Four-, Five-, and Six-Coordinate Complexes Containing 1,1,7,7-Tetraethyldiethylenetriamine

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Abstract: Syntheses, properties, and electronic structures of $Ni(Et_4dien)X_2$ ($Et_4dien = 1,1,7,7$-tetraethyldiethylenetriamine; $X = Cl, Br, I$), $Co(Et_4dien)Cl_2$, and $Rh(Et_4dien)Cl_3$ are reported. The spectral and magnetic properties of $Ni(Et_4dien)X_2$ depend on the nature of the solvent and the concentration of X^-. The $Ni(Et_4dien)Cl_2$ complex is diamagnetic and presumably square planar in the solid state and in ethanol solution. This complex exhibits paramagnetism in several organic solvents, including CH_3CN, DMF, and acetone. The $Co(Et_4dien)Cl_2$ complex is paramagnetic both in the solid state and in solution. It is suggested that $Ni(Et_4dien)Cl_2$ exists as a high-spin, five-coordinate species in certain solutions and that $Co(Et_4dien)Cl_2$ is five-coordinate and high-spin both in the solid state and in solution.

Recent studies[2] of transition metal ions in five-coordination have dealt largely with d^8 complexes containing good π-acceptor ligands such as CO[3] and $SnCl_3^-$[4] or ligands with heavy donor atoms such as phosphorus and arsenic.[5–8] The d^8 five-coordinate complexes containing these types of ligands are invariably low-spin, in part because the interelectronic repulsions in molecular orbitals derived from d valence orbitals are greatly reduced from free-atom values.

A possible strategy to obtain examples of high-spin, five-coordinate complexes is to employ simple σ bonding but very bulky nitrogen- and oxygen-donor chelating groups, so that the tendency to attain six-coordination with central metals such as Ni(II) and Co(II) is suppressed. In the course of our studies,

plexes.[10] The present paper reports our studies of complexes of Ni(II), Co(II), and Rh(III) containing the bulky ligand 1,1,7,7-tetraethyldiethylenetriamine (Et_4-dien).

Experimental Section

Preparation of $Ni(Et_4dien)Cl_2$. $NiCl_2 \cdot 6H_2O$ (3 g) was dissolved in 75 ml of absolute ethanol. The clear green solution was heated to about 60° and 3.3 g of the ligand was added slowly with continuous stirring. To the resulting red solution, LiCl (0.3 g) was added. The solution was then evaporated to about 20 ml and filtered. The red crystals, which were obtained on cooling the solution to about −10°, were dissolved in ethanol and recrystallized from an ethanol–acetone solution to give a pure sample of $Ni(Et_4$-dien)Cl_2$. The complexes $Ni(Et_4dien)Br_2$ and $Ni(Et_4dien)I_2$ were prepared in the same manner. Analytical and physical data for these compounds are given in Table I.

Table I. Analytical Data and Physical Properties of the $M(Et_4dien)X_n$ Complexes

Compound	Color	μ_{eff}, BM[a]	% C Calcd	% C Found	% N Calcd	% N Found	% X Calcd	% X Found	% H Calcd	% H Found
$Ni(Et_4dien)Cl_2$	Red	Diamagnetic	41.78	41.52	12.18	12.34	20.60	20.44	8.41	8.31
$Ni(Et_4dien)Br_2$	Red-violet	Diamagnetic	33.42	33.30	9.68	9.88	36.79	36.70	6.74	6.69
$Ni(Et_4dien)I_2$	Violet-blue	Diamagnetic	27.30	27.46	7.96	7.99	48.00	47.83	5.54	5.69
$Co(Et_4dien)Cl_2$	Red-violet	4.71	41.74	42.11	12.17	12.23	20.58	20.12	8.41	8.39
$Rh(Et_4dien)Cl_3$	Yellow-brown	Diamagnetic	34.15	33.95	9.88	9.83	24.99	24.85	6.86	6.95

[a] All measurements were made at 20–23°.

