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CONTRIBUTION FROM THE BROWN CHEMICAL LABORATORY,
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The Effects of the Nature of the Counteranion on the Structure of 1,1,7,7-Tetraethyldiethylenetriamine- and Diethylenetriaminecobalt(II), -nickel(II), and -copper(II) Pseudohalide Complexes¹

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The occurrence of stable, square-planar, N-bonded complexes of the type $[M(Et_4dien)NCX][B(C_6H_5)_4]$ ($M = Ni(II), Cu(II)$; $X = O, S, Se$; $Et_4dien = 1,1,7,7$ -tetraethyldiethylenetriamine) is contrasted with the $N \rightarrow X$ -bonded reorganizations which have been observed for $[Pd(Et_4dien)NCX][B(C_6H_5)_4]$ ($X = S, Se$) complexes in the solid state. The latter reestablishes a soft-soft interaction, whereas, in the former case, a preferential hard-hard interaction would be destroyed. The nickel(II) cyanate and thiocyanate complexes were found to be thermochromic. The corresponding Co(II) complexes could not be prepared; instead, five-coordinate complexes of the type $Co(Et_4dien)(NCX)_2$ ($X = O, S, Se$) are formed. The corresponding Ni(II) complexes, $Ni(Et_4dien)(NCX)_2$ ($X = O, S, Se$), exhibit a variety of geometries: the cyanate is five-coordinate, both in the solid state and in acetonitrile solution; the thiocyanate is dimeric in the solid state, with bridging thiocyanates creating an octahedral environment, but exists as an equilibrium mixture of four- and five-coordinate species in acetonitrile solution, and the selenocyanate is four-coordinate in the solid state and primarily so in acetonitrile solution. The diethylenetriamine complexes $[Cu(dien)NCS]NCS$, $[Cu(dien)NCO][B(C_6H_5)_4]$, and $[M(dien)_2](NCSe)_2$ ($M = Co, Ni$) were also prepared. The structural conclusions are based on the results of molar conductance and infrared and electronic spectral data.

Introduction

Among the several factors² which determine the bonding modes adopted by ambidentate ligands in coordination complexes, counterion control was undoubtedly the least anticipated. Control by both counteranions,³ e.g., $[Pd(Et_4dien)NCS]SCN$ vs. $[Pd(Et_4dien)SCN][B(C_6H_5)_4]$ ($Et_4dien = 1,1,7,7$ -tetraethyldiethylenetriamine), and counterations,⁴ e.g., $K_3[Co(CN)_5SCN]$ vs. $[(n-C_4H_9)_4N]_3[Co(CN)_5NCS]$, has been demonstrated. Likewise, $Pd(Et_4dien)SeCN^+$ isomerizes to the N-bonded isomer in solution but re-isomerizes to the Se-bonded isomer in the solid state following its isolation as the tetraphenylborate salt.³ The selenocyanate ion also displays⁵ a different bonding preference in the complexes $K_3[Co(CN)_5SeCN]$ and $[(n-C_4H_9)_4N]_3[Co(CN)_5NCSe]$. The counteranion control has been attributed³ to steric effects in the solid state since $[Pd(Et_4dien)NCO][B(C_6H_5)_4]$, with a smaller exo atom in the cation, does not isomerize,⁶ whereas the counteranion control has been attributed⁴ to preferential hard-hard and soft-soft interactions in the solid state. In addition to the effects of changing the ambidentate group, our exploration of the limitations of counterion control has involved a study of the effects of changing the metal coordination center. We now

wish to report the results of this study involving Et_4dien and diethylenetriamine (dien) pseudohalide complexes of cobalt(II), nickel(II), and copper(II).

Experimental Section

Preparation of Complexes.— $M(Et_4dien)Cl_2^7$ ($M = Co, Ni$), $Ni(dien)_2Cl_2^8$, $Cu(dien)Cl_2^9$ and $Co(Et_4dien)(NCS)_2^9$ were prepared according to literature methods.

$[M(Et_4dien)(NCO)_2]$ Complexes.—Sodium cyanate (1.3 g, 0.02 mol) and the appropriate anhydrous metal(II) halide (0.01 mol) were stirred in 100 ml of anhydrous methanol, whereupon 3.0 g (0.02 mol) of silver cyanate was added, and the stirring continued for an additional period. The precipitated silver halide was removed by filtration, and 6 ml (0.033 mol) of Et_4dien was added to the filtrate. After standing overnight, the solution was again filtered. Cooling the filtrate to -15° yielded the crystalline product, which was isolated by filtration, washed, and dried *in vacuo*. Details of preparation are as follows: for $M = Co(II)$, 1.3 g of $CoCl_2$, stirring periods of 5 and 10 min, violet crystals washed with ethanol and ether; for $M = Ni(II)$, 2.2 g of $NiBr_2$, stirring periods of 5 and 0.5 hr, green crystals washed with a little cold methanol, changing color to yellow on drying.

$[M(Et_4dien)(NCX)_2]$ ($X = S, Se$) Complexes.—Alcoholic solutions of the appropriate potassium or sodium pseudohalide and hydrated metal(II) nitrate were mixed and the precipitated potassium or sodium nitrate removed by filtration. After adding Et_4dien to the filtrate, the resulting solution was stirred, cooled, or reduced in volume to yield the crystalline product, which was isolated by filtration. Details of preparation are as follows: for $M = Ni(II)$ and $X = S$ (dimeric in solid state, *vide infra*), 2.0 g (0.02 mol) of $KNCS$ in 50 ml of ethanol (at boiling point prior to mixing), 2.9 g (0.01 mol) of $Ni(NO_3)_2 \cdot 6H_2O$ in 25 ml of ethanol, 2.2 g (0.01 mol) of Et_4dien , solution allowed to stand overnight, green crystals washed with ethanol and dried *in vacuo*; for $M = Cu(II)$ and $X = S$, 2.0 g (0.02 mol) of $KNCS$ in 50 ml of methanol, 2.4 g (0.01 mol) of $Cu(NO_3)_2 \cdot 3H_2O$ in 50 ml of methanol, 2.2 g (0.01 mol) of Et_4dien in 25 ml of methanol, solution evaporated to 75 ml under reduced pressure, blue crystals re-

(1) Presented at the Fifth Middle Atlantic Regional Meeting of the American Chemical Society, Newark, Del., April 1-3, 1970; see Abstracts, p 47; abstracted in part from the Ph.D. dissertation of T. P. O., University of Delaware, June 1969.

