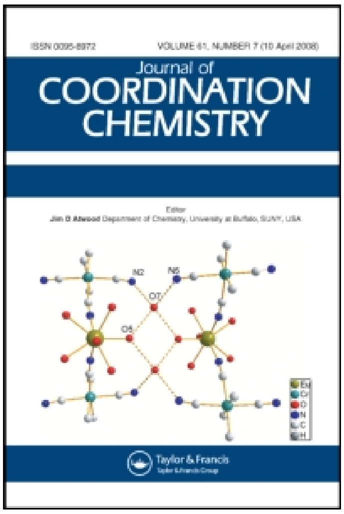

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Extraction Equilibria of Nickel(II) with 3-Mercapto-1,5-Diarylformazans in the Presence of 2,2'-Bipyridyl or 1,10-Phenanthroline

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EXTRACTION EQUILIBRIA OF NICKEL(II) WITH 3-MERCAPTO-1,5-DIARYLFORMAZANS IN THE PRESENCE OF 2,2'-BIPYRIDYL OR 1,10-PHENANTHROLINE

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The equilibria associated with nickel(II) extraction from aqueous solutions with 3-mercapto-1,5-diarylformazans (dithizone analogues, RPh–N=N–C(=S)NH–NH–PhR; H_2R_2Dz) in the presence of 2,2'-bipyridyl or 1,10-phenanthroline (L) has been investigated. The reactions between H_2R_2Dz and $[NiL]^{2+}$, $[NiL_2]^{2+}$ and $[NiL_3]^{2+}$ were also studied and found to give identical ternary nickel(II) complexes, $Ni(HR_2Dz)_2L$. The absorption spectral characteristics of ternary complex species extracted from perchlorate solutions were found to be different from those of the corresponding ternary complex species extracted from chloride, acetate, phosphate or sulfate solutions. The reaction equilibria between binary nickel(II) 3-mercapto-1,5-diarylformazan complexes, $Ni(HR_2Dz)_2$ and 2,2'-bipyridyl or 1,10-phenanthroline were also investigated and the formation constants of the ternary complex species were calculated. The effect of substituents R, on the extraction or formation constants of the ternary complexes are discussed and correlated with Hammett's σ^+ values.

Keywords: Nickel(II) extraction, dithizone, 2,2'-bipyridyl, 1,10-phenanthroline

INTRODUCTION

The synergic extraction of nickel(II) by a mixture of 3-mercapto-1,5-diphenylformazan (dithizone, Ph–N=N–C(=S)–NH–NH–Ph; H_2Dz) and 1,10-phenanthroline (phen) leads to the formation of a highly coloured ternary complex[1] $[Ni(HDz)_2\text{-}phen)]$; λ_{max} 520 nm and ε_{max} $49.1 \times 10^3\ M^{-1}\,cm^{-1}$). This has been utilized for the selective and highly sensitive extraction determination of nickel(II).[2–4] However, the extraction equilibria of the ternary nickel(II) complex are not clearly understood. According to Freiser and Freiser,[1] the formation of $[Ni(HDz)_2phen]$ takes place through the initial formation of bisdithizonatonickel(II), $[(Ni(HDz)_2]$, followed by its reaction with 1,10-phenanthroline, (*1*) and (*2*).

$$Ni^{2+} + 2H_2Dz_{org} \rightleftharpoons [Ni(HDz)_2]_{org} + 2H^+ \qquad (1)$$

$$[Ni(HDz)_2]_{org} + phen_{org} \rightleftharpoons [Ni(HDz)_2(phen)]_{org} \qquad (2)$$

On the other hand, Ohashi *et al.*[5] have recently suggested that the formation of $[Ni(HDz)_2(phen)]$ involves the reaction between dithizone and (1,10-phenanthroline)nickel(II), $[(Ni\ phen)^{2+}]$, according to (*3*) to (*5*).

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$$Ni^{2+} + phen \overset{\text{slow}}{\rightleftharpoons} [Ni(phen)]^{2+} \quad (3)$$

$$[Ni(phen)]^{2+} + HDz^{-} \overset{\text{fast}}{\rightleftharpoons} [Ni(phen)(HDz)]^{+} \quad (4)$$

$$[Ni(phen)(HDz)]^{+} + HDz^{-} \overset{\text{fast}}{\rightleftharpoons} [Ni(HDz)_2(phen)] \quad (5)$$

In their investigation of the synergistic extraction of the ternary nickel(II) complex $[Ni(HDz)_2(phen)]$, Kawamoto and Akaiwa[6] reported that the formation of $[Ni(HDz)_2Phen)]$ involves the reaction between dithizone and $[Ni(phen)_2]^{2+}]$ as the rate-controlling step. They also suggested that $[Ni(phen)_3]^{2+}$ is inert towards dithizone.