Sacconi and co-workers reported examples of high-spin, five-coordinate Mn(II), Co(II), and Ni(II) complexes containing substituted salicylaldimines.[9] Also, Ciampolini, Nardi, and Speroni independently have used bulky triamine ligands to prepare high-spin, five-coordinate Mn(II), Fe(II), Co(II), and Ni(II) com-

Preparation of $Co(Et_4dien)Cl_2$. $CoCl_2 \cdot 6H_2O$ (3 g) was dissolved in 75 ml of absolute ethanol. The solution was heated to boiling and 3.3 g of the ligand was added slowly. Very finely divided crystalline material precipitated immediately. The crystals of $Co(Et_4dien)Cl_2$ were filtered, washed with hot ethanol, and recrystallized from acetonitrile solution. The $Rh(Et_4dien)Cl_3$ complex was prepared in the same manner. Analytical and physical data for these compounds are given in Table I.

Spectroscopic Measurements. Absorption spectra were recorded on a Cary 14 spectrophotometer using 1-cm path-length cells. Spectral grade solvents were used as received. Low-temperature spectra were also recorded on a Cary 14 spectrophotometer, using double-beam absorption cells designed and constructed in this laboratory.[11] Temperature control was accurate to ±2°.

Magnetic Measurements. Magnetic susceptibilities were measured by the Gouy method, using solid $Hg[Co(NCS)_4]$ and nickel chloride solutions as calibrants.[12]

(1) Alfred P. Sloan Research Fellow.
(2) Pertinent references are collected in the following reviews: J. A. Ibers, *Ann. Rev. Phys. Chem.*, **16**, 380 (1965); E. L. Muetterties and R. A. Schunn, *Quart. Rev.* (London), to be published.
(3) S. S. Bath and L. Vaska, *J. Am. Chem. Soc.*, **85**, 3500 (1963).
(4) R. D. Cramer, R. V. Lindsey, C. T. Prewitt, and U. G. Stolberg, *ibid.*, **87**, 658 (1965).
(5) G. S. Benner, W. E. Hatfield, and D. W. Meek, *Inorg. Chem.*, **3**, 1544 (1964).
(6) G. Dyer, J. G. Hartley, and L. M. Venanzi, *J. Chem. Soc.*, 1293 (1965).
(7) G. Dyer and L. M. Venanzi, *ibid.*, 2771 (1965).
(8) A. D. Westland, *ibid.*, 3060 (1965).
(9) L. Sacconi, P. L. Orioli, and M. DiVaira, *J. Am. Chem. Soc.*, **87**, 2059 (1965); P. L. Orioli, M. DiVaira, and L. Sacconi, *Chem. Commun.* (London), 103 (1965); L. Sacconi, P. Nannelli, N. Nardi, and U. Campigli, *Inorg. Chem.*, **4**, 943 (1965).

(10) M. Ciampolini, N. Nardi, and G. P. Speroni, Abstracts of papers for the meeting on "Mechanistic and Structural Aspects in the Chemistry of Metal Complexes," Bressanone, Italy, July 1965.
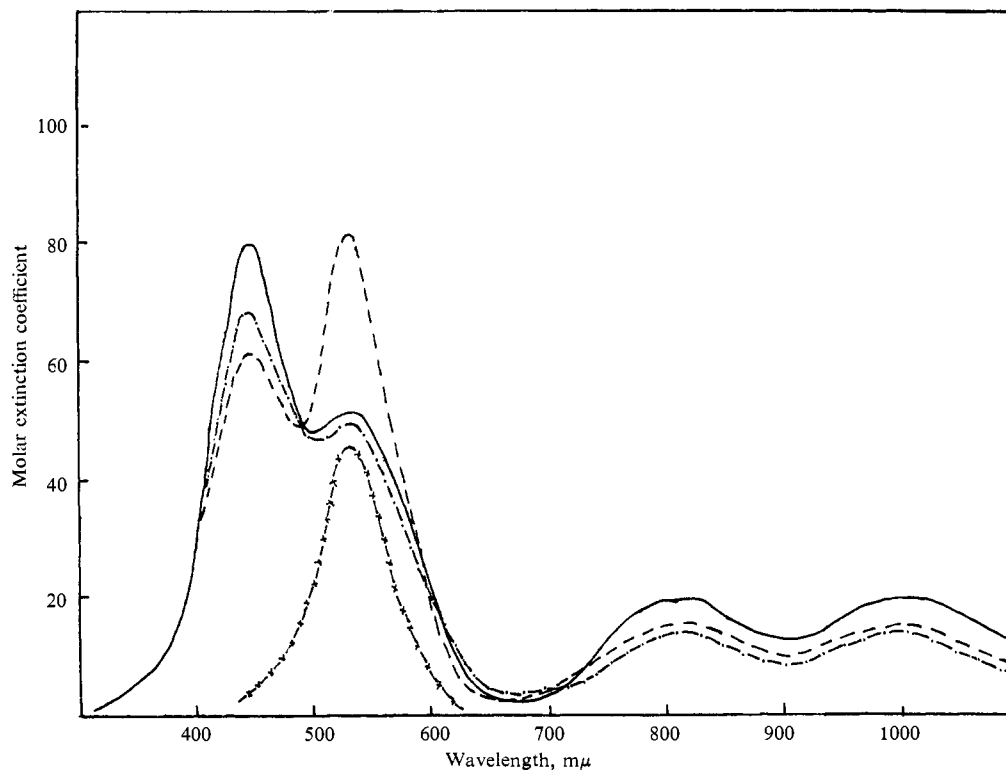(11) Details will be provided upon request.

