

proceeds through the intermediacy of a σ complex, I. This complex may then dissociate to an ion pair, $M^+O_2SC_6H_5X^-$, or form the *O*-sulfinate in a concerted fashion through simultaneous scission of the $M-C_6H_5X$ bond and formation of the $M-OS(O)$ bond, or do both. The remaining aspects of the reaction, although not specifically elucidated, are probably similar to those for the alkyl complexes.

Before concluding we wish to address ourselves to two points which are relevant to the theme of this investigation. First, we wish to emphasize that the reaction picture presented herein may not apply to the SO_2 insertion in various coordinatively unsaturated metal alkyls and aryls. In fact, the recent isolations of $Rh[P(C_6H_5)_3]_2(CO)(SO_2)CF_2CHF_2$ ⁶¹ and $Ir[P(C_6H_5)_3]_2(CO)(SO_2)C\equiv CR$ ⁶² from the appropriate four-coordinate complexes and SO_2 suggest that the SO_2 insertion in $PtL_2(R)Cl$ ($L = P, As, Se, \text{ and } Te$ -donor ligands) to give $PtL_2[S(O)_2R]Cl$ ⁶³ may proceed through a five-coordinate intermediate, $PtL_2(SO_2)(R)Cl$. Similarly, $(h^5-C_5H_5)_2Ti(CH_3)Cl$ may undergo the inser-

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tion⁶⁴ *via* initial coordination of SO_2 to the titanium. Our second point is that this study has revealed significant mechanistic differences between the CO insertion and the SO_2 insertion, the former having been shown earlier to involve an intramolecular transfer of R onto a coordinated CO.³ These differences further underscore absence of mechanistic connotations in the term "insertion reaction."

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Supplementary Material Available. A listing of analytical data and rate constants will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-73-6962.

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Reactions of Dithiolene Complexes with Amines. II. The Formation and Properties of Mixed-Ligand Dithiolene α -Diimine Complexes of Nickel

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Abstract: A series of neutral, four-coordinate, square-planar nickel complexes composed of one dithiolene and one α -diimine ligand have been prepared by (a) substitution of bis(dithiolene) nickel complexes, (b) substitution of a bis(α -diimine) nickel complex, and (c) ligand exchange between bis(dithiolene) and bis(α -diimine) nickel complexes. The dithiolene ligands $RC(S)C(S)R$ contain $R = CN, CF_3, \text{ and } Ph$, and the α -diimine ligands are *o*-phenylenediimine, biacetylisanil, 1,10-phenanthroline, and derivatives. The complexes undergo electron-transfer reactions, studied voltammetrically, and exist as members of an electron-transfer series of complexes with charges +1, 0, -1, -2. Species other than the neutral complexes have not been isolated. Spectra of the strongly colored complexes show the same pattern as the bis-ligand complexes, with the exception that the low energy (12–20 kK) intense charge-transfer absorption is negatively solvatochromic. The complexes evidently possess a substantial ground-state electric dipole which is reduced or reversed by this low-energy dithiolene to α -diimine charge-transfer transition. On the basis of the spectral and electrochemical potential data a partial molecular orbital model for the mixed-ligand complexes is proposed.

Numerous four-coordinate bis(dithiolene) nickel complexes, I, are known.¹ Analogous bis(α -diimine) complexes, II, have been described.² However, the literature contains but passing reference, without details, to two examples of the mixed ligand, dithiolene α -diimine type of complex, III. The compound $Ni(mnt)(dipy)$ ³ is listed as red and diamagnetic in a review,⁴ and

$Ni(S-S,Ph)(dipy)$ was prepared by reaction of $Ni(S-S,Ph)((CH_3S)_2C_2Ph_2)$ with molten 2,2'-dipyridyl and "identified by its nmr spectrum."⁵ We report here the

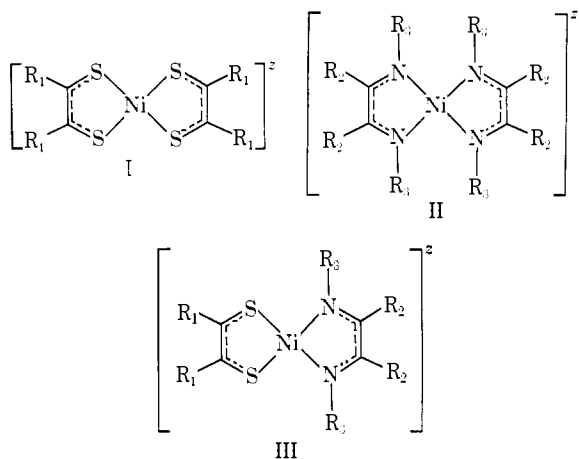
(3) The general abbreviations for dithiolene and diimine ligands are $(S-S, R_1)$ and $(N-N, R_2, R_3)$, respectively. Also, $(S-S, CN) \equiv mnt$, $(S-S, CF_3) \equiv tfd$; $phen \equiv 1,10$ -phenanthroline, $5-NO_2phen \equiv 5$ -nitro-1,10-phenanthroline, $dipy \equiv 2,2'$ -dipyridyl, and $o-C_6H_4(NH)_2 \equiv o$ -phenylenediimine.

(4) Reference 1, p 186.

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synthesis and characterization of a series of neutral dithiolene α -diimine nickel complexes, III.

Although bis(dithiolene) and bis(diimine) complexes participate in pure electron-transfer reactions ($z = -2, -1, 0, +1$ for I; $z = -2, -1, 0, +1, +2$ for II), their electron affinities and the preferred electron populations of comparable complexes of classes I and II are very different. Thus $[\text{Ni}(\text{S}-\text{S}, \text{CH}_3)_2]$ is reduced to the monoanion at -0.14 V (*vs.* sce) whereas a potential of -1.60 V (*vs.* sce) is necessary to reduce $[\text{Ni}(\text{N}-\text{N}, \text{CH}_3, \text{Ph})_2]$ to the monoanion. Therefore a mixed-ligand dithiolene diimine complex might be expected to possess a valence electron distribution which is asymmetric through the metal atom. The electrochemical and spectroscopic properties of the mixed-ligand complexes support such a description of electronic structure.

Experimental Section

$[\text{Ni}(\text{tfd})_2]$, $[\text{Ni}(\text{S}-\text{S}, \text{Ph})_2]$, and $[\text{Ni}(\text{o}-\text{C}_6\text{H}_4(\text{NH})_2)_2]$ were prepared and purified by standard methods.^{2,6,7} The bis-Schiff base from biacetyldihydrazone and benzaldehyde was prepared by adding the former (1 g) to the latter (5 ml) in ethanol (15 ml). The yellow crystals which formed were recrystallized from dichloromethane-ethanol, mp 121–123°. 5-Nitro-1,10-phenanthroline was prepared following Conrad and Rund.⁸

Ni(tfd)(phen). A solution of 1,10-phenanthroline (0.2 g, 1.1 mmol) in toluene (30 ml) was added to a filtered solution of $\text{Ni}(\text{tfd})_2$ (0.5 g, 0.97 mmol) in toluene (30 ml) at ambient temperature. The solution immediately changed from dark blue-violet to magenta and an orange precipitate formed. The precipitate was collected by filtration, washed with a little acetone, and recrystallized from acetone-ethanol, yield 0.33 g (72%).

The filtrate from this reaction was allowed to stand overnight, during which time small brown crystals formed. These were collected by filtration, washed with toluene, and air-dried. Elemental analysis of this second product suggested the composition $[\text{Ni}(\text{phen})_3^{2+}][\text{Ni}(\text{tfd})_2^{2-}]_2$, perhaps slightly contaminated with hydrocarbon solvent. *Anal.* Calcd: C, 38.52; H, 1.49; N, 5.18; S, 15.82. Found: C, 39.11; H, 1.79; N, 4.96; S, 15.10.

Ni(tfd)(5-NO₂-phen). A solution of $\text{Ni}(\text{tfd})_2$ (0.5 g) in dichloromethane (50 ml) was added to a solution of 5-nitro-1,10-phenanthroline (0.3 g) in dichloromethane (50 ml). The red crystals which formed were collected by filtration, washed with ethanol and a small amount of acetone, and recrystallized from acetone-ethanol.

Ni(S-S,Ph)(phen). $\text{Ni}(\text{S}-\text{S}, \text{Ph})_2$ (0.5 g) and 1,10-phenanthroline (0.3 g) were heated together in refluxing toluene (50 ml) for 90 min, during which time dark violet crystals formed. The product was separated by filtration from the hot mixture, washed with hot toluene, and dried *in vacuo*. Further purification was unnecessary.

The same reaction was performed in dichloromethane solution

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(8) R. C. Conrad and J. V. Rund, *Inorg. Chem.*, **11**, 129 (1972).

(100 ml) for 3 hr at room temperature. From the resulting blue-green solution a violet crystalline product identical with the above sample was separated by filtration. During 3 days at room temperature long black needles crystallized from the filtrate. Although not fully characterized this latter product has properties consistent with the formulation $[\text{Ni}(\text{phen})_3^{2+}][\text{Ni}(\text{S}-\text{S}, \text{Ph})_2^{2-}]_2$.

