

# Co-ordination of Solvent Molecules to Square-planar Mixed-ligand Nickel(II) Complexes: a Thermodynamic and Quantum-mechanical Study†

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Equilibria between four-, five- and six-co-ordinated substituted and unsubstituted  $[\text{Ni}(\beta\text{-dik})(\text{diam})]^+$  complexes associated with various solvents like acetonitrile, acetone, *n*-butanol, formamide dimethylformamide, dimethyl sulfoxide and pyridine have been investigated in nitroethane solution at 293 K. Increasing donor strength of the donor solvents (L) as well as increasing electron-withdrawing properties of the substituents at the  $\beta$ -diketonate ( $\beta\text{-dik}$ ) and the diamine ( $\text{diam}$ ) ligands favours the formation of six-co-ordinated species. The results are interpreted using correlations with IR, Hammett and electrochemical data, and results of semiempirical quantum-mechanical calculations carried out within an extended CNDO/2 framework. *cis-trans* Isomerism is proposed for  $[\text{Ni}(\beta\text{-dik})(\text{diam})\text{L}_2]^+$  due to the mechanism of stepwise co-ordination.

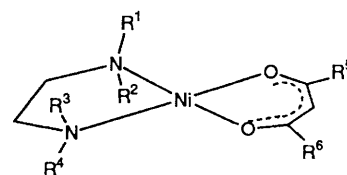
Detailed spectroscopic, thermodynamic and electrochemical studies on the solvato- and thermo-chromic behaviour of  $[\text{Ni}(\beta\text{-dik})(\text{diam})]\text{BPh}_4$  ( $\beta\text{-dik}$  =  $\beta$ -diketonate,  $\text{diam}$  = diamine) dissolved in 1,2-dichloroethane have been reported previously.<sup>1-3</sup> For the present investigations nitroethane is used because this medium shows stronger acceptor properties and might in comparison yield insight into the role of the diluting solvent with respect to complex formation.<sup>4,5</sup> Quantum-mechanical calculations on 'unsolvated and solvated species' of nickel(II) chelates have been performed in analogy to copper(II) complexes<sup>6</sup> to yield insight into the charge redistribution due to different substituents on the  $\beta$ -diketonate and on the diamine ligands, as well as to the solvating solvents.

## Experimental

**Chemicals.**—Reagents were obtained from Merck and Rathburn Chemicals. Mixed-ligand nickel(II) complexes with the  $\beta$ -diketonates and diamines were synthesised according to refs. 7 and 8. Solvents were purified according to standard procedures.<sup>9,10</sup> Acetone and pyridine were purified according to ref. 1. Nitroethane was distilled twice, dried over 3 Å molecular sieve and finally fractionated using a 1000 mm Vigreux column. The water content of the solvents was found to be below 30 mg l<sup>-1</sup> by means of Karl-Fischer titration (except for ketones).

**Measurements.**—Visible spectra were obtained with a Tracor Northern TN-1710 spectrophotometer from Photo-Applied Physics Corporation using a cell with a path length of 3 cm, thermostatted by means of a Haake F4 thermostat to 20 °C ( $\pm 0.05$  °C). The temperature within the cell was measured before and after recording the spectra. Far-IR measurements were made with a Nicolet 20F (FTIR) vacuum spectrometer with a TGS (room temperature) detector using polyethylene wafers. The data were collected with the Happ-Genzel apodization function.

To a  $3 \times 10^{-3}$  mol dm<sup>-3</sup> stock solution of the nickel



	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>	R <sup>5</sup>	R <sup>6</sup>
$[\text{Ni}(\text{acac})(\text{tmen})]^+$	Me	Me	Me	Me	Me	Me
$[\text{Ni}(\text{bzac})(\text{tmen})]^+$	Me	Me	Me	Me	Me	Ph
$[\text{Ni}(\text{dbm})(\text{tmen})]^+$	Me	Me	Me	Me	Ph	Ph
$[\text{Ni}(\text{tfacac})(\text{tmen})]^+$	Me	Me	Me	Me	Me	CF <sub>3</sub>
$[\text{Ni}(\text{dpm})(\text{tmen})]^+$	Me	Me	Me	Me	Bu <sup>†</sup>	Bu <sup>†</sup>
$[\text{Ni}(\text{acac})(\text{trmen})]^+$	Me	Me	Me	H	Me	Me
$[\text{Ni}(\text{acac})(\text{teen})]^+$	Et	Et	Et	Et	Me	Me
$[\text{Ni}(\text{acac})(\text{treen})]^+$	Et	Et	Et	H	Me	Me