Figure 1. Absorption spectra of Ni(Et₄dien)Cl₂ in different solvents: ———, acetone; —·—··—·, DMF; — — — —, CH₃CN; - × - × -, Nujol spectra (arbitrary units).

Conductance Measurements. Conductivities were determined on an Industrial Instruments Bridge Model RC16B2, using a cell calibrated with 0.010 M KCl solution.

Results

Ni(Et₄dien)X₂. The compound Ni(Et₄dien)Cl₂[13] is a red, diamagnetic solid. As shown in Figure 1, a solid sample exhibits an electronic absorption maximum at 18,800 cm⁻¹. The X-ray powder patterns of Ni(Et₄-dien)Cl₂ and [Pd(Et₄dien)Cl]Cl are identical, and it has been assumed that solid [Pd(Et₄dien)Cl]Cl contains square-planar Pd(Et₄dien)Cl⁺ groups.[14] The Ni(Et₄-dien)Br₂ and Ni(Et₄dien)I₂ complexes are also diamagnetic solids with X-ray powder patterns similar to that of Ni(Et₄dien)Cl₂ and low-energy electronic absorption bands at 18,300 and 17,550 cm⁻¹, respectively.

Table II. Conductance Data for the M(Et₄dien)Xₙ Complexes

Compound	Ethanol	DMF	Aceto-nitrile	Acetone	Nitro-meth-ane
Pd(Et₄dien)Cl₂	51	100	118	Insoluble	b
Ni(Et₄dien)Cl₂	50	57	50	4	40
Ni(Et₄dien)Br₂	48	94	85	22	b
Ni(Et₄dien)I₂	50	142	190	66	91
Co(Et₄dien)Cl₂	14	18	14	10	b
Rh(Et₄dien)Cl₃	4	8	b	b	b

Header: Λ (cm² mole⁻¹ ohm⁻¹)[a]

[a] All measurements were made at 28° on 0.0005 M solutions.
[b] Not measured.

(12) B. N. Figgis and J. Lewis, "Modern Coordination Chemistry," J. Lewis and L. Wilkins, Ed., Interscience Publishers, Inc., New York, N. Y., 1960.
(13) The Ni(Et₄dien)Cl₂ complex was first prepared by Dr. W. H. Baddley at Northwestern University. Dr. Baddley kindly supplied us with his sample of Ni(Et₄dien)Cl₂; the physical properties of his sample and our sample are the same.
(14) W. H. Baddley and F. Basolo, J. Am. Chem. Soc., 86, 2075 (1964).

