Redistribution Reactions of Some Transition-metal Chelates. Part I. Thermodynamics of Bidentate Ligand Exchange between Nickel(II) Chelates

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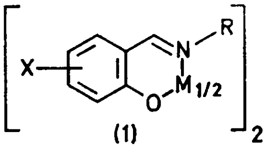
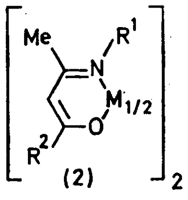
The redistribution reaction between chelates NiL^1_2 and NiL^2_2 to give NiL^1L^2 where L^1 and L^2 are bidentate salicylaldimine or β-keto-imine residues has been monitored by use of contact shifts in the ^1H or ^{19}F n.m.r. spectra of the chelates. Equilibrium constants, enthalpies, and entropies for the redistribution are presented for several systems. The mixed compound is in general formed in less than statistical amount, enthalpies of redistribution then usually being positive. This unusual result is discussed in relation to previous work. In a number of systems no reaction was observed. The redistribution between NiL^1_2 and ML^2_2 (where M is Cu, Zn, or Co) has also been examined. These reactions have shed light on the reason for non-reactivity of the bis-(*N*-n-propylsalicyaldiminato)nickel(II)–bis-(*N*-t-butylsalicylaldiminato)nickel(II) system.

THIS series will be concerned mainly with studies of equilibria such as (1), where $L^1 \neq L^2$ are bidentate ligands. Most of the compounds used were of types (1) and (2). Structural information for these compounds in solution is plentiful.[1-3] A most useful property is the paramagnetism which gives rise to contact shifts [4] in the n.m.r. spectra of complexes (1) and (2) (where these have any tetrahedral character). Whereas the n.m.r. spectrum of the diamagnetic ligand covers a range of 10 p.p.m. the spectrum of the co-ordinated ligand may cover a range of 250 p.p.m., effectively providing a non-linearly expanded spectrum of the ligand. Thus quantitative analysis of the reactants and products in equation (1)


(1)


(2)

$$NiL^1_2 + NiL^2_2 \rightleftharpoons 2NiL^1L^2 \qquad (1)$$

[(NiL^1_2, NiL^2_2 = (1) or (2)] which would be difficult in diamagnetic systems can be achieved by use of n.m.r. signal areas as a measure of concentration.[5] We have used this method of analysis to determine the kinetics and thermodynamics of a number of redistribution reactions [6] such as (1) and some thermodynamic results are discussed. A preliminary account has appeared.[5]

The redistribution shown in equation (2) has also been examined where M is Co, Cu, or Zn. A third equilibrium (3) together with equations (1) and (2) is necessary to

$$NiL^1_2 + ML^2_2 \overset{K_2}{\rightleftharpoons} NiL^2_2 + ML^1_2 \qquad (2)$$

describe the mixed-metal reaction completely. Although there are six components in the mixture we were

$$ML^1_2 + ML^2_2 \overset{K_3}{\rightleftharpoons} 2ML^1L^2 \qquad (3)$$

able to monitor only the nickel compounds by contact shift spectra. The presence of other components was inferred from mass-spectral analyses and material balance or (for diamagnetic zinc compounds) unshifted n.m.r. signals.

EXPERIMENTAL

Preparation of Complexes.—All the complexes were prepared by previously published procedures, the β-keto-imine derivatives by a non-aqueous chelation procedure,[3] and the salicylaldimines by the reaction of preformed metal salicylaldehydate with amine.[1,2]