complexes in nitroethane, the respective donor solvent (when necessary diluted with nitroethane) was added in a titration procedure. Up to ten recorded spectra were stored in a multichannel memory unit. The obtained spectral titration curves were fitted by means of a combined Marquardt Newton method<sup>11</sup> to evaluate  $K_1$  and  $K_2$  (see below).

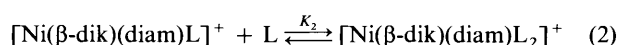
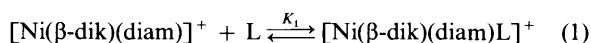
**Theoretical Methods.**—Quantum-mechanical calculations were performed within the usual CNDO/2-MO-SCF framework extended to include transition metals.<sup>12</sup> The input parameters have already been described.<sup>13</sup> Molecular geometries for the  $[\text{Ni}(\beta\text{-dik})(\text{diam})]^+$  chelates were taken from X-ray diffraction data for nickel(II) chelates.<sup>14</sup> For these calculations the co-ordinating solvent molecules have been assumed to attack the axial sites of the nickel(II) chelate.<sup>8,14,15</sup> Atomic charges were defined as  $Q = n - \sum P_{\lambda\sigma}$ , where the summation runs over all occupied atomic orbitals of the atom,  $n$  being the number of

† Non-SI unit employed: eV  $\approx 1.60 \times 10^{-19}$  J.

valence electrons in the atom. The  $P_{\lambda\sigma}$  are the elements of the density matrix,  $P_{\lambda\sigma} = \sum C_{i\lambda} C_{i\sigma}$ , where  $C_{i\lambda}$  and  $C_{i\sigma}$  are the coefficients of the atomic orbitals  $\lambda$  and  $\sigma$  in the occupied molecular orbital  $i$ . The complex  $[\text{Ni}(\text{dpm})(\text{tmen})]^+$  has not been calculated as a reliable geometry for the orientation of the Bu' substituents could not be obtained by experiment or by means of common optimisation methods.

## Results and Discussion

The square-planar species  $[\text{Ni}(\beta\text{-dik})(\text{diam})]^+$  absorb light at  $\lambda_{\text{max}} \approx 500$  nm when dissolved in nitroethane. This absorption decreases with addition of donor solvents, so that a titration procedure can be used to evaluate formation constants. A least-squares evaluation of the resulting titration curves shows that the co-ordination of donor solvent molecules (L) proceeds *via* a two-step process involving a five-co-ordinated intermediate [equations (1) and (2)].



The evaluated equilibrium constants  $K_1$  and  $K_2$  are listed in Table 1 with the exception of  $[\text{Ni}(\text{acac})(\text{teen})]^+$  where, due to steric hindrance, the equilibrium constants are too low to be measured exactly by the given methods. An isosbestic point near 600 nm holds for all nickel(II) complexes and for all donor solvents investigated. This is in agreement with the high ratio of  $K_2/K_1$  showing that the intermediate is only present in low concentrations. An exception is  $[\text{Ni}(\text{tfacac})(\text{tmen})]^+$  where the isosbestic point does not hold for all solvents. A deviating behaviour of this complex has been observed before<sup>3</sup> and might be explained by the high electron-withdrawing properties of the  $\text{CF}_3$  substituent leading to high stability constants, especially for some of the five-co-ordinated species. Owing to its different behaviour it should be considered separately and is therefore not included in the correlations depicted below.