Conductances and magnetic moments are listed in Tables II and III, respectively. In ethanol solution

Table III. Magnetic Data for Ni(Et₄dien)Cl₂ and Co(Et₄dien)Cl₂ in Different Solvents

Compound	Ethanol	Ace-tone	DMF	Nitro-toni-trile	Nitro-meth-ane	DMSO
Ni(Et₄dien)Cl₂	Diamagnetic	3.40	3.13	2.88	2.78	...[b]
Co(Et₄dien)Cl₂	4.72	4.70	4.78	...[b]	...[b]	4.74

Header: μₑff, BM[a]

[a] All measurements were made at 20–23°. [b] Not measured.

all three Ni(Et₄dien)X₂ complexes are diamagnetic and 1:1 electrolytes (molar conductances are compared with those of the [Pd(Et₄dien)Cl]Cl complex, which is known[14] to be a 1:1 electrolyte). In acetone solution the Ni(Et₄dien)Cl₂ complex is essentially a nonelectrolyte and paramagnetic (3.40 BM). In other polar organic solvents Ni(Et₄dien)Cl₂ exhibits lower magnetic moments and higher molar conductances than observed in acetone solution. In most solutions the Ni(Et₄-dien)Br₂ and Ni(Et₄dien)I₂ complexes have higher molar conductances than observed for Ni(Et₄dien)Cl₂. In DMF, Ni(Et₄dien)Br₂ and Ni(Et₄dien)I₂ are approximately 1:1 and 2:1 electrolytes, respectively.

The electronic absorption spectra of the three Ni(Et₄-dien)X₂ complexes are listed in Table IV. The spectrum of each complex in ethanol solution is the same as observed in the solid state. However, in each case spectra in several other polar organic solvents differ markedly from the spectrum observed in ethanol solution.

Co(Et₄dien)Cl₂. The red-purple solid Co(Et₄dien)Cl₂ is paramagnetic (4.71 BM) and exhibits electronic
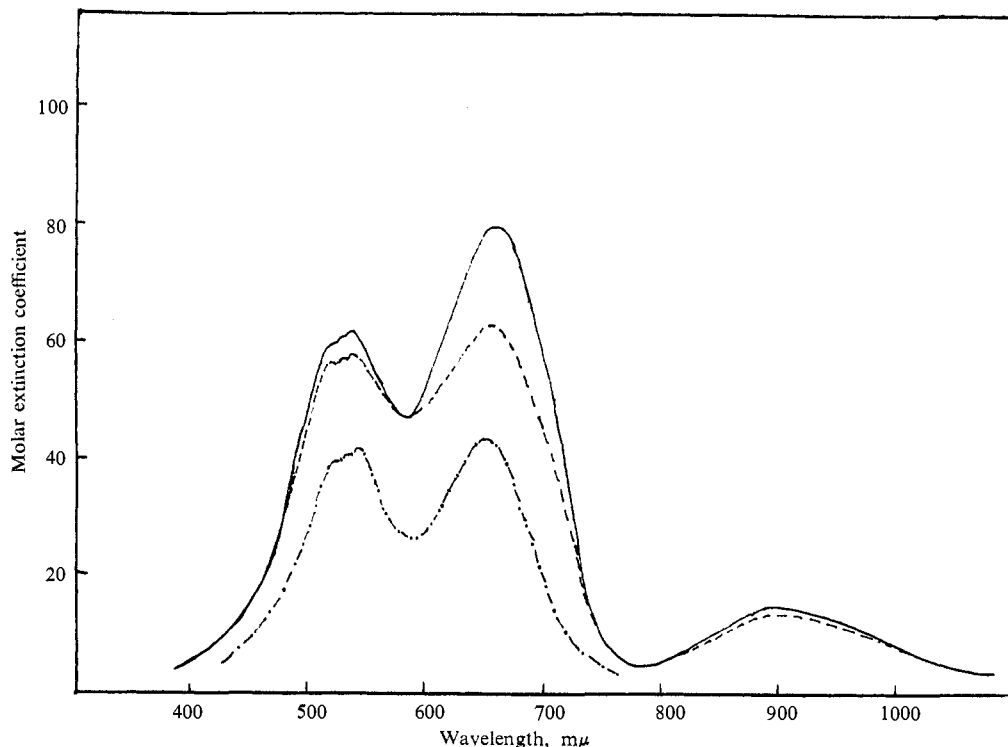
Figure 2. Absorption spectra of Co(Et₄dien)Cl₂ in different solvents: ————, acetone; — — — —, EtOH; —·—·—·—, Nujol spectra (arbitrary units).

absorption bands at 10,500, 15,200, and 19,300 cm⁻¹. Its X-ray powder pattern differs considerably from that of [Pd(Et₄dien)Cl]Cl. In solution, the Co(Et₄dien)Cl₂ complex is essentially a nonelectrolyte and has magnetic moments that are nearly equal to the solid-state value.

resemble closely the spectrum observed for a solid sample in Nujol.