Redistribution Studies.—To a weighed mixture of two solid reactants was added a known volume of solvent from an Agla micrometer syringe. After dissolution the reaction mixture was transferred to an n.m.r. tube and cooled to −78 K. The tube was sealed and transferred to the n.m.r. spectrometer, adjusted to the appropriate temperature. Spectra were recorded as soon as possible. For slow reactions (which took up to 30 h to reach equilibrium) spectra were recorded at intervals until equilibrium was reached. For fast reactions, which reached equilibrium before the first spectrum was recorded, spectra were measured at a minimum of five temperatures in the range 290—380 K. Normally two or three ' equilibrium ' spectra were measured at each temperature. All n.m.r. spectra were recorded in tetrachloroethylene or deuteriochloroform, relative to Me_4Si or $CFCl_3$, with a Bruker Spectrospin HFK-6 instrument. N.m.r. signal areas were integrated with the aid of a Dupont 310 Curve Analyser. Preliminary studies showed that signal area could be used as a measure of concentration for the NiL^1_2 and NiL^2_2 complexes and the same is assumed for NiL^1L^2 complexes which cannot in general be isolated. Reactions were normally run at several different initial concentrations and with equimolar ratios of reagent. The concentration range (*ca.* 10^{-1}—10^{-2}M) was limited on the one hand by the solubility of the reagents and on the other by the resolution possible with the n.m.r. instrument.

RESULTS

Three categories of equation (1) were studied, arbitrarily distinguished thus: (i) fast reactions (complete in less than 5 min), (ii) slow reactions (for which equilibrium was reached in longer periods), and (iii) systems for which no reaction could be detected by the n.m.r. technique described.

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The thermodynamic parameters for equilibrium (1) in both fast and slow systems (i) and (ii) are in Table 1.

Values of the equilibrium quotient $K_1 = [NiL^1L^2]^2/([NiL^1_2][NiL^2_2])$ were determined at several different temperatures and the values quoted (all at 298 K) were obtained graphically from a ' least-squares ' treatment of the plot of log K against the reciprocal of the temperature. From the slope of this plot values of the enthalpy (Table 1) were obtained. The values of ΔS were obtained from the second law. The errors in peak measurement are of the order ±4% and lead to large errors in the value of K which lie within the limits ±20%. The errors in ΔH and ΔS quoted in Table 1 were obtained from the least-squares analysis.

TABLE 1

Thermodynamic parameters for equation (1) in C_2Cl_4 solution (unless otherwise noted)

	NiL^1_2			NiL^2_2					
	R^1	X or R^2		R^1	X or R^2	K_1 [a] (298 K)	ΔH / kJ mol^{-1}	ΔS / J mol^{-1} K^{-1}	
(1)	Bu^t	H	(2)	Pr^i	Me	13	−2·8 ± 3	12 ± 9	S [d]
(1)	Bu^t	H	(2)	Pr^i	Ph	8·2	−2·2 ± 2	10 ± 10 [b]	S
(2)	Pr^i	CF_3	(2)	Pr^i	Me	4	−0·1 ± 0·5	11·2 ± 2 [b,c]	S
(1)	Bu^t	5Me	(2)	Pr^i	Me	3·6	1 ± 3	13 ± 9	S
(1)	Et_2CH	H	(2)	Pr^i	Ph	3·6	−1 ± 3	7 ± 9 [b]	S
(1)	Bu^t	H	(1)	Pr^i	H	1·44	5·5 ± 2	21 ± 7 [b]	F
(1)	Pr^i	H	(1)	Pr^n	H	1·32	18 ± 9	62 ± 25	F
(1)	Bu^t	H	(1)	Pr^i	4Me	1·2	5·2 ± 2	19 ± 15	F
(1)	Et_2CH	H	(2)	Pr^i	Me	0·82	11 ± 1·6	35 ± 15	S
(1)	Pr^i	H	(2)	Pr^i	Me	0·80	13 ± 3	42 ± 9	S
(1)	Bu^t	H	(1)	Et_2CH	H	0·62	5·5 ± 1	14·5 ± 10	F
(1)	Bu^t	H	(1)	Pr^i	3MeO	0·16	15 ± 2	38 ± 17	F
(1)	Bu^t	H	(1)	Ph	H	0·13	28 ± 4	77 ± 15 [b]	F
(1)	Ph	H	(2)	Pr^i	Me	0·087	38 ± 1	107 ± 3 [b]	F

[a] These values are calculated from total concentrations of a particular compound in all its stereochemical forms present in solution (*i.e.*, square planar, tetrahedral, and associated). Only for the first four reactions in the Table does this represent equilibrium between three compounds of the same (tetrahedral) geometry. In principle two values of K_1 (K_1 tetrahedral and K_1 planar) could be obtained for each of the other systems but in practice it is not possible to establish the percentage of tetrahedral geometry present in the mixed compounds since these cannot be isolated directly. [b] $CDCl_3$ solution. [c] Data obtained at two temperatures only. [d] S, slow, F, fast reaction.