Both formation constants,  $K_1$  and  $K_2$ , are found to be significantly lower for nitroethane solutions than the corresponding values obtained with 1,2-dichloroethane.<sup>1</sup> This may be attributed to the higher acceptor number of excess of nitroethane compared to 1,2-dichloroethane, leading to increased solvation of the added donor solvent.<sup>16</sup> The ratio  $K_2/K_1$  in nitroethane is lower than in 1,2-dichloroethane reflecting the higher stability of the five-co-ordinated intermediate in the former solution. In both solvents this intermediate is further stabilised by increasing donor strength of

the donor solvent. The same effect occurs on decreasing donor strength of the diamine and the  $\beta$ -diketonate ligands when electron-withdrawing substituents are present.<sup>1</sup>

The increase in  $K_1$  and  $K_2$  with increasing electron-withdrawing and decreasing electron-releasing effects of the substituent groups  $\text{R}^1\text{--R}^6$  can be seen from Hammett plots (Fig. 1). The logarithms of the formation constants ( $\log K_1$  or  $\log K_2$ ) are linearly related with the position of IR absorption frequencies assigned<sup>3</sup> to C=O stretching vibrations (see Fig. 2). The strength of the C=O bond in the ligand increases in the sequence  $[\text{Ni}(\text{dpm})(\text{tmen})]^+ < [\text{Ni}(\text{acac})(\text{treen})]^+ < [\text{Ni}(\text{acac})(\text{tmen})]^+ = [\text{Ni}(\text{acac})(\text{trmen})]^+ < [\text{Ni}(\text{bzac})(\text{tmen})]^+ < [\text{Ni}(\text{dbm})(\text{tmen})]^+ \ll [\text{Ni}(\text{tfacac})(\text{tmen})]^+$ , where  $\nu(\text{C}=\text{O})$  1555, 1569, 1578, 1578, 1585, 1591 and 1606  $\text{cm}^{-1}$ , respectively.<sup>3</sup> This is paralleled by the solvent association equilibria shifting towards the five- and six-co-ordinated species. The shift of  $\nu(\text{C}=\text{O})$  towards higher wavenumbers is in agreement with the predictions of the bond-length variation rules,<sup>17,18</sup> *i.e.* stronger co-ordination of the donor solvent molecules is associated with weakening of the Ni- $\beta$ -dik bonds. The changes in the electron distributions are also reflected in the redox behaviour of the complexes. An increase in  $K_1$  is related to a less negative potential for nickel(II) reduction [ $E_3$  was polarographically measured at a mercury electrode *versus* the bis(biphenyl)-chromium(I) iodide reference system<sup>2</sup>] (Fig. 3). The observed separation into two groups in Fig. 3 points to the occurrence of *cis-trans* isomerism as will be discussed below.

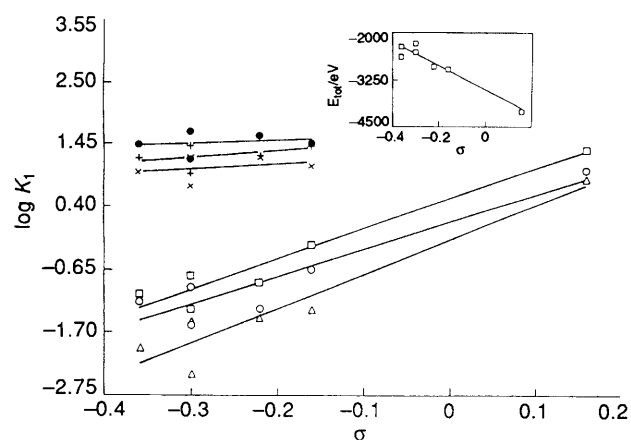


Fig. 1 Hammett plot of  $\log K_1$  in nitroethane solution at 20 °C. The insert shows the correlation between Hammett constants ( $\sigma$ ) and total energy ( $E_{\text{tot}}/\text{eV}$ ) for unsolvated nickel(II) chelates. Donor molecules:  $\text{Me}_2\text{SO}$  (●),  $\text{HCONMe}_2$  (+),  $\text{HCONH}_2$  (×),  $\text{MeCN}$  (□),  $\text{Bu}^o\text{OH}$  (○) and  $\text{Me}_2\text{CO}$  (△)