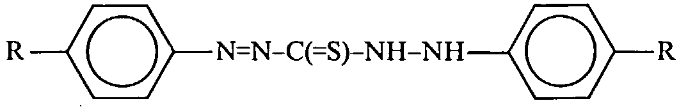
However, during our current studies on metal complexes of dithizone and its analogues, we found that all three nickel(II) species, $[Ni(phen)^{2+}]$, $[Ni(phen)_2]^{2+}$ and $[Ni(phen)_3]^{2+}$ are reactive towards dithizone and give the same extractable ternary complex, $[Ni(HDz)_2(phen)]$. The corresponding mono-, bis- and tris(2,2'-bipyridyl)–nickel(II) complexes were also found to react with dithizone or dithizone analogues to give the same ternary complex $[Ni(HR_2Dz)_2(bipy)]$.

We report here our results on studies of the extraction equilibria of nickel(II) from aqueous solutions containing perchlorate, acetate, chloride, phosphate or sulfate ions with several dithizone analogues in the presence of 2,2,'-bipyridyl or 1,10-phenanthroline (L). The reactions between dithizone analogues and $[Ni(phen)_3]^{2+}$ or $[Ni(bipy)_3]^{2+}$ in two-phase systems were also studied. The reactions between $[Ni(HR_2Dz)_2]$ and 1,10-phenanthroline or 2,2'-bipyridyl were investigated and the formation constants of ternary nickel(II) complexes are reported. The effects of substituents on the absorption spectral characteristics of the ternary nickel(II) complexes and their extraction (or formation) constants are also discussed.

EXPERIMENTAL

Reagents

3-Mercapto-1,5-diarylformazans (dithizone analogues H_2R_2Dz, I) were prepared from the corresponding arylamines by the nitroformazyl method[7,8] and purified by recrystallization from chloroform/cyclohexane mixtures.



(I)

The stock nickel(II) solution was prepared by dissolving the appropriate amount of nickel(II) sulfate hexahydrate in water. A stock solution of 2,2'-bipyridyl or 1,10-phenanthroline was prepared by dissolving known amounts of the compounds (Merck) in analytical grade chloroform.

Tris(2,2'-bipyridyl)-, and tris(1,10-phenanthroline)nickel(II) chloride complexes were prepared according to the methods of Schweitzer *et al.*,[9] and Morgan *et al.*[10]

Aqueous solutions of $[\mathrm{Ni(bipy)_2}]^{2+}$, $[\mathrm{Ni(bipy)}]^{2+}$, $[\mathrm{Ni(phen)_2}]^{2+}$ and $[\mathrm{Ni(phen)}]^{2+}$ were prepared by mixing stoichiometric amounts of nickel(II) chloride and 2,2'-bipyridyl or 1,10-phenanthroline in water. The spectral characteristics of these nickel(II) complexes were similar to those reported by Cabain *et al.*[11] and Basolo *et al.*[12]

Determination of the extraction constants (K_{et}) of the ternary nickel(II) complexes [$Ni(HR_2Dz)_2L$]

In a typical experiment, 5 cm^3 aliquots of chloroform containing known amounts of 4,4'-difluorodithizone (4,4'-$\mathrm{F_2H_2Dz}$) and 2,2'-bipyridyl were shaken for 30 minutes in stoppered glass tubes with equal volumes of sodium perchlorate (0.50 M)–sodium acetate (0.02 M) mixture at different pH values in the presence of known amounts of nickel(II). Preliminary experiments showed that equilibrium was attained in 30 minutes. After phase separation, the pH of the aqueous phase was measured and the absorption spectrum of the organic phase recorded (Fig. 1). The extraction constant, K_{et}, of the ternary complex was calculated from (*6*),

$$\mathrm{Ni^{2+}} + 2\mathrm{H_2R_2Dz_{org}} + \mathrm{L_{org}} \overset{K_{et}}{\rightleftharpoons} [\mathrm{Ni(HR_2Dz)_2L}]_{\mathrm{org}} + 2\mathrm{H^+} \qquad (6)$$

where L is bipy or phen. The equilibrium concentrations of 3-mercapto-1,5-diarylformazan and its ternary nickel(II) complex were determined spectrophotometrically, whereas $[\mathrm{H^+}]$ was calculated from the pH and the activity coefficient. The equilibrium concentration of $[\mathrm{Ni^{2+}}]$ was computed from known values of stability constants[13] of the $[\mathrm{NiL_n}]^{2+}$ complexes.