(2) See J. L. Burmeister, R. L. Hassel, and R. J. Phelan, *Chem. Commun.*, 679 (1970), for references.

(3) J. L. Burmeister, H. J. Gysling, and J. C. Lim, *J. Amer. Chem. Soc.*, **91**, 44 (1969).

(4) D. F. Gutterman and H. B. Gray, *ibid.*, **91**, 3105 (1969).

(5) D. F. Gutterman, J. B. Melpolder, H. B. Gray, and J. L. Burmeister, unpublished results.

(6) J. L. Burmeister and N. J. DeStefano, *Inorg. Chem.*, **8**, 1546 (1969).

(7) Z. Dori and H. B. Gray, *J. Amer. Chem. Soc.*, **88**, 1394 (1966).

(8) J. G. Breckenridge, *Can. J. Res., Sect. B*, **26**, 11 (1948).

(9) Z. Dori and H. B. Gray, *Inorg. Chem.*, **7**, 889 (1968).

TABLE I
ANALYTICAL, MELTING POINT, AND CONDUCTANCE DATA

M	X	Analyses, %								Mp, °C	Δ_m , ^b ohm ⁻¹ cm ² mol ⁻¹
		C		H		N		M (Se)			
		Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found		
M(Et ₄ dien)X ₂ Complexes											
Co	Cl	41.75	41.78	8.47	8.63	12.17	12.34			180	11
Co	NCO	46.92	46.81	8.16	8.01	19.54	19.64	16.45	16.01		16
Co	NCS	43.06	43.16	7.49	7.69	17.94	17.96	15.09	14.73	159	12
Co	NCS _e	34.72	35.23	6.04	6.01	14.46	13.95			162 dec	21
Ni	Cl	41.78	41.28	8.47	8.65	12.18	11.66			142	31
Ni	NCO	46.95	46.63	8.16	8.48	19.56	19.93	16.39	16.19	155	5.9
Ni	NCS	43.09	42.83	7.49	7.76	17.95	17.85	15.04	15.01	138	64
Ni	NCS _e	34.74	34.99	6.04	6.10			32.58 (Se)	32.62	123 dec	84
Cu	NCS	42.56	42.25	7.40	7.10	17.73	17.56	16.08	16.20	122	71
[M(Et ₄ dien)X][B(C ₆ H ₅) ₄] Complexes											
Ni	Cl	68.77	68.48	7.85	7.99	6.68	6.62	9.34	9.41	199	116
Ni	NCO	69.95	69.88	7.77	7.87	8.82	9.01	9.24	9.33	179	123
Ni ^a	NCO	68.39	68.16	8.00	8.07	8.39	8.47	8.80	8.90	190	
Ni	NCS	68.22	68.25	7.58	7.46	8.60	8.47	9.01	8.94	192	116
Ni	NCS _e	63.64	63.73	7.07	7.07	8.02	7.98	11.31 (Se)	11.40	175 dec	105
Cu	Cl	68.24	68.26	7.80	8.07	6.63	6.72	10.03	10.14	79	84
Cu	Br	63.77	63.72	7.28	7.16	6.20	6.21	9.37	9.27	76	101
Cu	I	59.64	59.40	6.81	6.89	5.80	5.90	8.76	9.05	67	124
Cu	NCO	69.42	69.44	7.72	7.77	8.75	8.63	9.93	10.00	96	107
Cu ^{a,c}	NCO ^a	64.35	64.02	6.67	6.37	10.05	10.19	11.35	11.57	112	89
Cu	NCS	67.72	67.80	7.53	7.53	8.57	8.57	9.68	9.65	97	122
Cu	NCS _e	63.20	63.14	7.01	6.80	7.96	7.71	9.03	8.81	105 dec	100
Cu(dien)X ₂ Complexes											
Cu	Cl	20.22	20.32	5.51	5.47	17.68	17.53			231	Insoluble
Cu	NCS	25.48	25.36	4.63	4.69	24.76	24.71	22.46	22.68	152	105
[M(dien) ₂]X ₂ Complexes											
Co	NCS _e	25.27	25.75	5.51	5.47	23.58	23.28	33.23 (Se)	31.72		
Ni	Cl	28.60	28.47	7.80	7.93	25.05	25.15			>300	
Ni	NCS _e	25.29	25.43	5.52	5.38	23.59	23.28	33.25 (Se)	32.79	235 dec	266

^a Monomethanolate. ^b Acetonitrile solution, unless indicated otherwise; 1:1 electrolytes give Δ_m values >100; 2:1, >250; J. L. Burmeister, S. D. Patterson, and E. A. Deardorff, *Inorg. Chim. Acta*, **3**, 105 (1969). ^c These entries are for the corresponding dien complexes.

crystallized from acetone to give a green complex which, on pumping under vacuum, reconverted to the blue product (the green complex, which was not analyzed, presumably contains acetone as a solvent of crystallization, since its ir spectrum contains a strong peak at 1720 cm⁻¹ which is absent in the spectrum of the blue complex); for M = Co(II) and X = Se, 5.1 g (0.04 mol) of NaNCSe in 100 ml of ethanol, 5.8 g (0.02 mol) of Co(NO₃)₂·6H₂O in 50 ml of ethanol, 4.4 ml of Et₄dien, solution cooled in ice bath, dark blue crystals recrystallized from 150 ml of hot acetone; for M = Ni(II) and X = Se, 1.3 g (0.01 mol) of NaNCSe in 10 ml of ethanol, 1.45 g (0.005 mol) of Ni(NO₃)₂·6H₂O in 10 ml of ethanol, both solutions cooled to -20° before mixing, filtrate passed into a solution of 1.1 ml (0.005 mol) of Et₄dien in 15 ml of ethanol, solution stirred overnight, orange crystals air dried.

