mula 4 is symmetrical in c_1 and c_2. The parameter value closest to the experimental k_{13} value has been chosen for c_1. The agreement is rather good for the three $I(ClO_4)$ series. From the relations 5 it is seen that $k_{34} = {}^1/_4 a_1/c_2$. k_{34} is the only isomerization rate constant that can be calculated directly and in Table II an entry is made of the quotient $a_1/c_2 = 4k_{34}$. The change in k_{34} on varying the ionic strength reflects the uncertainty in c_2. As the sum of the rate constants k_{34} and k_{43} at 20° lies[6] between 1 and 10, the steady-state treatment outlined above is not invalidated by the absolute values obtained for k_{34}.

Alternate Mechanism.—The mathematical formulation of eq 4 is not altered when it is assumed that the rate-determining step is a dissociative reaction of the conjugate base formed by abstracting an ammine proton from the *trans*-$Co(NH_3)_4(OH)(H_2O)^{2+}$ ion.

$$\begin{array}{l} Co(NH_3)_4(OH)(H_2O)^{2+} + OH^- \underset{K_c}{\overset{}{\rightleftarrows}} \\ \qquad\qquad Co(NH_3)_3(NH_2)(OH)(H_2O)^+ + H_2O \quad (6) \\ \qquad\qquad\qquad\qquad \downarrow k_c \\ \qquad\qquad\qquad\qquad \text{tetramer} \end{array}$$

When the proper substitutions are made, the quotient a_1/c_2 still equals $4k_{34}$ and $c_1 = K_{13}$. Finally it must be noted that a direct check on the reactivity of the trans complexes is prohibited by the fact that no trans complex has as yet been isolated.

Conclusion

The most striking result of the present study is the fact that the polymerization reaction of the tetraammine complex is essentially of first order in the concentration of the monomer. In the mechanisms worked out in the preceding section, the rate-determining step must consequently proceed by a dissociative reaction;[12] this can be the splitting off of one ligand from the *trans*-$Co(NH_3)_4(OH)_2{}^+$ ion or from the N-conjugated base of the *trans*-$Co(NH_3)_4(OH)(H_2O)^{2+}$ ion to give a rapidly reacting intermediate. At present nothing can be said about the nature of the intermediate. The expected low concentration of the N-conjugated base probably makes this ion an unlikely reactive species, although this amido complex may have an unusually high reactivity analogous to the amido complex of the SN1cb mechanism for base hydrolysis.[13] The reactivity of the *trans*-dihydroxo ion may be explained from the fact that the hydroxyl ion as a ligand exerts a large cis labilization effect.[14,15] Thus cis labilizations could effect a loosening of the Co^{III}–NH_3 bonds in the CoN_4 plane of the *trans*-$Co(NH_3)_4(OH)_2{}^+$ ion and result in the splitting off of an ammine group.

Acknowledgment.—The authors wish to thank Professor P. Ros for writing the steepest descent program and Professor J. M. Los for computer facilities. They also acknowledge the construction of the pH-Stat by Mr. J. Brederveld and of the reaction cell by Mr. J. Ph. Musch and their staff.

[12] C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, New York, N. Y., 1966, p 7.

[13] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1961, p 177.

[14] M. L. Tobe, *Sci. Progr.* (*London*), **48**, 484 (1960).

[15] Reference 13, pp 170–177.

Notes

CONTRIBUTION FROM LABORATORIO CNR AND ISTITUTO DI CHIMICA GENERALE E INORGANICA, UNIVERSITÀ DI FIRENZE, FLORENCE, ITALY, AND ISTITUTO CHIMICO POLICATTEDRA, UNIVERSITÀ DI CAGLIARI, CAGLIARI, ITALY

Polarized Single-Crystal Spectrum of a High-Spin Trigonal-Bipyramidal NiN_5 Chromophore

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The high-spin pentacoordinate nickel(II) complexes with the quadridentate ligand Me_6tren (tris(2-dimethylaminoethyl)amine) having general formula $[Ni(Me_6tren)X]X$ (X = Cl, Br, I)[2] are known to be trigonal bipyramidal with a C_{3v} symmetry.[3] Despite their high symmetry, the halo complexes are not suitable for anisotropic measurements because they crystallize in the cubic system.[3]

We looked for Me_6tren derivatives which crystallize in a noncubic system. The thiocyanate derivative has been found to be crystallographically anisotropic, and its electronic spectrum is quite similar to those of the halo analogs. An X-ray structure determination has been undertaken in order to determine the exact geometry of the chromophore and the molecular orientation in the crystal. Such information has been used to discuss the single-crystal polarized spectra.