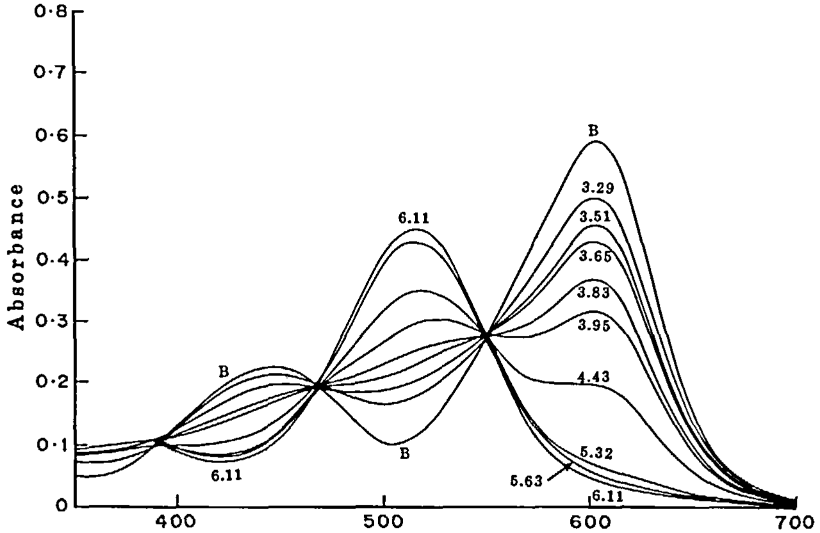


FIGURE 1 Reaction between 4,4'-$\mathrm{F_2H_2Dz}$ (2.65×10^{-5}M in $\mathrm{CHCl_3}$) and $\mathrm{Ni^{2+}}$ (8.96×10^{-5}M) in 0.50 M $\mathrm{NaClO_4}$–0.02 M sodium acetate and in the presence of 2,2'-bipyridyl (2.70×10^{-4}M in $\mathrm{CHCl_3}$). Figures on the absorption curves correspond to pH values of the aqueous phases and B is the initial 4,4'-$\mathrm{F_2H_2Dz}$ solution (l = 0.50 cm).

Reaction between tris(2,2'-bipyridyl)nickel(II) and 3-mercapto-1,5-diarylformazans

In a typical extraction experiment, 5 cm^3 aliquots of a chloroform solution containing known amounts of dithizone were equilibrated for 30 minutes with equal volumes of sodium perchlorate (0.50 M)–sodium acetate (0.02 M) solution mixture at different pH values and containing known amounts of $[Ni(bipy)_3]^{2+}$. Preliminary experiments showed that equilibrium was achiveved in 30 minutes. After phase separation, the absorption spectra of organic phases were recorded (Fig. 2), and the pH values of the aqueous phases were measured. The extraction constant K'_{et}, was calculated according to (7).

$$[Ni(bipy)_3]^{2+} + 2H_2Dz_{org} \overset{K'_{et}}{\rightleftharpoons} [Ni(HDz)_2(bipy)]_{org} + 2bipy + 2H^+ \qquad (7)$$

The equilibrium concentrations of H_2Dz and $[Ni(HDz)_2(bipy)]$ were determined spectrophotometrically, whereas $[H^+]$ was calculated from the pH measurements. The concentrations of $[Ni(bipy)_3]^{2+}$ and free bipy were computed from the known value[13] of the stability constant for $[Ni(bipy)_3]^{2+}$.