[M(Et₄dien)X][B(C₆H₅)₄] Complexes.—An alcoholic solution of Et₄dien was added to an alcoholic solution of the appropriate metal(II) halide. The products precipitated immediately upon the addition of an alcoholic solution of sodium tetraphenylborate. Details of preparation are as follows: for M = Ni(II) and X⁻ = Cl⁻, 1.6 g (0.008 mol) of Et₄dien in 5 ml of ethanol, 1.5 g (0.0065 mol) of NiCl₂·6H₂O in 35 ml of ethanol at 60°, solution heated to boiling prior to the addition of 2.1 g (0.006 mol) of Na[B(C₆H₅)₄] in 25 ml of ethanol, red-violet crystals recrystallized twice by dissolving in acetone and precipitating with ethanol, dried *in vacuo*; for M = Cu(II) and X⁻ = Cl⁻, 2.2 g (0.01 mol) of Et₄dien in 10 ml of methanol, 1.7 g (0.01 mol) of CuCl₂·2H₂O in 25 ml of methanol, both solutions at boiling point prior to mixing, 3.4 g (0.01 mol) of Na[B(C₆H₅)₄] in 20 ml of methanol, lustrous violet crystals washed with 10 ml of methanol, dried *in vacuo*; for M = Cu(II) and X⁻ = Br⁻, 1.1 ml of Et₄dien (neat), 1.1 g (0.005 mol) of CuBr₂ in 20 ml of methanol, solution filtered into 15 ml of methanol containing 1.7 g (0.005 mol) of Na[B(C₆H₅)₄], product light sensitive; for M = Cu(II) and X⁻ = I⁻, 1.1 ml of Et₄dien dissolved in 9 ml of methanol, 1.2 g (0.005 mol) of Cu(NO₃)₂·3H₂O in 20 ml of methanol, 1.5 g (0.01 mol) of NaI in 25 ml of methanol added, resulting solution filtered into 10 ml of methanol containing 1.7 g (0.005 mol) of Na[B(C₆H₅)₄].

[M(Et₄dien)NCO][B(C₆H₅)₄] Complexes.—Sodium cyanate was added to a methanolic solution of the appropriate anhydrous metal(II) bromide and stirred for 5 min. Silver cyanate was added and the resulting mixture was stirred in the dark for 1 hr, whereupon the precipitated silver bromide was removed by filtration. To the filtrate were added Et₄dien and a methanolic solution of sodium tetraphenylborate. Details of preparation are as follows: for M = Ni(II), 0.7 g (0.01 mol) of NaNCO, 1.1 g (0.005 mol) of NiBr₂ in 50 ml of anhydrous methanol, 1.5 g (0.01 mol) of AgNCO, 3 ml (0.016 mol) of Et₄dien, 1.7 g (0.005 mol) of Na[B(C₆H₅)₄] in 25 ml of methanol, solution immediately filtered after addition of Na[B(C₆H₅)₄] through a fine sintered glass filter, orange crystals of monomethanolate precipitated in filtrate (the methanol can be removed by pumping under vacuum for 12 hr at 25°, whereupon the complex becomes red); for M = Cu(II); 1.3 g (0.02 mol) of NaNCO, 2.2 g (0.01 mol) of CuBr₂ in 200 ml of methanol, 3 g (0.02 mol) of AgNCO, 6 ml (0.033 mol) of Et₄dien, 3.5 g (0.01 mol) of Na[B(C₆H₅)₄] in 30 ml of methanol, the blue crystalline product, which formed immediately, was isolated by filtration and air dried.

[M(Et₄dien)NCX][B(C₆H₅)₄] (X = S, Se) Complexes.—Alcoholic solutions of the appropriate sodium pseudohalide and hydrated metal(II) salt were mixed and the precipitated sodium nitrate or chloride was removed by filtration. To the filtrate were added Et₄dien and an alcoholic solution of sodium tetraphenylborate. Details of preparation are as follows: for M = Ni(II) and X = S, boiling solution of 1.7 g (0.02 mol) of NaNCS in 50 ml of ethanol, 2.9 g (0.01 mol) of Ni(NO₃)₂·6H₂O in 25 ml of ethanol, 2.8 g (0.013 mol) of Et₄dien, resulting solution diluted to 150 ml and reheated prior to addition of 3.4 g (0.01 mol) of Na[B(C₆H₅)₄] in 25 ml of ethanol, solution heated to boiling and stirred for 5 min, filtered while hot, orange crystals obtained upon cooling, washed with ethanol and dried *in vacuo*; for M = Cu(II) and X = S, 1.7 g (0.02 mol) of NaNCS in 50 ml of methanol, 1.7 g (0.01 mol) of CuCl₂·2H₂O in 50 ml of methanol, 2.3 g (0.011 mol) of Et₄dien in 20 ml of methanol, solution cooled to -20° prior to addition of 3.4 g (0.01 mol) of Na[B(C₆H₅)₄] in 50 ml of methanol, green sticky precipitate formed which, on

standing, converted into blue crystals of the product, dried *in vacuo*; for M = Ni(II) and X = Se, 2.6 g (0.02 mol) of NaNCSe in 50 ml of ethanol, 2.9 g (0.01 mol) of Ni(NO₃)₂·6H₂O in 25 ml of ethanol, solutions cooled to -78° in a Dry Ice-acetone bath prior to mixing, 2.8 g (0.013 mol) of Et₄dien, solution diluted to 150 ml, heated, and filtered while hot into 3.4 g (0.01 mol) of Na[B(C₆H₅)₄] in 30 ml of ethanol, orange crystals formed upon cooling, dried *in vacuo*; for M = Cu(II) and X = Se, all solutions cooled to -78° prior to mixing, 3.4 g (0.02 mol) of CuCl₂·2H₂O in 40 ml of methanol, 4.3 ml of Et₄dien added *before* methanolic solution of NaNCSe (5.1 g (0.04 mol) in 30 ml), bright green precipitate (probably Cu(Et₄dien)(NCSe)₂) formed which was relatively stable in cooled solution, solution diluted to 400 ml with cooled methanol, then filtered into 6.8 g (0.02 mol) of Na[B(C₆H₅)₄] in 50 ml of methanol, new green precipitate formed was quickly removed by filtration, yielding a solution from which dark green crystals of the product separated, complex decomposed rapidly, losing elemental selenium.