The same reaction in dimethyl sulfoxide formed $\text{Ni}(\text{S}-\text{S}, \text{Ph})_2^{2-}$ with no indication of the mixed complex.

Ni(tfd)(N-N,CH₃,Ph). A solution of biacetyl-bisanil (0.3 g) in toluene (10 ml) was added to a solution of $\text{Ni}(\text{tfd})_2$ (0.5 g) in toluene (10 ml). The solution immediately turned dark green and a violet precipitate formed. The precipitate was collected by filtration, recrystallized from dichloromethane-ethanol as long black needles, washed with ethanol and ether, and dried.

Ni(tfd)(N-N,CH₃,*p*-CH₃OC₆H₄). To a solution of $\text{Ni}(\text{tfd})_2$ (0.5 g) in toluene (10 ml) the substituted biacetyl-bisanil (0.3 g) was added. The black precipitate which formed was collected by filtration, washed with methanol, and recrystallized from acetone-2-propanol.

Ni(tfd)(N-N,CH₃,*m*-ClC₆H₄). Biacetyl (18 ml) and *m*-chloroaniline (40 ml) were mixed and allowed to stand for 18 hr. The solution separated into two finely dispersed immiscible liquids. Two milliliters of this mixture was added to a solution of $\text{Ni}(\text{tfd})_2$ (0.5 g) in dichloromethane (100 ml). The solution turned blue-green within 2 min. After evaporation almost to dryness, the dark blue crystals which formed were collected, washed with a small amount of ethanol, and recrystallized twice from dichloromethane-2-propanol.

Ni(tfd)(N-N,CH₃,N=CHPh). To a solution of $\text{Ni}(\text{tfd})_2$ (0.5 g) in toluene (10 ml) was added 0.3 g of the bis-Schiff base formed from biacetyldihydrazone and benzaldehyde. The mixture was stirred for 5 min, and the dark red product was collected by filtration and recrystallized twice from acetone-2-propanol.

Ni(mnt)(N-N,CH₃,Ph) and Ni(mnt)(N-N,CH₃,Ph)·0.5CH₂Cl₂. (A) Biacetyl-bisanil (5.3 g, 23 mmol) and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (2.4 g, 10 mmol) were dissolved in hot acetone (100 ml), and the solvent was evaporated to produce an orange-brown crystalline solid. This product and Na_2mnt (2.0 g, 11 mmol) were suspended in dichloromethane (200 ml) and stirred for 18 hr, producing a deep blue solution. After filtration benzene was added and the dichloromethane removed at reduced pressure. The dark red lustrous crystals of the dichloromethane solvate which formed were collected by filtration, washed with benzene, and air-dried. The dichloromethane may be removed by heating at *ca.* 150°.

(B) A solution of Na_2mnt (1.9 g) and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1.45 g) in 100 ml of 3:1 (v) ethanol-water was added to a filtered solution of biacetyl-bisanil (2.4 g) and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1.45 g) in 200 ml of 3:1 (v) ethanol-water. Water was added to complete the formation of the dark brown precipitate, a solvate of $[\text{Ni}(\text{N}-\text{N}, \text{CH}_3, \text{Ph})_2^{2+}][\text{Ni}(\text{mnt})_2^{2-}]$, which was then filtered, washed with water, and air-dried. This product was dissolved in acetonitrile and the red solution refluxed for 1 hr, during which time the color changed to dark violet and a coppery brown microcrystalline precipitate of $\text{Ni}(\text{mnt})(\text{N}-\text{N}, \text{CH}_3, \text{Ph})$ formed. Recrystallization may be effected from acetone-2-propanol or acetonitrile-2-propanol.

Conversion of the salt to the mixed-ligand complex occurs also on heating the solid above 180° or on heating in acetone or DMSO solution.

Ni(mnt)(N-N,CH₃,*p*-CH₃OC₆H₄)·0.5CH₂Cl₂. The diimine ligand (1.8 g) was slurried in methanol (100 ml), and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (1.2 g) and Na_2mnt (0.9 g) were added. The resulting red solution was boiled for about 5 min, and the brown solid which formed was collected by filtration and washed with methanol. This solid was extracted with cold acetone to produce a violet filtrate and a red residue. After addition of 2-propanol to the filtrate and removal of the acetone at reduced pressure, the product was collected by filtration and recrystallized from dichloromethane-2-propanol, yield 0.45 g (20%, based on mnt).

Ni(tfd)(*o*-C₆H₄(NH)₂). A heterogeneous mixture of $\text{Ni}(\text{tfd})_2$ (0.511 g) and $\text{Ni}(\text{o}-\text{C}_6\text{H}_4(\text{NH})_2)_2$ (0.260 g) in dichloromethane was allowed to stand for 5 days. The resulting green solution was filtered, heptane was added to the filtrate, and the solvent was evaporated at reduced pressure. The dark brown crystals which formed were collected by filtration, washed with heptane, and recrystallized once from dichloromethane-2-propanol-water and once from dichloromethane-heptane.

Related Reactions. A mixture of $\text{Ni}(\text{S}-\text{S}, \text{Ph})_2$ (0.5 g) and biacetyldihydrazone (0.13 g) was refluxed in toluene (50 ml) for 5 hr. The yellow-brown crystals which formed were collected by filtration, washed with hot toluene, and air-dried. Solid- and solution-state

Table I. Microanalytical Data

Compound	Appearance of crystals	% C	% H	% N	% S
Ni(tfd)(S—S,Ph)	Green-black needles	41.33 (41.01)	1.92 (1.91)		24.52 (24.33)
Ni(tfd)(phen)	Orange needles	41.10 (41.32)	1.97 (1.73)	6.09 (6.02)	13.54 (13.79)
Ni(tfd)(5-NO ₂ phen)	Orange-red	38.02 (37.68)	1.43 (1.38)	8.25 (8.24)	12.15 (12.57)
Ni(S—S,Ph)(phen)	Blue-black needles ^a	65.57 (64.89)	3.56 (3.77)	5.70 (5.81)	13.13 (13.32)
Ni(tfd)(N—N,CH ₃ ,Ph)	Violet-black needles	46.07 (46.09)	2.94 (3.09)	5.31 (5.37)	11.92 (12.30)
Ni(mnt)(N—N,CH ₃ ,Ph)·0.5CH ₂ Cl ₂	Red-black flakes ^a	51.49 (51.54)	3.37 (3.59)	11.78 (11.72)	13.67 (13.42)
Ni(tfd)(N—N,CH ₃ , <i>p</i> -CH ₃ OC ₆ H ₄)	Blue-black	45.50 (45.46)	3.51 (3.47)	4.73 (4.81)	10.85 (11.03)
Ni(mnt)(N—N,CH ₃ , <i>p</i> -CH ₃ OC ₆ H ₄)·0.5CH ₂ Cl ₂	Red-black flakes	49.90 (50.25)	4.04 (3.93)	10.29 (10.42)	11.75 (11.92)
Ni(tfd)(N—N,CH ₃ , <i>m</i> -ClC ₆ H ₄)	Blue-black needles	40.88 (40.71)	2.26 (2.39)	4.69 (4.75)	11.01 (10.87)
Ni(tfd)(N—N,CH ₃ ,N=CHPh)	Red-brown	45.93 (45.94)	3.14 (3.15)	9.62 (9.74)	10.79 (11.15)
Ni(tfd)(<i>o</i> -C ₆ H ₄ (NH ₂))	Red-black ^a	30.99 (30.72)	1.50 (1.55)	7.07 (7.16)	16.25 (16.40)

^a Metallic luster.

Table II. Mass Spectral Data

Complex	Molecular ion		Most abundant peak	
	<i>m/e</i>	Rel abundance, %	<i>m/e</i>	Interpretation
Ni(tfd)(phen)	464	41	180	(N—N)
Ni(tfd)(5-NO ₂ phen)	509	10	179	(N—N)-NO ₂
Ni(S—S,Ph)(phen)	480	1	178	(N—N)-H ₂ (?)
Ni(tfd)(N—N,CH ₃ ,Ph)	520	1.1	118	(N—N)/2
Ni(mnt)(N—N,CH ₃ ,Ph)·0.5CH ₂ Cl ₂	Not observed		49	CH ₂ Cl
Ni(tfd)(N—N,CH ₃ , <i>p</i> -CH ₃ OC ₆ H ₄)	580	1.6	148	(N—N)/2
Ni(mnt)(N—N,CH ₃ , <i>p</i> -CH ₃ OC ₆ H ₄)·0.5CH ₂ Cl ₂	Not observed		49	CH ₂ Cl
Ni(tfd)(N—N,CH ₃ , <i>m</i> -ClC ₆ H ₄)	588	0.4	152	(N—N)/2
Ni(tfd)(N—N,CH ₃ ,N=CHPh)	574	0.9	186	(N—N)-NCHPh
Ni(tfd)(<i>o</i> -C ₆ H ₄ (NH ₂))	390	13.2	164	Ni(N—N)