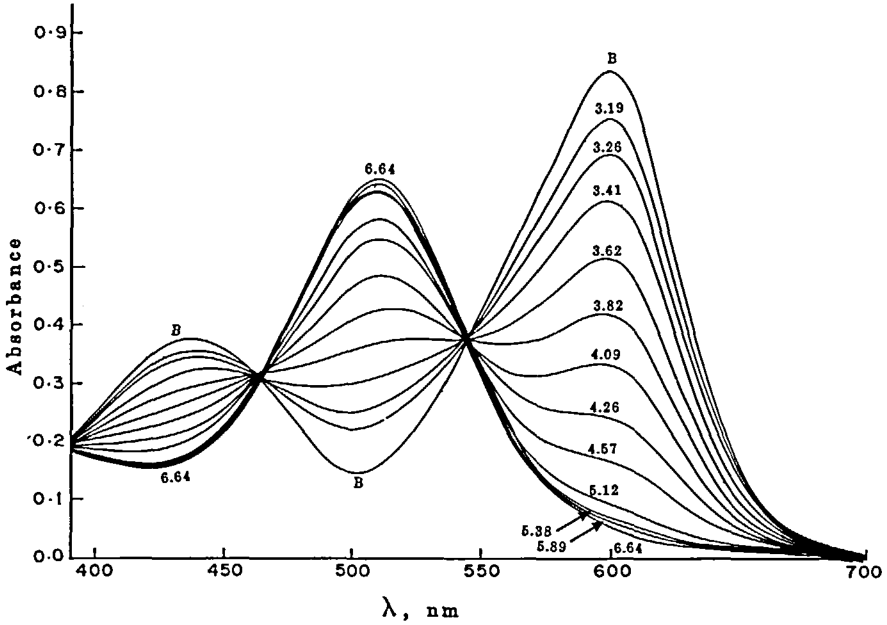


FIGURE 2 Reaction between dithizone (4.04 × 10^{-5}M in $CHCl_3$) and (1.10 × 10^{-4}M $[Ni(bipy)_3]^{2+}$ in 0.50 M $NaCl_4$–0.02 M sodium acetate solution. Figures on the absorption curves correspond to pH values of the aqueous phases and B is the initial dithizone solution (l = 0.50 cm).

Determination of the formation constants (K_{ft}) of the ternary nickel complexes $[Ni(HR_2Dz)_2L]$

Varying aliquots, x cm^3, of a chloroform solution of $[Ni(HR_2Dz)_2]$ were mixed with (5 − x) cm^3 aliquots of chloroform containing known amounts of the nitrogen base

L and the visible spectra of the mixtures were recorded. The formation constants, K_{ft}, of the ternary complexes in chloroform were calculated according to (*8*)

$$[Ni(HR_2Dz)_2]_{org} + L_{org} \overset{K_{ft}}{\rightleftharpoons} [Ni(HR_2Dz)_2L]_{org} \tag{8}$$

The equilibrium concentrations of $[Ni(HR_2Dz)_2]$ and $[Ni(HR_2Dz)_2L]$ were determined spectrophotometrically, whereas the concentration of free L was computed from the difference between the initial concentration of L and that of $[Ni(HR_2Dz)_2L]$.

Shimadzu 260 and Unicam SP 800 recording spectrophotometers were used for measurements of the visible absorption spectra of the complexes. The pH readings were measured with a Radiometer 64 pH meter.

RESULTS AND DISCUSSION

Spectral characteristics of $[Ni(HR_2Dz)_2L]$

Nickel(II) is extracted from aqueous solutions with a mixture of 3-mercapto-1,5-diarylformazan, H_2R_2Dz, and 2,2′-bipyridyl or 1,10-phenanthroline in chloroform as a highly coloured ternary complex, $[Ni(HR_2Dz)_2L]$. Typical absorption spectral changes in the organic phases as a function of pH of the aqueous perchlorate solutions are shown in Fig. 1. Within the pH range given for the curves, the successive absorption curves pass through isosbestic points at 468 and 550 nm, confirming the presence of constant stoichiometry: 3-mercapto-1,5-di(4-fluorophenylformazan, 4,4′-F_2H_2Dz, and its ternary nickel(II) complex with 2,2′-bipyridyl, *viz*, $[Ni(4,4'\text{-}F_2H_2Dz)_2(bipy)]$.

TABLE I

Spectral characteristics of the ternary nickel(II) complexes $[Ni(HR_2Dz)_2(bipy)]$ extracted from different aqueous solutions, or formed by reacting $[Ni(HR_2Dz)_2]$ with 2,2′-bipyridyl in chloroform.

	Two phase species				Single phase[@] species	
	Perchlorate media		Other media**			
H_2R_2Dz	λ_{max} (nm)	ε_{max}[a] $\times 10^{-3}$	λ_{max} (nm)	ε_{max}[a] $\times 10^{-3}$	λ_{max} (nm)	ε_{max}[a] $\times 10^{-3}$
H_2Dz	512	62.1	520	52.3	520	52.6
4,4′-$(CF_3)_2H_2Dz$	520	59.8	525	51.4	524	51.6
4,4′-Cl_2H_2Dz	523	72.6	529	56.1	529	55.9
3,3′-Cl_2H_2Dz	519	54.3	524	47.1	525	46.9
4,4′-F_2H_2Dz	517	69.3	519	55.9	520	55.0
3,3′-F_2H_2Dz	519	55.0	520	49.7	520	49.8
3,3′-$(CH_3O)_2H_2Dz$	521	54.7	524	42.9		
4,4′-$(CH_3)_2H_2Dz$	518	67.9	526	52.3	526	51.7
3,3′-$(CH_3)_2H_2Dz$	518	62.5	522	51.5	522	51.0

[a] Molar absorptivity (M^{-1} cm^{-1}). ** Chloride, acetate, phosphate or sulfate solutions. [@] Formed by reacting $[Ni(HR_2Dz)_2]$ with 2,2′-bipyridyl in $CHCl_3$.

