

$\Delta_{hs} < \pi < \Delta_{ls} = 13\,700 < 16\,000 < 19\,000$, is verified and that within the large experimental errors, $|\Delta - \pi|$ is of the order of 2000 cm^{-1} , another condition suggested by Griffith⁴² for the existence of spin equilibrium.

Acknowledgment. We thank Professor R. A. Osteryoung for helpful discussions and Colorado State University for some of the magnetic measurements. The financial support from

the Fundação de Amparo à Pesquisa de Estado de São Paulo is gratefully acknowledged. Profitable discussions with Drs. J. H. Christie, G. Vicentini, D. Soria, W. Hatfield, and K. Sone are also acknowledged.

Registry No. [Fe(AMP)₃](ClO₄)₂, 64020-61-7; [Fe(AMP)₃](PF₆)₂, 80105-98-2; [Fe(AMP)₃]Cl₂, 18433-69-7; [Fe(AMP)₃]Br₂, 18433-70-0.

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Spectroelectrochemical Studies of Nickel(I) Complexes: One-Electron Reduction of Nickel(II) Complexes of Dithiocarbamate and Phosphine Ligands [Ni(R₂NCS₂)_x(Ph₂PCH₂CH₂PPh₂)_{2-x}]^{2-x} (x = 0, 1, 2)

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Received February 4, 1981

The electrochemical generation and stability of nickel(I) complexes of the type [Ni(R₂NCS₂)_x(dpe)_{2-x}]^{1-x} (x = 0, 1, 2; dpe = Ph₂PCH₂CH₂PPh₂) have been investigated with use of the methods of electron spin resonance (ESR) spectroscopy and cyclic voltammetry. Reduction of the bis(dithiocarbamate) complexes Ni^{II}(R₂NCS₂)₂ at a Pt electrode in dichloromethane solution yields an initial planar nickel(I) species, which interconverts to a new nickel(I) species with "reversed" g values. In contrast Ni(dpe)₂²⁺ undergoes two closely spaced reductions, the first of which corresponds to a nickel(I) complex with four equivalent phosphorus ligands bound to the metal. The mixed-ligand complex [Ni^{II}(R₂NCS₂)(dpe)]PF₆ may be reduced to a nickel(I) species with two equivalent phosphorus ligands bound to the metal. This species undergoes a series of further reactions, resulting in an overall disproportionation to Ni^{II}(R₂NCS₂)₂ and Ni⁰(dpe)₂. The kinetics and mechanism of this reaction have been investigated with use of ESR spectra and cyclic voltammetry. The nickel(I) complexes [Ni(R₂NCS₂)₂]⁻ can also be generated by γ irradiation of frozen solutions of Ni(R₂NCS₂)₂, and these have been characterized with use of ESR spectroscopy.

Introduction

Relatively few studies of the redox behavior of nickel(II) complexes have combined the electrochemical and electron spin resonance (ESR) spectroscopy techniques. In one such study an extensive series of complexes of nickel(II) with tetraaza macrocyclic ligands were found to undergo reversible one-electron reductions. The species produced were found to be either d⁹ nickel(I) complexes or nickel(II) stabilized radical anions. These two cases were distinguished on the basis of their ESR spectra, the former having anisotropic g values greater than 2.0, the latter having isotropic g values near 2.0.² In one case an equilibrium between two species was detected by ESR, and this was attributed to a valence isomerization between a nickel(I) complex and the isomeric nickel(II) radical anion complex.^{2b} Several of these complexes have been shown to form carbonyl adducts whose ESR spectra are different from those of the parent nickel(I) complex. The one-electron reduction of square-planar M(mnt)₂²⁻ ions (M = Ni(II), Pd(II), Pt(II); mnt = maleonitriledithiolate) shows reversible behavior, and the ESR spectra of the palladium and the ⁶¹Ni (I = 3/2) enriched nickel complex are consistent with their formulation as M(I) d⁹ complexes.^{3,4}

A number of voltammetric studies of the redox behavior of nickel(II) dialkyldithiocarbamate complexes, Ni(R₂NCS₂)₂, have been reported.⁵⁻¹² In some cases there is evidence of a quasi-reversible one-electron reduction to [Ni(R₂NCS₂)₂]⁻, although it is not yet known whether the reduction is metal- or ligand-based. [Ni(R₂NCS₂)₂]⁻ is reported to react with 2,2'-bipyridyl to form Ni(R₂NCS₂)(bpy),¹¹ although it has also been reported that [Ni(R₂NCS₂)₂]⁻ reduces 2,2'-bipyridyl to the radical anion.¹²

In the present work, the techniques of voltammetry and ESR spectroscopy have been combined to study the species produced by the reduction of nickel(II) dialkyldithiocarbamate complexes of the type Ni(R₂NCS₂)₂ and [Ni(R₂NCS₂)(dpe)]⁺ (dpe = 1,2-bis(diphenylphosphino)ethane). The dpe ligand was chosen because a number of relatively stable nickel(I) complexes involving this ligand have been reported previously.¹³⁻¹⁵ The reduction of [Ni(dpe)₂]²⁺ has also been studied

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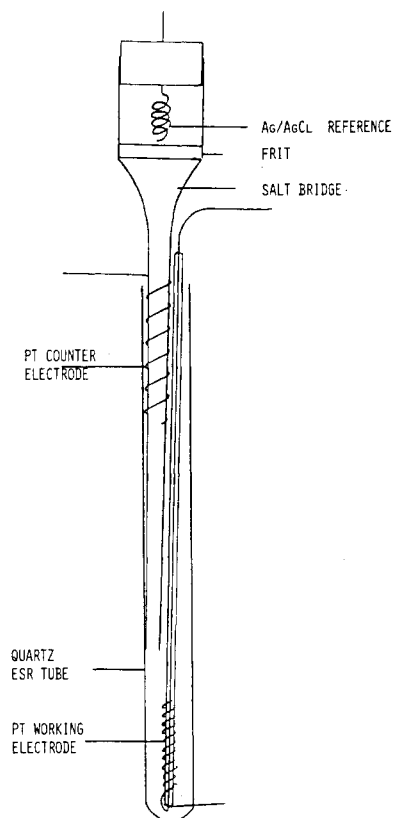


Figure 1. ESR cell for in situ electrolyses.

for comparison purposes and for resolution of some uncertainties still remaining in the literature concerning the one-electron reduction product $[\text{Ni}(\text{dpe})_2]^+$.

Experimental Section

Materials. Complexes $\text{Ni}(\text{R}_2\text{NCS}_2)_2$,⁷ $[\text{Ni}(\text{R}_2\text{NCS}_2)(\text{dpe})]\text{PF}_6$ ¹⁶ (R = ethyl (Et), *n*-butyl (Bu), cyclohexyl (Cy), benzyl (Bz)), and $[\text{Ni}(\text{dpe})_2](\text{ClO}_4)_2$ ¹⁷ were prepared by literature methods. ⁶¹Ni metal was converted to nickel(II) nitrate by digestion in concentrated nitric acid and used to prepare labeled complexes as above.

