

important, although in view of the large activation energy for the homogeneous process this now seems unlikely.

If we consider now the so-called "homogeneous" reaction, it is apparent that the final state or stages of this must also occur heterogeneously. Firstly, there is the experimental observation that the reaction is faster, and of more reproducible rate, when carried out in the presence of a nickel surface than in the presence of a glass surface. Secondly, the free-energy change⁷ (ΔG°) for reaction 1, which refers to the formation of solid nickel, is negative only above *ca.* 80°. The hypothetical homogeneous reaction, with the formation of gaseous nickel, is only energetically favorable at much higher

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temperatures. Therefore, step 3 (Figure 2) must be, in part at least, heterogeneous. We assumed earlier, in order to apply eq 3, that the postulated $\text{Ni}(\text{CO})_2$ intermediate undergoes rapid decomposition (*i.e.*, $k_{34} \gg k_{32}$). In view of the agreement between the experimental data and eq 3, and also of the magnitude of the enthalpy of activation (45 kcal mol⁻¹), which is reasonable for the removal of two CO groups, we conclude that the assumption is justified and that step 3 proceeds heterogeneously with a low enthalpy of activation.

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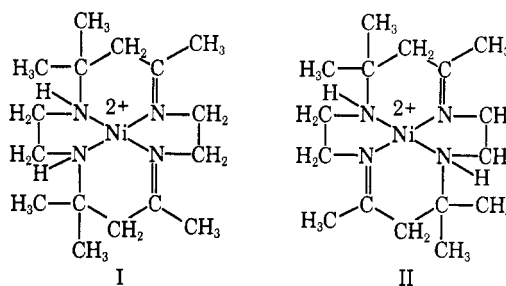
A Proton Magnetic Resonance Study of the Stereochemistry of a Macrocyclic Schiff Base–Amine Complex of Nickel(II)

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Abstract: The stereochemistry of the complex hexamethyl-1,4,8,11-tetraazacyclotetradecadienenickel(II) has been investigated. The data derived from proton magnetic resonance spectra and from complimentary physical chemical studies have provided detailed information concerning chelate ring conformations for three types of isomers. Differing relative positions of the two imine functions, which result in 1,4-diene and 1,7-diene forms, are readily distinguished by pmr spectra. More subtle forms of isomerism lead to *meso* and racemic forms of the 1,7-diene. These isomers have been isolated, characterized, and shown to be derived from variations in the configurations of the two asymmetric amine nitrogens. Qualitative determinations of the relative stabilities of the various ring conformations have been deduced. Homoallylic coupling through the imine bonds of the 1,7-diene isomers and a deshielding effect due to the anisotropy of the square-planar d^8 transition metal ion system have been observed.

The complex hexamethyl-1,4,8,11-tetraazacyclotetradecadienenickel(II), $\text{Ni}(\text{CT})^{2+}$, first described by Curtis,^{1,2} exists in a variety of isomeric forms which exhibit a number of features that are of particular stereochemical interest. Two noninterconvertible forms have been isolated by Curtis, Curtis, and Powell,³ who have concluded on the basis of chemical and X-ray evidence that these forms are the imine positional isomers 5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-1(14),4-dienickel(II) (structure I, $\text{Ni}(1,4\text{-CT})^{2+}$) and 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-1(14),7-dienickel(II) (structure II, $\text{Ni}(1,7\text{-CT})^{2+}$). These were formally designated as the *cis* and *trans* isomers, respectively. The $\text{Ni}(1,7\text{-CT})^{2+}$ isomer was also separated into interconvertible forms designated $A\alpha$ and $A\beta$ by Curtis, Curtis, and Powell, who considered them to be "conformational isomers stabilized by steric hindrance."³ We had simultaneously and independently discovered and characterized the latter isomers.^{4,5}



In the following study we discuss three types of isomerism other than imine positional isomerism that are characteristic of the $\text{Ni}(\text{CT})^{2+}$ system. These subtle polymorphisms^{4,5} are diastereoisomerism, enantiomorphism, and coordination number isomerism. Detailed attention is given to aspects of chelate ring conformations and to orientations of the peripheral methyl substituents within each of the known isomers. All structural assignments rest heavily upon interpretation of proton magnetic resonance spectra.

Results and Discussion

Coordination Number Isomerism. The coordination template condensation reaction between $\text{Ni}(\text{en})_3^{2+}$

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Table I. Electronic Spectra of Isomers of Ni(CT)²⁺

Isomer	Medium	ν_{\max} , cm ⁻¹	ϵ_{\max} (0.5 hr)	ϵ_{\max} (36 hr)
<i>dl</i> -Ni(1,7-CT)(NCS) ₂ ·H ₂ O	Nujol ^a	22,570
	H ₂ O	22,900	94	93
	Acid	22,900	96	96
<i>meso</i> -Ni(1,7-CT)(NCS) ₂ (low spin)	Nujol ^a	23,040
	H ₂ O	22,900	81	93
	Acid	22,900	81	81
<i>dl</i> -Ni(1,4-CT)(NCS) ₂	Nujol ^a	23,150
	H ₂ O	22,400	105	105
	Acid	22,400	105	105
<i>dl</i> -Ni(1,7-CT)(PF ₆) ₂	Acetone	22,800	98	98
<i>meso</i> -Ni(1,7-CT)(PF ₆) ₂	Acetone	22,800	84	97
<i>meso</i> -Ni(1,7-CT)(NCS) ₂ (high spin)	Nujol ^a	28,480 s ^b
		20,490 m
		15,500 w, br
		12,500 sh
		10,810 w, br

^a Diffuse transmittance. ^b s = strong, m = medium, w = weak, br = broad, sh = shoulder.

Table II. Characteristic Infrared Absorption Bands^a of the Isomers of Ni(CT)(NCS)₂

Isomer	$\nu(\text{OH})^b$	$\nu(\text{NH})$	$\nu(\text{CN of NCS})$	$\nu(\text{CN of imine})$	$\delta(\text{H}_2\text{O})$
<i>dl</i> -Ni(1,7-CT)(NCS) ₂ ·H ₂ O	3571 w				
	3483 s	3185 s, sp	2070 s, sp	1661 s	1624 m, sp
	3425 s	3068 s, br	2045 sh		
	3247 w		2030 s, br		
<i>meso</i> -Ni(1,7-CT)(NCS) ₂ (low spin)	...	3049 s	1986 w, sp	1647 s	...
			2049 s, sp		
			2007 w, sp		
<i>meso</i> -Ni(1,7-CT)(NCS) ₂ (high spin)	...	3236 s	2079 s, sp	1667 s	...
			2036 w, sp		
			2056 s, sp	1658 s	...
<i>dl</i> -Ni(1,4-CT)(NCS) ₂	...	2075 s	2045 sh		
			2010 w, sp		
			2005 sh		

^a All spectra obtained with Nujol mulls and data are given in cm⁻¹. ^b Conclusively shown to arise due to the presence of H₂O: K. Long, The Ohio State University, unpublished results.

and acetone yields two imine positional isomers (structures I and II) which have been conclusively identified as the Ni(1,4-CT)²⁺ and Ni(1,7-CT)²⁺ forms *via* the pmr data^{4,5} contained herein and X-ray crystallographic analysis by Dunitz⁶ and Bailey,⁷ respectively. Metathetical reaction between potassium thiocyanate and the perchlorate or tetrafluoroborate derivatives of Ni(CT)²⁺ has yielded three isomeric dithiocyanato derivatives.^{4,5,8} The Ni(1,7-CT)²⁺ form yields an orange hydrated and a yellow anhydrous derivative. These are interconvertible and correspond respectively to the A α and A β ⁹ isomers reported by Curtis.^{3,8} The Ni(1,4-CT)²⁺ form yields a yellow-green anhydrous derivative. All three of these dithiocyanate derivatives are of low-spin electronic configurations and exhibit a single electronic absorption maximum that is typical of square-planar nickel(II) (Table I).¹⁰ Molar conductances in water and methanol⁸ show them to be 2:1 electrolytes. These data indicate, as do the thiocyanate infrared frequencies⁸ (Table II), that these isomers are four-coordinate and contain square-

planar structures in which the anions are not functioning as ligands.