All ternary nickel complexes [Ni(HR_2Dz)$_2$L] are intensely coloured with ε_{max} ranging from 47.1×10^3 (for [Ni(3,3'-Cl_2HDz)$_2$)bipy)] to 75.6×10^3 $M^{-1} cm^{-1}$ (for [Ni(4,4'-Cl_2HDz)$_2$(phen)] as shown in Tables I and II. The latter value is about 54% greater than values reported for [Ni(HDz)$_2$(bipy)] (49.1×10^3 at 520 nm) and which was regarded to form the basis of a highly sensitive method for the spectrophotometric determination of nickel(II).[1,14] Inspection of the spectral data for [Ni(HR_2Dz)$_2$L] (Tables I and II) reveals that the ternary complex species extracted from perchlorate solutions have higher ε_{max} values than corresponding values for the species extracted from acetate, chloride, phosphate or sulfate solutions, and that they absorb maximally at lower wavelengths. On the other hand, the spectral characteristics of [Ni(HR_2Dz)$_2$L] extracted from acetate, chloride, phosphate or sulfate solutions are identical. They are also similar to those of the corresponding ternary species formed from the reactions between authentic Ni(HR_2Dz)$_2$ and 2,2'-bipyridyl or 1,10-phenanthroline in chloroform.

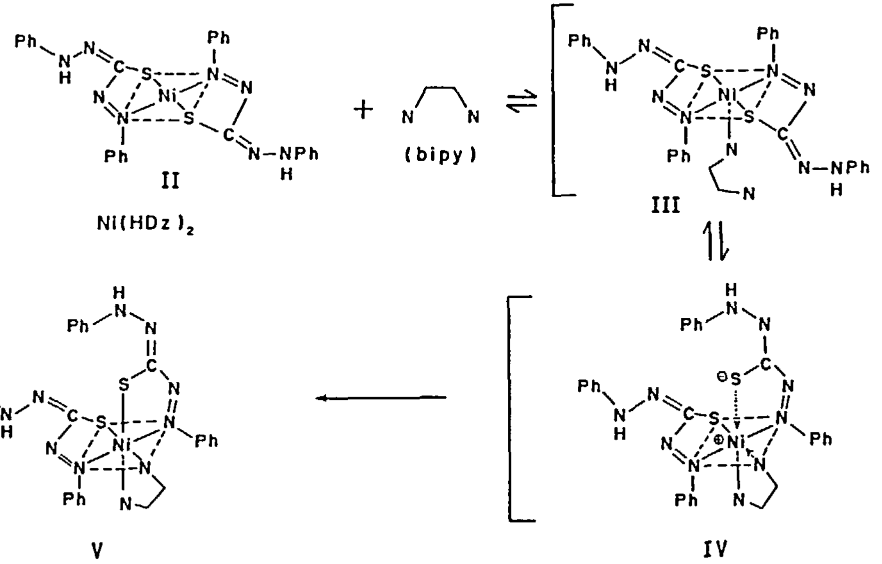
TABLE II

Spectral characteristics of the ternary nickel(II) complexes [Ni(HR_2Dz)$_2$(phen)] extracted from different aqueous solutions, or formed by reacting [Ni(HR_2Dz)$_2$] with 1,10-phenanthroline in chloroform.

	Two phase species				Single phase[a] species	
	Perchlorate media		Other media**			
H_2R_2Dz	λ_{max} (nm)	ε_{max}* $\times 10^{-3}$	λ_{max} (nm)	ε_{max}* $\times 10^{-3}$	λ_{max} (nm)	ε_{max}* $\times 10^{-3}$
H_2Dz	512	67.6	519	53.8	519	53.2
					520[1]	49.1[1]
4,4'-$(CF_3)_2H_2Dz$	520	56.3	525	52.3	524	51.6
4,4'-Cl_2H_2Dz	524	75.6	529	57.7	529	56.9
3,3'-Cl_2H_2Dz	518	59.9	525	48.4	525	47.8
4,4'-F_2H_2Dz	516	69.1	520	57.5	521	58.0
3,3'-F_2H_2Dz	518	54.7	522	51.6	522	52.0
3,3'-$(CH_3O)_2H_2Dz$	518	52.2	521	49.6		
4,4'-$(CH_3)_2H_2Dz$	518	66.4	526	54.5	527	53.9
3,3'-$(CH_3)_2H_2Dz$	517	62.0	523	53.6	522	53.0

*Molar absorptivity (M^{-1} cm^{-1}). **Chloride, acetate, phosphate or sulfate solutions. [a] Formed by reacting [Ni(HR_2Dz)$_2$] with 1,10-phenanthroline in $CHCl_3$.