Table 1 Formation constants ( $\text{dm}^3 \text{mol}^{-1}$ ) of  $[\text{Ni}(\beta\text{-dik})(\text{diam})]\text{BPh}_4$  with various donor solvents in nitroethane at 293 K

Complex		MeCN	Me <sub>2</sub> CO	Bu <sup>o</sup> OH	HCONH <sub>2</sub>	HCONMe <sub>2</sub>	Me <sub>2</sub> SO	C <sub>5</sub> H <sub>5</sub> N
[Ni(acac)(tmen)]BPh <sub>4</sub> *	$K_1$	0.095	0.011	0.072	9.30	16.08	27.27	
	$K_2$	9.97	3.57	6.00	240.60	111.20	402	
[Ni(bzac)(tmen)]BPh <sub>4</sub> *	$K_1$	0.137	0.034	0.05	16.15	16.83	39.10	—
	$K_2$	17.03	1.24	5.95	334.6	497.2	1533	—
[Ni(dbm)(tmen)]BPh <sub>4</sub> *	$K_1$	0.552	0.048	0.22	11.25	26.7	28.0	—
	$K_2$	6.13	9.50	7.40	647.40	2299	2466	—
[Ni(tfacac)(tmen)]BPh <sub>4</sub>	$K_1$	23.24	6.51	9.17	$6.5 \times 10^6$	$2.1 \times 10^7$	$6.5 \times 10^9$	
	$K_2$	369.2	0.66	25.60	$5.5 \times 10^4$	$4.9 \times 10^4$	$8.9 \times 10^9$	
[Ni(dpm)(tmen)]BPh <sub>4</sub>	$K_1$	0.10	0.010	0.032	6.54	9.76	14.0	11.52
	$K_2$	2.72	1.50	2.00	60.0	200	308.6	282.4
[Ni(acac)(trmen)]BPh <sub>4</sub>	$K_1$	0.17	0.03	0.12	16.5	26.1	45.0	101
	$K_2$	28.87	3.87	18.28	576	756	1278	4139
[Ni(acac)(treen)]BPh <sub>4</sub>	$K_1$	0.05	0.004	0.028	5.3	8.44	15.8	53.8
	$K_2$	3.27	0.57	1.75	51.9	111.40	300	649

\* Taken from ref. 1.

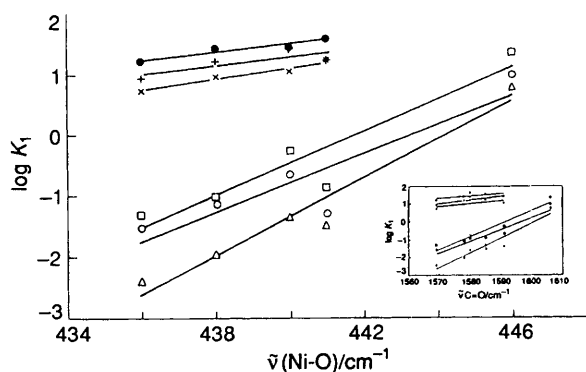


Fig. 2 Equilibrium constant  $\log K_1$  for the co-ordination of various donor solvents to  $[\text{Ni}(\beta\text{-dik})(\text{diam})]\text{BPh}_4$  in nitroethane solution at 20 °C versus Ni-O stretching frequencies of the complexes.<sup>3</sup> The correlation with C=O stretching vibrations is given as an insert. Donor solvents as in Fig. 1