A fourth dithiocyanate isomer has been prepared by recrystallization of the yellow dithiocyanate from boiling chloroform. The resulting product is a metastable violet material which readily reverts to its yellow parent upon grinding or contact with water. It exists in a high-spin electronic configuration ($\mu_{\text{eff}} = 3.27$ BM), and its electronic absorption spectrum is typical of tetragonally distorted, pseudo-octahedral nickel(II)¹¹⁻¹⁵ (Table I). The data, coupled with the fact that the C \equiv N stretching mode of the thiocyanate anions is shifted to a higher energy than in the parent complex (Table II), indicate that the ionic thiocyanates of the square-planar parent complex have become coordinated¹⁶ at the axial sites of the Ni(II). On the basis of the electronic absorption spectrum and its known chemistry, and by comparison with other systems,¹⁸ *Dq* for this macrocycle is tentatively assigned the high value of 1550 cm⁻¹. This isomer and its parent provide a rare example of coordination number isomerism which is similar to that reported by

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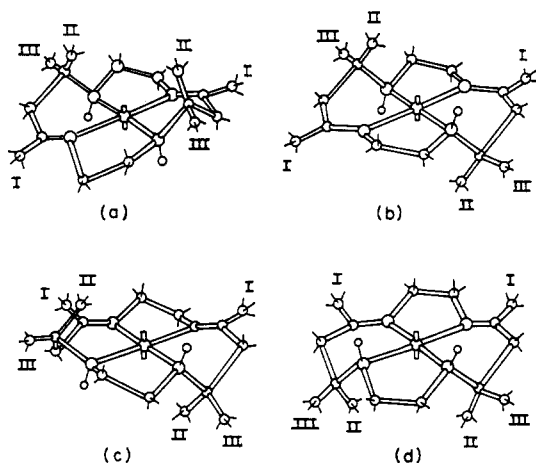


Figure 1. Idealized structures of stereoisomers of $\text{Ni}(\text{CT})^{2+}$: (a) $dl\text{-Ni}(1,7\text{-CT})^{2+}$, (b) $meso\text{-Ni}(1,7\text{-CT})^{2+}$, (c) $dl\text{-Ni}(1,4\text{-CT})^{2+}$, (d) $meso\text{-Ni}(1,4\text{-CT})^{2+}$.

Rosenthal and Drago¹⁷ for the tetrapyridinenickel(II) perchlorate and fluoroborate systems.

Perhaps the most unusual characteristic of this species is the fact that a paramagnetic complex can be obtained with Ni(II) and the macrocyclic ligand in question. Only two other examples of paramagnetic derivatives containing this ligand have been reported: the hemioxalato dimer,¹⁸ $\{[\text{Ni}(\text{CT})_2(\text{C}_2\text{O}_4)](\text{ClO}_4)_2\}$, and an unstable adduct formed in aqueous solution with cyanide ion.¹⁹

Several factors may be operating which do not favor axial coordination in the $\text{Ni}(\text{CT})^{2+}$ complexes, even in the presence of strongly coordinating ligands such as thiocyanate. One is the strong tendency of the secondary amine protons to hydrogen bond to the anions in both the solid and solution states.^{7,8} The second is the tendency toward decreased coordination in the axial positions of six-coordinate Ni(II) complexes which contain strong inplane fields.¹³ Steric crowding of the axial sites may also be a contributing factor, although this seems unlikely in view of the fact that the cobalt(III) complexes which contain the CT macrocyclic ligand readily allow axial coordination.^{20,21} Also the nickel complexes which contain the reduced form of the macrocyclic ligand (CTH = tet a, b, c, and d)^{22,23} readily allow axial coordination even though pmr studies indicate that the axial methyl substituents lie further over the plane containing the Ni and four nitrogen atoms and thus are closer to the axial site of the metal ion than in the $\text{Ni}(\text{CT})^{2+}$ system.²⁴ Curtis has suggested that increased ligand flexibility and increased chelate ring size accompany reduction of the imine functions, thereby relieving axial crowding and allowing axial coordination.^{8,25}

Diastereoisomers. There are two coordinated secondary amines in the $\text{Ni}(\text{CT})^{2+}$ complexes and both are

asymmetric. The presence of these two asymmetric centers affords the possibility of two diastereoisomers for each positional isomer of the ligand (see Figure 1). The existence of such a diastereometric relationship between the orange and yellow $\text{Ni}(1,7\text{-CT})(\text{NCS})_2$ isomers was established by partial resolution of the orange isomer into optical antipodes.^{4,5,24} This resolution was achieved by passing an acidic aqueous solution of this isomer through a column packed with microcrystalline cellulose or potato starch. All attempts to resolve the yellow dithiocyanate failed. Consequently, the orange form is confidently assigned the racemic configuration, $dl\text{-Ni}(1,7\text{-CT})(\text{NCS})_2 \cdot \text{H}_2\text{O}$, and the yellow form, the meso isomer, $meso\text{-Ni}(1,7\text{-CT})(\text{NCS})_2$. These assignments have been corroborated by an X-ray crystallographic study.⁷

The convertibility of the diastereoisomers in neutral solution demonstrates the expected lability of the protons of the coordinated secondary amines. Both pure $dl\text{-Ni}(1,7\text{-CT})^{2+}$ and $meso\text{-Ni}(1,7\text{-CT})^{2+}$ convert to the same equilibrium mixture in neutral aqueous and in acetone solutions. Each diastereoisomer exhibits a single electronic absorption maximum between 22,800 and 23,000 cm^{-1} , but different extinction coefficients are observed. After several hours the extinction coefficient of solutions of the $meso\text{-Ni}(1,7\text{-CT})^{2+}$ isomer approaches that of the $dl\text{-Ni}(1,7\text{-CT})^{2+}$ isomer, thereby indicating that the equilibrium between meso and racemic forms in solution is strongly shifted toward the latter. Proton magnetic resonance spectral data, to be discussed below, corroborate this shift in that the spectra of equilibrium mixtures in D_2O show the racemic isomer to constitute at least 83% of the compound present. The obvious mechanism for isomerization (racemic to meso) involves ionization of the proton from one secondary amine nitrogen followed by inversion of that nitrogen atom. The mechanism for the disappearance of optical rotation must be directly coupled with this simple isomerization mechanism.²⁶ However the actual racemization must involve ionization from, and inversion of, both asymmetric secondary amine nitrogens in simultaneous or consecutive steps, with the meso diastereoisomer forming as an intermediate species. In accordance with the long known pH dependence of proton exchange reactions involving coordinated secondary amine groups,²⁶ acidification of pure diastereoisomer solutions completely inhibits the isomerization process. The above-mentioned resolution has only been achieved in aqueous solutions at a pH of 2 or lower. Acid solutions of partially resolved isomer retain their observed rotations for at least 2 days. Thus it is expected and observed that the extinction coefficients for the racemic and meso diastereoisomers in aqueous solutions of pH 2 remain constant over periods of several days.