Discussion

Ni(Et₄dien)X₂ Complexes. The magnetic, spectral, and X-ray powder data for the Ni(Et₄dien)X₂ complexes

Table IV. Electronic Spectral Data for Ni(Et₄dien)X₂ in Different Solvents[a]

Compound	Solvent	ν_{max}, cm⁻¹ (ϵ_{max})			
Ni(Et₄dien)Cl₂	Ethanol	. . .	. . .	18,800 (80)	. . .
	Acetonitrile	10,150 (15)	12,800 (15)	18,800 (80)	22,100 (60)
	Acetone	10,000 (20)	12,500 (20)	18,900 (55)	22,150 (80)
	DMF	10,100 (15)	12,700 (15)	18,850 (50)	22,500 (70)
Ni(Et₄dien)Br₂	Ethanol	. . .	. . .	18,300 (80)	. . .
	Acetone[b]	10,100 (15)	12,700 (15)	18,300 (185)	21,650 (90)
	Acetonitrile	10,000 (10)	12,900 (10)	18,200 (120)	21,750 (40)
	DMF	8,700 (8)	14,700 (8)	18,200 (14)	23,350 (24)
Ni(Et₄dien)I₂	Ethanol	. . .	. . .	17,500 (80)	. . .
	Acetone[b]	10,500 (8)	. . .	17,400 (150)	. . .
	DMF	9,200 (10)	15,300 (10)	. . .	26,000 (26)

[a] All solutions were 0.01 M in complex unless otherwise stated; spectral data were obtained at room temperature. [b] Solutions were 0.0025 M in complex.

Table V. Electronic Spectral Data for Co(Et₄dien)Cl₂ in Different Solvents

Solvent	ν_{max}, cm⁻¹ (ϵ_{max})		
Ethanol	11,200 (18)	15,400 (58)	19,050 (60)
Acetone	10,700 (20)	15,300 (80)	18,900 (57)
DMSO	11,250 (15)	15,200 (54)	19,000 (40)

The electronic absorption spectra of Co(Et₄dien)Cl₂ in Nujol, EtOH, and acetone are shown in Figure 2. Spectra in different organic solvents are set out in Table V. The spectra are essentially the same and

suggest that the square-planar, low-spin Ni(Et₄dien)X⁺ complex is present in the solid state and in ethanol solution. The electronic absorption spectrum of Ni(Et₄dien)Cl₂ in acetone solution shows four principal d–d bands. At least part of the intensity of the band at 18,900 cm⁻¹ is probably due to the square-planar Ni(Et₄dien)Cl⁺ complex in low concentration. Since the positions and intensities of the principal d–d bands are not compatible with octahedral[15] or tetrahedral[16]

(15) The three d–d bands at 10,000, 12,500, and 22,150 cm⁻¹ are too closely spaced to be due to Ni(II) in octahedral coordination. That is, the lowest energy band is too high energy and the highest energy band is too low energy for an octahedral Ni(II) complex of the type

coordination for Ni(II), the combined spectral, magnetic, and conductance data strongly support the assignment of a five-coordinate structure to the paramagnetic species in an acetone solution containing $Ni(Et_4dien)Cl_2$. The absorption spectra in other polar organic solvents show that both $Ni(Et_4dien)Cl^+$ and $Ni(Et_4dien)Cl_2$ are present, with $Ni(Et_4dien)Cl^+$ in higher mole ratios than in acetone solution. This is in agreement with the higher molar conductances and lower magnetic moments observed for these solutions. The behavior of $Ni(Et_4dien)Cl_2$ in these solutions can be summarized by the equilibrium