Electrochemistry. Electrochemical measurements were performed with use of either PAR 170 three-electrode instrumentation with *iR* compensation¹⁸ (ANU) or a PAR 173 potentiostat with PAR 179 digital coulometer with *iR* compensation, a ECG 175 universal programmer, and a HP 7046A XY recorder. The reference electrode was Ag–AgCl (0.1 M LiCl in acetone) separated from the voltammetric cell by a 0.1 M $[\text{Bu}_4\text{N}]\text{ClO}_4$ in acetone salt bridge. Measurements were carried out in acetone or acetonitrile (0.1 M $[\text{Et}_4\text{N}]\text{ClO}_4$ supporting electrolyte) or dichloromethane (0.1 M $[\text{Bu}_4\text{N}]\text{ClO}_4$ supporting electrolyte). In this system the oxidation potential of $[\text{Pt}(\text{maleonitriledithiolate})_2]^{2-}$ in CH_2Cl_2 was found to +0.16 V. It has been found that potentials measured in nonaqueous solvents are not reproducible in differing solvent systems. Accordingly we have referenced all potentials to the ferrocene/ferrocenium couple taken as 0.46 V relative to the Ag/AgCl 0.1 M LiCl couple. In practice for each measurement the potential for the oxidation of ferrocene in the particular system is also determined and potentials of other processes are adjusted.

Electron Spin Resonance Spectra. X-Band electron spin resonance (ESR) spectra were recorded with use of a JEOL PES 3 or Varian E4 spectrometer. Spectra were measured in CH_2Cl_2 solution at room

temperature and as a frozen CH_2Cl_2 solution between –160 and –170 °C. The electrochemically produced species were generated on a platinum wire in situ by controlled-potential electrolysis, with use of a three-electrode configuration, at potentials slightly greater than the measured reduction potential of the complex (Figure 1). Reductions in this cell could be carried out at ambient or lower temperatures with use of the Varian variable-temperature attachment. For more rapid sampling of electrolytically produced species such as in the reduction of $\text{Ni}(\text{R}_2\text{NCS}_2)_2$ complexes, an external cell was used, the solution being frozen rapidly in liquid nitrogen after anaerobic transfer to an oxygen-free quartz ESR tube. Spectra of γ -irradiated samples were measured with ESR tubes, which were used for both the irradiation and ESR measurements.

The ESR spectra of frozen solutions were simulated by calculation of the ESR line shape by integration over all orientations of the ESR-active species to give

$$f(H) = \sum_{K=1}^u \int_{\phi=0}^{\phi=90^\circ} \int_{\theta=0}^{\theta=90^\circ} (P(K, \theta, \phi))(G(H, K, \theta, \phi)) d(\cos \theta) d\phi$$

where u = number of transitions, $P(K, \theta, \phi)$ is the transition probability of the K th transition, and $G(H, K, \theta, \phi)$ is the first-derivative component line shape.¹⁹ Normalized Gaussian first-derivative line shapes were used, and the transition probability was taken to include the g term anisotropy.²⁰ The line shapes were evaluated numerically with use of the method of Smith and Pilbrow¹⁹ by summation of the appropriately weighted line shapes over the angle ranges $\theta = 0$ – 90° , $\phi = 0$ – 90° for rhombic symmetry and $\theta = 0$ – 90° , $\phi = 0$ – 180° for monoclinic symmetry.

γ -Irradiation Experiments. Saturated solutions of the nickel(II) complexes in a mixed *o*-, *m*- and *p*-xylene solvent were irradiated in quartz ESR tubes at 77 K for about 10 min with use of a ⁶⁰Co γ source with a dose rate of 1.0 Gy s^{–1} (100 rd s^{–1}). The samples were maintained at 77 K during transfer to the ESR spectrometer, and their spectra were recorded at 77 K.

Results and Discussion

Reduction of $\text{Ni}^{II}(\text{R}_2\text{NCS}_2)_2$ Complexes. Nickel(II) bis-(dialkylthiocarbamate) complexes, $\text{Ni}^{II}(\text{R}_2\text{NCS}_2)_2$, undergo a quasi-reversible one-electron reduction at a platinum electrode in acetone or dichloromethane solvents in the range –1.2 to –1.5 V relative to an Ag–AgCl electrode. Martin and co-workers⁷ found that a change in scan rates from 20 to 200 mV s^{–1} increased the cathodic–anodic peak separation in cyclic voltammograms of such complexes while i_p^r/i_p^f tended to 1. Figure 2 shows the effect of scan rate on the cyclic voltammogram for the reduction of $\text{Ni}^{II}(\text{Bu}_2\text{NCS}_2)_2$. The ratio of the peak currents of the reverse (i_p^r) to forward (i_p^f) scans varies from 0.77 to 0.94 for scan rates in the range 50–200 mV s^{–1}. This suggested that the species initially formed in the reduction process changed to some other form or decomposed to products that are not reoxidized at the same potential as the first-formed species. Analysis of the variation of i_p^r/i_p^f with scan rate for 5 different scan rates in the range 50–200 mV s^{–1} by the method of Nicholson and Shain for an electrochemical process followed by a first-order chemical process (EC mechanism)²¹ gave a first-order rate constant of $(6.2 \pm 0.2) \times 10^{-2}$ s^{–1} at 20 °C for the chemical process. The same rate constant was obtained for solutions of concentration 2.1×10^{-3} and 5.5×10^{-3} M with respect to the nickel(II) complex, supporting the first-order nature of the process. The half-life of this reaction, calculated from the measured rate constant, is 11.2 ± 0.4 s.

ESR Spectra of Reduced $\text{Ni}^{II}(\text{R}_2\text{NCS}_2)_2$ Complexes. The ESR spectra of frozen solutions sampled from controlled-potential electrolysis consisted of several lines, which could not be attributed to a single species. By variation of the time of sampling during electrolysis the relative intensities of some peaks changed in a manner suggesting a mixture of two

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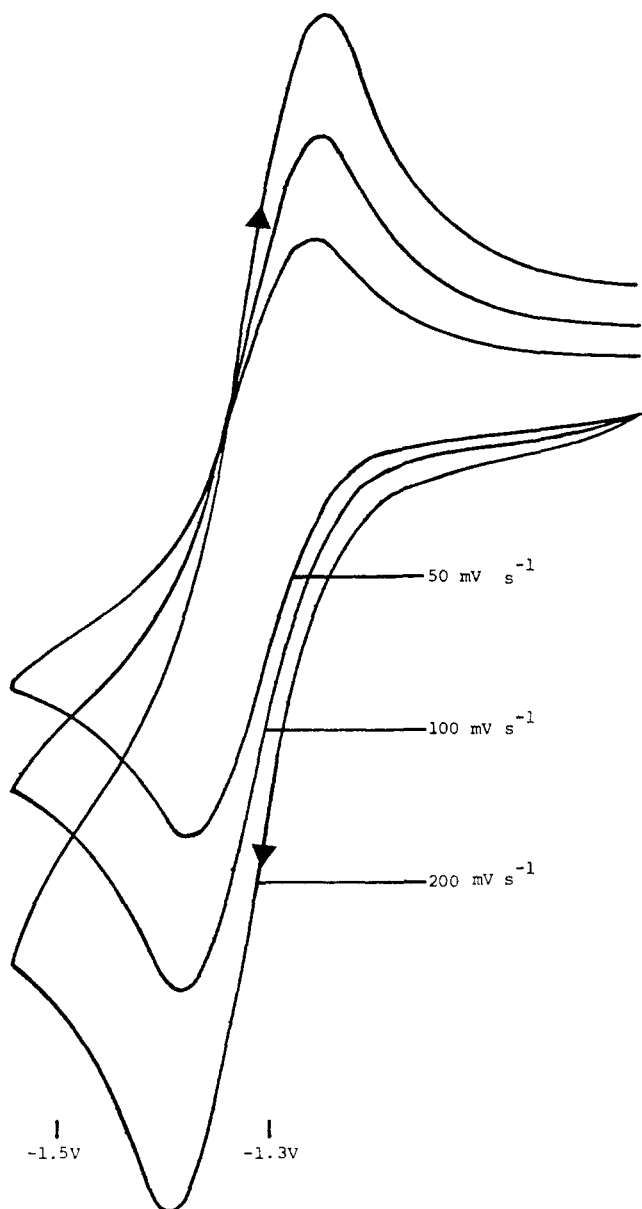