Since dithizone analogues (H_2R_2Dz) investigated here react in a stoichiometrically identical manner to dithizone, their ternary nickel(II) complexes [Ni(HR_2Dz)$_2$L] extracted from acetate, chloride, phosphate or sulfate solutions, or those directly formed from the reaction between [Ni(HR_2Dz)$_2$] and L, (*8*), should have identical structures to [Ni(HDz)$_2$bipy], (II), reported by Math and Freiser.[13] According to X-ray crystallographic data, [Ni(HDz)$_2$] is a square planar complex and has a *trans* configuration with respect to the Ni–S bonds.[15] On the other hand, [Ni(HDz)$_2$-(bipy)] is an octahedral complex with a *cis* configuration with respect to the two Ni–S bonds, (III). Math and Freiser[16] suggested that the conversion from *trans*(S) to *cis*(S) structure occurs as a result of a 90° rotation of the dithizone chelate rings about an axis defined by the two dithizone nitrogen (bonding) atoms. Alternatively, this conversion may proceed according to Scheme 1 without the need of rotation of the rather bulky dithizone chelates about the Ni atom. The essential feature of Scheme 1 is the cleavage of an Ni–S bond as a result of the nucleophilic attack of 2,2'-bipyridyl at the Ni atom in [Ni(HDz)$_2$] or [NiHR$_2$Dz)$_2$]. This step is followed by a structural rearrangement process (III, IV), which ultimately results in the formation of the *cis*(S) octahedral ternary complex (V). There are other examples in the literature in which *trans*(S) square planar nickel complexes react with bidentate Lewis bases to form *cis*(S) octahedral ternary complexes.[17,18]

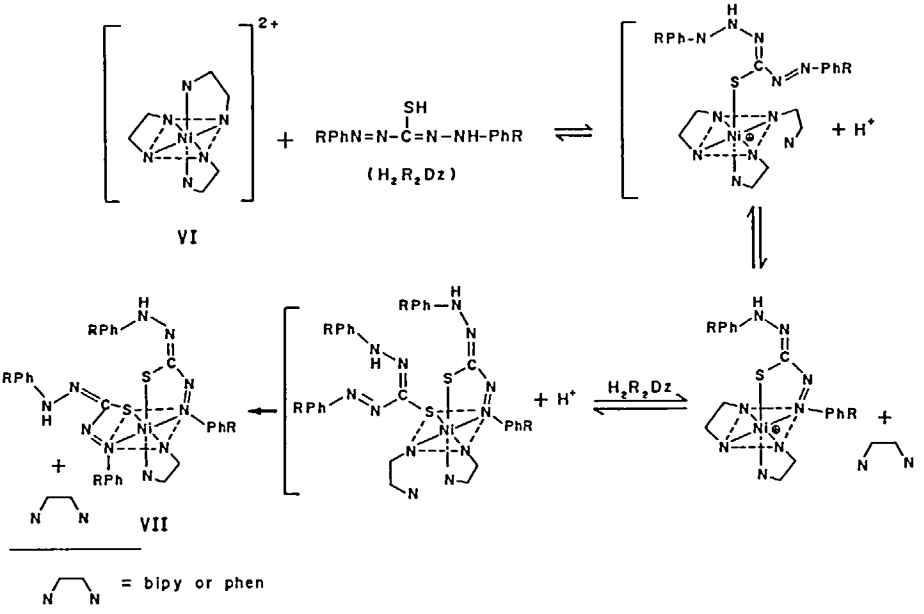


Scheme 1 Proposed mechanism for the reaction between bis(dithizonato)nickel(II) and 2,2'-bipyridyl in CHCl$_3$.

Extraction equilibria of ternary nickel(II) complexes

Although the ternary species extracted from acetate, chloride, sulfate or phosphate media may be structurally identical to those formed from the reaction between Ni(HR$_2$Dz)$_2$ and L, (*8*), they are most likely formed by a different mechanism to that shown in Scheme 1. The extraction of nickel(II) by dithizone is known to be slow[1,19] and the equilibrium requires several hours to be attained in the pH range 6.5 to 8.0. In the presence of bipy or phen, however, the extraction of nickel(II) by dithizone is greatly enhanced and the equilibrium is reached within 25–30 minutes in the same pH range.

Ohashi *et al.*[5] have proposed that, in the presence of phen, the extraction of nickel(II) by dithizone involves the reaction of the latter with (1,10-phenanthroline)-nickel(II) (*3–5*) rather than with nickel(II) ions as suggested by Freiser *et al.*[1] (*1,2*). However, on investigating the reaction between dithizone (as well as several dithizone analogues) and authentic samples of the complexes [NiL]$^{2+}$, [NiL$_2$]$^{2+}$ and [NiL$_3$]$^{3+}$, where L is 2,2'-bipyridyl or 1,10-phenanthroline, we found that all three nickel(II) complexes give the same ternary nickel(II) complex species [Ni(HR$_2$Dz)$_2$L], thus suggesting that its formation may be represented by Scheme 2.