$$Ni(Et_4dien)Cl^+ + Cl^- \rightleftarrows Ni(Et_4dien)Cl_2 \qquad (1)$$
$$\text{four-coordinate} \qquad\qquad \text{five-coordinate}$$
$$\text{low-spin} \qquad\qquad\qquad \text{high-spin}$$
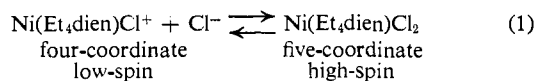
Consistent with eq 1, addition of Et_4NCl to DMF, DMSO, or acetonitrile solutions containing $Ni(Et_4dien)Cl_2$ markedly increases the intensities of the bands at 10,000, 12,500, and 22,000 cm^{-1}. At high Cl^- concentrations almost all of the complex is in the five-coordinate form. The detailed dependence of the coordination structure on Cl^- concentration was studied in DMSO solution. The initial state is a solution containing no Cl^-, and a 1:1 mole ratio of $Ni(ClO_4)_2$ and Et_4dien. The absorption spectrum of this solution, with bands at 9600 cm^{-1} (ϵ 5), 14,600 (5), and 25,600 (12), is typical of Ni(II) in octahedral coordination, and we assume that an octahedral complex of formula $Ni(Et_4dien)(DMSO)_3{}^{2+}$ is present. Conductance measurements support this formulation. On addition of 1 equiv of Et_4NCl, a new band appears at 18,800 cm^{-1} (ϵ 20), and the other band maxima are 9800 cm^{-1} (ϵ 2) and 23,800 cm^{-1} (ϵ 10). At this point the major species in solution is presumably the square-planar complex $Ni(Et_4dien)Cl^+$, with $Ni(Et_4dien)$-$(DMSO)_3{}^{2+}$ and $Ni(Et_4dien)Cl_2$ in lower concentrations. After 2 equiv of Cl^- has been added, all the bands can be assigned to two species, square-planar $Ni(Et_4dien)Cl^+$ and five-coordinate $Ni(Et_4dien)Cl_2$. Further addition of Cl^- to this solution simply intensifies the three "five-coordinate" bands at the expense of the 18,800-cm^{-1} band assigned to $Ni(Et_4dien)Cl^+$. This behavior is expected from the equilibrium described by eq 1.

We suggest that the $Ni(Et_4dien)Cl_2$ complex is observable in stable four- and five-coordinate modifications owing to the bulky nature of Et_4dien. Apparently the stability of a six-coordinate structure is decreased relative to structures of lower coordination number. In this connection it is of interest to note the effect of the anion size on the solution behavior of $Ni(Et_4dien)X_2$ complexes. In acetone the $Ni(Et_4dien)Br_2$ complex has a higher molar conductance than observed for

$Ni(Et_4dien)Cl_2$. This fact and the relatively high intensity of the 18,300-cm^{-1} band suggest that in acetone $Ni(Et_4dien)Br_2$ exists mainly in the low-spin, square-planar form $Ni(Et_4dien)Br^+$. In the relatively good coordinating solvent DMF, no five-coordinate form is observed. The electronic spectrum of $Ni(Et_4dien)Br_2$ in DMF indicates that the low-spin, square-planar complex $Ni(Et_4dien)Br^+$ and a six-coordinate species are present. The spectrum of the six-coordinate species is different from that of $Ni(Et_4$-$dien)(DMF)_3{}^{2+}$ ($Ni(Et_4dien)(ClO_4)_2$ in DMF solution), which shows bands at 9200 cm^{-1} (ϵ 10), 15,300 (10), and 26,000 cm^{-1} (26). Since the bands due to the six-coordinate complex are at slightly lower energy than those observed for $Ni(Et_4dien)(DMF)_3{}^{2+}$, we suggest the formula $Ni(Et_4dien)(DMF)_2Br^+$ for the six-coordinate complex. This formulation is in agreement with the molar conductance of $Ni(Et_4dien)Br_2$ in DMF.