Figure 2. Effect of scan rate on the cyclic voltammogram for the one-electron reduction of $\text{Ni}^{\text{II}}(\text{Bu}_2\text{NCS}_2)_2$ (in acetone, 0.1 M $[\text{Bu}_4\text{N}]\text{ClO}_4$).

species. By very rapid sampling and freezing of the electrolysis product it was possible to observe the spectrum, shown in Figure 3, of a single species (species I). The spectrum was typical of an axially symmetric $S = 1/2$ system. Freezing-thawing experiments revealed that this species converted to a second (species II, Figure 4) whose spectrum was that observed in the initially measured mixtures. Species II was typical of a rhombically distorted $S = 1/2$ species with "reversed" g values. It was also found to be possible to observe both spectra by carrying out the controlled-potential electrolysis in the cavity of the spectrometer and freezing the sample immediately or freezing it after a suitable time interval. This method required less sample than the above and was used to obtain the spectra of the corresponding ^{61}Ni -enriched species. The spectrum for the ^{61}Ni -enriched species I showed a small amount of species II to be present, but ^{61}Ni hyperfine structure $[I(^{61}\text{Ni}) = 3/2]$ was clearly resolved in the parallel region of the spectrum. Similarly the spectrum of species II shows a small contribution of species I; however, reasonably well-resolved ^{61}Ni hyperfine structure was seen in the parallel region. The hyperfine lines showed an anomalous intensity distribution, which is not reproduced in computer simulations of this

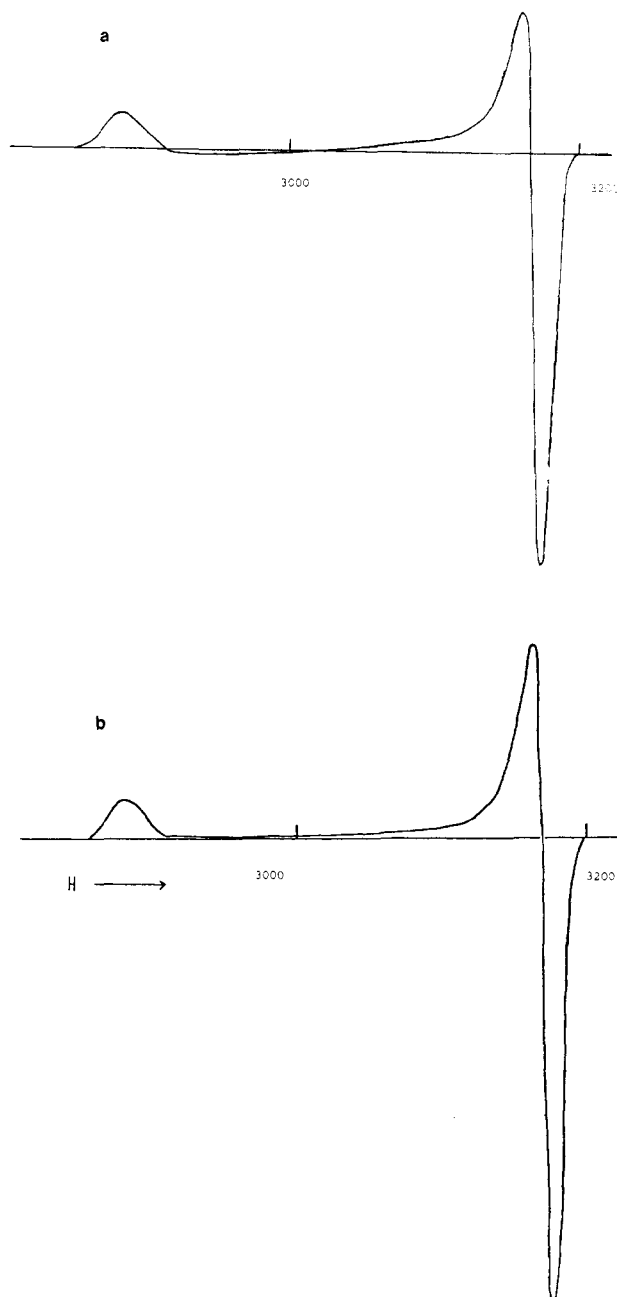


Figure 3. (a) ESR spectrum (9.197 GHz) of reduced $\text{Ni}(\text{Bu}_2\text{NCS}_2)_2$ (species I) in frozen acetone solution (77 K). The spectrum was obtained by rapid sampling of the product from controlled-potential electrolysis. (b) Simulated ESR spectrum for g values $g_{\parallel} = 2.272$ and $g_{\perp} = 2.062$ and line widths $\sigma_{\parallel} = 10.0$ G and $\sigma_{\perp} = 7.0$ G.

Table I. ESR Parameters for Nickel Dithiocarbamate Complexes and Related Species^a

complex	g_1	g_2	g_3	A_1^b	A_2^b	A_3^b
$[\text{Ni}(\text{Bu}_2\text{NCS}_2)_2]^{-c,d}$ (species I)	2.272	2.062	2.062	53	9	9
$[\text{Ni}(\text{Bu}_2\text{NCS}_2)_2]^{-c}$ (species II)	2.025	2.207	2.260	16.5	13	13
$[\text{Ni}(\text{Cy}_2\text{NCS}_2)_2]^{-d}$	2.253	2.065	2.065			
$[\text{Ni}(\text{Bz}_2\text{NCS}_2)_2]^{-d}$	2.266	2.068	2.068			
$[\text{Ni}(\text{MeOCS}_2)_2]^{-}$	2.282	2.076	2.076			
$[\text{Ni}(\text{EtOCS}_2)_2]^{-}$	2.280	2.074	2.074			
$[\text{Ni}(\text{mnt})_2]^{3-}$	2.205	2.081	2.061	53	6	6
$[\text{Cu}(\text{Et}_2\text{NCS}_2)_2]$	2.108	2.023	2.023	142.4	22.4	22.4

^a Data for $[\text{Ni}(\text{MeOCS}_2)_2]^{-}$ from ref 22; data for $[\text{Ni}(\text{mnt})_2]^{3-}$ from ref 4; data for $\text{Cu}(\text{Et}_2\text{NCS}_2)_2$ from ref 25. ^b ^{61}Ni or ^{63}Cu hyperfine coupling constants/ 10^{-4} cm^{-1} . Absolute magnitudes only are given. ^c Generated electrochemically in acetone. ^d Generated by γ irradiation in *o*-, *m*-, and *p*-xylene.