The aim of this research is (I) the circumstantiated assignment of the electronic transitions of a trigonal-bipyramidal high-spin nickel chromophore and (II) the study of the spectral and magnetic properties of a ^3E ground state which is expected to experience a zero-field splitting.

Experimental Section

Preparation and Characterization of the $[Ni(NCS)Me_6tren](SCN)\cdot H_2O$ Complex.—The complex was prepared by the general method already reported.[2] *Anal.* Calcd for $C_{14}H_{32}N_6ONiS_2$: N, 19.85; C, 39.72; H, 7.62. Found: N, 20.16; C, 40.00; H, 7.76. The compound is green and paramagnetic

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[2] M. Ciampolini and N. Nardi, *Inorg. Chem.*, **5**, 41 (1966).

[3] M. Di Vaira and P. L. Orioli, *ibid.*, **6**, 490 (1967).

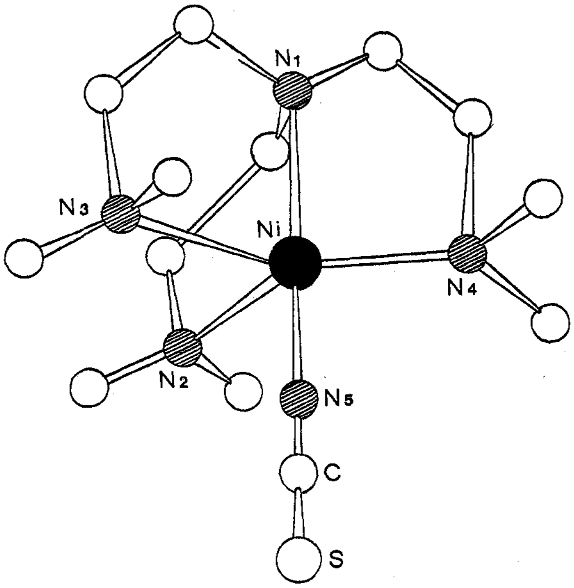

Figure 1.—A perspective view of the configuration of the complex cation $[Ni(NCS)(Me_6tren)]^+$.

with a magnetic moment of 3.3 BM at room temperature. The infrared spectrum shows the O–H stretching vibrations characteristic of non-hydrogen-bonded water molecules and two C–N stretching bands at 2050 and 2085 cm^{-1} characteristic of one bound and one free NCS ion, respectively.[4] A band at 760 cm^{-1}, assigned to the C–S stretching, is diagnostic of the Ni–NCS bond.[4] The compound behaves as a 1:1 electrolyte in nitroethane (Λ_M for a 10^{-3} solution is 81 Ω^{-1} M^{-1} cm^2; for reference Λ_M of tetrabutylammonium bromide is 80 Ω^{-1} M^{-1} cm^2). The solution spectrum has the same features as the solid spectrum with bands at 7.7 (ϵ 35.5), 11.3 (24.4), 12.5 (27.6), 16.2 (34.4), and 24.6 (185) kK. These spectral data correlate quite closely with those of the halo derivatives.[2]

X-Ray Analysis.—The $[Ni(Me_6tren)NCS]NCS \cdot H_2O$ crystals, grown as green rhombic plates from 1-butanol, are orthorhombic, space group *Pbca*. The crystal data are a = 20.408 (4), b = 13.759 (2), c = 15.002 (2) Å, V = 4212.46 Å^3, Z = 8. Intensity data were obtained by photographic methods, using the Weissenberg equiinclination technique. The reciprocal lattice levels *hk*0–*hk*12 were collected on a Nonius integrating camera with Ni-filtered Cu Kα radiation, and the intensities of 1112 reflections were measured with a microdensitometer.

The structure determination was carried out using the direct methods which gave the positions of the heavy atoms (the nickel and the two sulfur atoms). Three subsequent Fourier syntheses showed the positions of all nonhydrogen atoms of the structure. The refinement is still in progress using the least-squares technique. At the present stage of refinement the R factor is 0.090.