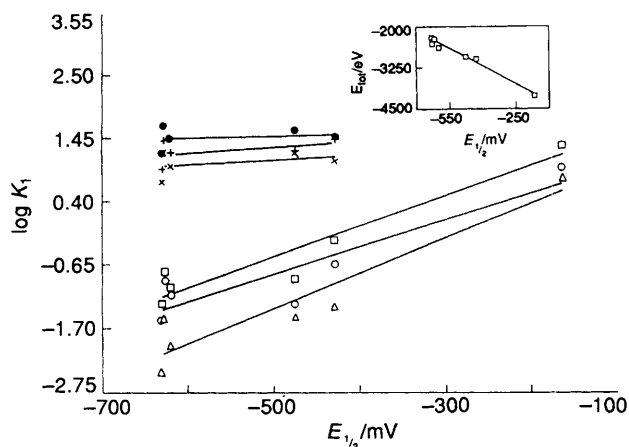


Fig. 3 Relation of  $\log K_1$  in nitroethane solution at 20 °C versus polarographic reduction potential of the complexes measured in 1,2-dichloroethane at a dropping mercury electrode versus bis(biphenyl)-chromium(i) iodide.<sup>2</sup> The insert shows the correlation between  $E_3$  and total energy ( $E_{\text{tot}}$ /eV) for unsolvated nickel(II) chelates. Donor solvents as in Fig. 1

The experimental results can be compared with results from a semiempirical quantum-mechanical description based on CNDO/2 calculations (Table 2). The calculated total energies ( $E_{\text{tot}}$ ) yield good linear correlations with Hammett constants ( $\sigma$ ), electrochemical data,<sup>2</sup> IR data<sup>3</sup> and formation constants. An increase in electron-withdrawing effect of the substituent groups leads to decreasing  $E_{\text{tot}}$  (see insert in Fig. 1):  $E_{\text{tot}} = -3530 - 3230\sigma$ ,  $r = 0.97$ . Higher total energies of the square-planar species are related to lower  $\log K$  values as well as to more cathodic reduction potentials ( $E_3$ ) of the complexes in 1,2-dichloroethane (see insert in Fig. 3):  $E_{\text{tot}} = -4610 - 3.53E_3$ ,  $r = 0.99$ . The  $\nu(\text{Ni-O})$  and  $\nu(\text{C=O})$  values decrease linearly with increasing total energy ( $E_{\text{tot}}$ ) of the nickel(II) chelates [ $E_{\text{tot}} = 65\,000 - 154\nu(\text{Ni-O})$ ,  $r = 0.95$ ;  $E_{\text{tot}} = 71\,000 - 46.6\nu(\text{C=O})$ ,  $r = 0.91$ ] reflecting a weakening of the respective bonds.

The charges of the central nickel atom ( $Q_{\text{Ni}}$ ) for the unsolvated species are linearly related to the IR absorptions assigned to the Ni-O stretching frequencies [ $Q_{\text{Ni}} = 20.53 - 0.045\nu(\text{Ni-O})$ ,  $r = 0.94$ ]. Increasing strength of the Ni-O bond leads to increasing electron density at the central nickel atom. The negative charges at the co-ordination centre confirm that almost no back donation effects occur [see Fig. 4(a)]. Increasing negative charge density on the nickel co-ordination centre is related to decreasing formation constants for the co-ordination of solvent donor molecules.