Ni(tfd)(phen)			Ni(tfd)(N—N,CH ₃ ,Ph)			Ni(tfd)(<i>o</i> -C ₆ H ₄ (NH ₂))		
Prominent peaks ^a <i>m/e</i>	Rel abundance, %	Interpretation	Prominent peaks ^a <i>m/e</i>	Rel abundance, %	Interpretation	Prominent peaks ^a <i>m/e</i>	Rel abundance, %	Interpretation
143	5.3	C ₄ F ₅	113	3.2	(S—S)/2	108	8.0	
152	5.9		118	100	(N—N)/2	113	8.0	(S—S)/2
153	10		162	2.7	C ₄ F ₆	136	11.3	
154	14	(N—N)-C ₂ H ₂	226	2.7	(S—S)	137	10.6	
162	6.5	C ₄ F ₆	235	7.1	(N—N)-H	143	5.2	C ₄ F ₅
179	32	(N—N)-H	236	17	(N—N)	162	5.6	C ₄ F ₆
180	100	(N—N)	294	1.1	Ni(N—N)	163	5.0	
226	3.3	(S—S)	520	1.1	Ni(S—S)(N—N)	164	100	Ni(N—N)
238	98	Ni(N—N)				226	2.0	(S—S)
257	6.0					390	13.2	Ni(S—S)(N—N)
464	41	Ni(S—S)(N—N)						

^a Peaks below *m/e* 100, peaks corresponding to ⁶⁰Ni, ¹³C, etc., and most peaks below 5% relative abundance are not listed.

spectra indicated that this product was Ni(S—S,Ph)(N—N,CH₃,NH₂) contaminated with salts of Ni(S—S,Ph)₂⁻.

The reaction of approximately equimolar amounts of (Bu₄P)[Ni(mnt)₂] and biacetylisanil in acetone, acetonitrile, or *o*-dichlorobenzene gave in about 10 min a solution containing both Ni(mnt)(N—N,CH₃,Ph) and Ni(mnt)₂²⁻.

Ni(tfd)(S—S,Ph). Ni(tfd)₂ (1.0 g) and Ni(S—S,Ph)₂ (1.09 g) were dissolved in dichloromethane (200 ml), and the solution was refluxed for 30 min, during which time the color change from blue-green to dark red was essentially complete. After cooling and standing the solution was filtered, heptane (50 ml) added, and the solvent evaporated at reduced pressure to produce lustrous black needles, which were washed with heptane and dried *in vacuo*. The mass spectrum of this sample had peaks at *m/e* 510, 526, and 540, corresponding to both the original symmetrical complexes as well as the mixed-ligand complex, but the peak for the latter was the most intense of the three. Cyclic voltammetry of a 10⁻³ M solution of the product in dichloromethane demonstrated that it was predominantly the mixed complex with only traces of the symmetrical complexes present.

None of the complexes melts or decomposes below 275°. Microanalytical data (by Galbraith Laboratories, Inc.) for all complexes are contained in Table I.

Mass spectra were obtained with an AEI-MS-9 spectrometer, operating at 70 V. Molecular ion and representative fragmentation data are listed in Table II. For all but the two mnt complexes the

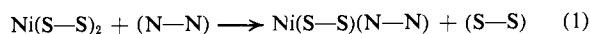
monomeric mixed-ligand formulation of the complexes is confirmed. For each compound the most abundant fragment contained nitrogen but not sulfur; characteristic fragments from the dithiolene ligands were observed but at low intensities compared with the diimine ligand and its fragments.

Solid-state magnetic susceptibility data were obtained with a Faraday balance. Electronic spectra were recorded on a Cary 14 spectrometer at 22°; the diffuse reflectance spectra were obtained from finely powdered solids spread on adhesive tape. Electrochemical experiments were performed with a PAR Model 170 potentiostat, with a stationary platinum sphere working electrode and (*n*-Bu₄)P⁺ClO₄⁻ supporting electrolyte. All potentials are *vs.* sce (KCl). Acetonitrile was distilled once from calcium hydride then from P₄O₁₀, dichloromethane was distilled from P₄O₁₀ and toluene from sodium, and DMSO was distilled at reduced pressure. All solvents were stored over molecular sieves.

Results

Synthetic Reactions. Three general reactions were used to prepare the neutral dithiolene diimine nickel complexes.

(A) Substitution of a dithiolene ligand from a bis-(dithiolene) complex by the diimine ligand, eq 1, was

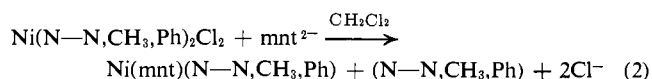


applicable for the neutral dithiolene precursors $\text{Ni}(\text{tfd})_2$ and $\text{Ni}(\text{S—S,Ph})_2$ (and in some cases for $\text{Ni}(\text{mnt})_2^-$). There is, however, a pronounced variation in the rates of these substitution reactions. The substitution of $\text{Ni}(\text{tfd})_2$ by all diimine ligands investigated is complete within several minutes at room temperature in toluene or dichloromethane, whereas the substitution of $\text{Ni}(\text{S—S,Ph})_2$ is very much slower, to the extent that diimines such as biacetylbianil and its derivatives did not displace the dithiolene ligand during several hours at reflux temperature in toluene. A significant observation in this regard is that the neutral mixed dithiolene complex $\text{Ni}(\text{tfd})(\text{S—S,Ph})$ was substituted by 1,10-phenanthroline and by biacetylbianil at rates comparable with the rates of substitution of $\text{Ni}(\text{tfd})_2$ by these diimines. Further, the reaction of $\text{Ni}(\text{tfd})(\text{S—S,Ph})$ with phen in dichloromethane produced $\text{Ni}(\text{tfd})(\text{phen})$ in about 80% yield, with no more than a trace of $\text{Ni}(\text{S—S,Ph})(\text{phen})$.

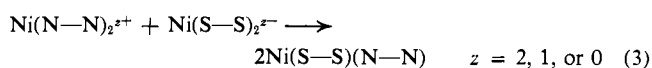
The formation of a mixed-ligand complex by dithiolene ligand substitution is dependent on other identifiable factors, and is subject to competition by an alternative substitution reaction sequence which leads to a comparatively stable reduced form of the bis(dithiolene) complex. The monoanionic complexes $\text{Ni}(\text{tfd})_2^-$ and $\text{Ni}(\text{S—S,Ph})_2^-$ did not react at an appreciable rate with any of the diimine ligands under any of the high- or low-temperature conditions investigated. The reaction of $\text{Ni}(\text{mnt})_2^-$ ($\text{Ni}(\text{mnt})_2^0$ has not yet been isolated) with biacetylbianil in acetonitrile or *o*-dichlorobenzene at 60° produced a mixture of $\text{Ni}(\text{mnt})(\text{N—N,CH}_3,\text{Ph})$ and $\text{Ni}(\text{mnt})_2^{2-}$. Dianionic bis(dithiolene) complexes such as $\text{Ni}(\text{mnt})_2^{2-}$ appear to be totally inert to substitution by neutral diimine ligands (but see method C, below).

Small amounts of disproportionation complexes $[\text{Ni}(\text{phen})_3^{2+}][\text{Ni}(\text{S—S})_2^-]_2$ were obtained in the substitution reactions leading to the mixed complexes $\text{Ni}(\text{S—S})(\text{phen})$, $(\text{S—S}) = \text{tfd}$ and (S—S,Ph) . This competition is solvent dependent; both $\text{Ni}(\text{S—S,Ph})(\text{phen})$ and $\text{Ni}(\text{S—S,Ph})_2^-$ were obtained from the reaction of $\text{Ni}(\text{S—S,Ph})_2$ with phen in dichloromethane,⁹ but in toluene only $\text{Ni}(\text{S—S,Ph})(\text{phen})$ was produced and in acetone or DMSO only $\text{Ni}(\text{S—S,Ph})_2^-$ was detected. Formation of the mixed-ligand complex is also dependent on the unsaturated nature of the chelating amine, all substitution reactions with ethylenediamine having produced only disproportionation salts with reduced bis(dithiolene) complex anions.

(B) Substitution of a bis(diimine) complex by a dithiolene ligand. One successful example of this reaction type has been found to date, namely



(C) Ligand exchange reactions (eq 3). The brown



crystalline salt $[\text{Ni}(\text{N—N,CH}_3,\text{Ph})_2^{2+}][\text{Ni}(\text{mnt})_2^{2-}]$ is converted to $\text{Ni}(\text{mnt})(\text{N—N,CH}_3,\text{Ph})$ on heating the solid at 180° or on heating in aprotic polar organic solvents (refluxing a solution of the salt in acetonitrile for 1 hr is a convenient procedure). The rate of this

(9) In CH_2Cl_2 solutions containing excess $(n\text{-Bu})_4\text{P}^+\text{ClO}_4^-$ the formation of $\text{Ni}(\text{S—S,Ph})_2^-$ is faster and more complete.

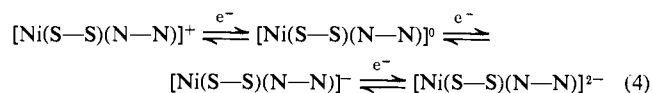
ligand exchange reaction appears to decrease with increasing solvent polarity, being slower in DMSO than in acetonitrile or acetone; the reaction does not occur in DMSO–water mixtures containing more than ca. 30% (v/v) water.