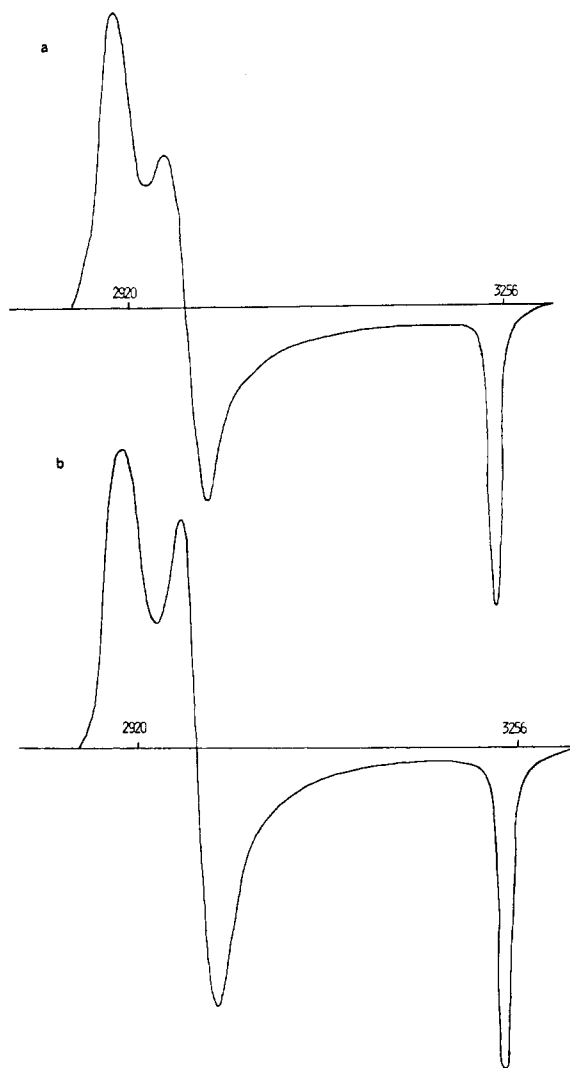


Figure 4. (a) ESR spectrum (9.217 GHz) of reduced $\text{Ni}^{\text{II}}(\text{Bu}_2\text{NCS}_2)_2$ (species II) in frozen acetone solution (77 K). (b) Simulated ESR spectrum for g values $g_z = 2.035$, $g_x = 2.207$, and $g_y = 2.260$ and line widths $\sigma_z = 6.0$ and $\sigma_x = 12.0$ G.

spectrum, and the reason for this is not known at present. For both species no splitting was resolved in the perpendicular region, but estimates of the perpendicular coupling constants were obtained by spectrum simulation using the line widths obtained from the ^{58}Ni spectra.

The ESR parameters for both species are listed in Table I. ESR spectra have been reported for several Ni^{I} complexes produced by γ irradiation of glassy solutions of Ni^{II} complexes at 77 K.^{22,23} Similar species are produced by UV irradiation in the presence of the electron donor molecule N,N,N',N' -tetramethylphenylenediamine.²⁴ The results of this work for some Ni^{II} xanthates $\text{Ni}(\text{ROCS}_2)_2$ ($R = \text{Me}, \text{Et}$) are included in Table I. For the determination of whether Ni^{I} dithiocarbamates could be generated in this manner, frozen solutions of $\text{Ni}(\text{R}_2\text{NCS}_2)_2$ ($R = \text{Bu}, \text{Cy}, \text{Bz}$) in xylene were γ -irradiated and their ESR spectra recorded. In the case of the butyl compound an axial spectrum identical with that of species I was observed. For the other two compounds similar spectra were obtained and the g values obtained by simulation are given in Table I. The conditions under which these species are formed strongly suggest that they are four-coordinate

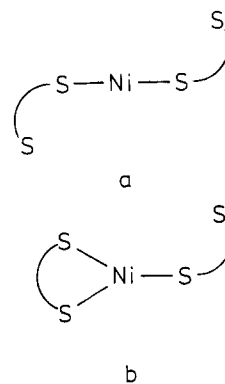


Figure 5. Possible (a) 2-coordinate and (b) 3-coordinate structures for species II.

planar complexes formed from the Ni^{II} complex by direct electron attachment. This provides strong evidence that species I is the four-coordinate planar $[\text{Ni}(\text{Bu}_2\text{NCS}_2)_2]^-$ complex and that the quasi-reversible electrochemical reduction process involves electron transfer without any essential change in structure.

The question of whether the one-electron reduction of Ni complexes is metal- or ligand-based (i.e., whether the resulting complex is a $d^9 \text{Ni}^{\text{I}}$ complex or a Ni^{II} complex involving a radical anion ligand) has been discussed by other workers in connection with complexes involving tetraaza macrocyclic ligands. Both cases have been observed and have been distinguished on the basis of their ESR spectra. The $d^9 \text{Ni}^{\text{I}}$ complexes have anisotropic g values greater than 2.0, while the Ni^{II} -stabilized radical anions have isotropic g values near 2.0.² According to this criterion both species observed here should be formulated as $d^9 \text{Ni}^{\text{I}}$ complexes. Species I cannot have true axial symmetry, but it is significant that the closely related d^9 complex $\text{Cu}(\text{Et}_2\text{NCS}_2)_2$ also shows an essentially axially symmetric ESR spectrum (Table I).²⁵ Thus it is clear that the ligand field produced by a square-planar arrangement of two dithiocarbamate ligands can have effective axial symmetry. It is proposed that species II is the initial product of the observed first-order decay of species I. Since the cyclic voltammograms showed no evidence of a peak corresponding to the oxidation of free dithiocarbamate ion, this species cannot be formed from species I by a process involving ligand loss. Its g values are similar in magnitude to those of species I, so this species too is formulated as a Ni^{I} complex. A possible structure for this species is one derived from species I by one-ended dissociation of one or both of the dithiocarbamate ligands to produce a three- or two-coordinate complex, respectively (Figure 5). The most likely ground state for a two-coordinate complex would be one in which the unpaired electron occupies the d_{z^2} orbital. For such a ground state $g_z < g_x = g_y$,²⁶ i.e., "reversed" g values are expected. It is not so clear what the expected ground state for a three-coordinate complex with one bidentate and one monodentate ligand would be, but for some geometries a d_{z^2} ground state would be possible, and the low symmetry of such a complex would be consistent with the rhombic nature of the observed ESR spectrum. Either of the above possibilities would be consistent with the production of species II from species I by a first-order rate process. Species II must have a redox potential that is more negative than that of species I, since no peak corresponding to its reoxidation is seen on the reverse sweep in the cyclic voltammetry experiments. The rate of interconversion of species I to species II is not sufficiently rapid to affect the cathodic peak in the manner observed in the oxidation of

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trans-bis(2,4-dimethyl-1,2,4-triazolin-3-ylidene)molybdenum tetracarbonyl.²⁷ In this case the oxidized *trans* complex very rapidly interconverts to the *cis* complex at a potential much more negative than the reduction potential of the *cis* anion, leading to immediate reduction to the neutral *cis* molecule and no net current flow.