Table 2 lists systems which gave no detectable reaction.

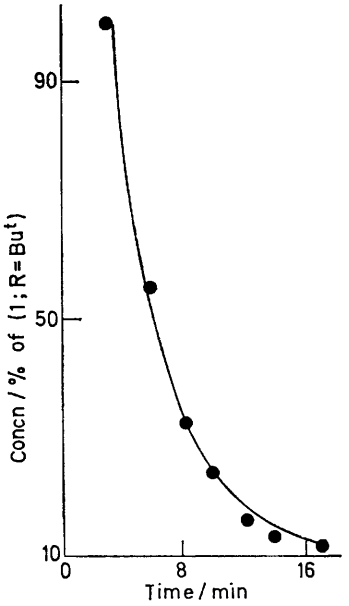
TABLE 2

Mixtures in which no reaction according to equation (1) was observed after several days at room temperature [a]

	NiL_2^1			NiL_2^2	
	R^1	X or R^2		R^1	X or R^2
(1)	Pr^n	H	(2)	Pr^i	Me
(1)	Pr^n	H	(2)	Pr^i	CF_3 [b]
(2)	Pr^i	Me	(2)	Pr^i	Ph
(1)	Bu^t	H	(2)	Pr^i	CF_3 [c]
(1)	Bu^n	H	(1)	Bu^t	H
(1)	Bu^t	H	(1)	$MeO\cdot[CH_2]_3\cdot$	H
(1)	Bu^t	H	(3 [d])	Pr^n	H
(2)	Pr^i	Me	(3 [d])	Pr^n	H

[a] No reaction after heating to 360 K for several hours. These reactions however occurred in the mass spectrometer, since parent ions corresponding to NiL^1L^2 were observed for every mixture. [b] Addition of pyridine (which changes the geometry of the nickel complexes) caused this reaction to proceed rapidly. [c] Addition of free ligand causes reaction. [d] (3) = Square planar nickel chelate of *N*-(n-propyl)-*o*-hydroxyacetophenone-imine.

Mixed-metal Reactions.—The reactions were investigated in $CDCl_3$ solution by the method outlined above and were too fast for kinetic studies. In some cases an approach to equilibrium could be followed (*e.g.*, see Figure). In this reaction the t-butyl group of *N*-t-butylsalicylaldiminato-nickel compounds gave suitable ^1H n.m.r. signals and was used to monitor the reaction which took *ca.* 20 min to come to completion. The systems can be characterised by three independent equilibrium constants K_1, K_2, and K_3. It is possible to determine K_1 for the all-nickel equilibrium [equation (1)] and the values of K_1 agree quite well with values for the system (1) in isolation. For the nickel–copper and nickel–cobalt systems it was not possible to determine the areas of the signals due to copper or cobalt compounds since the signals were very broad. The zinc complexes are diamagnetic and by material balance the concentrations of each ligand on zinc could be found. The resolution was insufficient for K_3 to be determined, and a value of 4 (statistical value) was assumed in order to calculate K_2, the intersystem equilibrium constant. Table 3 contains the equilibrium constants.



Plot of concentration against time for NiL_2 = (1; R = Bu^t) in system *A*, bis-(*N*-t-butylsalicylaldiminato)nickel(II) and bis-(*N*-n-propylsalicylaldiminato)zinc(II) in $CDCl_3$ at 303 K

A qualitative order of reaction rates was observed and this was D and $E > A > C \approx B$ (see Table 3 for labelling).