The mixed-complex $\text{Ni}(\text{tfd})(o\text{-C}_6\text{H}_4(\text{NH})_2)$ was prepared by ligand exchange between $\text{Ni}(\text{tfd})_2$ and $\text{Ni}(o\text{-C}_6\text{H}_4(\text{NH})_2)_2^{2+}$ in dichloromethane.¹⁰ This is the only known route to mixed-ligand complexes with this diimine ligand, which has limited stability when uncoordinated.²

An analogous ligand exchange reaction occurs when $\text{Ni}(\text{tfd})_2$ and $\text{Ni}(\text{S—S,Ph})_2$ interact in dichloromethane, affording $\text{Ni}(\text{tfd})(\text{S—S,Ph})$. A noteworthy feature of this reaction is its rate (reaction complete in ca. 30 min at 40° in dichloromethane) which is in contrast to the very much slower (ca. 6 days to reach equilibrium under the same conditions) dithiolene ligand exchange between $\text{Ni}(\text{tfd})_2^-$ and $\text{Ni}(\text{S—S,Ph})_2^-$ to produce $\text{Ni}(\text{tfd})(\text{S—S,Ph})^-$.¹¹

The dithiolene diimine nickel complexes are strongly colored crystalline solids, stable to air and water. None of the complexes decomposed or disproportionated in dichloromethane solution during a period of several weeks. The complexes manifest a varied reactivity toward bases and basic solvents, $\text{Ni}(\text{tfd})(\text{N—N,CH}_3,\text{N}=\text{CHPh})$ being the most reactive, turning to an unidentified pale yellow species during several hours in DMF or DMSO solution. The remainder of the complexes appeared to be stable in DMSO solution, but all with $(\text{N—N,CH}_3,\text{R})$ ligands decomposed in pyridine. $\text{Ni}(\text{S—S,Ph})(\text{phen})$ and $\text{Ni}(\text{tfd})(\text{phen})$ turned pale yellow rapidly when dissolved in morpholine or other alkylamines, but were stable for at least 24 hr in pyridine. All complexes were decomposed by mineral acids, none reacted with iodide ion in nonaqueous solution, and only $\text{Ni}(\text{S—S,Ph})(\text{phen})$ reacted with iodine, producing $\text{Ni}(\text{S—S,Ph})_2$ among other unidentified products.

Electrochemical Properties. Cyclic voltammetry data are presented in Table III. All of the mixed complexes undergo two one-electron reductions and one one-electron oxidation, and therefore the general electron-transfer series for these complexes is



The $0 \rightleftharpoons -1$ couple is uniformly chemically reversible,¹² and all monoanionic complexes are stable in solution for periods of at least several minutes. The second reduction process is chemically reversible in DMSO only for complexes not containing derivatives of biacetylbianil. Each complex exhibits at least one oxidation peak, the chemical reversibility of the first oxidation depending on the complex and on the solvent. The lifetimes of the first oxidized species are greatest in dichloromethane and least in DMSO and generally follow the order of lifetimes known for the parent

(10) According to the electrochemical potentials the electron transfer reaction $[\text{Ni}(\text{tfd})_2] + [\text{Ni}(o\text{-C}_6\text{H}_4(\text{NH})_2)_2] \rightarrow [\text{Ni}(\text{tfd})_2]^- + [\text{Ni}(o\text{-C}_6\text{H}_4(\text{NH})_2)_2]^+$ is exergonic, and is presumed to precede the ligand exchange reaction.

(11) A. Davison, J. A. McCleverty, E. T. Shawl, and E. J. Wharton, *J. Amer. Chem. Soc.*, **89**, 830 (1967).

(12) Chemical reversibility was assessed from the current in the reverse scan. No detailed investigation has been made of homogeneous processes coupled to electron transfer or of electrochemical reversibility.

Table III. Electrochemical Data

Complex	Solvent	+1 \rightleftharpoons 0			0 \rightleftharpoons -1			-1 \rightleftharpoons -2				
		Scan rate ^a	$E_{1/2}^b$	ΔE_p^c	Solvent	Scan rate ^a	$E_{1/2}^b$	ΔE_p^c	Solvent	Scan rate ^a	$E_{1/2}^b$	ΔE_p^c
Ni(tfd)(phen)	CH ₂ Cl ₂	5.0	+0.82 ^d	280	CH ₂ Cl ₂	5.0	-1.20	200				
	CH ₃ CN	5.0	+0.79 ^d	<i>e</i>	CH ₃ CN	5.0	-1.16	190				
	DMSO	5.0	+0.74 ^d	<i>e</i>	DMSO	5.0	-1.08	120	DMSO	5.0	-1.80 ^d	120
Ni(tfd)(5-NO ₂ phen)	DMSO	5.0	+0.90 ^d	<i>e</i>	DMSO	5.0	-0.57	100	DMSO	0.05	-1.13	60
	Ni(S-S,Ph)(phen)	CH ₂ Cl ₂	0.50	+0.33	80	CH ₂ Cl ₂	5.0	-1.40	120			
Ni(tfd)(N-N,CH ₃ ,Ph)	DMSO	0.50	+0.30 ^d	240	DMSO	5.0	-1.29	100	DMSO	5.0	-1.93	140
	CH ₃ CN	5.0	+0.84 ^d	330	CH ₃ CN	5.0	-0.88	200				
	DMSO	5.0	+0.90 ^d	<i>e</i>	CH ₃ CN	0.05	-0.88	70	DMSO	5.0	-1.64 ^d	<i>e</i>
Ni(mnt)(N-N,CH ₃ ,Ph)	CH ₃ CN	5.0	+0.90 ^d	<i>e</i>	CH ₃ CN	5.0	-0.72	200				
	DMSO	5.0	+0.98 ^d	<i>e</i>	DMSO	5.0	-0.64	100	DMSO	5.0	-1.6 ^d	<i>e</i>
	DMSO	0.05	-0.61	70								
Ni(tfd)(N-N,CH ₃ , <i>p</i> -CH ₃ OC ₆ H ₄)	CH ₂ Cl ₂	5.0	+0.93 ^d	240	CH ₂ Cl ₂	0.50	-0.92	130				
	CH ₂ Cl ₂	0.50	+0.90	160	CH ₃ CN	5.0	-0.91	110				
	CH ₃ CN	5.0	+0.80 ^d	190	CH ₃ CN	0.05	-0.91	60				
	DMSO	5.0	+0.80 ^d	<i>e</i>	DMSO	5.0	-0.85	80	DMSO	5.0	-1.66 ^d	<i>e</i>
Ni(mnt)(N-N,CH ₃ , <i>p</i> -CH ₃ OC ₆ H ₄)	CH ₃ CN	5.0	+0.88 ^{d,f}	<i>e</i>	CH ₃ CN	5.0	-0.75	130	CH ₃ CN	5.0	-1.8 ^d	<i>e</i>
	Ni(tfd)(N-N,CH ₃ , <i>m</i> -ClC ₆ H ₄)	DMSO	5.0	+0.94 ^d	<i>e</i>	DMSO	5.0	-0.78	200	DMSO	5.0	-1.5 ^d
Ni(tfd)(N-N,CH ₃ ,N=CHPh)	DMSO	0.05	-0.71	70	DMSO	0.05	-0.71	70				
	CH ₃ CN	5.0	+0.86 ^{d,g}	170	CH ₃ CN	5.0	-0.76	240	CH ₃ CN	0.50	-1.28	90
	DMSO	0.05	-0.78	75								
Ni(tfd)(C ₆ H ₄ (NH) ₂)	DMSO	5.0	+1.08 ^d	<i>e</i>	DMSO	5.0	-0.31	90	DMSO	5.0	-1.04	160
	DMSO	0.05	-0.28	60	DMSO	0.05	-0.28	60	DMSO	0.05	-1.02	60
	Ni(tfd) ₂		<i>i</i>				+0.90 ^h		CH ₃ CN		-0.12	
Ni(S-S,Ph) ₂		+1.35 ^h				+0.12 ^h		CH ₃ CN		-0.82		
Ni(mnt) ₂		<i>i</i>				+1.28 ^h		CH ₃ CN		+0.23		
Ni(C ₆ H ₄ (NH) ₂) ₂ ⁱ	Acetone		+0.14		DMSO		-0.88		DMSO		-1.59	
Ni(N-N,CH ₃ ,Ph) ₂ ⁱ	CH ₃ CN		-0.61 ^k		CH ₃ CN		-1.60		CH ₃ CN		-1.80	

^a V/sec. ^b Volts vs. saturated calomel electrode. ^c Anodic-cathodic peak separation, mV. ^d The potential reported is that at which the current on the forward scan reaches half its peak value. ^e No peak was observed on a reverse scan. ^f Peak current corresponds to two-electron transfer. ^g Peak current indicates transfer of between one and two electrons. ^h Data from A. L. Balch, I. G. Dance, and R. H. Holm, *J. Amer. Chem. Soc.*, **90**, 1139 (1968), in CH₂Cl₂ vs. Ag/AgI, converted to the sce/CH₃CN scale by the equation $E(\text{sce}, \text{CH}_3\text{CN}) = 1.03E(\text{Ag}/\text{AgI}, \text{CH}_2\text{Cl}_2) - 0.14$. ⁱ Process has not been detected. ^j Data from A. L. Balch and R. H. Holm, *J. Amer. Chem. Soc.*, **88**, 5201 (1966). ^k Two electron process, +2 \rightleftharpoons 0.