The ⁶¹Ni hyperfine coupling constants for species I are very similar to those found previously for Ni(mnt)₂³⁻ (Table I) the only other Ni^I complex for which ⁶¹Ni hyperfine coupling has been reported to date.⁴ These coupling constants can be used to obtain information about the metal–ligand bonding in the complexes. If metal–ligand σ bonding only is considered, the following equations for *A*_{||} and *A*_⊥ can be derived for a d⁹ complex with a d_{x²-y²} ground state:⁴

$$A_{||} = -K + P_0[\frac{4}{7}\alpha^2 + (g_{||} - g_e) + \frac{3}{7}(g_{\perp} - g_e)] \quad (1)$$

$$A_{\perp} = -K + P_0[\frac{2}{7}\alpha^2 + \frac{1}{14}(g_{\perp} - g_e)] \quad (2)$$

where *P*₀ is a coupling constant for magnetic dipole–dipole coupling between the unpaired electron and the nucleus, $-K$ is the isotropic hyperfine coupling constant, and α² is a covalency parameter that describes the in-plane metal–ligand σ bonding (α² = 1 for pure ionic bonding, and α² < 1 for covalent bonding). These equations have previously been used to compare the bonding in the isoelectronic ions [Ni(mnt)₂]³⁻ and [Cu(mnt)₂]²⁻, and it was found that the degree of covalency is considerably lower in the Ni complex.⁴ A similar comparison can be made between [Ni(Bu₂NCS₂)₂]⁻ and Cu(Et₂NCS₂)₂ (ESR parameters for Cu(Bu₂NCS₂)₂ have not been reported to date). With use of the spin Hamiltonian parameters shown in Table I for Cu(Et₂NCS₂)₂, with negative signs for both *A*_{||} and *A*_⊥²⁵ and *P*₀(⁶³Cu) = 389 × 10⁻⁴ cm⁻¹,²⁸ it is found that α² = 0.47, corresponding to a high degree of metal–ligand covalency. (A value α² = 0.50 has been reported previously from an analysis that includes the effects of metal–ligand π bonding.²⁵) The calculation for species I, again with negative signs for both *A*_{||} and *A*_⊥ and *P*₀(⁶¹Ni) = 102 × 10⁻⁴ cm⁻¹,^{4,28} yields α² = 0.8. The signs of *A*_{||} and *A*_⊥ cannot be determined experimentally from the present results but the only other reasonable possibility is *A*_{||} negative and *A*_⊥ positive, and this yields α² = 1.0. Thus, as found previously for the mnt complexes, the degree of σ covalency in the Ni^I complexes is considerably lower than that in the Cu^{II} complexes. A similar conclusion has been reached by other workers for a number of Ni^I complexes produced by γ irradiation of frozen solutions of Ni^{II} complexes.²² This conclusion was based on the *g* values for these complexes, which are generally higher than those of corresponding Cu^{II} complexes. This is also evident in the *g* values for species I and Cu(Et₂NCS₂)₂ in Table I.

A noticeable feature of the ⁶¹Ni hyperfine coupling for species II is that *A*_{||} for this species (i.e., *A*₁ in Table I) is considerably smaller than that for species I. This can be understood in terms of the proposed d_{z²} ground state for this species. For a d⁹ complex with a d_{z²} ground state, the equations corresponding to (1) and (2) are²⁹

$$A_{||} = -K + P_0[\frac{4}{7}\alpha^2 - \frac{1}{7}(g_{\perp} - g_e)] \quad (3)$$

$$A_{\perp} = -K + P_0[-\frac{2}{7}\alpha^2 + \frac{1}{14}(g_{\perp} - g_e)] \quad (4)$$

The smaller value of *A*_{||} for species II compared with that of species I is due to the fact that the first two terms in eq 3 are of opposite sign, whereas those in eq 1 are of the same sign

Table II. Reduction Potentials for the Process [Ni^{II}(R₂NCS₂)(dpe)]⁺ → Ni^I(R₂NCS₂)(dpe) (vs. Ag–AgCl in 0.1 M LiCl)

R	<i>E</i> _{1/2} /V ^a	
	CH ₃ CN	CH ₂ Cl ₂ ^b
benzyl	-0.775	-0.99
<i>n</i> -butyl	-0.838	-1.07
ethyl	-0.842	-1.05
cyclohexyl	-0.887	-1.13

^a Measured by cyclic voltammetry. *E*_{1/2} taken as the midpoint between the potentials corresponding to the forward and reverse peak currents. ^b For the ferrocene/ferrocenium couple at 0.46 V relative to Ag–AgCl in 0.1 M LiCl.

Table III. Kinetic Parameters for the First-Order Decomposition of Electrochemically Generated Ni^I(R₂NCS₂)(dpe) (in Dichloromethane Solvent) and Some Related Complexes

complex	rate constant/s ⁻¹	activation energy/kJ mol ⁻¹
Ni ^I (R ₂ NCS ₂)(dpe)		
R = cyclohexyl ^{a, b}	(3.1 ± 0.1) × 10 ⁻² (20 °C)	24.2
R = benzyl ^a	(1.3 ± 0.1) × 10 ⁻² (20 °C)	18.1
Ni ^I (dpe)(CN) ₂ ^{-c}	0.41 ± 0.03 (25 °C)	
Ni ^I (Ph ₂ EtP) ₂ (CN) ₂ ^{-c}	2.8 ± 0.2 (25 °C)	

^a Determined by the ESR kinetic method. ^b A rate constant of (3.2 ± 0.3) × 10⁻² s⁻¹ was determined by cyclic voltammetry. ^c Reference 31b (measured in acetonitrile by cyclic voltammetry).

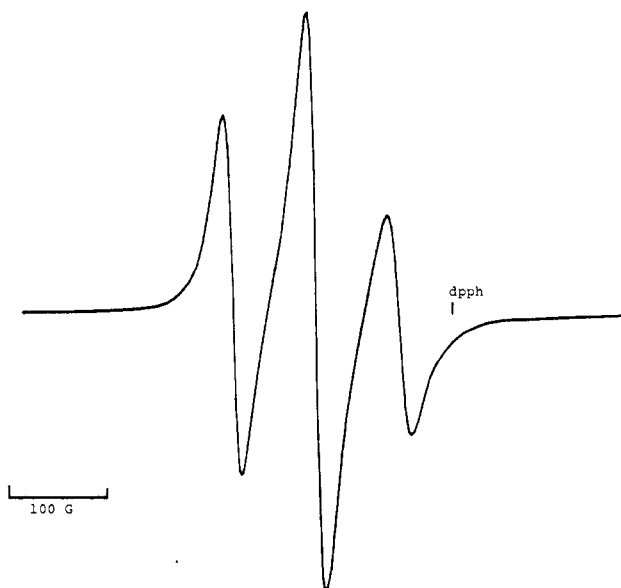


Figure 6. ESR spectrum of Ni^I(Et₂NCS₂)(dpe) in dichloromethane at -40 °C.

(both negative). This is a direct consequence of the fact that the principal component of the dipolar coupling tensor is positive for a d_{z²} orbital and negative for a d_{x²-y²} orbital. Thus the proposed d_{z²} ground state for species II accounts for the observed magnitude of the ⁶¹Ni hyperfine coupling constant as well as for the reversed *g* values.