TABLE 3

Equilibrium constants obtained from studies of mixed-metal systems [equation (2)]; NiL_2 = (1; R = Bu^t, X = H)

(1) = ML^2_2

	M	R	X	K_1	K_2	T/K
A	Zn	Pr^n	H	$6 \cdot 9 \times 10^{-3}$	$0 \cdot 5$ [a]	303
				$2 \cdot 6 \times 10^{-2}$		332
B	Zn	Pr^i	H	1·9		
C	Cu	Pr^i	H	1·5		303
D	Co	Pr^i	H	2·0		303
E	Ni	Pr^i	H	1·5		303

[a] This was estimated assuming the zinc exchange to be random with $K_3 = 4$.

Mass Spectra.—The presence of all components in equations (1)—(3) was demonstrated in mass spectra of mixtures. The mixture of bis-(N-n-propylsalicylaldiminato)zinc and bis-(N-t-butylsalicylaldiminato)nickel had as major parent ions the products of equation (2), but the mixed species [equations (1) and (3)] and starting materials of equation (2) were in very small abundance. Although ion abundance cannot be taken as a direct measure of concentration, these observations are in accord with a highly non-random reaction, suggested also by the solution n.m.r. studies.

U.v. Spectra.—The cobalt–nickel mixed metal system was examined by u.v. spectroscopy. Although there was a change in the spectrum, overlap of peaks prevented quantitative analysis.

DISCUSSION

Table 1 shows a variation of 10^2 in the values of K^{298} for individual reactions. All but three of the K^{298} values are less than the statistical value $K_1 = 4$. We discuss these low values first. The corresponding enthalpies are in general positive and unfavourable to the mixed NiL^1L^2 compound. The entropy gain for equation (1) from statistical considerations should be $+11 \cdot 6$ J K^{-1} but the experimental results are in general more positive than this value, which tends to stabilise NiL^1L^2 opposing the effect of the positive enthalpy. It is exceptional to find a system in which the mixed compound is not favoured. Only a few instances have been recorded.[6,7]

Very few data have been available concerning exchange of bidentate ligands. Holm and his co-workers supposed the exchange of bidentate salicylaldimines on nickel to be random,[8] while the exchange of dithiolates on nickel gave more product than expected on statistical considerations.[9] Exchange of β-diketonate ligands has been studied on aluminium [10] and gallium [11] (six-co-ordinate) and zirconium [12,13] and hafnium (eight-co-ordinate).[13] In the six-co-ordinate systems reactions involving two β-diketonates with simple alkyl substituents (*e.g.*, acac,* tmhd *) were approximately random but if one ligand contained fluorinated alkyl groups (hfac) exchange was very strongly in favour of the mixed compound. The enthalpy [11] in the reaction [equation (4)] was $-17 \cdot 2 \pm 3$ kJ mol^{-1} and the entropy $0 \cdot 4 \pm 10$ J K^{-1}. In contrast the eight-co-ordinate zirconium and hafnium compounds $M(acac)_4$ and $M(tfac)_4$ gave slightly more than the statistical amount of mixed compounds: the enthalpies for the Zr systems were found to be nearly zero, but the entropies were greater than expected.[12] The co-ordination number of the central atom seems to be important in determining the enthalpy of these processes. Exothermic reactions are the usual pattern for non-random redistributions and can be interpreted in terms of increased bond energies in the mixed compounds (a synergic effect). In the six-co-ordinate compounds this reinforced (synergic) bonding occurs when two different ligands (acac and hfac) are bound to the same central atom, but synergism is not evident in the eight-co-ordinate compounds. There has been no comparable study of asymmetric bidentate ligands such as the systems examined here. Our finding of unfavourable enthalpies suggests that far from being reinforced, bonds are relatively weaker in the mixed nickel salicylaldimine complexes. Since the ligands are asymmetric O,N donors, the reinforced bonding associated with the presence of ligands of different bonding capabilities may already operate in the starting materials (1) (NiL^1_2), and be destroyed in the mixed compound NiL^1L^2. This finding is extremely important, since the construction of mixed-ligand catalyst systems of enhanced reactivity is a current synthetic aim.[14,15] Extensive redistribution studies for a variety of multidentate ligands and central atoms of different stereochemistry are needed. At present, trends in redistribution chemistry are documented mostly for monofunctional substituents on Main Group elements.[6,7] There has been a somewhat different approach to the problem of mixed-ligand complexes, which can however yield information similar to that from redistribution studies.[14] Extensive studies of formation constants for mixed-ligand complexes of copper indicate reinforced bonding.[14,15]

$$\tfrac{1}{3}Ga(acac)_3 + \tfrac{2}{3}Ga(hfac)_3 \rightleftharpoons Ga(hfac)_2(acac) \quad (4)$$