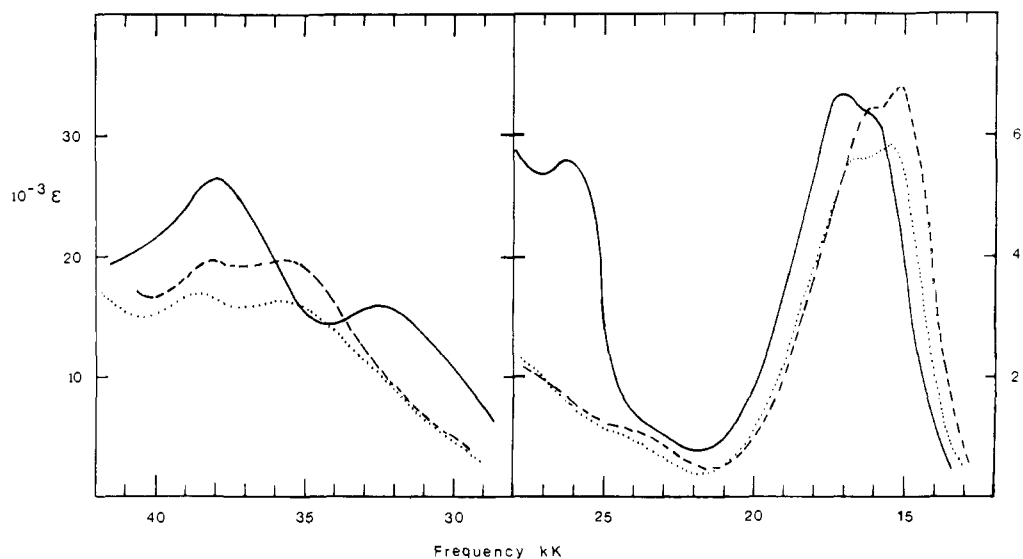


Figure 1. Spectra of Ni(mnt)(N-N,CH₃,Ph) (—), Ni(tfd)(N-N,CH₃,Ph) (· · · · ·), and Ni(tfd)(N-N,CH₃,*m*-ClC₆H₄) (-----), all 2×10^{-4} M in dichloromethane.

neutral bis(dithiolene) complexes, namely (S-S,Ph) > tfd > mnt. The chemically reversible oxidations (with the possible exception of Ni(tfd)(N-N,CH₃,N=CHPh)) are one-electron processes, but some of the irreversible

oxidative processes may correspond to two-electron transfers or catalytic sequences.

Significant medium effects are also apparent in the data, oxidations occurring at more positive potentials

Table IV. Spectral Data^a

Complex	Medium	18.7	19.35 (5.1)	20.0	23.0 (w)	26.2 (sh)	29.6	37.9 (37)	44.5 (49)
Ni(tfd)(phen)	Crystal ^b	18.7	19.35 (5.1)	20.0	23.0 (w)	26.2 (sh)	29.6	37.9 (37)	44.5 (49)
	CH ₂ Cl ₂	19.35 (5.1)	20.5 (5.0)	20.5 (sh, vw)	23.5 (sh, <1.5)		29.6 (sh, 4.5)	37.9 (33)	
	CH ₃ CN-CH ₂ Cl ₂ ^c	20.5 (5.0)	18.4 (5.1)				29.9 (5.0)	36.2 (sh)	
Ni(tfd)(5-NO ₂ phen)	Toluene-CH ₂ Cl ₂ ^c	18.2	18.2	19.9 (sh, vw)	23.4	26.0 (sh, 2)	29.6 (sh, 4.3)	36.4 (sh)	43.4
	Crystal ^b	17.1	15.4 (sh, w)	18.5 (sh, vw)	24.0 (vw)		28.4 (sh, vw)		
	Toluene	14.6 (7.2)		18.5 (sh, w)	23.0 (sh)	26.5 (sh)		38.5 (16.9)	
Ni(tfd)(N-N,CH ₃ ,Ph)	CH ₂ Cl ₂	15.6 (5.7)	16.5 (sh)	16.5 (sh)	24.0 (sh)	27.0 (sh)	36.2 (16.1)	38.7 (16.4)	
	CH ₃ CN	17.9 (5.2)							
	Crystal ^b	17.15	15.45 (sh, w)	18.2 (sh, vw)	22.8 (sh, vw), 24.0 (sh, vw)				
Ni(tfd)(N-N,CH ₃ , <i>m</i> -ClC ₆ H ₄)	Crystal ^b	16.95		16.3 (sh)	23.5 (sh, <1)	26.5 (sh, <1.8)	35.5 (20.0)	38.1 (20.0)	
	CH ₂ Cl ₂	15.2 (6.8)							
	Crystal ^b	19.5	18.2 (sh, vw)	21.1 (3.6)	23.0 (sh, vw)	26.8 (sh, 1.7)	26.25	31.3 (3.3)	40.1 (25.8)
Ni(tfd)(C ₆ H ₄ (NH) ₂)	Crystal ^b	14.2 (15.5)							
	CH ₂ Cl ₂	16.4	15.4 (sh)		23.0 (sh, vw)	26.25	27.0 (7.4)	37.0 (48)	43.6 (57)
	Crystal ^b	16.4							
Ni(mnt)(N-N,CH ₃ ,Ph)	Crystal ^b	18.1	16.8 (sh)	18.1 (1.6)	24.0 (sh, 1.0)	27.5	33.75 (23.1)	37.5 (sh)	43.7 (18.1)
	CH ₂ Cl ₂	17.55	15.9 (sh)	17.1 (6.6)	23.8 (sh)		32.3 (32)	39.7 (26)	
	Crystal ^b	13.87 (12.0)	12.95 (20.7)	18.35 (1.85)	22.7 (sh)	26.3 (5.6)	31.6 (48)	37.2 (35)	
Ni(tfd)(S-S,Ph)	CH ₂ Cl ₂	11.70 (29.6)	11.70 (29.6)	16.8 (2.0)	17.9 (sh, 2.1), 19.2 (1.6)	23.8 (sh, 1.3)	25.0 (1.2)	32.3 (sh, 4.7)	36.3 (9.0)
	CH ₃ CN	12.7 (54.9)	15.4 (5.6)						
	DMSO								

^a Frequencies in kK; millimolar extinction coefficients given in parentheses. Key: sh = shoulder, vw = very weak, w = weak, < = not measured. ^b Reflectance spectrum of powder diluted with MgSO₄; the spectrometer high frequency cut-off was 33 kK. ^c Saturated solution. ^d Data from A. L. Balch and R. H. Holm, *J. Amer. Chem. Soc.*, **88**, 5201 (1966). ^e 4:1 v/v.

and reductions at more negative potentials in dichloromethane than in acetonitrile or DMSO.

Electronic Spectra. Representative solution spectra are presented in Figure 1, and all spectral data for solid and solution phases are tabulated in Table IV. All complexes possess one intense ($\epsilon = (5-10) \times 10^3 M^{-1} \text{ cm}^{-1}$) absorption in the low-frequency visible region, several lower intensity ($\epsilon \sim 1 \times 10^3 M^{-1} \text{ cm}^{-1}$) transitions 20–28 kK, and several high-intensity absorptions 28–45 kK. This spectral pattern is also characteristic of parent bis(dithiolene) complexes Ni(S—S)₂⁰ and Ni(S—S)₂⁻¹ and of the bis(diimine) complexes Ni(N—N)₂^{0,2}.

Ni(tfd)(phen) and Ni(mnt)(N—N,CH₃,Ph)·0.5CH₂Cl₂ are diamagnetic in the solid state. In view of the invariance of the spectral pattern observed for all mixed-ligand complexes, and its correspondence with the pattern for the diamagnetic neutral bis(dithiolene) and bis(diimine) nickel complexes, it is presumed that all of the mixed-ligand complexes possess spin singlet ground states in crystalline and solution phases.

It is the lowest frequency intense absorption which provides most information about the electronic structure of these complexes. This transition is unique in the spectral pattern in that it is markedly medium dependent and is influenced by substituents on the dithiolene and diimine ligands. This low-frequency intense transition in the dithiolene diimine complexes exhibits a strong negative solvatochromism^{13–15} which does not appear to any appreciable extent in the higher frequency transitions. The solvent-dependent frequency shift is illustrated for Ni(tfd)(phen) in mixtures of acetonitrile, dichloromethane, and toluene in Figure 2, and data for 19 pure solvents are plotted in Figure 3 against the product of the solvent gas-phase dipole moment and its molar concentration in the liquid phase at 25°.