Reduction of [Ni^{II}(R₂NCS₂)(dpe)]PF₆ Complexes. Complexes [Ni^{II}(R₂NCS₂)(dpe)]PF₆ undergo a near-reversible reduction, for scan rates of 200 mV s⁻¹, around -1.0 V vs. Ag–AgCl (Table II) at a platinum electrode in dichloromethane solution. The reduction potentials show the expected dependence of the dithiocarbamate substituent.⁷ Similar reductions are observed in acetone and acetonitrile solutions. From the cyclic voltammetric data for the R = cyclohexyl compound it was found that the ratio of peak currents of the forward (*i*_p^f) and reverse (*i*_p^r) scans varied from 0.907 to 0.977

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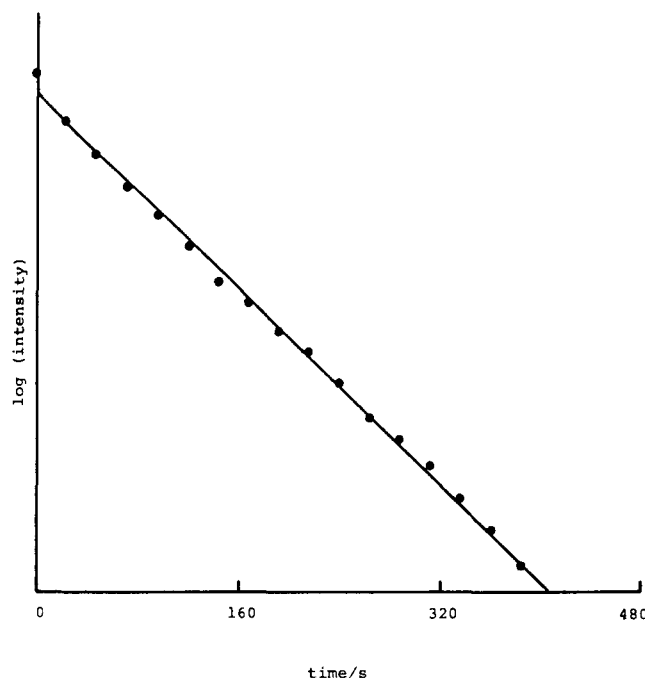
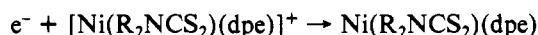


Figure 7. Analysis of the first-order decay of the $\text{Ni}^{\text{I}}(\text{Bz}_2\text{NCS}_2)(\text{dpe})$ ESR signal in dichloromethane at 0 °C.

for scans rates in the range 50–150 mV s⁻¹. ESR spectra were obtained at -40 °C of the initial reduction product by controlled-potential electrolysis at slightly greater than the reduction potential. The solution spectra showed three lines ($g = 2.089$, $a = 84.2$ G), indicative of two equivalent phosphorus ligands bound to the metal ion (Figure 6). The intensity of the solution ESR signal decreases with time, the decrease being first order in the concentration of the initially reduced species Ni(R₂NCS₂)(dpe) (R = Cy, Bz) (Figure 7). The rate of reaction was most rapid for R = cyclohexyl and least for R = benzyl (Table III). The ESR and electrochemical data then suggest an initial reduction process of the form



followed by a further reaction of the reduced product.

A study of the effect of scan rate on the cyclic voltammogram of the cyclohexyl derivative was then made with use of solutions of the same ionic strength as for the ESR kinetic experiments. The variation of the ratio of forward (i_p^f) and reverse (i_p^r) peak currents with scan rate were found to be consistent with a reversible electrochemical process followed by an irreversible chemical process (E_C).³⁰ The rate constant K_f for the chemical reaction was obtained by the method of Nicholson and Shain for an EC mechanism.²¹ The rate constants derived from the spectroscopic (ESR) and electrochemical methods are in good agreement. The rate of the reaction as a function of temperature was measured in the ESR kinetic experiments, and the resulting activation energies are given in Table III.

An exhaustive controlled-potential electrolysis of solutions of $[\text{Ni}(\text{Et}_2\text{NCS}_2)(\text{dpe})]\text{PF}_6$ at potentials lower than the reduction potential for the complex followed by an ac cyclic voltammogram to more positive potentials showed peaks in positions expected for the oxidation of $\text{Ni}^0(\text{dpe})_2$ and $\text{Ni}^{\text{II}}(\text{Et}_2\text{NCS}_2)_2$. Further, in concentrated solutions, it was found that green $\text{Ni}^{\text{II}}(\text{Et}_2\text{NCS}_2)_2$ was precipitated at the cathode during the reduction. The powder could be isolated and was confirmed to be the bis(dithiocarbamate)nickel(II) complex.

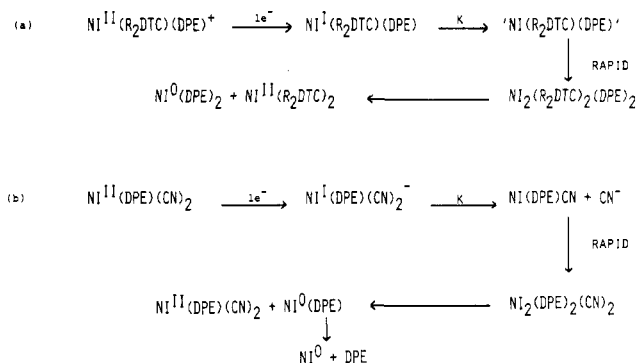


Figure 8. (a) Proposed mechanism of reaction of reduced $[Ni^{II}-(R_2NCS_2)(dpe)]^+$. (b) Mechanism of reaction of reduced $Ni^{II}-(dpe)(CN)_2$ (ref 31).

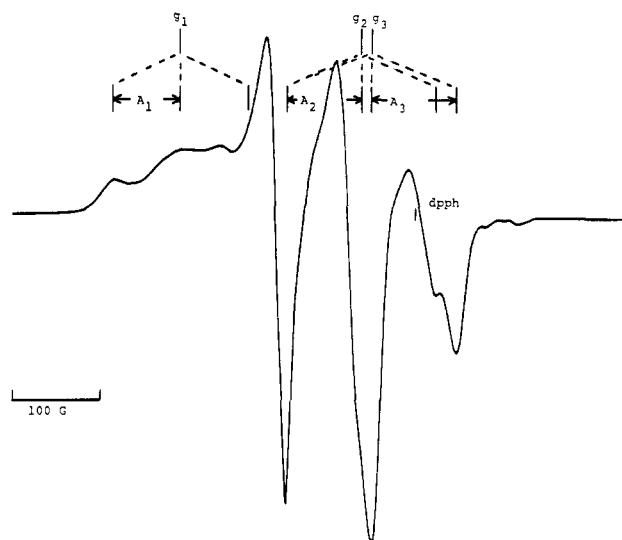


Figure 9. ESR spectrum of $\text{Ni}^{\text{I}}(\text{Et}_2\text{NCS}_2)(\text{dpe})$ in frozen dichloromethane solution.

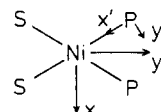


Figure 10. Principal axis of g and phosphorus hyperfine coupling tensors in $\text{Ni}^{\text{I}}(\text{R}_2\text{NCS}_2)(\text{dpe})$ (z and z' are perpendicular to the plane of the molecule).