In the case of the $Ni(Et_4dien)I_2$ complex, the conductance and spectral data in acetone solution suggest that $Ni(Et_4dien)I_2$ exists almost entirely in the low-spin, square-planar form $Ni(Et_4dien)I^+$. In the relatively good coordinating solvent DMF, only an octahedral Ni(II) spectrum is observed. The high molar conductance and the absence of a low-energy, charge-transfer band indicate that there is no coordinated I^-, and therefore the complex is logically formulated as $Ni(Et_4dien)(DMF)_3{}^{2+}$. Independent evidence for this formulation is the fact that in DMF solution the spectra of $Ni(Et_4dien)(ClO_4)_2$ and $Ni(Et_4dien)I_2$ are identical.

The different solution behavior of the three $Ni(Et_4$-$dien)X_2$ complexes may be attributed to the difference in anion size. For example, it is apparently very difficult to crowd two iodides into an inner-coordination sphere containing an Et_4dien ligand bound to Ni(II). To further investigate this point we have examined halide substitution reactions in the square-planar complexes $Ni(Et_4dien)Cl^+$, $Ni(Et_4dien)Br^+$, and $Ni(Et_4$-$dien)I^+$ in ethanol solution. In ethanol, the coordinated chloride in $Ni(Et_4dien)Cl^+$ is not replaced by Br^- or I^-, even in solutions in which the latter ions are in great excess (10:1 mole ratios). This is most remarkable behavior in a square-planar system, because bromo and iodo complexes are usually more stable than an analogous chloro complex. Recall that $Pd(Et_4dien)Cl^+$ reacts with Br^- and I^- to yield the bromo and iodo derivatives.[14] Both $Ni(Et_4dien)Br^+$ and $Ni(Et_4dien)I^+$ react very rapidly with Cl^- in ethanol to give $Ni(Et_4$-$dien)Cl^+$. These reactions appear to go to completion even under initial conditions of a 1:1 mole ratio of $Ni(Et_4dien)X^+$ and Cl^-. As a final observation, Br^- rapidly and completely replaces I^- in $Ni(Et_4dien)I^+$ in an ethanol solution initially containing a 1:1 mole ratio of the two reactants. From these data we infer the stability order $Ni(Et_4dien)Cl^+ > Ni(Et_4dien)Br^+ > Ni(Et_4dien)I^+$. Although electronic factors are expected to shift the halide stability order in the direction of M–Cl > M–I in going from Pd(II) to Ni(II), the obviously *enormous* preference of $Ni(Et_4dien)^{2+}$ for Cl^- suggests that a large contribution to the relative instabilities of the bromo and iodo complexes is due to crowding of the coordinated anion by the bulky Et_4dien group. This crowding is presumably not as effective in the square-planar $Pd(Et_4dien)X^-$ complexes, be-

[Ni(Et_4dien)(acetone)Cl_2]. For comparison, D. M. L. Goodgame and L. M. Venanzi [*J. Chem. Soc.*, 5909 (1963)] report d–d bands for $Ni(Me_4en)_2Cl_2$ in CH_3OH at 9390, 12,300, 15,750, and 25,850 cm^{-1}.

(16) The spectrum of $Ni(Et_4dien)Cl_2$ in acetone solution bears no resemblance whatsoever to a typical tetrahedral Ni(II) spectrum. [For examples of tetrahedral Ni(II) spectra, see C. P. Smith, C. H. Liu, and T. R. Griffiths, *J. Am. Chem. Soc.*, **86**, 4796 (1964).] The observed spectrum is not compatible with an interpretation involving Et_4dien behaving as a bidentate ligand in an acetone solution of $Ni(Et_4dien)Cl_2$. Further evidence inconsistent with a bidentate Et_4dien structure is the fact that the infrared spectra of $Ni(Et_4dien)Cl_2$ and $Co(Et_4dien)Cl_2$ are identical in acetone solution. Recently $Co(Me_4dien)Cl_2$ has been found to have a five-coordinate structure [M. DiVaira and P. L. Orioli, *Chem. Commun.* (London), 590 (1965)], and we have observed that $Co(Me_4dien)Cl_2$ and $Co(Et_4dien)Cl_2$ have very similar electronic spectra in solid samples. We show in this paper that the structure of Co-$(Et_4dien)Cl_2$ is the same in the solid and in acetone solution.

cause Pd(II) is effectively larger than Ni(II) as a central ion.