The relatively large difference in the extinction coefficients shown by these two diastereoisomers (Table II) is most probably due to their different absolute symmetries. As can be readily seen from the structures in Figure 1, the $rac\text{-Ni}(1,7\text{-CT})^{2+}$ diastereoisomer has C_2 symmetry and the $meso\text{-Ni}(1,7\text{-$

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Table III. Proton Magnetic Resonance Spectra for the Isomers of $\text{Ni}(\text{CT})^{2+}$ ^{a, b}

Isomer	Anion	Solvent	CH ₃ groups			Amine dimethyl-ene protons	Methylene protons	Imine dimethyl-ene protons	$\Delta(\text{II} - \text{III})$	$\Delta(\text{I} - \text{III})$
			III	II	I					
<i>meso</i> -Ni(1,7-CT) ²⁺	SCN ⁻	D ₂ O (H ⁺) ^c	1.75	2.21	2.69	3.11 ^d	3.29	4.07 ^d	0.46	0.94
<i>dl</i> -Ni(1,7-CT) ²⁺	SCN ⁻	D ₂ O (H ⁺)	1.75	2.52	2.67	3.10 ^d	2.35	3.97 ^d	0.77	0.92
<i>dl</i> -Ni(1,4-CT) ²⁺	SCN ⁻	D ₂ O (H ⁺)	1.75	2.54	2.70	3.11	3.35	3.92	0.79	0.95
<i>dl</i> -Ni(1,4-CT) ²⁺ ^e	SCN ⁻	D ₂ O (H ⁺)	1.75	2.53	...	3.11	...	3.92	0.78	...
<i>meso</i> -Ni(1,7-CT) ²⁺	BF ₄ ⁻	D ₂ O (H ⁺)	1.72	2.18	2.67	3.14 ^d	3.28	4.06 ^d	0.46	0.95
<i>dl</i> -Ni(1,7-CT) ²⁺	BF ₄ ⁻	D ₂ O (H ⁺)	1.71	2.50	2.60	3.06 ^d	3.28	3.90 ^d	0.79	0.89
<i>dl</i> -Ni(1,7-CT) ²⁺ ^c	BF ₄ ⁻	D ₂ O (H ⁺)	1.71	2.50	...	3.06 ^d	...	3.90 ^d	0.79	...
<i>dl</i> -Ni(1,4-CT) ²⁺	BF ₄ ⁻	D ₂ O (H ⁺)	1.71	2.48	2.63	3.11	3.33	3.92	0.77	0.92

^a Spectra obtained with a Varian A-60 spectrometer. ^b Chemical shifts in parts per million downfield from an external TMS standard. ^c pD ~2 (HCl added). ^d Centers of gravity for complex patterns. ^e The imine methyl and the methylenic protons have been replaced by deuterium.

CT)²⁺ diastereoisomer has C_i symmetry. The latter is expected to show a lower extinction coefficient for d to d transitions than does the former.²⁷

Conclusive evidence which identified the Ni(1,4-CT)²⁺ isomer as the racemic form has been provided by Dunitz and associates.⁶ They have shown *via* X-ray crystallographic analysis that *d* and *l* enantiomers exist in equal numbers within the crystal lattice of Ni(1,4-CT)(ClO₄)₂. Through the use of column chromatography, utilizing optically active absorbents, attempts have been made to resolve the NCS⁻ and BF₄⁻ derivatives of this isomer. Small rotations and ORD and CD curves attributable to the complex were obtained.²⁴

Our studies on the interconversion of the diastereoisomers of Ni(1,7-CT)²⁺ suggested that the missing isomer, *meso*-Ni(1,4-CT)²⁺, might be generated by labilization of the nitrogen protons in the *dl* isomer. Several such experiments showed no evidence of isomerization of *dl*-Ni(1,4-CT)²⁺, and it is tentatively concluded that the equilibrium concentration of the *meso* isomer is below the detection limit of the methods employed (see Experimental Section). This isomer may be of limited stability because of the possible nonbonding interactions between the two axial methyl groups (Figure 1d) and the strained, eclipsed five-membered chelate rings.⁷

Proton Magnetic Resonance Spectra. The assignments of proton resonances for both of the Ni(1,7-CT)²⁺ diastereoisomers and for the *dl*-Ni(1,4-CT)²⁺ isomer are given in Table III, and typical spectra are shown in Figure 2. Detailed analysis of these spectra have permitted the conclusive demonstration of the more subtle conformational aspects of the five- and six-membered chelate ring systems within these isomers.

Methyl Proton Resonances. The most prominent features in the pmr spectrum of each isomer are the three equally intense resonances which appear in the high-field portion of the spectra (Figure 2, Table III). These resonances are due to the six methyl groups within each isomer and require these groups to be pairwise equivalent. Consequently, the two six-membered chelate rings must be of equivalent and stable conformations. The location of the geminal carbon atom produces an axial and equatorial distinction between the two geminal methyl groups. Thus, there are three types of methyl groups associated with each isomer

(see Figure 1): (1) CH₃-I, the imine methyl group is oriented in an equatorial manner and is essentially in the NiN₄ plane; (2) CH₃-II, the axial methyl groups of the geminal pairs lie over the NiN₄ plane; (3) CH₃-III, the equatorial geminal methyl groups lie out away from the metal ion center and their bond axes are roughly parallel to the NiN₄ plane.

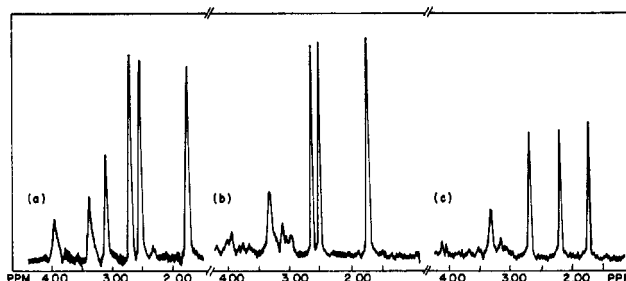
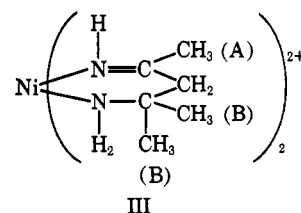


Figure 2. Pmr spectra of Ni(CT)(NCS)₂ isomers: (a) Ni(1,4-CT)(NCS)₂ in neutral D₂O, (b) *dl*-Ni(1,7-CT)(NCS)₂·H₂O in acidic D₂O, (c) *meso*-Ni(1,7-CT)(NCS)₂ in acidic D₂O. Spectra calibrated in ppm downfield from external TMS.