[Cu(dien)NCO][B(C₆H₅)₄]·CH₃OH.—This preparation was carried out in a drybox and all glassware was dried at 120°. The methanol used contained less than 0.01% water.

Diethylenetriamine (1.03 g, 0.01 mol) was added to a solution of 2.23 g (0.01 mol) of anhydrous copper(II) bromide in 50 ml of methanol, yielding a blue precipitate. Silver cyanate (4.50 g, 0.03 mol) was added and the mixture was stirred for 20 min. The resulting blue solution was filtered to remove a yellow precipitate and the precipitate was washed with methanol. The washings were combined with the filtrate. A solution of 3.42 g (0.01 mol) of sodium tetraphenylborate in 25 ml of methanol was added and the solution was immediately filtered through a large surface area, fine sintered glass filter. The filtrate was allowed to stand for 0.5 hr, yielding blue crystals of the product, which were isolated by filtration, washed with methanol and methylene chloride, and dried on the filter.

Cu(dien)(NCS)₂.—A solution of 3.9 g (0.04 mol) of potassium thiocyanate in 50 ml of methanol was added to a solution of 4.8 g (0.02 mol) of copper(II) nitrate trihydrate in 50 ml of methanol. The resulting brown solution was filtered to remove a white precipitate and the precipitate was washed with 50 ml of methanol. The washings were combined with the filtrate and 2.0 g (0.02 mol) of dien in 25 ml of methanol was added. The resulting blue solution was filtered and the filtrate was allowed to stand overnight. Blue crystals were obtained by filtration, washed with ethanol, and dried *in vacuo*.

[Co(dien)₂](NCSe)₂.—The preparation was carried out in a glove bag with a nitrogen atmosphere. A solution of 2.56 g (0.02 mol) of sodium selenocyanate in 20 ml of absolute ethanol was combined with a solution of 2.91 g (0.01 mol) of cobalt(II) nitrate hexahydrate in 25 ml of ethanol. The resulting blue solution was filtered into a solution of 2.1 ml of dien in 20 ml of ethanol. The flask and filter were washed with 30 ml of ethanol. A pale orange product was isolated and dried *in vacuo*. The complex rapidly decomposed in the solid state, becoming brown. Decomposition upon dissolution precluded the determination of any solution physical data.

[Ni(dien)₂](NCSe)₂.—After dissolving 1.45 g (0.005 mol) of nickel(II) nitrate hexahydrate in 10 ml of absolute ethanol and cooling the solution in a Dry Ice-acetone bath, a second cooled solution of 1.30 g (0.01 mol) of sodium selenocyanate in 10 ml of ethanol was added. The sodium nitrate which precipitated was removed by filtration, the filtrate passing into a solution of 1.05 ml of dien in 10 ml of ethanol. A lavender product was isolated and washed with ethanol.

Analyses.—Carbon, hydrogen, and nitrogen analyses were performed by the Alfred Bernhardt Microanalytical Laboratory, Elbach über Engelskirchen, Germany, and MHW Laboratories, Garden City, Mich. Cobalt,¹⁰ nickel,¹¹ copper,¹² and selenium¹³ analyses were carried out according to methods given in the literature. The results of these analyses are shown in Table I, along with the melting points of the complexes.

Molar Conductances.—Measurements on 10⁻³ M solutions were carried out at 25°, using an Industrial Instruments, Inc., Model RC 16B2 conductivity bridge and a cell with platinized electrodes. The results are shown in Table I.

Infrared Spectra.—Survey spectra were measured using a

Perkin-Elmer 337 spectrophotometer in the range 4000–400 cm⁻¹, using either Nujol mulls between KBr plates or pressed KBr disks. A Perkin-Elmer 421 double-beam grating spectrophotometer was also used, both for recording survey spectra and, in a fourfold wave number scale expansion, for precise assignment of ν_{CN} bands. Solution spectra were measured in 1.01 × 10⁻² cm matched NaCl cavity cells using solutions of known concentration. The integrated absorption intensity of the ν_{CN} band was determined using Ramsay's method of direct integration.¹⁴ All samples for which

TABLE II
INFRARED DATA

M	X	ν _{CX} , ^a cm ⁻¹	δ _{NCX} , ^a cm ⁻¹	ν _{CN} , cm ⁻¹		M ⁻¹ cm ⁻²
				Solid ^a	Soln	
M(Et ₄ dien)(NCX) ₂ Complexes						
Co	O	1336	613	2244	2222 ^c	19 ^c
		1325		2217	2202 ^c	16 ^c
Co	S	820	480	2080	2080 ^d	13 ^d
				2065	2069 ^d	13 ^d
Co	Se	640	418	2080	2080 ^d	11 ^d
				2067	2071 ^d	
Ni	O	1320	615	2242	2225 ^c	13 ^c
			605	2223	2208 ^c	10 ^c
Ni	S	849	487	2142	2092 ^d	13 ^d
		783	475	2130		
			466 sh	2090		
			464	2045		
Ni	Se	667	416	2090	2093 ^d	9.5 ^d
				2105 sh		
Cu	S	862	475	2110	2100 ^d	12 ^d
				2061	2068 ^d	10 ^d
Cu ⁱ	S ⁱ	800	470	2102	2098 ^d	6.6 ^d
				2069	2062 ^d	8.4 ^d
[M(Et ₄ dien)NCX][B(C ₆ H ₅) ₄] Complexes						
Ni	O	1348	600	2255	2242 ^c	17 ^c
Ni ^e	O ^e	1350	608	2237		
Ni	S	819	470	2100	2105 ^d	13 ^d
Ni	Se	?	420	2094	2098 ^d	12 ^d
Cu	O	1345	602	2252	2226 ^c	14 ^c
				2225		
Cu ^{e,i}	O ^{e,i}	1320	601	2218	2215 ^c	18 ^c
Cu	S	810	470	2109	2095 ^d	15 ^d
Cu	Se	666	?	2115	2097 ^f	18 ^f
[M(dien) ₂](NCSe) ₂ Complexes						
Co				2070		
Ni				2070	2070 ^d	3.8 ^d
Ionic Pseudohalides						
Ionic cyanate		1300 ^g	636 ^g	2165 ^g	2158 ^{c,h}	8.4 ^{c,h}
		1205 ^g	626 ^g			
KNCS		749	486	2053	2061 ^f	4.4 ^f
			471			
KNCS ₂		558	424	2070	2069 ⁱ	3.1 ⁱ
			416			