Description of the Structure

The structure consists of discrete $Ni(Me_6tren)NCS^+$ and NCS^- ions and the interposed H_2O molecules. The nickel atom is pentacoordinate, linked to the four nitrogen atoms of the Me_6tren ligand and to the nitrogen atom of the NCS group. The coordination polyhedron geometry can be described as a distorted trigonal bipyramid, having the central nitrogen of the Me_6tren ligand and the nitrogen of the isothiocyanate in the apical positions and the other three nitrogens of the Me_6tren in the equatorial positions (Figure 1). The water molecule is not bound to the nickel atom, the shortest Ni · · · O distance being 5.02 Å.

The positional parameters of the atoms of the coordination polyhedron are reported in Table I and the corresponding distances and angles in Table II.

TABLE I

POSITIONAL PARAMETERS ($\times 10^4$) WITH THEIR ESTIMATED STANDARD DEVIATIONS FOR THE ATOMS OF THE COORDINATION POLYHEDRON

Atom	x/a	y/b	z/c
Ni	1243 (2)	3700 (2)	2528 (3)
N(1)	1239 (12)	5029 (15)	1920 (15)
N(2)	422 (9)	3381 (18)	1696 (15)
N(3)	2122 (9)	3485 (15)	1858 (15)
N(4)	1223 (12)	4524 (15)	3700 (15)
N(5)	1240 (12)	2431 (15)	3138 (16)

TABLE II

DISTANCES AND ANGLES IN THE COORDINATION GROUP WITH THEIR ESTIMATED STANDARD DEVIATIONS

	Distance, Å	
Ni–N(1)	2.04	0.02
Ni–N(2)	2.13	0.02
Ni–N(3)	2.08	0.02
Ni–N(4)	2.09	0.02
Ni–N(5)	1.97	0.02
	Angle, Deg	
N(1)–Ni–N(2)	85.4	0.9
N(1)–Ni–N(3)	85.1	0.9
N(1)–Ni–N(4)	83.7	0.8
N(1)–Ni–N(5)	178.8	0.9
N(2)–Ni–N(3)	111.5	0.8
N(2)–Ni–N(4)	126.0	0.9
N(2)–Ni–N(5)	95.0	0.9
N(3)–Ni–N(4)	120.0	0.9
N(3)–Ni–N(5)	95.8	0.9
N(4)–Ni–N(5)	95.1	0.9

We notice a remarkable displacement from C_{3v} symmetry in the values of the equatorial angles which are 111.5, 126.0, and 120.0°. The N(1)–Ni–N(5) angle, on the contrary, has a value very close to 180° (178.8°). Furthermore, the nickel atom is displaced from the equatorial plane by 0.19 Å toward the nitrogen atom of the NCS group. This displacement was also found in the $[Ni(Me_6tren)Br]Br$ structure[3] and seems to be characteristic of all the Me_6tren derivatives. The linked NCS group is linear with a Ni–N–C angle of 167.8°.

Single-Crystal Polarized Spectra.—The crystals had the (100) face most highly developed and the spectra were recorded along the b and c axes. The z molecular axis has been chosen parallel to the N(1)–Ni bond. The spectra were recorded with the Unicam SP 700 spectrophotometer modified as previously described.[5]

Results

The single-crystal polarized spectra as well as the reflectance spectrum of this NiN_5 chromophore are shown in Figure 2 together with the reflectance spectrum of the bromo derivative.[2] The two reflectance spectra are quite identical save for the displacements due to spectrochemical effects although the structures show same differences. The spectrum recorded along the b direction is mostly $\parallel$ whereas the spectrum recorded along c is mostly $\perp$ in character (see Table III). The weak band (or system of bands) at *ca.* 13 kK is essentially nonpolarized whereas the band at 7.7 is $\parallel$ polarized and the band at 16.2 is $\perp$ polarized.

The band at 24.6 kK is apparently only slightly $\perp$

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[4] I. Bertini and A. Sabatini, *Inorg. Chem.*, **5**, 1025 (1966).

[5] B. J. Hathaway, P. Nicholls, and D. Barmerd, *Spectravision*, **22**, 4 (1969).