The negative solvatochromism, a consequence of the Franck–Condon principle, reveals that there is a large electric dipole associated with the ground state of the solute and that the transition in question reduces, reverses, or rotates that dipole. The observed effect is a measure of the interactions between the solute complex and the solvent. From the spectra in Figure 1 and the data in Table IV it can be seen that this low-frequency transition in some of the complexes is accompanied by one or two weaker shoulders. Additional studies in solvent mixtures indicate that only one transition in this manifold shows a frequency dependence on the solvent. These detailed results and their interpretation in terms of the solvation of the dithiolene diimine complexes will be reported in full in a separate paper. For the present purposes of elucidating the electronic structures of the mixed-ligand complexes, it is sufficient to conclude that the ground state is markedly dipolar, and one (only) of the lower excited states is much less so.

The frequency of the low-frequency intense transition is increased by electron-withdrawing substituents on the dithiolene ligand and decreased by electron-withdrawing substituents on the diimine ligand. Thus the dithiolene character of the orbital populated in this low-energy excited state is less than the dithiolene character of the depopulated ground-state orbital, whereas the diimine

(13) C. Reichardt, *Angew. Chem., Int. Ed. Engl.*, **4**, 29 (1965).

(14) W. Liptay, *Angew. Chem., Int. Ed. Engl.*, **8**, 177 (1969).

(15) E. M. Kosower, "An Introduction to Physical Organic Chemistry," Wiley, New York, N. Y., 1968, Part Two, Medium Effects.

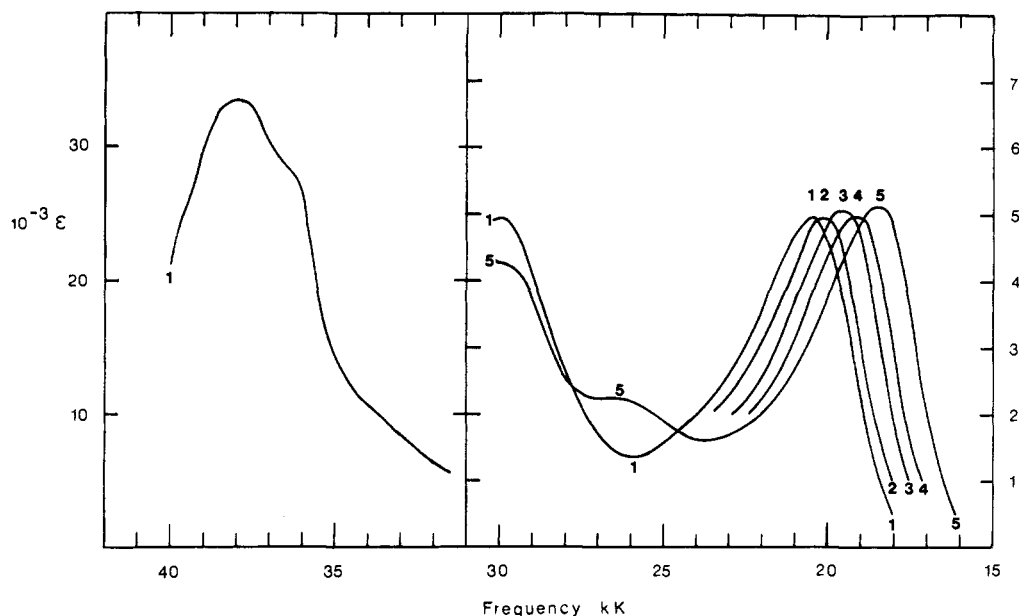


Figure 2. Spectra of Ni(tfd)(phen), 1×10^{-4} M, in the following solvents (mixtures by volume): 1, CH₂Cl₂-CH₃CN (1:4); 2, CH₂Cl₂-CH₃CN (3:2); 3, CH₂Cl₂; 4, CH₂Cl₂-toluene (3:2); 5, CH₂Cl₂-toluene (1:4).

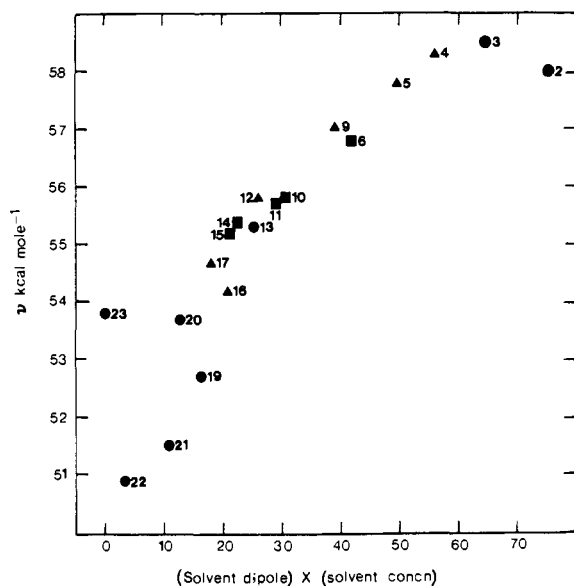


Figure 3. Plot of the frequency (in kcal mol⁻¹) of the lowest frequency absorption maximum of Ni(tfd)(phen) in various solvents against the product of the gas-phase dipole moment of the solvent and the molar concentration of the solvent in the liquid phase. Solvent key: 2, CH₃CN; 3, CH₃NO₂; 4, DMSO; 5, DMF; 6, CH₃OH; 9, acetone; 10, acetic acid; 11, ethanol; 12, pyridine; 13, CH₂Cl₂; 14, 1-propanol; 15, 2-propanol; 16, THF; 17, ethyl acetate; 19, bromobenzene; 20, CHCl₃; 21, diethyl ether; 22, toluene; 23, dioxane.

character is greater in the excited-state orbital than the ground-state orbital.

Vibrational spectra (4000–600 cm⁻¹) of the mixed complexes were recorded, but they are generally too complex to permit unambiguous assignment of informative vibrations. The compounds were insufficiently soluble in unreactive solvents for molecular weight or dipole moment determinations.

Discussion

All results are consistent with description of the

neutral dithiolene diimine nickel complexes as monomeric square-planar complexes in crystalline and solution phases, analogous to the parent neutral bis(dithiolene)^{1, 16, 17} and bis(diimine) nickel complexes.^{2, 18} The mixed complexes undergo electron-transfer reactions¹⁹ and belong to a four-membered electron-transfer series (eq 4) with complex charges $z = +1, 0, -1,$ and -2 . This behavior is intermediate between the observations for the parent bis(dithiolene) and bis(diimine) complexes.

The unique property of the mixed-ligand complexes is their electronic structure, which is revealed primarily by the electrochemical and spectral data. There are certain significant relationships contained within the set of electron-transfer potential data (Table III) which we believe reflect directly the electronic structure of the mixed-ligand complexes. These comparative relationships are presented in Table V.

For a transition metal complex the connection between the potential for a pure electron-transfer process in solution and an orbital description of electronic structure^{20, 21} often contains more theoretical parameters than observables. However, for the present set of complexes it is possible to circumvent the uncertainties associated with the variable solvation energies of species with different charges. Where there exists a series of isostructural and isoelectronic complexes with the same spin state, comparisons of the potentials for electron-transfer processes involving the same charges and in the

(16) R. Eisenberg, *Progr. Inorg. Chem.*, **12**, 295 (1970).

(17) K. W. Browall, T. Bursh, L. V. Interrante, and J. S. Kasper, *Inorg. Chem.*, **11**, 1800 (1972).




(18) The frequency of the lowest frequency intense transition in crystals of the mixed complexes is indicative of a strongly polar crystalline environment and suggests the possibility of some molecular association. X-Ray crystallographic investigations are in progress.

(19) The "purity" of this electron transfer, namely the absence of associated atom rearrangements, is suggested by the chemical reversibility of the voltammetric processes under the more inert conditions but cannot be confirmed without structural information for the reduced and oxidized species.

(20) A. A. Vlcek, *Electrochim. Acta*, **13**, 1063 (1968).

(21) A. A. Vlcek, Abstracts, XIV International Conference on Coordination Chemistry, Toronto, 1972, p 220.

