Solvatochromic Dithiolene α-Di-imine Nickel Complexes

By Ian G. Dance* and Thomas R. Miller
(*Department of Chemistry, University of Wisconsin, Madison, Wisconsin* 53706)

Summary The syntheses, dipolar electronic structures, and solvent-dependent electronic spectra of square-planar dithiolene α-di-imine nickel complexes are reported.

We report the synthesis and characterization of a new class of mixed-ligand transition-metal complexes which exhibit pronounced solvatochromism. The four-co-ordinate square planar nickel complexes, (I), (II), and (III) contain one dithiolene and one α-di-imine ligand.

Preparative reactions involve (i) substitution of a bis-dithiolene complex by an α-di-imine ligand in a medium of low polarity, equations (1) and (2),†

$$\mathrm{Ni(S\text{–}S,R^1)_2 + (N\text{–}N) \rightarrow Ni(S\text{–}S,R^1)(N\text{–}N) + (S\text{–}S,R^1)} \quad (\mathrm{R^1 = CF_3,Ph}) \qquad (1)$$

$$\mathrm{Ni(mnt)_2^- + (N\text{–}N,Me,Ph) \rightarrow Ni(mnt)(N\text{–}N,Me,Ph)} + \text{other products} \qquad (2)$$

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† Dithiolene ligand $(\mathrm{S\text{–}S,R^1}) \equiv$ mnt when $\mathrm{R^1 = CN}$, tfd when $\mathrm{R^1 = CF_3}$; (N–N) ≡ α-di-imine ligand, biacetylbisanil ≡ (N–N,Me,Ph); 1,10-phenanthroline ≡ phen.

(ii) substitution of a bis-α-di-imine complex with a dithiolene ligand, equation (3),

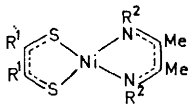
$$\mathrm{Ni(N{-}N,Me,Ph)_2^{2+} + (mnt)^{2-} \rightarrow Ni(mnt)(N{-}N,Me,Ph) + (N{-}N,Me,Ph)} \quad (3)$$

and (iii) ligand exchange, equations (4) and (5).

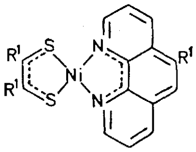
$$\mathrm{Ni(tfd)_2 + Ni[\mathit{o}\text{-}C_6H_4(NH)_2]_2 \rightarrow Ni(tfd)[\mathit{o}\text{-}C_6H_4(NH)_2]} \quad (4)$$

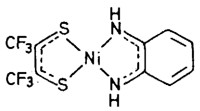
$$\mathrm{[Ni(N{-}N,Me,Ph)_2{}^{2+}][Ni(mnt)_2{}^{2-}] \rightarrow Ni(mnt)(N{-}N,Me,Ph)} \quad (5)$$

All the complexes occur as intensely coloured, high melting, diamagnetic crystals, (Ib) and (Id) being able to form dichloromethane solvates. Cyclic voltammetry reveals that the mixed-ligand complexes undergo one one-electron oxidation and two one-electron reductions, which are chemically reversible under appropriately inert conditions. Therefore the compleses are members of a four-membered electron-transfer series:



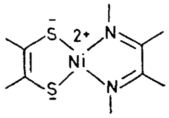
(I)



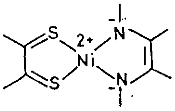


a; $R^1 = CF_3$, $R^2 = Ph$
b; $R^1 = CN$, $R^2 = Ph$
c; $R^1 = CF_3$, $R^2 = p\text{-}MeOC_6H_4$
d; $R^1 = CN$, $R^2 = p\text{-}MeOC_6H_4$
e; $R^1 = CF_3$, $R^2 = m\text{-}ClC_6H_4$
f; $R^1 = CF_3$, $R^2 = N{=}CHPh$

(II) a; $R^1 = CF_3$, $R^2 = H$
b; $R^1 = CF_3$, $R^2 = NO_2$
c; $R^1 = Ph$, $R^2 = H$



(IV)



(V)

$$\mathrm{[Ni(S{-}S)(N{-}N)]^{+} \rightleftharpoons [Ni(S{-}S)(N{-}N)] \rightleftharpoons [Ni(S{-}S)(N{-}N)]^{-} \rightleftharpoons [Ni(S{-}S)(N{-}N)]^{2-}}$$

Electronic spectra of dithiolene α-di-imine complexes show the pattern of bands that is characteristic of the parent bis-ligand complexes,[1] namely one low frequency (12—20 kK) intense (ϵ *ca.* 5×10^3 M^{-1} cm^{-1}) band, a series of less intense bands 20—28 kK, and several high intensity bands 28—45 kK. The salient spectroscopic property is, however, the substituent and medium dependence of the low frequency intense band (see Table). The (IIa), (IIb), (IIc) spectra show that the transition frequency is decreased by electron-withdrawing substituents on the α-di-imine ligand and increased by electron-withdrawing substituents on the dithiolene ligand, indicating that the transition is from a predominantly dithiolene orbital to one mainly di-imine in character. The negative solvatochromism, increasing transition frequency with solvent 'polarity', is a consequence of a substantial ground state molecular dipole which is reduced, reversed, or rotated by this low frequency charge-transfer transition. The ground state may be represented with (IV) as the principal resonance form, while the first excited state contains more of form (V). The acceptor orbital for this first transition is also the reduction orbital. Comparison of the electron transfer potentials for the mixed ligand complexes with those of the parent bis-ligand compounds reveals that the ligand component of this lowest unfilled molecular orbital is *ca.* 70% di-imine, 30% dithiolene.

TABLE. *Charge-transfer transition frequencies* (kK)

Complex	Toluene	CH_2Cl_2	MeCN	Me_2SO	Crystal
(IIa)	17·7	19·3	20·3	20·4	18·7
(IIb)		18·2			
(IIc)	14·3	16·5	17·3	16·9	16·4
(Ia)	14·6	15·6	17·9		17·1
(Ib)		17·1			18·1
(If)	16·6	17·5	18·9	19·0	19·5
(III)	13·8	14·2			

The solvatochromism of these complexes can be developed as a sensitive indicator of detailed solute–solvent interactions. Frequency shifts in an extensive series of solvents are not the same for all complexes, and it is possible to discern the contributions of solvent-to-solute hydrogen bonding and Lewis acid(solute)–base(solvent) interactions in addition to the intrinsic polar interaction arising from the solvent molecular dipole.

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[1] J. A. McCleverty, *Progr. Inorg. Chem.*, 1968, **10**, 49; A. L. Balch and R. H. Holm, *J. Amer. Chem. Soc.*, 1966, **88**, 5201.