The calculated energies of the lowest unoccupied and highest

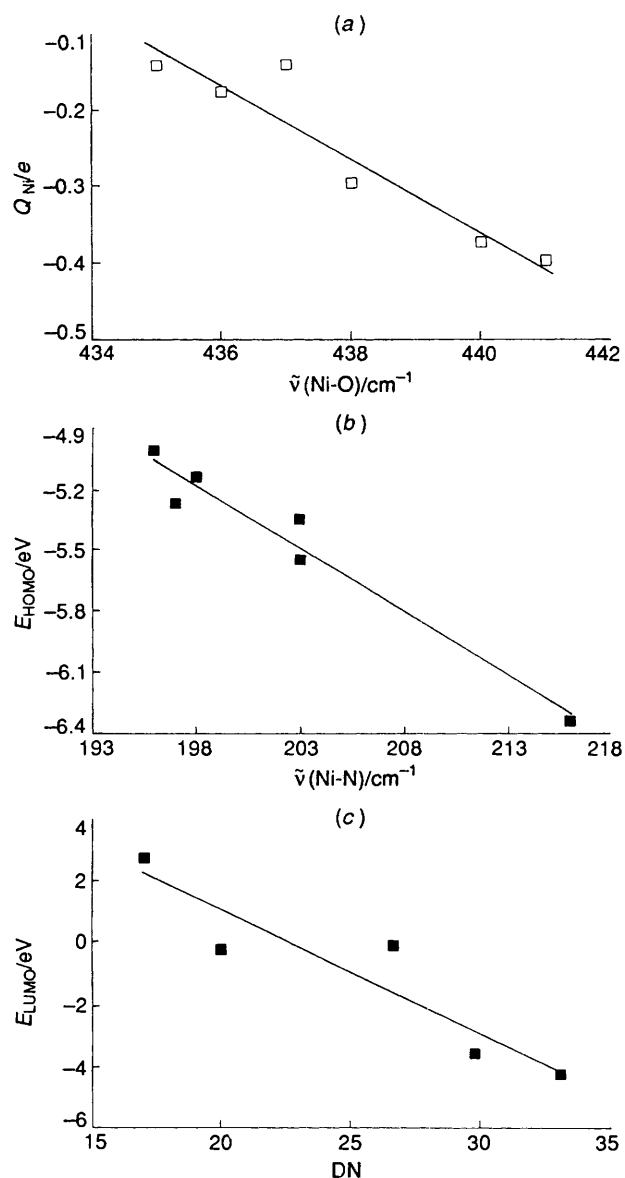


Fig. 4 (a) Charge on nickel versus Ni-O stretching frequencies of the complexes. (b) The HOMO energy levels of the unsolvated species  $[\text{Ni}(\beta\text{-dik})(\text{diam})]^+$  versus Ni-N stretching frequencies of the complexes. (c) The LUMO energy levels of the solvated species  $[\text{Ni}(\beta\text{-dik})(\text{diam})\text{L}_2]^+$  versus donor numbers

occupied molecular orbitals ( $E_{\text{LUMO}}$  and  $E_{\text{HOMO}}$ ) increase with increasing equilibrium constants ( $K_1$  and  $K_2$ ) and therefore with decreasing Ni-O and Ni-N stretching frequencies [ $E_{\text{HOMO}} = 7.26 - 0.06\nu(\text{Ni-N})$ ,  $r = 0.98$ ;  $E_{\text{HOMO}} = 46.2 - 0.12\nu(\text{Ni-O})$ ,  $r = 0.90$ ;  $E_{\text{LUMO}} = 2.18 - 0.013\nu(\text{Ni-N})$ ,  $r = 0.86$ ]. Furthermore increasing LUMO and HOMO energy levels of unsolvated species are associated with higher ligand-field stabilisation energies of these species, *i.e.* decreasing affinity of the square-planar nickel centre to co-ordinate with donor solvent molecules [Fig. 4(b)]. This explains the lowering of  $E_{\text{HOMO}}$  with strengthening of the Ni-N and Ni-O bonds. An increase in donor number of the co-ordinating solvents leads to decreasing  $E_{\text{LUMO}}$  values ( $E_{\text{LUMO}} = 8.89 - 0.40\text{DN}$ ,  $r = 0.93$ ) calculated for the solvated species [see Fig. 4(c)]. This is in accord with results for copper(II) chelates.<sup>6</sup>