Table V. Comparisons of Electron-Transfer Potentials^a

Part A. Comparison of Mixed-Ligand Complex with Parent Bis-Ligand Complexes				
(S—S)	(N—N)	Process	$\frac{E[\text{Ni}(\text{N—N})(\text{S—S})] - E[\text{Ni}(\text{S—S})_2]}{E[\text{Ni}(\text{N—N})_2] - E[\text{Ni}(\text{S—S})_2]}$	
tfd	(N—N, CH ₃ , Ph)	0 ⇌ -1 -1 ⇌ -2	0.71 0.91	
mnt	(N—N, CH ₃ , Ph)	0 ⇌ -1 -1 ⇌ -2	0.69 0.90	
tfd	C ₆ H ₄ (NH) ₂	0 ⇌ -1 -1 ⇌ -2	0.68 0.63	
Part B. Substituent Effects at One Ligand (L ₂) in Comparison with That in Parent Bis Complexes, Ni(L ₂) ₂				
L ₁	L ₂	L ₂ '	Process	$\frac{E[\text{Ni}(\text{L}_1)(\text{L}_2)] - E[\text{Ni}(\text{L}_1)(\text{L}_2')]}{E[\text{Ni}(\text{L}_2)] - E[\text{Ni}(\text{L}_2')_2]}$
tfd	C ₆ H ₄ (NH) ₂	(N—N, CH ₃ , Ph)	+1 ⇌ 0 0 ⇌ -1 -1 ⇌ -2	<0.24 ^b 0.72 2.6 ^c
phen	tfd	(S—S, Ph)	0 ⇌ -1 -1 ⇌ -2	0.26 0.19
(N—N, CH ₃ , Ph)	tfd	mnt	0 ⇌ -1 -1 ⇌ -2	0.43 ca. 0.1
Part C. Comparisons of Literature Data ^d for Centrosymmetrical Complexes, According to Donor Atom Variation				
N—N ligand	N—S ligand	S—S ligand	Process	$\frac{E[\text{NiN}_2\text{S}_2] - E[\text{NiS}_4]}{E[\text{NiN}_4] - E[\text{NiS}_4]}$
			0 ⇌ -1 -1 ⇌ -2	0.48 0.49
Part D. Diimine Ligand Substituent Effects				
Process	$E[\text{Ni}(\text{tfd})(5\text{-NO}_2\text{phen})] - E[\text{Ni}(\text{tfd})(\text{phen})], \text{V}$			
+1 ⇌ 0 0 ⇌ -1 -1 ⇌ -2	+0.16 +0.51 ca. +0.67			
Complex	$E_{1/2} (0 \rightleftharpoons -1), \text{V}$			
Ni(tfd)(N—N, CH ₃ , <i>m</i> -ClC ₆ H ₄)	-0.78			
Ni(tfd)(N—N, CH ₃ , C ₆ H ₅)	-0.83			
Ni(tfd)(N—N, CH ₃ , <i>p</i> -CH ₃ OC ₆ H ₄)	-0.85			
Part E. Differences between Successive Potentials				
Complex	$E(0 \rightleftharpoons -1) - E(-1 \rightleftharpoons -2), \text{V}$			
Ni(S—S) ₂	Ni(tfd) ₂ Ni(mnt) ₂ Ni(S—S, Ph) ₂	1.06 1.04 0.94		
Ni(N—N) ₂	Ni(C ₆ H ₄ (NH) ₂) ₂	0.71		
Ni(N—S) ₂	Ni(C ₆ H ₄ (NH)(S)) ₂	0.85–0.90		
Ni(N—N)(S—S)	Ni(tfd)(C ₆ H ₄ (NH) ₂) Ni(tfd)(N—N, CH ₃ , Ph) Ni(tfd)(phen) Ni(S—S, Ph)(phen) Ni(tfd)(5-NO ₂ phen) Ni(tfd)(N—N, CH ₃ , N=CHPh)	0.73 0.76 0.70 0.64 0.56 0.51		

^a In all cases the ratios involve comparable potentials ($E_{1/2}$, E_p , or $E_{p/2}$) in the same solvent with the same reference. ^b Obtained using the +2 ⇌ 0 potential for Ni(N—N, CH₃, Ph)₂: A. L. Balch and R. H. Holm, *J. Amer. Chem. Soc.*, **88**, 5201 (1966). It is assumed that the potential for the unobserved +1 ⇌ 0 process would not be more negative than this value. ^c The actual value of this ratio is insignificant, due to the small potential difference (0.21 V) between the parent complexes Ni(L₂)₂ and Ni(L₂')₂. It is significant that this ratio is substantially greater than 0.5. ^d R. H. Holm, A. L. Balch, A. Davidson, A. H. Maki, and T. E. Berry, *J. Amer. Chem. Soc.*, **89**, 2866 (1967). ^e In DMSO, *vs.* sce.

same medium reveal differences which may be directly associated with the one-electron and two-electron energies which characterize the orbital containing the transferred electron.²² Then the analytical principle is that the influence of substituents at various locations upon the electron-transfer potential is a measure of the

(22) In these comparisons the implied attribution of electronic energy changes to only the redox orbital is not an unreasonable approximation. The occurrence of pure electron-transfer necessitates that the redox orbital be delocalized over at least several atoms.²⁰ Then geometrical and core orbital energy changes engendered by a change in population of the redox orbital are expected to be relatively small and without major contribution to comparisons over a series of very similar complexes.

contribution of atomic or group orbitals at those locations to the redox molecular orbital.^{23,24} For the present mixed-ligand complexes this approach, utilizing comparison with the parent bis-ligand complexes, reveals the relative contributions of the diimine and dithiolene ligand orbitals to the complex valence orbitals.

The following conclusions are developed from the comparisons in Table V. (a) The two one-electron reductions resemble more closely the reductions of the

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(24) A. Wolberg and J. Manassen, *J. Amer. Chem. Soc.*, **92**, 2982 (1970).

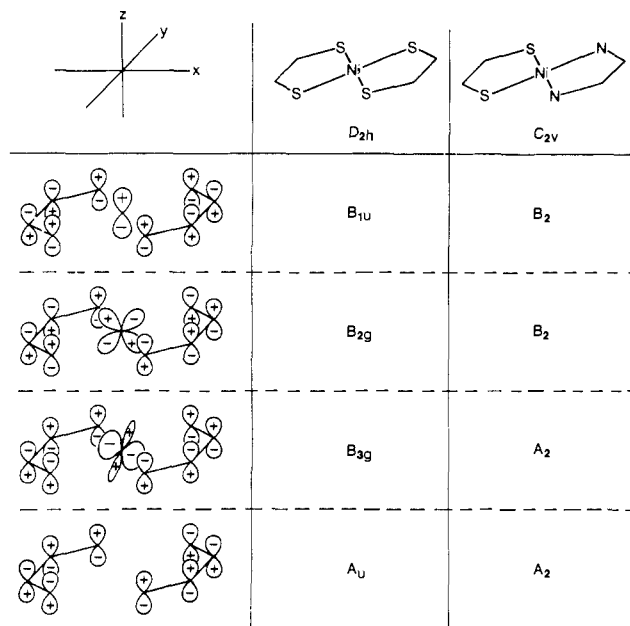


Figure 4. Symmetry representations for the pertinent π^* orbitals of bis(dithiolene) and dithiolene α -diimine nickel complexes.

parent bis(diimine) complexes than the bis(dithiolene) complex reductions (Table V, Part A) and respond more to diimine ligand variation (part B). Therefore the lowest unfilled molecular orbital (LUMO) in the neutral mixed-ligand complexes possesses more diimine than dithiolene character. With the assumption that the metal contribution to the LUMO in the mixed complexes is midway between its contributions in the parent complexes,²⁵ the ligand contributions to the mixed complex LUMO are assigned as 70% diimine, 30% dithiolene. (The results in Table VA indicate further that the reduction orbital in the (N—N,CH₃,Ph) complexes acquires more diimine character (90% diimine, 10% dithiolene) after introduction of the first electron.²⁶) (b) One electron oxidation is relatively unresponsive to diimine ligand variation. (The dependence on dithiolene ligand variation cannot be assessed directly due to the limited data on oxidation of the parent bis(dithiolene) complexes.) (c) Differences between potentials for successive one-electron reductions of the mixed complexes are relatively small (0.5–0.75 V), like the value (0.71 V) for the bis(diimine) complex Ni(*o*-C₆H₄(NH)₂)₂ but unlike the values of this energy for the bis(dithiolene) complexes (1.0 ± 0.1 V) (Table VE). This further supports assignment of predominant diimine character to the reduction orbital. (d) Substitution of the phenanthroline ligand produces a pronounced change in the reduction potentials and not more than one-third of this change in the oxidation potential. However, substituent effects on the phenyl rings of biacetylbisaniol are almost negligible²⁷ (Table VD). The extra-chelate anil π system is very weakly conjugated with the diimine chelate ring reduction orbital.

A partial molecular orbital description able to account

(25) The validity of this assumption is supported by the results in Table VC, where the same analysis for centrosymmetrical complexes with analogous ligands yields the expected ratios of 0.5.

(26) The $-1 \rightleftharpoons -2$ potentials for (N—N,CH₃,Ph) mixed complexes approach the potential (-1.82 V vs. sce) for the two-electron reduction of uncoordinated (N—N,CH₃,Ph).

(27) This substituent effect is about one-fourth of that in Ni(S—S,Ph)₂ derivatives.²³

for all observed properties of the mixed complexes can be derived from the π -orbital scheme for the neutral bis(dithiolene) nickel complexes. The butadiene-like ligand π orbitals and metal orbitals of importance are displayed in Figure 4 with the symmetry labels for D_{2h} (bis(dithiolene) or bis(diimine) complexes) and C_{2v} (dithiolene diimine complexes). The influential difference between mixed-ligand complexes and bis-ligand complexes is the nondegeneracy of the ligand π orbitals in the former, the diimine π orbitals residing at higher energy than the corresponding dithiolene orbitals.²⁸ The essential parts of the MO diagrams for bis(dithiolene) and dithiolene diimine nickel complexes are shown in Figure 5. The orbital energies and compositions for Ni(S—S)₂ are those calculated by Teo²⁹ for Ni(mnt)₂,⁹ and the diimine ligand orbitals are placed at an arbitrarily higher energy than comparable dithiolene orbitals. Molecular orbital labels are those utilized by Schrauzer³⁰ for Ni(S—S,H)₂. The only consequential difference between the bis(dithiolene) complex MO schemes of Schrauzer and Teo lies in the relative energies of 4a_g (almost pure metal 3d) and 2b_{3g} ($\geq 75\%$ metal 3d_{yz}); Schrauzer assigns 4a_g as the HOMO, whereas Teo calculates 2b_{3g} to be 0.3 eV above 4a_g. There is good agreement between the two calculations (Schrauzer 18%; Teo 23%) of the 3d_{zz} character for the LUMO 3b_{2g}.