Scheme 2 Proposed mechanism for the reaction between $[Ni(bipy)_3]^{2+}$ and H_2R_2Dz in a two-phase system.

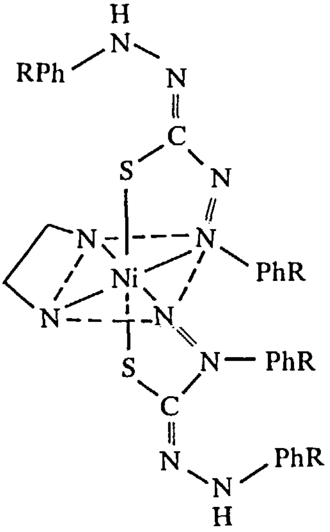
TABLE III
Extraction and formation constants for the ternary nickel complex species $[Ni(HR_2Dz)_2(bipy)]$ and $[Ni(HR_2Dz)_2(phen)]$.

	$[Ni(HR_2Dz)_2(bipy)]$			$[Ni(HR_2Dz)_2(phen)]$	
H_2R_2Dz	$\log K_{et}$	$\log K'_{et}$	$\log K_{ft}$	$\log K_{et}$	$\log K_{ft}$
H_2Dz	11.5	−8.6	4.4 (4.65)[14]	15.3	6.0 (5.96)[14]
$4,4'\text{-}(CF_3)_2H_2Dz$	13.2	−6.9	6.3		
$3,3'\text{-}Cl_3H_2Dz$	12.6	−7.5	5.3	16.5	7.1
$4,4'\text{-}Cl_2H_2Dz$	11.8	−8.4	4.8	15.8	6.5
$4,4'\text{-}F_2H_2Dz$	11.4	−8.8	4.4	15.0	5.8
$3,3'\text{-}(CH_3O)_2H_2Dz$	11.2	−9.0	4.5	15.1	6.1
$3,3'\text{-}(CH_3)_2H_2Dz$	10.8	−9.3	4.1	14.6	5.7
$4,4'\text{-}(CH_3)_2H_2Dz$	10.5	−9.6	3.8 (3.8)[14]	14.3	5.2 (5.16)[14]

Fig. 2 is a typical example of the reaction between tris(2,2′-bipyridyl)nickel(II) and dithizone. Within the pH range 3.19 to 6.14, the successive absorption curves pass through clean isosbestic points at 464 and 545 nm (confirming the existence of a constant stoichiometry involving dithizone and the ternary nickel(II) complex $[Ni(HDz)_2(bipy)]$. The spectral characteristics of the latter species were found to be identical to those (Table I) of the nickel(II) complex extracted from perchlorate solutions by a mixture of dithizone and 2,2′-bipyridyl. Accordingly, the reaction between dithizone or dithizone analogues and nickel(II) in the presence of 2,2′-bipyridyl or 1,10-phenanthroline (L) may be represented by the general equation (*9*).

$$[NiL_n]^{2+} + 2H_2R_2Dz_{org} \overset{K'_{et}}{\rightleftharpoons} [Ni(HR_2Dz)_2L]_{org} + (n\text{-}1)L + 2H^+ \qquad (9)$$

As the spectral characteristics of $[Ni(HR_2Dz)_2L]$ extracted from perchlorate solutions differ from those of the corresponding species extracted from other aqueous solutions (Tables II and III), stereoisomeric complexes, *e.g.*, *trans* (S) ternary species (VIII), may be formed by a basically similar mechanism to that proposed in Scheme 2.



VIII

Although the spectral characteristics of ternary nickel(II) complexes formed by the reactions between H_2R_2Dz and $[NiL]^{2+}$, $[NiL_2]^{2+}$ or $[NiL_3]^{2+}$ (*10–12*) were identical, their extraction constants were found to be different. Thus, the reaction

$$2H_2RDz_{org} + [NiL]^{2+} \overset{K'_{et}}{\rightleftharpoons} [Ni(HR_2Dz)_2L]_{org} + 2H^+ \qquad (10)$$

$$2H_2R_2Dz_{org} + [NiL_2]^{2+} \overset{K'_{et}}{\rightleftharpoons} [Ni(HR_2Dz)_2L]_{org} + L + 2H^+ \qquad (11)$$

$$2H_2R_2Dz_{org} + [NiL_3]^{2+} \overset{K'_{et}}{\rightleftharpoons} [Ni(HR_2Dz)_2L]_{org} + 2L + 2H^+ \qquad (12)$$

between H_2Dz and $[Ni(bipy)]^{2+}$, $[Ni(bipy)_2]^{2+}$ or $[Ni(bipy)_3]^{2+}$ in the perchlorate/chloroform two-phase system (as an example), resulted in the formation of the same $[Ni(HDz)_2(bipy)]$ species (λ_{max} 512 nm and ε_{max} 62.1×10^3 M^{-1} cm^{-1}), yet their log K'_{et} values were 0.58, −3.7 and −8.9, respectively. The reaction between H_2Dz and

$[Ni(bipy)]^{2+}$, (*10*), may be considered to be an addition reaction, whereas (*11*) and (*12*) are substitution reactions and so their low K'_{et} values may be attributed to competitive reactions of liberated L with $[Ni(HR_2Dz)_2L]$.