The lowest field methyl resonance in the pmr spectra of each isomer is assigned to CH₃-I on the basis of deuteration experiments. The proximity of these methyl protons to the imine function and the electron-withdrawing effect of the metal ion causes them to be acidic and to exchange for deuterium in basic D₂O.^{28, 29} The loss of the resonance attributable to CH₃-I can actually be followed in freshly prepared D₂O solutions which are basic. Finally this assignment is strongly supported by the unambiguous assignments made for the methyl protons of a similar nickel(II) complex which is derived from acetone and ammonia (structure III). In this case, the imine methyl protons of group A give rise to a low-field singlet of relative intensity one,



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Table IV. Chemical Shifts for Methyl Protons as a Function of Solvent

Isomer	Salt	Solvent	CH ₃ -I	Rel int	CH ₃ - II	Rel int	CH ₃ - III	Rel int	$\Delta(I - III)$	$\Delta(I - II)$	$\Delta(II - III)$
<i>dl</i> -Ni(1,7-CT) ²⁺	NSC ⁻	D ₂ O(H ⁺) ^a	2.67	1	2.52	1	1.75	1	0.92	0.15	0.77
<i>dl</i> -Ni(1,7-CT) ²⁺	PF ₆	C ₆ D ₆ O ^b	2.67	1	2.20	1	1.36	1	0.94	0.10	0.84
<i>dl</i> -Ni(1,7-CT) ²⁺	PF ₆	C ₆ H ₅ NO ₂ ^b	2.45	(2)			1.54	1	0.91	0	0.91
<i>meso</i> -Ni(1,7-CT) ²⁺	NCS ⁻	D ₂ O(H ⁺) ^a	2.69	1	2.21	1	1.75	1	0.94	0.48	0.46
<i>meso</i> -Ni(1,7-CT) ²⁺	PF ₆	C ₆ D ₆ O ^b	2.32	1	1.83	1	1.36	1	0.96	0.49	0.47
<i>meso</i> -Ni(1,7-CT) ²⁺	PF ₆	C ₆ H ₅ NO ₂ ^b	2.51	1	2.06	1	1.56	1	0.95	0.45	0.50
<i>dl</i> -Ni(1,4-CT) ²⁺	NCS ⁻	D ₂ O(H ⁺) ^a	2.70	1	2.54	1	1.75	1	0.95	0.16	0.79
<i>dl</i> -Ni(1,4-CT) ²⁺	PF ₆	C ₆ D ₆ O ^b	2.25	1	2.09	1	1.33	1	0.92	0.16	0.76
<i>dl</i> -Ni(1,4-CT) ²⁺	PF ₆	C ₆ H ₅ NO ₂ ^b	2.43	1	2.37	1	1.51	1	0.93	0.06	0.87

^a Chemical shifts in parts per million downfield from an external TMS standard. ^b Chemical shifts in parts per million downfield from an internal TMS standard.

and those of the geminal methyl groups B give rise to a high-field singlet of relative intensity two in neutral D₂O.³⁰

The two remaining higher field methyl resonances of the Ni(CT)²⁺ isomers are those due to the axial and equatorial geminal methyl protons, CH₃-II and CH₃-III, respectively. Specific assignment of these two resonances can be inferred from the following. As shown in Tables III and IV, the chemical shift difference between the highest field methyl proton resonance and the imine methyl resonance, $\Delta(I - III)$, remains relatively constant from isomer to isomer and from solvent to solvent; $\Delta(I - III) = 0.94$ ppm with an average derivation of ± 0.01 ppm. Such constancy might well be expected from groups whose environment is similar from isomer to isomer and from groups allowing ready access to solvents so that the relative effects of small structural variations are minimized. On this basis, CH₃-I and CH₃-III must be identified with the imine methyl (CH₃-I) and the equatorial geminal methyl (CH₃-III). These groups are oriented away from the metal ion and away from all other atoms in the complex. Because the imine methyl group, CH₃-I, has already been assigned to the lowest field methyl proton resonance, it is reasonable to assign the equatorial geminal methyl group, CH₃-III, to the highest field methyl proton resonance position.

By elimination then, the center methyl proton resonance is assigned to the axial geminal methyl protons, CH₃-II. This assignment is strongly supported by the variations in relative positions of this methyl proton resonance noted as a function of isomer and solvent. The orientation of the axial geminal methyl group makes its proton resonance position sensitive to solvation and chelate ring conformational changes because of their proximity to other atoms and bonds in the complex. The magnitude of the low-field shift of the axial geminal methyl proton resonance with respect to the equatorial geminal methyl proton resonance for each isomer is striking. It would otherwise be expected that protons, such as these, which are in the same bonded chemical environment, would give rise to resonances in very nearly the same region of the pmr spectrum and only show relatively small chemical shift differences due to slightly different nonbonding effects. The relatively large chemical shift differences observed here (0.46–0.91 ppm) indicate that a relatively large nonbonding effect

is occurring. In all of the isomers of the Ni(CT)²⁺ complex, the axial geminal methyl groups are over the NiN₄ plane. Based on this geometrical consideration it seems most reasonable to explain the large chemical shifts in terms of a theoretical prediction made by Buckingham and Stevens.³¹ They predict large deshielding effect for protons situated above the plane of square-planar platinum(II) complexes. In so far as d⁸ systems resemble each other, a similar situation should be expected for analogous nickel(II) complexes. As in the case of the shielding effects on protons in the plane of square-planar platinum(II) complexes, the magnitude of the deshielding observed here should be a function of the radial and angular orientation of the axial geminal methyl groups with respect to the NiN₄ plane and the perpendicular axis through the metal ion center. Changes in the conformation of the six-membered chelate ring within the Ni(CT)²⁺ system would alter the methyl group orientation. Such changes are expected to be a function of isomer and, perhaps, of solvent and would account for the solvent and isomer dependence of the low-field shifts observed for the CH₃-III proton resonance (Tables III and IV). The obvious alternative explanation, that of deshielding due to the anisotropy of the imine function, has been abandoned on the assumption that imine functions are analogous to carbonyl and olefinic functions. The long-range diamagnetic effect predicted for protons that lie in the vicinity of the π -electron cloud of these double bonds is a high-field rather than a low-field shift.³²

The interesting solvent effect reported in Table IV can be rationalized from a geometrical point of view. The two isomers, *dl*-Ni(1,7-CT)²⁺ and *dl*-Ni(1,4-CT)²⁺, which shows this effect are unsymmetrical (C₂ symmetry). One side of the complex ion is more hydrophobic than the other; therefore they would be expected to be unsymmetrically solvated. As the solvation sphere changes from solvent to solvent, the chelate ring conformations might be expected to vary, thus significantly changing the chemical environment of the axial geminal methyl group, but not that of the equatorial methyl groups. No solvent-induced chemical shift was observed for the methyl resonances of *meso*-Ni(1,7-CT)²⁺ which has an inversion center (C_i symmetry). The chelate ring conformations of this

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(32) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, pp 124, 129.

(30) N. J. Rose, M. S. Elder, and D. H. Busch, *Inorg. Chem.*, 6, 1924 (1967).