^a Nujol mull. ^b Integrated absorption intensity, calculated per mole of NCX⁻. ^c Acetone solution. ^d Acetonitrile solution. ^e Monomethanolate. ^f N,N-Dimethylformamide solution. ^g As KNCO. ^h As [(C₆H₅)₄As]NCO·2H₂O. ⁱ 2-Butanone solution. ^j These entries are for the corresponding dien complexes.

integrated absorption intensities are reported were shown to obey Beer's law in the concentration range studied. The infrared data for the complexes are shown in Table II.

Proton Nuclear Magnetic Resonance Spectra.—Proton nmr spectra were measured with a Varian Model A-60-A nuclear magnetic resonance spectrometer. Acetone-d₆ and Matheson Coleman and Bell Spectroquality acetone (containing less than 0.05% water) were used as solvents.

Ultraviolet, Visible, and Near-Infrared Spectra.—Uv-visible spectra were measured with a Cary Model 14 double-beam prism spectrophotometer from 12,000 to 3000 Å. Matched 1.01-cm quartz cells were used for the solution spectra. Nujol mull spectra were measured using glass slides and filter paper impregnated with Nujol as a scattering agent both in the sample and reference beams. Quartz plates (Spectrosil B, proprietary material of Thermal American Fused Quartz Co., Montville, N. J.) were also used as support material for the Nujol mulls. Reflectance spectra were measured using a cell space total diffuse re-

(10) A. Vogel, "A Textbook of Quantitative Inorganic Analysis," 3rd ed. Longmans, Green and Co., London, 1961, pp 528–532.

(11) Reference 10, pp 271–274 or 526–528.

(12) Reference 10, pp 351–360 or 496–499.

(13) Reference 10, pp 508–509.

(14) D. A. Ramsay, *J. Amer. Chem. Soc.*, **74**, 72 (1952).

flectance accessory with the Cary 14, using MgO as a standard. The results are shown in Tables III and IV.

TABLE III
ACETONITRILE SOLUTION ELECTRONIC SPECTRAL DATA

Co(Et ₄ dien)X ₂ complexes				
X = Cl	X = -NCO	X = -NCS	X = -NCSe	
ν_{\max} , kK (ϵ_{\max})	ν_{\max} , kK (ϵ_{\max})	ν_{\max} , kK (ϵ_{\max})	ν_{\max} , kK (ϵ_{\max})	
11.0 (18)	12.2 (5.9)	13.3 (34)	13.5 (37)	
15.3 (83)	15.6 (89)	16.0 (133)	16.4 (121)	
18.3 (78)				
19.2 (78)	19.6 (88)	20.0 (104)	20.0 (93)	
20.2 (70)	20.9 (68)	21.1 (110)	21.3 (110)	
Ni(Et ₄ dien)X ₂ complexes				
X = Cl	X = -NCO	X = -NCS	X = -NCSe	
ν_{\max} , kK (ϵ_{\max})	ν_{\max} , kK (ϵ_{\max})	ν_{\max} , kK (ϵ_{\max})	ν_{\max} , kK (ϵ_{\max})	
10.2 (11)	11.0 (52)	11.4 (17)		
11.7 (11)	12.2 (48)	12.3 (17)		
13.1 (12)	14.1 (52)	15.4 (20)	15.6 vw	
18.9 (55)	18.2 (72)	20.4 (85)	20.3 (161)	
22.5 (51)	23.4 (188)	24.7 (73)		
[Ni(Et ₄ dien)(NCS) ₂] ₂ plus excess KNCS				
[Ni(Et ₄ dien)X][B(C ₆ H ₅) ₄]	X	[Cu(Et ₄ dien)X][B(C ₆ H ₅) ₄]	X	ν_{\max} , kK
Cl	18.7 (162)	Cl	15.6 (232)	7.7
			18.5 (140)	12.6
		Br	15.2 (226)	16.5
			17.5 sh (171)	26.3
		I	16.8 (340)	
-NCO	19.9 (272)	-NCO	15.8 (270)	
-NCS	20.2 (265)	-NCS	15.4 (270)	
-NCSe	20.4 (391)	-NCSe	15.9 (331)	
Cu(Et ₄ dien)(NCS) ₂ [Cu(dien)NCO][B(C ₆ H ₅) ₄]·CH ₃ OH Cu(dien)(NCS) ₂				
ν_{\max} , kK (ϵ_{\max})		ν_{\max} , kK (ϵ_{\max})		ν_{\max} , kK (ϵ_{\max})
15.3 (310)		15.9 (126)		15.8 (138)

TABLE IV
SOLID-STATE ELECTRONIC SPECTRAL DATA

Complex	ν_{\max} , kK
[Ni(Et ₄ dien)Cl]Cl ^a	18.9
[Ni(Et ₄ dien)Cl][B(C ₆ H ₅) ₄] ^a	18.9
[Ni(Et ₄ dien)(NCS) ₂] ₂ ^a	16.0, 25.6
[Ni(Et ₄ dien)NCS][B(C ₆ H ₅) ₄] ^a	20.2
[Ni(Et ₄ dien)(NCO) ₂] ^a	12.4, 13.3, 14.4, 20.0, 23.8
[Ni(Et ₄ dien)NCO][B(C ₆ H ₅) ₄] ^a	19.9
[Ni(Et ₄ dien)NCO][B(C ₆ H ₅) ₄]·CH ₃ OH ^a	Ca. 21.3 (broad)
[Ni(Et ₄ dien)NCSe]NCSe ^b	20.0
[Ni(Et ₄ dien)NCSe][B(C ₆ H ₅) ₄] ^b	20.0

^a Transmission spectrum of Nujol mull. ^b Reflectance spectrum.