Substituent effects on K_{et}, K'_{et} and K_{ft}

The extraction constant K'_{et}, (*9*), of a given reaction is related to the corresponding value of K_{et}, (*6*), according to (*13*),

$$K_{et}/K'_{et} = \frac{[NiL_3{}^{2+}]}{[Ni^{2+}][L]^3} = \beta_3 \qquad (13)$$

where β_3 (the stability constant of $[NiL_3]^{2+}$) is $10^{20.13}$ and $10^{24.91}$ for $[Ni(bipy)_3]^{2+}$ and $[Ni(phen)_3]^{2+}$, respectively.[13] Both K_{et} and K'_{et} are composite parameters and depend on the acid dissociation constants of H_2R_2Dz, the stability constants of $Ni(HR_2Dz)_2L$ and their partition coefficients.[20]

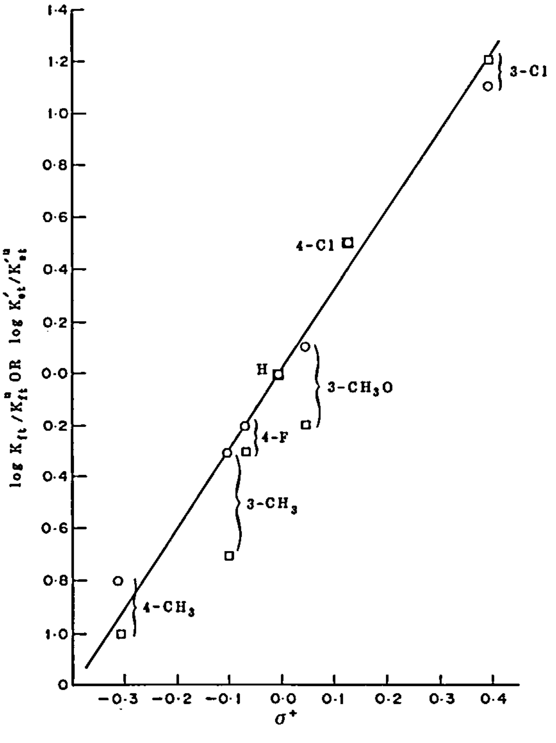


FIGURE 3 Correlation between Hammett's σ^+ values and formation constants, K_{ft}(○) and extraction constants, K'_{et} (□) for the $[Ni(HR_2Dz)_2(bipy)]$ complexes.

Inspection of the extraction or formation constants of the ternary nickel complexes (Table III) shows that, K_{et}, and K_{ft} for $[Ni(HR_2Dz)_2(phen)]$ are relatively greater than the corresponding values for $[Ni(HR_2Dz)_2(bipy)]$; this may be attributed to the relatively higher basicity of 1,10-phenanthroline ($pK_{LH}+$ 5.03)[13] compared to that of 2,2′-bipyridyl ($pK_{LH}+$ 4.4).[13] The same trend is known for the stability constants of binary nickel(II) bipyridyl and phenanthroline complexes.[13] The extraction (or formation) constants of $[Ni(HR_2Dz)_2L]$ also reflect the effect of substituents (R) in the phenyl rings of dithizone analogues. Electron withdrawing substituents (*e.g.* Cl or CF_3) were found to increase the extraction and formation constants of $[Ni(HR_2Dz)_2L]$, whereas electron donating substituents (*e.g.* 4-CH_3 or 3-CH_3O) have opposite effects. A correlation was found between Hammett's σ^+ values and log K_{ft}/K^u_{ft} or log K'_{et}/K'^u_{et} (Fig. 3) for the $[Ni(HR_2Dz)_2(bipy)]$ complexes (where K^u_{ft} or K'^u_{et} are the formation and extraction constants for $[Ni(HDz)_2(bipy)]$, respectively, with a ρ value ≈ 2.5). A similar correlation was also found by plotting the corresponding data (log K_{et} or log K_{ft}) for $[Ni(HR_2Dz)_2(phen)]$ complexes *vs* Hammett's σ^+ values ($\rho \approx 3.0$). This correlation may be attributed to the effect of substituents on Lewis acidities of the binary nickel(II) complexes $[Ni(HR_2Dz)_2]$ towards reactions with 2,2′-bipyridyl or 1,10-phenanthroline.

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