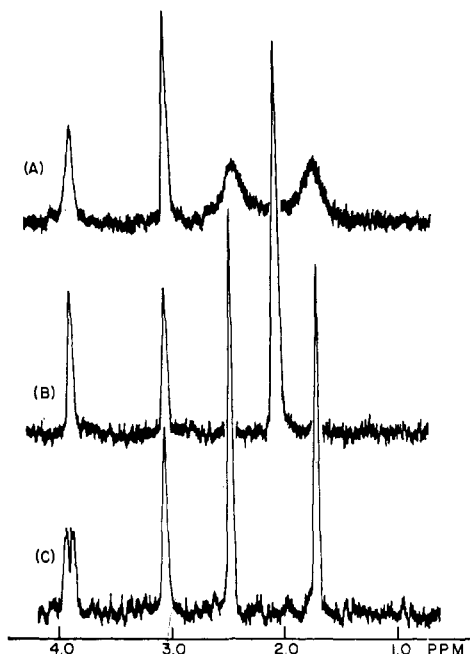


Figure 3. Pmr spectra of deuterated $\text{Ni}(1,4\text{-CT})^{2+}$: (A) D_2O (pD ~ 10) at 37° , (B) D_2O (pD ~ 10) at 100° , (C) D_2O (pD ~ 2). The imine methyl and methylene proton positions have been deuterated.

isomer and, therefore, the positions of the methyl groups are not a function of solvent because of symmetrical solvation.

The methyl proton region of the pmr spectra provides a convenient and trustworthy method for distinguishing between the racemic and *meso* diastereoisomers of the 1,7-diene complexes (Figure 2, Table III). In this regard, it is significant to note that the pmr spectrum of $\text{Ni}(\text{CT})(\text{BF}_4)_2$ isolated directly from the condensation reaction mixture shows that the only 1,7-diene isomer present is the racemate. An identical observation was made by Curtis, *et al.*,³ in the case of $\text{Ni}(\text{CT})(\text{ClO}_4)_2$.

The methyl proton resonance region of the pmr spectrum also provides a second method of observing the racemate-*meso* equilibrium. Freshly prepared solutions of pure *meso* and pure racemic isomers show the distinct methyl proton resonance patterns of Figure 2. After significant time has elapsed, solutions of both isomers show a mixture of the *meso* and *dl*-1,7-diene isomer resonance patterns. Integrated intensity data indicate a racemate:*meso* ratio of approximately 6:1 at 37° .

The dependence of the *meso*-racemate isomerization on the lability of the secondary amine proton has been demonstrated using pmr spectra. In aprotic solvents, such as nitrobenzene and acetone, where the lability of this proton is thought to be low, equilibrium is established only after several days and several hours, respectively, whereas, in water at 35° , the equilibrium is established within 1 hr. As in the case of electronic absorption spectra no isomerization is observed in acidic aqueous solutions.

The results obtained from pmr studies in acidic and basic D_2O substantiate the view that the chelate ring conformations and stability are inherently a function of the secondary amine nitrogens and their configurations. Under conditions for retention of nitrogen

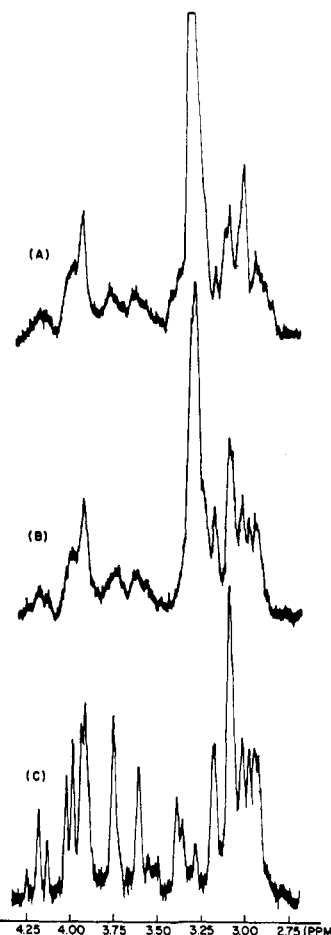


Figure 4. Pmr spectra of the five-membered chelate ring dimethylene chains of $dl\text{-Ni}(1,7\text{-CT})(\text{BF}_4)_2$: (A) no positions deuterated; (B) the secondary amines have been deuterated; (C) the secondary amines, the imine methyl functions, and the methylene function of the six-membered chelate rings have been deuterated.

configuration (acidic D_2O), the pmr spectra are sharp, and therefore the chelate rings are undoubtedly rigid (Figures 2-4). Under conditions for rapid inversion of the coordinated secondary amine nitrogens (basic D_2O), the pmr spectrum of the 1,4-diene isomer shows that the chelate rings are flexing. The conformational changes resulting from this flexing lead to an interchange of the geminal methyl groups between the axial and equatorial positions. At 35° the resonances due to the axial and equatorial geminal methyl protons are extensively broadened because of this chelate ring flexing; *i.e.*, the axial-equatorial interchange is relatively slow. At 100° this flexing and, therefore, the interchange, is very rapid, and the two geminal methyl resonances collapse into a single sharp absorption peak (Figure 3). In basic D_2O at 35° , the *dl*-1,7-diene isomer also shows extensive broadening of the geminal methyl resonances. This indicates a corresponding flexing of the six-membered chelate rings. The five-membered chelate rings also experience conformational interchange under conditions for rapid inversion of the secondary amine nitrogens, as is evident from the broadening of the 1,7-diene resonance patterns (Figure 4) associated with the dimethylene protons and the collapse of the imine dimethylene multiplet resonance of the $\text{Ni}(1,4\text{-CT})^{2+}$ isomer (Figure 3) when the complexes are dissolved in basic media.

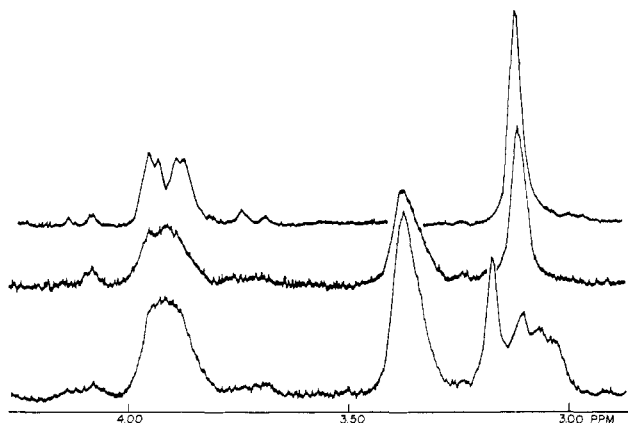


Figure 5. Low-field protons of the pmr spectra of *dl*-Ni(1,4-CT)-(NCS)₂: (top) in acidic D₂O (pD ~2), (middle) in neutral D₂O, (bottom) in acidic D₂O after recrystallization from basic D₂O.