Effect of Substitution.—Reactions within the salicylaldimine series [equation (1), NiL^1_2, NiL^1_2 = (1)] show only a tenfold variation in K_1 [200-fold if the reaction in Table 3 of (1; R = Pr^n) is included]. Substituents X on the aryl ring of (1) and substituents R on nitrogen have significant effects. If NiL_2 = (1; R = Bu^t) is

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* acac = Acetylacetonate; tmhd = tetramethylheptanedionate; hfac = hexafluoroacetylacetonate; and tfac = trifluoroacetylacetonate.

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taken as reference compound, exchange deviates most from random for NiL^2_2 = (1; R = Ph or Pr^n). We can also compare the reactions of a set of complexes with NiL_2 = (2; R^1 = Me, R^2 = Pr^i) as reference. Fully tetrahedral complexes such as (1; R = Bu^t) and (2; R^2 = CF_3, R^1 = Pr^i) gave random or greater than random values of K and reaction (1) is exothermic. For other salicylaldimines, the reaction is endothermic, most particularly for R = Ph.

The variation of substituents R is known to have a critical effect on the geometry at the nickel centre.[1,4] Substituents X affect the geometry most when in the 3-position of the aryl ring. It is clear that the R substituents will to a first approximation determine the geometry of the mixed complex NiL^1L^2. Where the geometries of the starting compounds NiL^1_2 and NiL^1L^2 differ, the largest deviations from random behaviour are to be expected. The reactions which were found to give the greatest deviations were those (i) of square planar (1; R = Pr^n) with fully tetrahedral (1; R = Bu^t) to give a mixed complex with partial tetrahedral character, and (ii) of associated (octahedral?) (1; R = Ph) with fully tetrahedral (1; R = Bu^t) or (2; R^1 = Pr^i, R^2 = CF_3). The first three reactions in Table 1 with more favourable enthalpies are between compounds which are fully tetrahedral.

Nickel(II) in four-co-ordination has Lewis acid tendencies which are satisfied in two ways: (i) self-association *via* bridging ligands to increase the co-ordination number and (ii) π-bonding internally in the four-co-ordinate monomer. Series (1) has a stronger tendency for association, (2) for π-bonding. Contact shift measurements suggest that series (2; R^2 = Me, R^1 = Pr^i) are more strongly π-bonding by a factor of *ca.* 1·5 than series (1; R = Pr^i).[3] We suggest tentatively that ligands giving rise to π-bonding tetrahedral monomers can take part more effectively in synergic bonding. However when a ligand with associating tendencies is exchanged with a π-bonding ligand the mixed complex is less able either to associate or to π-bond and is thus unstable with respect to the starting complexes.

Mixed-metal Reactions.—One of the most obvious features of the nickel redistributions noted by Holm and his co-workers[8] is the failure of certain square-planar nickel complexes to react. We have noted (Table 2) a number of such systems which did not react even at high temperatures. The reason for Holm's observation (which we have confirmed) that *N*-n-propylsalicylaldiminatonickel(II) and *N*-t-butylsalicylaldiminatonickel(II) do not react became immediately clear from the reaction in the zinc–nickel system *A* (Table 3). Tetrahedral (1; R = Bu^t) does not appear to react with square planar (1; R = Pr^n) because the system is already in its most stable form. When the ligand *N*-n-propylsalicylaldimine is introduced [equation (3)] as its tetrahedral zinc chelate, the most stable nickel chelate (1; R = Pr^n) is formed. It appears that the two ligands (R = Bu^t, R = Pr^n) are about equally stable on zinc. The equilibrium constant for equation (1) has been obtained from the zinc–nickel system. The intersystem constant could be obtained from material balance if the assumption was made that $K_3 = 4$ for the zinc system [equation (3)].

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