A possible mechanism for this overall disproportionation reaction of the reduction products of $[\text{Ni}^{\text{II}}(\text{R}_2\text{NCS}_2)(\text{dpe})]\text{PF}_6$ complexes appears to be an initial one-electron reduction to $\text{Ni}^{\text{I}}(\text{R}_2\text{NCS}_2)(\text{dpe})$ (ESR active) followed by a rate-determining reaction to an intermediate " $\text{Ni}^{\text{I}}(\text{R}_2\text{NCS}_2)(\text{dpe})$ ", which reacts rapidly to give a diamagnetic metal-metal bonded species or a strongly antiferromagnetically coupled dimer with bridging dithiocarbamates $\text{Ni}_2(\text{R}_2\text{NCS}_2)_2(\text{dpe})_2$, which disproportionates with ligand rearrangement to give $\text{Ni}^{\text{II}}-(\text{R}_2\text{NCS}_2)_2$ and $\text{Ni}^0(\text{dpe})_2$ (Figure 8). This mechanism is based on the known overall end products of the reaction, the nature of the initial reduction product as characterized by ESR spectroscopy, and no evidence for the loss of dithiocarbamate ligand during the reaction as determined by cyclic voltammetry measurements. Bontempelli and co-workers have proposed a similar type of mechanism for the further reaction of reduced $\text{Ni}^{\text{II}}(\text{dpe})(\text{CN})_3$.³¹ In their case the rate-determining reaction

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Table IV. ESR Parameters for Some dpe Complexes of Nickel(I) in Dichloromethane

complex	g_1	g_2	g_3	g	A_1^b	A_2^b	A_3^b	a^b
Ni(Et ₂ NCS ₂)dpe	2.186	2.043	2.035	2.093	79	81	92	83
Ni(Bu ₂ NCS ₂)dpe	c	2.045	2.039	2.090	c	82	92	82
Ni(Cy ₂ NCS ₂)dpe	2.199	2.046	2.038	2.089	80	80	93	82
Ni(Bz ₂ NCS ₂)dpe	c	2.048	2.040	2.093	c	80	93	82
[Ni(dpe) ₂] ⁺	2.134	2.030	2.030	2.074	48	64	64	59
Ni(dpe) ₂ X ^d	2.160	2.031	2.031	2.078	50	64	64	59

^a Isotropic parameters are from solution spectra at -40 °C; anisotropic parameters are from frozen solution spectra at -160 °C (parameters defined in Figure 9). ^b ³¹P hyperfine coupling constants/10⁻⁴ cm⁻¹. Absolute magnitudes only are given.

^c Parallel region poorly resolved. ^d X = Cl, Br, I; data for these species (in toluene solution) from ref 15.

is loss of cyanide followed by coupling to form a metal-metal bonded species. For the dithiocarbamate complex the rate-determining reaction may be, by comparison, the "unhinging" of the ligand to form a monodentate dithiocarbamate ligand.

ESR Spectra of Reduced [Ni^{II}(R₂NCS₂)(dpe)]PF₆ Complexes. Frozen solution ESR spectra of the initially reduced species, Figure 9, show a g value anisotropy consistent with a planar d⁹ species and anisotropic phosphorus hyperfine interactions. For a planar structure the principal axes of the g tensor and phosphorus hyperfine coupling tensor would be expected to be as shown in Figure 10. In the parallel region of the spectrum, the ³¹P hyperfine splitting would be equal to A_z , so this quantity can be measured directly from the spectrum. In the perpendicular region, however, the principal axes of the g and hyperfine tensors do not coincide. In this region the center line of the triplet is broadened and the high-field component is split into a partially resolved doublet. This behavior can be understood most readily if $g_x \neq g_y$ and the effective splittings A_x and A_y in these directions are also unequal. A_x and A_y are not principal components of the ³¹P hyperfine coupling tensor, but they can be related to the principal components A_x' and A_y' by means of the equations

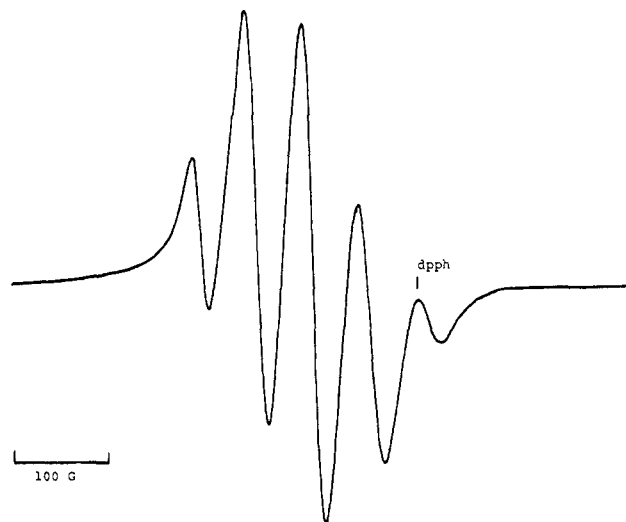
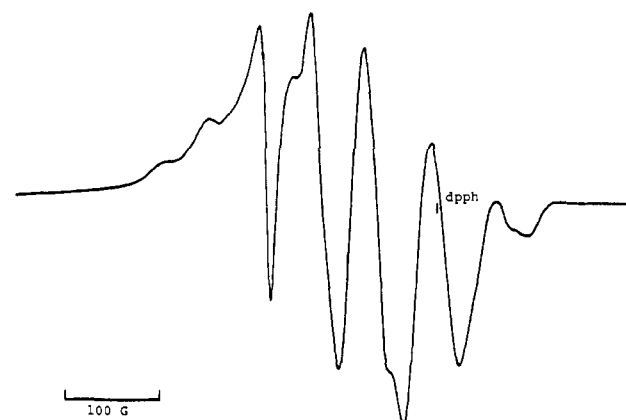
$$A_x^2 = A_x'^2 \sin^2(\alpha/2) + A_y'^2 \cos^2(\alpha/2) \quad (5)$$

$$A_y^2 = A_x'^2 \cos^2(\alpha/2) + A_y'^2 \sin^2(\alpha/2) \quad (6)$$

where α is the P-Ni-P bond angle. A similar observation has recently been made by other authors with respect to ¹⁴N hyperfine coupling in planar amine complexes of Ag^{II}.³² It is clear from eq 5 and 6 that when $\alpha = 90^\circ$

$$A_x^2 = A_y^2 = \frac{1}{2}(A_x'^2 + A_y'^2) \quad (7)$$

Thus, any observed departure of the A_x and A_y values from axial symmetry ($A_x = A_y$) must be due to a departure of the angle α from 90°. Computer simulations show that the effective splittings in the x and y directions for randomly oriented species with principal axes, as shown in Figure 10, do indeed correspond to A_x and A_y as given by eq 5 and 6, and spectra with the same appearance as the experimental ones can be obtained for a range of values of A_x' , A_y' , and α . However, no reasonable fit has yet been found for values of α near 83°, which appears to be typical of P-M-P angles in transition-metal dpe complexes.³³ This might be an indication that the principal axis x' of the ³¹P hyperfine tensor does not lie along the line joining the metal and the phosphorus atom, but more work involving a wider range of phosphine ligands is necessary

Figure 11. ESR spectrum of [Ni^{II}(dpe)₂]⁺ in dichloromethane at -40 °C.Figure 12. ESR spectrum of [Ni^{II}(dpe)₂]⁺ in frozen dichloromethane solution.

before any definite conclusions can be reached.

Since unique values of the principal components of the g and ³¹P hyperfine coupling tensors could not be obtained by simulation of the frozen solution spectra, parameters have been measured from these spectra as shown in Figure 9, and the results are given in Table IV. In terms of the directions defined in Figure 10, $A_1 = A_z = A_x'$ and A_2 and A_3 correspond to A_x and A_y (not necessarily in that order).