Predictions deriving directly from the higher energy of the diimine ligand π orbitals are all substantiated by the observed properties of the mixed complexes.

(1) The LUMO, the reduction orbital, b₂(3b_{2g}) is predominantly a diimine orbital, as is confirmed by the electrochemical correlations (a). Combination of the calculated value of the metal character of this orbital in bis(dithiolenes) with the semiquantitative electrochemical estimates of the subdivision of the ligand portion of this orbital leads to the prediction that in mixed complexes such as Ni(mnt)(N—N,CH₃,Ph) or Ni(tfd)-(*o*-C₆H₄(NH)₂)₂ the LUMO is composed of 20% metal 3d_{zz}, 55% diimine B₂, and 25% dithiolene B₂. It will be interesting to see whether this is confirmed by calculations.

(2) The oxidation orbital (HOMO) is mainly metal 3d_{yz} in character, consistent with the small diimine ligand influence on one-electron oxidation of the complexes. There is good agreement between the observation that the influence of 5-nitro substitution of phenanthroline is three times greater in reduction than in oxidation, and the theoretical predictions that both reduction and oxidation orbitals contain more diimine than dithiolene character but that the reduction orbital contains approximately three times less metal character than the oxidation orbital.

(3) The low-frequency intense absorption is assigned as the strongly allowed transition b₂(2b_{1u}) → b₂(3b_{2g}). Its dithiolene → diimine character is supported by both dithiolene and diimine substituent effects.³¹ This

(28) The justification for this derives from the markedly more negative reduction potentials of bis(diimine) nickel complexes compared with bis(dithiolene) analogs.

(29) B. K. Teo, private communication, using the method of R. F. Fenske, *Pure Appl. Chem.*, **27**, 61 (1971).

(30) (a) G. N. Schrauzer and V. P. Mayweg, *J. Amer. Chem. Soc.*, **87**, 3585 (1965); (b) G. N. Schrauzer, *Accounts Chem. Res.*, **2**, 72 (1969).

(31) The solvatochromic transition in other accentric metal complexes with diimine ligands is ascribed to charge transfer into the diimine ligand: J. Burgess, *Spectrochim. Acta, Part A*, **26**, 1369, 1957 (1970); J. Burgess, *J. Organometal. Chem.*, **19**, 218 (1969).

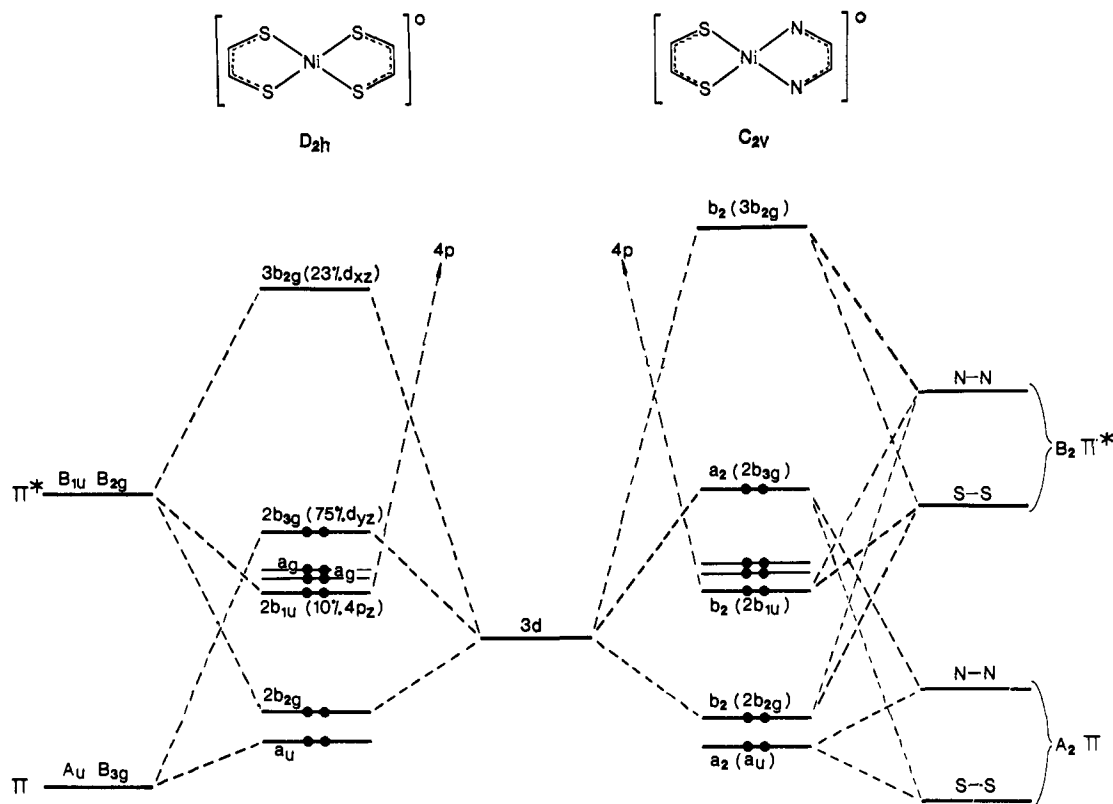
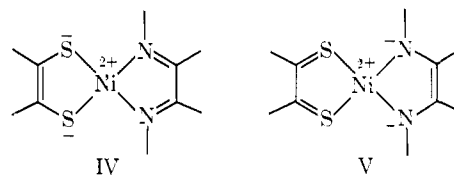


Figure 5. Diagrams showing the higher filled and lowest unfilled molecular orbitals for bis(dithiolene) and dithiolene α -diimine nickel complexes. D_{2h} symmetry labels are marked parenthetically in C_{2v} . All orbitals are π_v type except the two close lying $a_g(\sigma)$ levels. The bis(dithiolene) nickel complex orbital energies and compositions are those calculated for $Ni(mnt)_2^0$.

transition is analogous to the $2b_{1u} \rightarrow 3b_{2g}$ transition in bis(dithiolene) and bis(diimine) complexes except that it has somewhat higher frequency; the frequency of this transition in $Ni(tfd)(o-C_6H_4(NH)_2)$ is greater than the corresponding frequencies for $Ni(tfd)_2$ and $Ni(o-C_6H_4(NH)_2)_2$ (see Table IV). This observation also evolves from the qualitative MO scheme of Figure 5, as a consequence of the dithiolene and diimine π orbital non-degeneracy.

It is noted that although the $a_2(2b_{3g}) \rightarrow b_2(3b_{2g})$ transition is formally allowed, the required asymmetry of the $a_2(2b_{3g})$ orbital arises only from donor atom inequivalence and not the full ligand π -orbital symmetry as is the case for the $b_2(2b_{1u})$ orbital. Furthermore, $a_2(2b_{3g}) \rightarrow b_2(3b_{2g})$ is mainly diimine \rightarrow diimine and is tentatively assigned as the shoulder at *ca.* 16 kK in (N—N,CH₃,Ph) mixed complexes.

(4) The ground state fully populates all MO's derived from the A_2 ligand orbitals. However, $b_2(2b_{1u})$, which is mainly dithiolene B_2 , is also populated whereas $b_2(3b_{2g})$, mainly diimine B_2 , is not. This corresponds to ground-state accumulation of negative charge on the dithiolene chelate, or, in VB terms, to contribution by a dipolar resonance form, IV, to an otherwise almost symmetrical total electron distribution. The low-frequency charge-transfer transition $b_2(2b_{1u}) \rightarrow b_2(3b_{2g})$ shifts this "dithiolate" electron density to an orbital which is predominantly diimine π^* . Therefore an important resonance contributor to the excited state is V. Thus the MO



Scheme of Figure 5 accounts for the strong ground-state dipole of the dithiolene diimine complexes and the change (annulment and possibly reversal) of the excited state molecular dipole and thereby for the negative solvatochromism.

(5) Higher frequency intense absorptions generally correlate with parent bis-ligand complex absorptions and are attributed to intra-dithiolene or intra-diimine transitions.

Thus we are able to account in a semiquantitative fashion for all characteristic properties of these mixed-ligand complexes, in which the two ligands are quite dissimilar and the asymmetry of the electronic structure is more pronounced than in other mixed-ligand complexes such as mixed 1,2-dithiolenes^{12,32,33} and 1,2-dithiolene 1,1-dithiolate complexes.^{34,35}

Acknowledgment. This work was supported by the National Science Foundation (GP 24443X).

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(34) J. G. M. Van der Linden, *J. Inorg. Nucl. Chem.*, **34**, 1645 (1972).

(35) A. Hermann and R. M. Wing, *Inorg. Chem.*, **11**, 1415 (1972).