Discussion

Pseudohalide Bonding Modes.—The behavior of the [Pd(Et₄dien)NCX][B(C₆H₅)₄] (X = S, Se) complexes⁸ mentioned earlier results from the interplay of a number of factors: a basic preference on the part of the soft palladium(II) for X bonding,^{15,16} as in Pd(XCN)₄²⁻; the steric hindrance of the ethyl groups of the Et₄dien, which causes an X→N-bonded isomerization to take place in solution,³ and the presumed interaction between the X atom and the tetraphenylborate ion, which leads to an N→X-bonded isomerization in the solid state.³ In the present case, the hard cobalt(II), nickel(II), and copper(II) all display¹⁶⁻¹⁷ a preference for N bonding in their simple cyanate, thiocyanate, and selenocyanate complexes. (A simple selenocyanate

complex of copper(II) has never been prepared due to a redox reaction between the two which yields copper(I) and selenocyanogen.) Part of the driving force behind any N→X-bonded solid-state isomerization is thereby removed in the complexes [M(Et₄dien)NCX][B(C₆H₅)₄] (M = Ni, Cu; X = S, Se). (The corresponding cobalt(II) complexes could not be prepared because of their tendency to form five-coordinate complexes, *vide infra*.) This is evidently sufficient to render them stable N-bonded species, both in solution and in the solid state, for isomerization would create a hard-soft interaction at the expense of one which is hard-hard. Evidence in support of this conclusion is presented in Tables II and III. N bonding is indicated^{6,18} by the increased (relative to the free ion values) ν_{CX} stretching frequencies and ν_{CN} integrated absorption intensities, the δ_{NCX} frequencies, which are only shifted slightly from the free ion values, and the higher energy ligand field bands (relative to the chloro complexes) which are exhibited by the pseudohalide complexes. Indeed, the same conclusion is appropriate for all of the coordinated pseudohalide groups in all of the complexes prepared in this study. Moreover, the order of ligand field strengths for the N-bonded pseudohalides (-NCO < -NCS < -NCSe) deduced from the electronic spectra (Table III) of the M(Et₄dien)(NCX)₂ and [M(Et₄dien)NCX][B(C₆H₅)₄] complexes parallels that observed earlier¹⁹ for Co(NH₃)₅NCX²⁺ complexes.

Geometry of the Complexes.—The results of an X-ray study²⁰ have shown that the complex Co(Et₄dien)Cl₂ is five-coordinate, with the chlorides occupying cis positions in the structure which is intermediate between a trigonal bipyramid and a square pyramid. Based on their similar conductance values (Table I), which indicate very little dissociation in acetonitrile solution, their split ν_{CN} bands (Table II), both in the solid state and in solution, and their similar electronic spectra (Table III—the solid-state spectra, not shown, exhibit the same peaks), we would conclude that the cyanate and selenocyanate complexes, like the thiocyanate complex,⁹ also are five-coordinate and probably exhibit structures which are quite similar to that of the chloro complex. The driving force to attain five-coordination is quite strong, as evidenced by the failure to isolate tetraphenylborate salts of four-coordinate species, when only 1 equiv of pseudohalide was utilized. The same five-coordinate species were obtained.

In the case of nickel(II), however, four-coordinate geometry in the form of a square plane is favored, as has been shown⁷ to exist for [Ni(Et₄dien)Cl]Cl, [Ni(Et₄dien)Br]Br, and [Ni(Et₄dien)I]I, in the solid state and in ethanol solution. However, in various other solvents, *e.g.*, dimethylformamide, acetonitrile, or acetone, the four-coordinate Ni(Et₄dien)Cl⁺ species is involved in an equilibrium with the five-coordinate species Ni(Et₄dien)Cl₂, the amount of five-coordinate species present at equilibrium increasing as the polarity of the solvent is decreased (reaching a maximum in acetone). The bromo complex, on the other hand, exists mainly in the square-planar form in acetone, and the iodo complex, which would involve the greatest steric interaction of all, tends to dissociate completely in acetone to the four-coordinate species.⁷

(15) A. Sabatini and I. Bertini, *Inorg. Chem.*, **4**, 959 (1965).

(16) I. L. Burmeister and L. E. Williams, *ibid.*, **5**, 1113 (1966).

(17) D. Forster and D. M. L. Goodgame, *ibid.*, **4**, 715 (1965).

(18) J. L. Burmeister, *Coord. Chem. Rev.*, **1**, 205 (1966); **3**, 225 (1968).

(19) J. L. Burmeister and N. J. DeStefano, *Inorg. Chem.*, **9**, 972 (1970).

(20) Z. Dori, R. Eisenberg, and H. B. Gray, *ibid.*, **6**, 483 (1967).

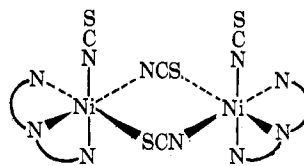
The $\text{Ni}(\text{Et}_4\text{dien})(\text{NCX})_2$ complexes exhibit different behavior in acetonitrile solution (Table I). The cyanate appears to be completely five-coordinated, whereas the thiocyanate, which apparently is dimeric in the solid state, as will be discussed later, and the selenocyanate complexes are involved in equilibria between four- and five-coordinate species, the selenocyanate dissociating to the greater extent. This reflects both trends in decreasing bond strength and increasing solvation of the free pseudohalides; *i.e.*, whereas KCl and KNCO are virtually insoluble in acetonitrile, KNCS and KNCS₂ are fairly soluble.