Methylene and Dimethylene Resonances. The low-field region of the pmr spectrum (2.7–4.2 ppm) for each isomer arises from the protons on the methylene carbons in the six-membered chelate ring and from the protons of the dimethylene chains which constitute the backbone of the five-membered chelate rings (Figure 1). Ready identification of the major portions of the low-field regions of the pmr spectrum of the *dl*-1,7-diene isomer is made on the basis of deuteration experiments. Figure 4A presents that portion of the pmr spectrum of *dl*-Ni(1,7-CT)(BF₄)₂ due to all protons except those of the methyl groups and the secondary amines. Shown in Figure 4B is the change in the high-field portion of the spectrum caused by substitution of deuterium for hydrogen at the secondary amine. A change of this nature would be expected to attend elimination of coupling between the amine protons and those protons on the methylene carbon adjacent to the amine nitrogen. The portion of the spectrum arising primarily from the methylene protons nearest to the amine nitrogen is thereby identified. The down-field portion of the pmr spectrum of *dl*-Ni(1,7-CT)(BF₄)₂ which has been recrystallized several times from basic D₂O is shown in Figure 4C. The figure shows only those resonances assignable to the dimethylene protons of the five-membered chelate rings. This assignment has been substantiated by condensing Ni(en)₃(BF₄)₂ with acetone-*d*₆. After one recrystallization from D₂O the resulting *dl*-Ni(1,7-CT)(BF₄)₂ salt is expected to have all proton positions deuterated except those of the dimethylene chains which comprise the five-membered chelate ring backbones. The pmr spectrum of this sample in acidic D₂O is identical with that spectrum shown in Figure 4C. The elimination of the major resonance at 3.28 ppm (Table III, Figure 4A,C) permits assignment of that band to the methylene protons of the methylene carbon in the six-membered chelate ring. Like the imine methyl protons, these protons are bonded to a carbon α to the imine function. They are therefore acidic and exchange in basic D₂O. This methylene resonance occurs as a compressed AB pattern with the ratio $J_{AB}/(\delta_A - \delta_B)$ greater than 1.5.³³

The most striking feature of the spectrum shown in Figure 4C is the emergence of the relatively sharp lines in the low-field portion. This emergence, coupled

with the fact that the imine methyl resonance is split slightly into a doublet, suggests *cisoid* homoallylic coupling.³⁴ This coupling must involve one of the protons on that dimethylene carbon which is bonded to the imine nitrogen and the protons of the imine methyl group. *Cisoid* homoallylic coupling between the axial dimethylene proton and the imine methyl protons would split the imine methyl proton resonance into a doublet and cause splitting in all the transitions due primarily to the dimethylene proton. In consequence the low-field portion (3.50–4.50 ppm) of the pmr spectrum of *dl*-Ni(CT)(BF₄)₂ (Figure 4A–C) is believed to be due to those transitions assignable primarily to the protons of the carbon atom α to the imine nitrogen. The sharpening of the spectrum upon deuteration results from the elimination of *cisoid* homoallylic coupling where the coupling constant is approximately 0.6 cps.

The two dimethylene chains of each 1,7-diene isomer are equivalent (Figure 1). Each chain links an imine and an amine nitrogen. The dimethylene carbons are nonequivalent, and the two protons on each of these carbons are also nonequivalent due to a *gauche* chelate ring conformation. Therefore, the highly unsymmetrical pattern seen in Figure 4C constitutes a single ABCD pattern and serves as an unequivocal means of identifying the racemic 1,7-diene isomer. The presence of an ABCD pattern indicates that the 2-dimethylene chains are equal and are of a staggered conformation.

In contrast to the 1,7-diene isomers, where the two dimethylene chains are equivalent, these two chains are different in the 1,4-diene isomers. One chain links the two secondary amine nitrogens, and the other links the two imine nitrogens. Within each chain, the two carbon atoms are equivalent. As a result, the most complex pattern to be expected is composed of two A₂B₂ systems. Three simple distinct patterns occur in the low-field portion of the pmr spectrum of Ni(1,4-CT)(NCS)₂ (Figures 2a and 5). Two are due to the dimethylene chains of the two dissimilar five-membered chelate ring systems, and the third arises from the protons on the methylene carbon of the six-membered chelate rings. By deuteration in basic D₂O the resonance arising from the methylenic protons is easily identified as the center resonance occurring at 3.35 ppm.

The resonance pattern centered at 3.11 ppm (Figure 5) is assigned to the protons on the dimethylene chain which links the secondary amine nitrogens. In acidic D₂O it appears as a broad multiplet. The collapse of this multiplet into a sharp singlet in neutral or basic D₂O indicates that in acid solution the amine protons exchange only very slowly and that they couple with the amine dimethylenic protons. In neutral or basic solution, however, the amine protons rapidly exchange with the solvent or are completely replaced by deuterons. The collapse into a singlet is then indicative of the elimination of coupling to other protons, and, in basic D₂O, it may also reflect rapid flexing of the five-membered chelate ring. A single sharp resonance is also observed after reacidification of a basic solution. The singlet resonance is then an A₄ pattern and indicates that the dimethylene chain

(34) (a) J. T. Pinkey and S. Steinhilber, *Tetrahedron Letters*, **4**, 275 (1963); (b) H. G. Hecht and B. L. Victor, *J. Am. Chem. Soc.*, **89**, 2532 (1967).

(33) L. M. Jackman, ref 32, p 90.

which spans the secondary amines is in an eclipsed conformation. This is a rather surprising result when it is realized the imine dimethylene chain is in a staggered rather than an eclipsed conformation (see below).

The broad multiplet centered at 3.92 ppm (Figure 2a) is assigned to the protons of the dimethylene chain linking the imine functions. When the imine methyl proton and the six-membered ring methylenic proton positions are deuterated, this multiplet becomes an A_2B_2 pattern corresponding to the case of intermediate coupling as analyzed by Corio,³⁵ where the ratio of the coupling constant (J) to the chemical shift difference (δ) is $0.2 < J/\delta < 0.8$. Because of the relatively low limit of resolution obtained for this pattern, more detailed numerical analysis is not justified.

This A_2B_2 pattern is indicative of a staggered conformation for this imine dimethylene chain, with a small distinction between the two equivalent axial protons and the two equivalent equatorial protons. This result is somewhat surprising, for models suggest that this chelate ring should exist in an eclipsed conformation, thereby giving rise to an A_4 singlet rather than the symmetrical A_2B_2 multiplet.

The existence of a broad multiplet for the imine dimethylene proton resonances that is observed prior to deuteration of the proton positions α to the imine carbon is probably due to *transoid* homoallylic coupling. The axial methylene proton is coupling with at least one of the imine dimethylene protons. This superimposed coupling broadens the dimethylene A_2B_2 resonances and causes the A_4 or condensed AB resonance pattern of the methylene protons to be unsymmetrical (see Figure 5).

Experimental Section

Infrared spectra were determined from Nujol mulls and potassium bromide pellets of dry solids, using a Perkin-Elmer Model 337 spectrophotometer. Visible spectra were measured using a Cary 14 recording spectrophotometer. All reported proton magnetic resonance spectra were determined using a Varian A-60 nmr spectrometer. The chemical shift data were determined using the side-banding technique. Both the Gouy and Faraday methods were used to determine magnetic susceptibilities.

Elemental analyses were performed by Mr. Peter Kovi of the Department of Chemistry, Ohio State University, and by Galbraith Laboratories, Inc. Conductances were obtained for 10^{-3} *N* aqueous solutions using an Industrial Instruments bridge.

Preparations. Derivatives of 5,7,7,12,12,14-Hexamethyl-1,4,8,11-tetraazacyclotetradeca-1(14),4-dienenickel(II), Ni(1,4-CT)(ClO₄)₂. This derivative was prepared following the method of Curtis.³

Ni(1,4-CT)(NCS)₂. The dithiocyanato salt, Ni(1,4-CT)(NCS)₂, is prepared by dissolving 8 g of Ni(1,4-CT)(ClO₄)₂ and 36 g of potassium thiocyanate in 60 ml of hot water. Upon cooling this solution to 0° the potassium perchlorate precipitate is filtered off. The filtrate volume is slowly reduced to about 30 ml and cooled to 0°. The resulting yellow-green product is collected and then recrystallized from ethanol (yield 5.3 g). *Anal.* Calcd for C₁₈H₃₂N₆S₂Ni: C, 47.48; H, 7.05; N, 18.46; S, 14.08. Found: C, 47.40; H, 6.84; N, 18.28; S, 14.18.