## Conclusion

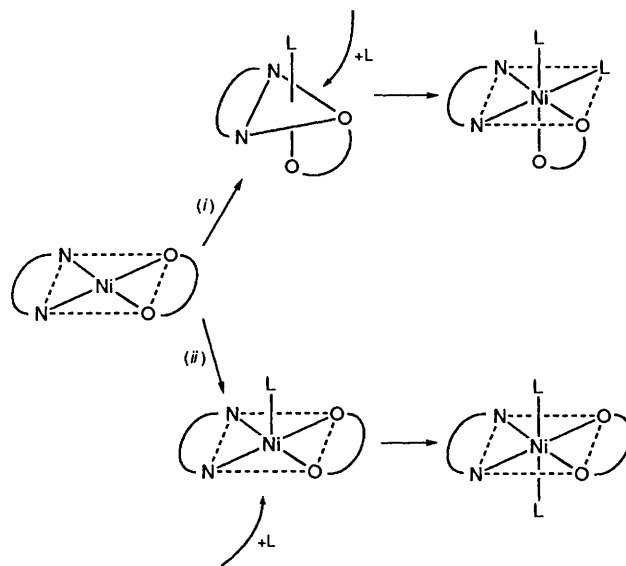
Correlations of the equilibrium constants ( $K_1$  and  $K_2$ ) with Hammett constants, IR, electrochemical and quantum-mechan-

**Table 2** Atomic charges ( $Q/e$ ), HOMO, LUMO energy levels and total energy (in eV) from a modified CDNO/2 calculation for  $[\text{Ni}(\beta\text{-dik})(\text{diam})]^+$  unsolvated and solvated complexes

Complex	$Q_{\text{Ni}}$	$E_{\text{HOMO}}$	$E_{\text{LUMO}}$	$E_{\text{tot}}$	$N_{\text{orbit}}^a$	$N_{\text{elec}}^b$
$[\text{Ni}(\text{acac})(\text{tmen})]^+$	-0.297	-6.06	-0.30	-2361	92	98
$[\text{Ni}(\text{acac})(\text{tmen})(\text{EtNO}_2)_2]^+$	-0.168	-3.93	-3.34	-4186	142	158
$[\text{Ni}(\text{acac})(\text{tmen})(\text{MeCN})_2]^+$	-0.236	-4.31	-4.18	-2998	122	130
$[\text{Ni}(\text{acac})(\text{tmen})(\text{H}_2\text{O})_2]^+$	-0.075	-5.83	-0.22	-2841	104	114
$[\text{Ni}(\text{acac})(\text{tmen})(\text{Me}_2\text{CO})_2]^+$	-0.59	-4.76	2.74	-3154	136	146
$[\text{Ni}(\text{acac})(\text{tmen})(\text{MeOH})_2]^+$	-0.01	-5.88	-0.235	-2936	116	126
$[\text{Ni}(\text{acac})(\text{tmen})(\text{HCONMe}_2)_2]^+$	-0.067	-5.90	-0.12	-3713	146	158
$[\text{Ni}(\text{acac})(\text{tmen})(\text{Me}_2\text{SO})_2]^+$	-0.074	-4.30	-3.58	-3594	146	150
$[\text{Ni}(\text{acac})(\text{tmen})(\text{C}_5\text{H}_5\text{N})_2]^+$	-0.30	-4.34	4.25	-3321	150	158
$[\text{Ni}(\text{bzac})(\text{tmen})]^+$	-0.398	-5.55	-0.542	-2900	114	120
$[\text{Ni}(\text{bzac})(\text{tmen})(\text{MeCN})_2]^+$	-0.40	-5.13	0.87	-3532	144	152
$[\text{Ni}(\text{bzac})(\text{tmen})(\text{H}_2\text{O})_2]^+$	-0.395	-5.24	0.76	-3387	126	136
$[\text{Ni}(\text{dbm})(\text{tmen})]^+$	-0.374	-5.27	-0.371	-2970	128	134
$[\text{Ni}(\text{dbm})(\text{tmen})(\text{MeCN})_2]^+$	-0.409	-5.03	0.91	-3582	158	166
$[\text{Ni}(\text{dbm})(\text{tmen})(\text{H}_2\text{O})_2]^+$	-0.326	-4.99	0.08	-3918	148	158
$[\text{Ni}(\text{tfacac})(\text{tmen})]^+$	-0.218	-6.34	-0.585	-4080	101	116
$[\text{Ni}(\text{tfacac})(\text{tmen})(\text{MeCN})_2]^+$	-0.162	-5.09	-4.92	-4712	131	148
$[\text{Ni}(\text{tfacac})(\text{tmen})(\text{H}_2\text{O})_2]^+$	-0.122	-6.21	-0.54	-4565	113	132
$[\text{Ni}(\text{acac})(\text{trmen})]^+$	-0.143	-6.13	-0.478	-2310	86	92
$[\text{Ni}(\text{acac})(\text{trmen})(\text{MeCN})_2]^+$	-0.235	-4.36	-4.21	-2962	116	124
$[\text{Ni}(\text{acac})(\text{trmen})(\text{H}_2\text{O})_2]^+$	-0.08	-5.92	-0.285	-2812	98	108
$[\text{Ni}(\text{acac})(\text{teen})]^+$	-0.176	-5.14	-0.519	-2510	104	110
$[\text{Ni}(\text{acac})(\text{teen})(\text{MeCN})_2]^+$	-0.62	-2.67	0.51	-3162	146	154
$[\text{Ni}(\text{acac})(\text{teen})(\text{H}_2\text{O})_2]^+$	-0.12	-4.88	-0.27	-3041	128	138
$[\text{Ni}(\text{acac})(\text{treen})]^+$	-0.142	-5.35	-0.381	-2630	116	122
$[\text{Ni}(\text{acac})(\text{treen})(\text{MeCN})_2]^+$	-0.305	-4.0	-3.96	-3079	134	142
$[\text{Ni}(\text{acac})(\text{treen})(\text{H}_2\text{O})_2]^+$	-0.22	-9.59	-9.54	-3038	116	126