Before turning to the electronic spectra of the $\text{Ni}(\text{Et}_4\text{dien})(\text{NCX})_2$ complexes, it would appear to be advantageous to introduce the $[\text{Ni}(\text{Et}_4\text{dien})\text{NCX}][\text{B}(\text{C}_6\text{H}_5)_4]$ complexes, which are undoubtedly square planar, into the discussion. Their molar conductances (Table I) are indicative of 1:1 electrolytes, their electronic spectra (Tables III and IV), both in solution and in the solid state, are characteristic³ of square-planar complexes, and their proton nmr spectra exhibit very sharp peaks which would have been considerably broadened if any paramagnetic species had been present. The cyanate complex also forms a stable monomethanolate with the methanol molecule probably weakly hydrogen bonded to the oxygen of the cyanate, since it is lost upon vacuum treatment. The enhancement of the ligand field strength upon bridging (compare the electronic spectra (Table IV) of the monomethanolate and the methanol-free complex) has been previously observed.¹⁸

An interesting feature of the $[\text{Ni}(\text{Et}_4\text{dien})\text{NCX}][\text{B}(\text{C}_6\text{H}_5)_4]$ ($\text{X} = \text{O}, \text{S}$) complexes is that they are thermochromic, reversibly changing color to violet upon heating to 100–160°, and convert back to their original color on cooling. Nujol mull spectra, measured at 100 and 160° using a specially made, heated cell, gave no evidence of isomerization to the X-bonded modes. The subject of reversible and irreversible thermochromism of coordination compounds, *e.g.*, $\text{Ni}(\text{N,N}'\text{-diethylethylenediamine})_2(\text{ONO})_2$, has recently been reviewed.²¹ Sone and Utsuno suggested that the phenomenon may be due to a decrease in the ligand field upon heating. It may also result from the populating of vibrational modes which couple to the electronic modes, thereby enhancing the oscillator strength.

The infrared and electronic spectral data (Tables II–IV) support the conclusion that the $\text{Ni}(\text{Et}_4\text{dien})(\text{NCO})_2$ complex is five-coordinate with *cis* cyanate groups, both in solution and in the solid state; *i.e.*, the ν_{CN} doublet and the five-band pattern in the electronic spectrum are independent of state. The infrared spectra of the $\text{Ni}(\text{Et}_4\text{dien})(\text{NCS})_2$ complex are unique, both with regard to the degree of splitting and the high ν_{CN} frequencies observed in the Nujol mull spectrum and, quite unlike the other complexes, the marked spectral changes which occur upon dissolution. The high pair of ν_{CN} frequencies indicate¹⁸ the presence of a double thiocyanate bridge and the splitting of the lower frequency ν_{CN} band indicates the presence of *cis*-terminal isothiocyanates. The frequencies and splittings observed for the ν_{CS} and δ_{NCS} bands also serve to

support the following structure which is postulated to exist in the solid state



The bridging ν_{CN} bands disappear entirely upon dissolution in acetonitrile, only N-bonded groups remaining.

The $[\text{Ni}(\text{Et}_4\text{dien})(\text{NCS})_2]_2$ complex also exhibits different visible spectra in the solid state and in solution. The solid-state spectrum is similar to that exhibited by octahedral species,²² in accord with the structure postulated on the basis of its infrared spectrum. For example, Goodgame and Venanzi²³ reported d-d bands for $\text{Ni}[(\text{CH}_3)_2\text{N}(\text{CH}_2)_2\text{N}(\text{CH}_3)_2]_2\text{Cl}_2$ in methanol at 9.4, 12.3, 15.8, and 25.9 kK. The first two bands are too weak and broad to be assigned in the Nujol mull spectrum of the $[\text{Ni}(\text{Et}_4\text{dien})(\text{NCS})_2]_2$ complex.

It should be noted that the complex could be optically active, depending on how the three nitrogens of the Et_4dien are coordinated. In solution, the $[\text{Ni}(\text{Et}_4\text{dien})(\text{NCS})_2]_2$ complex is postulated as being a mixture of four- and five-coordinated species on the basis of its molar conductivity and on the basis of a similarity between its electronic spectrum and that of the $[\text{Ni}(\text{Et}_4\text{dien})\text{Cl}]\text{Cl}$ species in solution. (Note the intensity of the band at 20.4 kK which is indicative of some square-planar species and the similarity of the rest of the spectrum to that of the five-coordinate $\text{Ni}(\text{Et}_4\text{dien})(\text{NCO})_2$ complex in solution.)

When the solution of $[\text{Ni}(\text{Et}_4\text{dien})(\text{NCS})_2]_2$ is saturated with KNCS, the spectrum changes drastically to one which is not only quite similar to the solid-state spectrum of $[\text{Ni}(\text{Et}_4\text{dien})(\text{NCS})_2]_2$ but is also indicative of octahedral $\text{Ni}(\text{II})$. The proposed formula for the predominant species in solution with excess KNCS is therefore $\text{Ni}(\text{Et}_4\text{dien})(\text{NCS})_3^-$.

The existence of the octahedral bridged structure in solution can be ruled out on the basis of the absence of the high-frequency bridging ν_{CN} bands. Furthermore, Dori and Gray⁷ have reported that $\text{Ni}(\text{Et}_4\text{dien})(\text{DMSO})_3^{2+}$ and $\text{Ni}(\text{Et}_4\text{dien})(\text{DMF})_3^{2+}$ exhibit bands at 14.6, 25.6 and 15.3, 26.0 kK, respectively.

In the case of the selenocyanate complex, a comparison of the solution and solid-state electronic spectral data indicates, as was inferred from the molar conductance data, that more of the square-planar four-coordinate form is present in solution than is the case with any of the other complexes of this type prepared in this study. The square-planar band at 20.3 kK completely dominates the spectrum and is fully half as intense as the corresponding band in the spectrum of the $[\text{Ni}(\text{Et}_4\text{dien})\text{NCSe}][\text{B}(\text{C}_6\text{H}_5)_4]$ complex, whereas the analogous bands of the other complexes are generally only one-fourth to one-third as intense as those of the corresponding tetraphenylborate salts.

Attempts to prepare the analogous cobalt(II) and nickel(II) dien-NCS₂ complexes resulted in the formation of the octahedral complexes $[\text{M}(\text{dien})_2](\text{NCS})_2$,

(21) K. Sone and S. Utsuno, *Kagaku No Ryoiki*, **22**, 222 (1968); *Chem. Abstr.*, **69**, 101128 (1968).