Ni(1,4-CT)(BF₄)₂. This salt is prepared by dissolving 1.8 g of Ni(1,4-CT)(NCS)₂ in 40 ml of H₂O and adding 1.5 g of AgNO₃ dissolved in 20 ml of H₂O. The resulting AgSCN is filtered off and to the filtrate is added 20 ml of a saturated aqueous NaBF₄ solution. The volume of this solution is slowly reduced by passing air across the surface. After several hours the yellow product is filtered off and recrystallized from water (yield 1.2 g). *Anal.* Calcd for C₁₈H₃₂N₆B₂F₈Ni: C, 37.47; H, 6.29; N, 10.93. Found: C, 37.6; H, 6.25; N, 11.1.

Ni(1,4-CT)(PF₆)₂. This salt is prepared by dissolving 6.8 g of Ni(1,4-CT)(NCS)₂ in 80 ml of hot water and adding 6 g of AgNO₃

in 50 ml of H₂O. The mixture is stirred at about 70° for 15 min and then cooled and the AgNCS filtered off. To the resulting filtrate is added a saturated solution of NH₄PF₆. The desired product is isolated by filtering and recrystallized from hot water. *Anal.* Calcd for NiC₁₈H₃₂N₆P₂F₁₂: C, 30.55; H, 5.13; N, 8.91. Found: C, 30.7; H, 4.98; N, 9.04.

Derivatives of *dl*- and *meso*-5,5,7,12,12,14-Hexamethyl-1,4,8,11-tetraazacyclotetradeca-1(14),7-dienenickel(II), Ni(1,7-CT)²⁺. Condensation of tris(ethylenediamine)nickel(II) fluoroborate (122 g) with acetone (300 ml) yields *dl*-Ni(1,7-CT)(BF₄)₂ after 5 days. The reaction mixture is evaporated down to an oil and 200 ml of ethanol is added to dissolve the polymeric side products and to precipitate the desired complex. This yellow product is isolated, washed with ethanol, and dried in a vacuum desiccator (yield 137 g). *Anal.* Calcd for C₁₈H₃₂N₆B₂F₈Ni: C, 37.47; H, 6.29; N, 10.93. Found: C, 37.33; H, 6.27; N, 11.14.

The pmr spectrum of this unrecrystallized product shows the *meso*-Ni(1,7-CT)(BF₄)₂ isomer to be absent. However, this product is not isomerically pure. A small amount of the 1,4-diene isomer has been found upon nearly quantitative conversion of the product to the diperchlorate salt by metathetical reaction with sodium perchlorate and numerous recrystallizations of this salt from water. The amount of the 1,4-diene isomer in the above product, *dl*-Ni(1,7-CT)(BF₄)₂, is small, less than 10%, and is difficult to detect *via* pmr spectroscopy as is evident from the nearly identical nature of its pmr spectrum with that of an isomerically pure sample of *dl*-Ni(1,7-CT)(BF₄)₂, whose preparation is described below.

Diastereoisomers of Ni(1,7-CT)(NCS)₂. To 20 g of the above prepared *dl*-Ni(1,7-CT)(BF₄)₂ in 450 ml of acetone is added, without agitation, 6.5 of sodium thiocyanate in 120 ml of acetone. After several hours, orange needles begin to precipitate. When the yellow needles of the *meso*-Ni(1,7-CT)(NCS)₂ begin to appear, the solids are filtered off and the filtrate is saved in order to obtain the *meso* isomer. Recrystallization of the solids by dissolution in water at room temperature and cooling in a refrigerator for 8 hr yield large orange needles of *dl*-Ni(1,7-CT)(NCS)₂·H₂O. These are isolated and air-dried (yield 5 g). *Anal.* Calcd for C₁₈H₃₂N₆S₂ONi: C, 45.67; H, 7.24; N, 17.76; S, 13.55. Found: C, 45.45; H, 7.29; N, 17.73; S, 13.27.

An alternate route to the *dl*-Ni(1,7-CT)(NCS)₂·H₂O proceeds *via* the condensation of tris(ethylenediamine)nickel(II) diperchlorate hemihydrate with acetone following the method of Curtis.³ After most of the Ni(1,4-CT)(ClO₄)₂ isomer has been removed by fractionation, the reaction mixture is evaporated to an oil. Ethanol is added to dissolve the polymeric side products and to precipitate the remaining complex. This material, which is an isomeric mixture, the *dl*-Ni(1,7-CT)(ClO₄)₂ isomer being predominant, is isolated and washed with ethanol. This product, Ni(CT)(ClO₄)₂ (47 g), is suspended in 250 ml of 95% ethanol which contains 20 g of potassium thiocyanate. After heating almost to boiling for 0.5 hr, the ethanolic solution is cooled to 0° and the potassium perchlorate is removed by filtration. The filtrate is then evaporated to dryness and the residue is recrystallized by dissolving in a minimum amount of water at room temperature and then cooling to 0°. The orange needles of isomerically pure *dl*-Ni(1,7-CT)(NCS)₂·H₂O are isolated, washed with ethanol, and air-dried (yield 22.2 g). *Anal.* Calcd for C₁₈H₃₄N₆S₂ONi: C, 45.67; H, 7.24; N, 17.76. Found: C, 45.6; H, 7.45; N, 17.9.

***meso*-Ni(1,7-CT)(NCS)₂ (Low Spin).** The acetone filtrate from the above metathetical reaction between KSCN and *dl*-Ni(1,7-CT)(BF₄)₂ is cooled in a refrigerator for several hours. The resulting yellow precipitate is isolated and rapidly recrystallized from room-temperature water by cooling to 0° (yield 3 g). Alternately, the *meso*-Ni(1,7-CT)(NCS)₂ can be prepared by suspension of *dl*-Ni(1,7-CT)(NCS)₂·H₂O (3 g) in boiling acetone (100 ml). After several hours the *meso* isomer is recovered (yield, 2 g). *Anal.* Calcd for C₁₈H₃₂N₆S₂Ni: C, 47.48; H, 7.08; N, 18.46; S, 14.08. Found: C, 47.54; H, 7.22; N, 18.58; S, 14.04.

***meso*-Ni(1,7-CT)(NCS)₂ (High Spin).** This coordination number isomer was prepared by dissolving the yellow low-spin isomer of *meso*-Ni(1,7-CT)(NCS)₂ (0.8 g) in 200 ml of boiling chloroform. The solution is boiled for 10 min and the volume reduced to approximately 100 ml. The hot solution is then placed in a freezer. After 4 days the pale violet product is isolated by filtration in a water-free nitrogen atmosphere, washed with ether, and dried in a vacuum desiccator (yield 0.3 g). This isomer readily reverts to its parent isomer upon contact with water or severe grinding. *Anal.* Calcd for C₁₈H₃₂N₆S₂Ni: C, 47.48; H, 7.08; N, 18.46; S, 14.08. Found: C, 47.41; H, 7.03; N, 18.45; S, 14.05.