<sup>a</sup> Number of included orbitals. <sup>b</sup> Number of electrons.

ical data show a clear distinction of strong co-ordinating solvents like  $\text{Me}_2\text{SO}$ ,  $\text{HCONMe}_2$ ,  $\text{HCONH}_2$  from the much weaker ones  $\text{MeCN}$ ,  $\text{BuOH}$  and  $\text{Me}_2\text{CO}$  (see Figs. 1–3). Such a separation was also observed previously, namely by application of the theoretically derived relations between linear free energy relationships and isokinetic relationships<sup>19,20</sup> to mixed-ligand complexes of the present type. The distinction suggests the existence of two mechanisms<sup>18,21</sup> which result in *cis* isomers upon attack of strong donors and in *trans* isomers for interaction with weaker donor solvents. This can be demonstrated by far-IR measurements<sup>18</sup> and by X-ray diffraction analysis of the obtained solvates.<sup>14</sup> The fact that the classification into two groups can be observed for  $K_1$  and for  $K_2$  suggests that the structural difference is also present in the five-co-ordinated species, namely that strong donating solvents react *via* the formation of a trigonal-bipyramidal intermediate (see Scheme 1). The new bound ligand forces the other ligands to bend away yielding a distorted trigonal bipyramid. The second solvent molecule therefore may attack more easily at the *cis* position. A similar geometrical distortion was found for chlorotrimethylstannane in the course of its interaction with Lewis-base molecules<sup>22,23</sup> where it was shown that a continuous set of molecular geometries between tetrahedral and trigonal bipyramidal exist depending on the donor number (DN) of the solvent.<sup>18</sup> On the other hand, weak co-ordinating solvents ( $\text{MeCN}$ ,  $\text{Me}_2\text{CO}$  and  $\text{Bu}^n\text{OH}$ ) are not able to destroy the symmetry around the nickel centre sufficiently so that only a slightly distorted square-pyramidal species is formed. This leads to a preferred attack of the second solvent molecule at the *trans* position. It has been shown by X-ray diffraction<sup>14</sup> that nitrate ion co-ordinates in a bidentate manner to  $\text{Ni}^{\text{II}}$  according to the *cis* mechanism similar to strongly donating solvent molecules. The  $\text{NO}_3^-$  ion itself in 1,2-dichloromethane has a donor number<sup>4</sup> of 21.1. The *trans* mechanism is followed by solvents with donor numbers equal or below 18. This suggests that the change from a *trans* to a *cis* mechanism occurs at a donor number of ca. 20.



**Scheme 1** (i) Strong donor L; (ii) weak donor L

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