(22) K. Nakamoto and P. J. McCarthy, "Spectroscopy and Structure of Metal Chelate Compounds," Wiley, New York, N. Y., 1968, p 148.

(23) D. M. L. Goodgame and L. M. Venanzi, *J. Chem. Soc.*, 5909 (1963).

wherein the selenocyanates are noncoordinated, emphasizing the effects of the steric hindrance due to the ethyl groups of the Et₄dien in determining the overall geometry of the complexes.

As can be seen from Table I, all of the Cu^{II}-Et₄dien and -dien complexes generally function as 1:1 electrolytes in acetonitrile. The [Cu(dien)NCO][B(C₆H₅)₄]·CH₃OH complex retains the methanol molecule even on pumping under vacuum for several days, in contrast to [Ni(Et₄dien)NCO][B(C₆H₅)₄]·CH₃OH, indicating that the methanol is probably coordinated to the copper(II). The ν_{CN} doublet in the solid-state infrared spectrum (Table II) of [Cu(Et₄dien)NCO][B(C₆H₅)₄] must be due to different crystal environments, since the extra band does not appear in the solution spectrum. Heating the solid compound at

40° for 2 weeks did not change the spectrum, indicating that linkage isomerism is most likely not involved. The visible spectra of these complexes (Table III) are typical of copper(II) complexes, consisting of broad bands which are, in some cases, resolved into a doublet.

Other complexes whose preparations were attempted included [Cu(dien)NCO]NCO, [Cu(dien)Cl][B(C₆H₅)₄], [Cu(dien)NCS][B(C₆H₅)₄], and [Cu(Et₄dien)NCO]NCO. In all cases a product was isolated and the infrared spectrum exhibited the appropriate absorption bands, but the analyses were unsatisfactory.

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The Crystal and Molecular Structure of 4-Methylpyridinium Triphenylphosphine Tribromozincate

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The structure of 4-methylpyridinium triphenylphosphine tribromozincate, [4-CH₃C₅H₄NH][ZnBr₃((C₆H₅)₃P)], has been determined from three-dimensional X-ray data collected by counter methods. The structure has been refined to a final unweighted *R* factor of 0.063 and a weighted *R* factor of 0.074 for 1533 independent nonzero reflections. The compound crystallizes in the space group *C*_{2h}⁵-*P*2₁/*c* of the monoclinic system containing four molecules per unit cell of dimensions *a* = 10.021 (12), *b* = 9.827 (15), *c* = 26.674 (40) Å, and β = 101.30 (7)°. The measured and calculated densities are 1.706 ± 0.015 and 1.700 g/cm³, respectively. The coordination geometry about the zinc atom is a distorted tetrahedron with one bromine atom strongly hydrogen bonded to the N-H proton of the 4-methylpyridinium cation, resulting in significant deviation from the expected *C*_{3v} symmetry. Phenyl groups of the triphenylphosphine molecule were refined as rigid groups with angles of 120° and carbon-carbon distances of 1.392 Å. Coordination geometry about the phosphorus atom is that of a slightly elongated tetrahedron. The distortion of the 4-methylpyridinium cation due to the hydrogen-bonding interaction with the bromine atom appears to be less than can be determined from the data.

With the intention of studying the magnetic properties of transition metal ions with fourfold coordination and *C*_{3v} symmetry, we have determined the crystal and molecular structure of 4-methylpyridinium triphenylphosphine tribromozincate, which could serve as a diamagnetic host lattice for other divalent paramagnetic ions. In this connection, the effect of lattice-anion interactions as well as the details of the anion geometry were of interest. In addition, we note that there is little structural data on four-coordination complexes of zinc(II).¹⁻⁴

Experimental Section

4-Methylpyridinium bromide was prepared by bubbling HBr through a solution of previously distilled 4-methylpyridine in diethyl ether. The white, hygroscopic product which immediately formed was filtered and washed under N₂ with dry ether.

[4-CH₃C₅H₄NH][ZnBr₃(C₆H₅)₃P] was prepared by combining

- (1) R. S. Sager and W. H. Watson, *Inorg. Chem.*, **7**, 1358 (1968).
- (2) C. W. Riemann, S. Block, and A. Perloff, *ibid.*, **5**, 1185 (1966).
- (3) T. Ikeda and H. Hagihara, *Acta Crystallogr.*, **21**, 611 (1966).
- (4) (a) B. Morosin and E. C. Lingafelter, *ibid.*, **12**, 611 (1959); (b) N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 3997 (1959); (c) P. Pauling, *Inorg. Chem.*, **5**, 1498 (1966).

ethanol solutions, each containing 0.01 mol of triphenylphosphine, 4-methylpyridinium bromide, and anhydrous zinc bromide. The resulting solution was boiled for about 5 min to ensure complete reaction and was then filtered. Upon cooling, crystals of the desired complex precipitated in good yield. These were washed with ethanol and ether and dried *in vacuo*. *Anal.* Calcd for C₂₄H₂₅Br₃NPZn: C, 43.58; H, 3.50; Br, 36.24; Zn, 9.88. Found: C, 43.85; H, 3.49; Br, 36.29; Zn, 9.87. Well-formed crystals were grown from ethanol-acetonitrile mixtures by slow evaporation under vacuum. The compound exhibited three crystal habits depending on the composition of the solution from which crystals were grown. X-Ray investigation showed all forms to be crystallographically equivalent.

Collection and Reduction of Intensity Data

Optical investigation immediately showed the crystals to be biaxial. Precession photographs of the *hk*0, *hk*1, *0kl*, and *1kl* reciprocal lattice nets using Mo Kα radiation (λ 0.71069 Å) indicated a monoclinic space group. The systematic absences, *l* = 2*n* for *h*0*l* and *k* = 2*n* for 0*k*0 uniquely determined the space group to be *C*_{2h}⁵-*P*2₁/*c*.⁵

For collection of intensity data, a small crystal approximating a hexagonal cylinder of dimensions ~0.3

(5) "International Tables for X-Ray Crystallography," Vol. I, Kynoch Press, Birmingham, England, 1962, p. 99.