'$). The increase in activation energy observed must be that required by further bond-breaking. This could occur *via* dissociation to free pyridine and the complex NiL_2, a process which would account for the increases in ΔS and E_a.

We thank the S.R.C. for a research studentship (to W. J. M.), Dr. A. K. Covington for the use of a Dupont Curve Resolver, and Mr. J. A. W. Akitt for helpful discussion.

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* The signals for any complex NiL_2 were shifted (a few Hz) in mixtures [equation (1)] as opposed to simple solutions of NiL_2. This could be due to a slight contribution to the shift from a rapidly equilibrating mixed aggregate (NiL_2NiL_2') in addition to the usual shift associated with the aggregate $(NiL_2)_n$. However the dependence of contact shifts on the reciprocal of the absolute temperature indicated no aggregate could be present in any concentration, except in systems containing L = (I) (R = Ph) (see Supplementary Publication).

[8] A. L. Balch, *Inorg. Chem.*, 1971, **10**, 338.

[9] A. Hermann and R. M. Wing, *Inorg. Chem.*, 1972, **11**, 1415.