Reduction of [Ni^{II}(dpe)₂]²⁺. [Ni^{II}(dpe)₂][BF₄]₂ or [Ni^{II}(dpe)₂][ClO₄]₂ undergo two closely spaced reductions at -0.23 and -0.52 V vs. Ag/AgCl in dichloromethane solution. Similar behavior was observed in acetonitrile solvents. Other workers have found two waves at -0.23 and -0.43 V vs. aqueous SCE for the reduction of [Ni^{II}(dpe)₂][ClO₄]₂ at a mercury drop electrode in acetonitrile solution. These workers attributed the first wave to the formation of mononuclear [Ni^I(dpe)₂]⁺, but they were unable to observe the expected ESR spectrum of this complex.¹⁴ In this present work it is found that solutions of [Ni^{II}(dpe)₂]²⁺ in CH₂Cl₂ reduced at -0.245 V at -40 °C or at ambient temperature give isotropic ESR spectra with five lines with intensity ratios corresponding to hyperfine splitting by four equivalent phosphorus atoms (Figure 11). This spectrum of the frozen solution, Figure 12, is anisotropic with approximate axial symmetry. The ESR parameters measured from the spectra are listed in Table IV. These spectra are similar to those reported previously for toluene solutions containing NiX₂ (X = Cl, Br, I), dpe, and Et₃Al, which have been attributed to tetragonal-pyramidal (dpe)₂NiX species. The observed relationship $g_{\parallel} > g_{\perp} > 2.0$ is consistent with a

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square-planar structure in which the unpaired electron occupies a $d_{x^2-y^2}$ orbital. This is in contrast with the situation for $[\text{Ni}(\text{PMe}_3)_4]^+$, which is known to have a tetrahedral structure and which gives only a very broad frozen solution ESR signal with no ^{31}P hyperfine structure.³⁴

Conclusion

The series of nickel(II) complexes $[\text{Ni}(\text{R}_2\text{NCS}_2)_x(\text{dpe})_{2-x}]^{2-x}$ all undergo one-electron reductions to give nickel(I) complexes, which can be identified by their ESR spectra. The reduction potential increases in magnitude from $x = 0$ to $x = 2$. In fact, a plot of reduction potential against x is always found to be linear or very nearly linear. Similar observations for other series of compounds have been made previously.

The stabilities of the nickel(I) complexes decrease markedly from $[\text{Ni}(\text{dpe})_2]^+$ to $[\text{Ni}(\text{R}_2\text{NCS}_2)_2]^-$. The observed decrease in the g values from $[\text{Ni}(\text{R}_2\text{NCS}_2)_2]^-$ to $[\text{Ni}(\text{dpe})_2]^+$ suggests that the extent of delocalization of the unpaired electron onto the ligands increases along this series. The ^{31}P hyperfine

coupling constants decrease from $\text{Ni}(\text{R}_2\text{NCS}_2)(\text{dpe})$ to $[\text{Ni}(\text{dpe})_2]^+$ by a factor of about 0.75. If R_2NCS_2^- was as effective as dpe in accepting unpaired spin density from the metal, no change in the ^{31}P hyperfine coupling constant would be expected to occur. Therefore these results, too, indicate that dpe promotes the delocalization of unpaired spin density from the metal to a greater extent than does the dithiocarbamate ligand. The simplest explanation for this is that the metal-ligand covalency is greater in the case of dpe so that the antibonding orbital containing the unpaired electron has more ligand character. However, even for $[\text{Ni}(\text{dpe})_2]^+$, the departure of the g values from the free electron value is still sufficient to warrant classification of this as a nickel(I) compound.

Acknowledgment. We thank the New Zealand University Grants Committee for financial assistance.

Registry No. $[\text{Ni}(\text{Bu}_2\text{NCS}_2)_2]^-$, 79972-29-5; $[\text{Ni}(\text{Cy}_2\text{NCS}_2)_2]^-$, 79972-30-8; $[\text{Ni}(\text{Bz}_2\text{NCS}_2)_2]^-$, 79972-31-9; $[\text{Ni}(\text{EtOCS}_2)_2]^-$, 42985-64-8; $[\text{Ni}^{\text{II}}(\text{Bz}_2\text{NCS}_2)(\text{dpe})]^+$, 79972-32-0; $[\text{Ni}^{\text{II}}(\text{Bu}_2\text{NCS}_2)(\text{dpe})]^+$, 55074-15-2; $[\text{Ni}^{\text{II}}(\text{Et}_2\text{NCS}_2)(\text{dpe})]^+$, 55074-14-1; $[\text{Ni}^{\text{II}}(\text{Cy}_2\text{NCS}_2)(\text{dpe})]^+$, 79972-33-1; $\text{Ni}^{\text{I}}(\text{Cy}_2\text{NCS}_2)(\text{dpe})$, 79972-34-2; $\text{Ni}^{\text{I}}(\text{Bz}_2\text{NCS}_2)(\text{dpe})$, 79972-35-3; $\text{Ni}^{\text{I}}(\text{Et}_2\text{NCS}_2)(\text{dpe})$, 79972-36-4; $\text{Ni}^{\text{I}}(\text{Bu}_2\text{NCS}_2)(\text{dpe})$, 79972-37-5; $[\text{Ni}(\text{dpe})_2]^+$, 79972-38-6.

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Raman Spectrometric Studies of "Cation-Cation" Complexes of Pentavalent Actinides in Aqueous Perchlorate Solutions^{1a}

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Received August 3, 1981

Complexation of actinyl(V) ions in aqueous solution has been studied by Raman spectral and spectrophotometric measurements. Addition of UO_2^{2+} to aqueous perchlorate solutions of NpO_2^+ or AmO_2^+ was found to result in the formation of distinct new species with lowered values of ν_1 , the symmetrical stretching frequency of the actinyl ion. The $\text{Np(V)}-\text{U(VI)}$ complexation constant was determined by Raman spectroscopy to be $K/T = 2.5 \pm 0.5$ at U(VI) concentrations below 1 M. For the weaker $\text{Am(V)}-\text{U(VI)}$ complex, the value of K/T was approximately 0.3. These complexation constants determined by Raman spectroscopy agreed well with the results of spectrophotometric ultraviolet-visible observations. For concentrated NpO_2^+ solutions, the Raman data gave evidence for a new form of cation-cation complex, that formed by the self-association of pentavalent actinyl ions. Above 0.2 M concentration, a dimer is formed with $K_2/T = 0.82 \pm 0.05$, while at higher neptunyl(V) concentrations, higher polymers are formed. The effects of a number of other complexing cations upon the ν_1 spectral band of NpO_2^+ were also observed.

Introduction

Since their discovery by Sullivan et al.,^{2a} the cation-cation complexes of pentavalent actinides have been studied by several different techniques. Absorption spectrophotometry has been used to a large extent to measure the strengths of the complexes.²⁻⁸ In concentrated solutions of uranyl perchlorate, Sullivan^{2a} also used proton spin relaxation measurements and potentiometric techniques that gave evidence of a shift of the

formal potential for the couple $\text{NpO}_2^+/\text{NpO}_2^{2+}$ in the presence of UO_2^{2+} . In other attempts to elucidate the structure of such actinyl(V) complexes, studies have been made with electron paramagnetic resonance,⁸ infrared spectroscopy,⁴ and Mössbauer spectroscopy.⁹

Raman spectrometry can often be used to detect and measure the formation of complexes in solution.^{10,11} In addition to providing basic information about structure and bonding of the complex, Raman methods can provide a direct measure of formation constants. Although the Raman scattering of actinides (in oxidation states V, VI, and VII) in solution has been reported,^{12,13} no Raman studies have previously been made of the vibrational spectra of cation-cation complexes. In the present work, we have used Raman scat-

- (1) (a) Work sponsored by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, under Contract W-7405-eng-26 with Union Carbide Corp., and by the Centre d'Etudes Nucléaires, Fontenay-aux-Roses, France. (b) Guest Scientist on assignment from Centre d'Etudes Nucléaires, Département de Génie Radioactif, Service d'Etude des Procédés, B.P. No. 6, 92260 Fontenay-aux-Roses, France.
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