The Ni(Et$_4$dien)Cl$^+$ complex in ethanol also does not undergo substitution by pyridine to give the four-coordinate Ni(Et$_4$dien)(py)$^{2+}$ complex. Instead, in the presence of a great excess of pyridine, a light blue solution forms which shows electronic spectral bands at 10,500, 17,600, and 27,800 cm^{-1}. This type of spectrum is typical of Ni(II)N$_6$ octahedral complexes,[17,18] and thus we propose that the solution contains Ni(Et$_4$dien)(py)$_3{}^{2+}$. The complex may be isolated as a light blue crystalline compound [Ni(Et$_4$dien)(py)$_3$]Cl$_2$, which is unstable and on standing loses pyridine to yield the red, diamagnetic [Ni(Et$_4$dien)Cl]Cl complex.

The Ni(Et$_4$dien)(py)$_3{}^{2+}$ complex may also be obtained by cooling an ethanol solution containing pyridine and Ni(Et$_4$dien)Cl$^+$ in a 3:1 mole ratio to about $-40°$. Analogous behavior is observed on cooling an ethanol solution containing [Ni(Et$_4$dien)Cl]Cl and excess Et$_4$dien to $-70°$. At the low temperature the solution is green and shows an octahedral Ni(II) spectrum with bands at 9700, 15,900, and 26,200 cm^{-1}. Upon warming, the solution turns red again, affording square-planar Ni(Et$_4$dien)Cl$^+$. An ethanol solution without excess Et$_4$dien (or pyridine) does not change from its room-temperature red color on cooling to $-70°$, and only the band at 18,800 cm^{-1} is observed. Thus one reasonable possibility is that the green, low-temperature form is Ni(Et$_4$dien)$_2{}^{2+}$, although forms containing coordinated EtOH and two Et$_4$dien groups, in which one or both of the Et$_4$dien's is not fully tridentate, cannot be ruled out.

Co(Et$_4$dien)Cl$_2$. The electronic absorption spectra of a solid sample of the Co(Et$_4$dien)Cl$_2$ complex is inconsistent with either tetrahedral or octahedral coordination for Co(II).[17] Further, the marked difference in

(17) See C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, Chapter 10.

(18) The d–d spectrum of [Ni(dien)$_2$]Cl$_2$ consists of maxima at 11,500, 18,500, and 28,800 cm^{-1}.

the X-ray powder patterns of Co(Et$_4$dien)Cl$_2$ and [Pd-(Et$_4$dien)Cl]Cl rules against a square-planar structure. Thus we assign a five-coordinate structure to the high-spin Co(Et$_4$dien)Cl$_2$ complex in the solid. In support of the five-coordinate assignment, the Co(Et$_4$dien)Cl$_2$ complex is a nonelectrolyte in several solutions that exhibit spectral and magnetic properties not significantly different from a solid sample.

The Co(Et$_4$dien)Cl$_2$ complex, the five-coordinate modifications of Ni(Et$_4$dien)Cl$_2$ and Ni(Et$_4$dien)Br$_2$, and the aforementioned complexes[9,10] discovered in Sacconi's laboratory represent examples of high-spin Ni(II) and Co(II) in five-coordination. We are now investigating the coordination geometry of Co(Et$_4$dien)Cl$_2$ by X-ray diffraction methods.

Rh(Et$_4$dien)Cl$_3$. With Rh(III) as the central metal ion, an octahedral complex of formula Rh(Et$_4$dien)Cl$_3$ is obtained on treating RhCl$_3$ with Et$_4$dien. The d^6 Rh(III) central ion is very stable in octahedral coordination and, although the complex may be very strained, three chlorides are firmly attached to the bulky Rh-(Et$_4$dien)$^{3+}$ system. The Rh(Et$_4$dien)Cl$_3$ complex is a nonelectrolyte in ethanol and DMF. In DMF the lowest electronic spectral band occurs at 23,800 cm^{-1} (ϵ 440), which may be compared with the values 19,300 cm^{-1} (ϵ 102) for RhCl$_6{}^{3-}$ and 33,200 cm^{-1} (ϵ 210) for Rh(en)$_3{}^{3+}$.[19]

(19) C. K. Jørgensen, *Acta Chem. Scand.*, 10, 500 (1956).