The elimination of possible contaminants from these dithiocy-

(35) P. L. Corio, *Chem. Rev.*, **60**, 363 (1960).

anato derivatives of the 1,7-diene isomers (mainly the 1,4-diene isomer) is ensured by recrystallization of the *dl* and *meso* (low spin) diastereoisomers from water. The dithiocyanato salt of the 1,4-diene isomer is several times more soluble in water at room temperature than is either of the dithiocyanato 1,7-diene isomers. This isomeric purity of the dithiocyanato isomers allows them to be the precursors for all other 1,7-diene derivatives.

***dl*- and *meso*-Ni(1,7-CT)(BF₄)₂.** These salts are prepared by dissolving the appropriate isomer, *dl*- or *meso*-Ni(1,7-CT)(NCS)₂ (1.8 g), in 0.01 *N* HBF₄ (40 ml). Silver nitrate (1.5 g) dissolved in 20 ml of 0.01 *N* HBF₄ is added and the mixture is vigorously stirred. The AgSCN is filtered off and to the filtrate is added 15 ml of a saturated NaBF₄ solution. The volume is reduced to approximately 50 ml by passing a stream of air across the surface of the solution. The yellow product is isolated by filtration, washed with small amounts of cold 0.01 *N* HBF₄, and dried under vacuum desiccation (yield ~50%). *Anal.* Calcd for C₅H₃₂N₄B₂F₈Ni: C 37.47; H, 6.29; N, 10.93. Found (*dl* isomer): C, 37.2; H, 6.86; N, 11.2. Found (*meso* isomer): C, 37.7; H, 6.36; N, 10.9.

***dl*- and *meso*-Ni(1,7-CT)(PF₆)₂.** The appropriate diastereoisomer, *dl* or *meso*-Ni(1,7-CT)(NCS)₂ (2 g), is dissolved in 70 ml of 0.01 *N* HCl. To this solution is added with stirring 8 g of NH₄PF₆ in 20 ml of H₂O. The yellow microcrystalline product is isolated by filtration, washed with water, and dried in a vacuum desiccator (yield ~85%). *Anal.* Calcd for C₁₆H₃₂N₄P₂F₁₂Ni: C, 30.55; H, 5.13; N, 8.91; F, 36.24. Found (*dl* isomer): C, 30.71; H, 5.17; N, 8.95; F, 36.10. Found (*meso* isomer): C, 30.77; H, 5.20; N, 8.26; F, 36.05.

***dl*- and *meso*-Ni(1,7-CT)(ClO₄)₂.** These derivatives are prepared following the procedure described for the preparation of the hexafluorophosphate derivatives; only perchloric acid and sodium perchlorate are substituted for HCl and NH₄PF₆, respectively. *Anal.* Calcd for C₁₆H₃₂N₄Cl₂O₈Ni: C, 35.71; H, 5.99; N, 10.41. Found (*dl* isomer): C, 35.8; H, 6.07; N, 10.7. Found (*meso* isomer): C, 35.6; H, 6.25; N, 10.59.

The isomeric purity of all derivatives of each isomer was determined using pmr spectroscopy. The only exception was the determination of possible 1,4-diene contamination in derivatives of the *dl*-1,7-diene isomer.

It should be noted that prolonged contact of any of the derivatives of either the *dl*- or *meso*-1,7-diene isomers with neutral aqueous solutions results in isomerization and equilibration of these two diastereoisomers.

Deuteration Experiments. Deuteration of the Ni(1,4-CT)²⁺ isomer was accomplished by dissolving any of its salts in basic D₂O. This accomplished the deuteration of the secondary amine, the imine methyl group, and the methylene function of the six-membered

chelate rings within a few minutes, as was evident from the pmr spectrum of each such solution. No solid deuterated derivatives of this isomer were isolated.

Two recrystallizations of the *dl*-Ni(1,7-CT)(BF₄)₂ isomer from D₂O resulted in deuteration of only the secondary amines. The infrared spectrum of the deuterated complex showed $\nu(\text{N-D})$ bands at 2410 and 2390 cm⁻¹ ($\nu(\text{N-D})/\nu(\text{N-H}) = 1.34$). Relative areas of the $\nu(\text{N-D})$ and $\nu(\text{N-H})$ bands indicated at least 90% deuteration of the amine function. The absence of any $\nu(\text{C-D})$ bands in the 2100–2300-cm⁻¹ region of the infrared spectrum indicated the absence of any further deuteration. This sample was found to be free of the *meso* diastereoisomer as indicated from its pmr spectrum shown in Figure 4B.

Deuteration of the secondary amines, imine methyl groups, and the methylene function of the six-membered chelate rings of the *dl*-Ni(1,7-CT)(BF₄) isomer was accomplished by twice recrystallizing from D₂O made basic with 4 *N* NaOH (pH 10 as indicated on Fisher Alkacid Test Ribbon). The infrared spectrum showed $\nu(\text{N-D})$ bands at 2410 and 2390 cm⁻¹ and at least 90% deuteration of the amine functions. A $\nu(\text{C-D})$ band centered at 2200 cm⁻¹ was also present and accompanied by gross changes in the $\nu(\text{C-H})$ region centered at 2930 cm⁻¹ ($\nu(\text{C-H})/\nu(\text{C-D}) = 1.33$) and in the finger-print region, 1200–1500 cm⁻¹. This sample was free of the *meso*-1,7-diene isomer as indicated by its pmr spectrum. The pmr spectrum shown in Figure 4C was obtained using this sample.

Tris(ethylenediamine)nickel(II) fluoroborate was condensed with acetone-*d*₆ and the deuterated product, *dl*-Ni(1,7-CT)(BF₄)₂, was isolated as described above and then recrystallized from D₂O. This product has all proton positions deuterated except those of the dimethylene chains which constitute the five-membered chelate rings. *Anal.* Calcd for C₁₆H₈D₂₄N₄B₂F₈Ni: C, 35.79; H (D), 6.48; N, 10.44; F, 28.31. Found: C, 35.72; H (D), 6.45; N, 10.52; F, 28.15.

The infrared spectrum of this *dl*-Ni(1,7-CT)(BF₄)₂-*d*₂₄ confirms the deuteration of the amine functions and some of the C-H positions: $\nu(\text{ND})$ 2400 br, $\nu(\text{C-D})$ 2230 cm⁻¹. The pmr spectrum confirms the deuteration of all methyl and methylene positions. The 2.5–4.5-ppm region of this spectrum is identical with that spectrum shown in Figure 4C, thus confirming the extent of the previously described deuteration.

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Spin-Delocalization Mechanisms in Some Paramagnetic Tris-2,2'-bipyridine Complexes of Nickel(II)¹

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Abstract: The proton nmr contact shifts of Ni(bipy)₃²⁺ (bipy = 2,2'-bipyridine) and some substituted bipyridyl complexes are reported, and the mechanisms of unpaired electron spin delocalization in these complexes are discussed. It is found that both σ - and π -delocalization mechanisms are important. The shifts can be interpreted quantitatively by comparing the experimental contact shifts with those predicted from extended Hückel molecular orbital calculations. These results and the change in direction of the shifts on substituting CH₃ for H at various ring positions are employed to indicate which ligand MO's are most extensively mixed with the metal ion in the MO's containing unpaired electrons.

In this laboratory we have been interested in the nmr contact shifts of paramagnetic transition metal complexes and in their use in the elucidation of the nature of metal-ligand bonding. From a simple ob-

servation of the shifts of different protons in a ligand, one can often infer whether or not spin delocalized in a

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