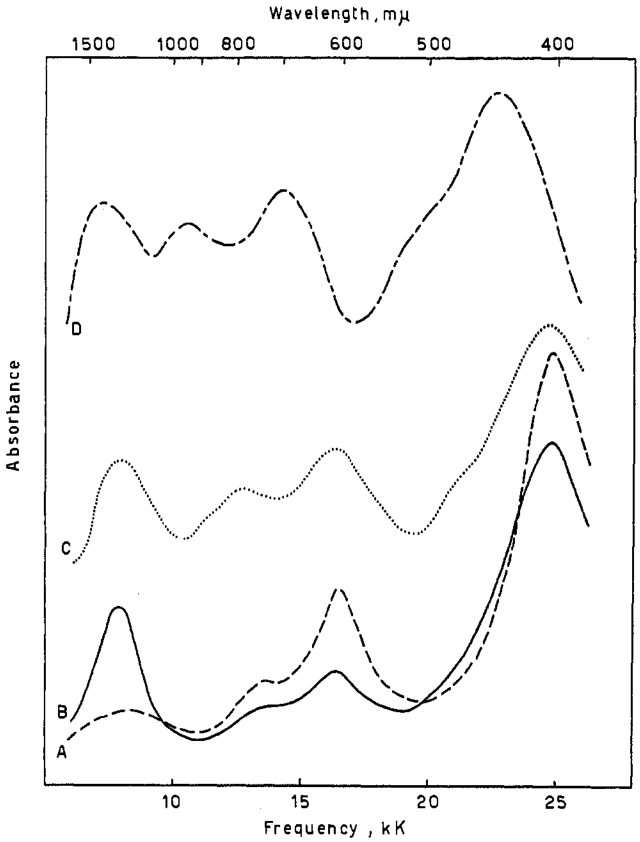

Figure 2.—Single-crystal polarized electronic spectra of the [Ni(NCS)(Me$_6$tren)](SCN)·H$_2$O complex recorded along the crystallographic *b* (B) and *c* (A) axes; diffuse reflectance spectra of the above complex (C) and of the [NiBr(Me$_6$tren)]Br complex (D).

TABLE III

SQUARES OF THE PROJECTIONS FOR A UNIT ELECTRIC VECTOR ALONG THE EXTINCTION DIRECTIONS OF [Ni(NCS)(Me$_6$tren)](SCN)·H$_2$O

Extinction direction	Square of the projection for a unit electric vector	
	$\parallel$	$\perp$
b	0.80	0.20
c	0.20	0.80

polarized; however, on the low-frequency side of its envelope, a $\parallel$ polarized transition is evident.

Discussion

Considering the present chromophore as having C_{3v} or D_{3h} symmetry, the lowest triplet level is the ^{3}E or ^{3}E′ level, respectively.[6] The expected polarization properties are reported below.

E $\longrightarrow$ E ($\parallel$, $\perp$)	E′ $\longrightarrow$ E″ ($\parallel$)
A$_2$ ($\perp$)	A$_2$″, A$_1$″ (no)
A$_1$ ($\perp$)	A$_2$′ ($\perp$)
C_{3v}	D_{3h}

If a C_{3v} symmetry were operative, a predominant $\perp$ polarized spectrum would be expected whereas $\parallel$, $\perp$, and nonallowed bands would be expected for a D_{3h} symmetry. The latter case is approximately the actual case as illustrated in the previous section. However, the 24.6-kK band is not as polarized as expected. This can be due to the presence of a $\parallel$ polarized transition under the same envelope (appearing as a shoulder at *ca.* 21 kK) and to spin–orbit coupling and small crystal-field distortions which may attenuate the orbital selection rules. Even the C_{3v} symmetry might explain the observed polarization properties if the $\parallel$ component of $\parallel$ and $\perp$ allowed transitions is larger than the $\perp$ component. However, this simply means that the most operative symmetry is D_{3h}. An approximate D_{3h} symmetry can be actually operative for this NiN$_5$ chromophore apart from the small deviation of the nickel atom from the equatorial plane and the nonequivalence of the equatorial angles. The effect of such distortions on the spectra appears to be small. Presumably the ^{3}E′ ground level will experience some splitting, but the low-symmetry effects (both from a crystal-field and a second-order λLS point of view) do not change the ground-state function to a large extent so that the polarization properties of the transitions are substantially preserved.

In Figure 3 the energy level diagrams for a nickel(II) ion in D_{3h} symmetry are shown together with the effect of relaxing the Dq_{ax}/Dq_{eq} ratio, the B_2/B_4 radial integral ratio,[7] the nephelauxetic parameter β, and a C_{3v} perturbation. Three F–F transitions and two F–P transitions are expected in D_{3h} symmetry as have been actually observed. The resulting proposed assignment is summarized in Table IV together with the calculated frequency values for a D_{3h} symmetry with $B_2/B_4 = 1.5$, $Dq_{ax} = Dq_{eq} = 1.25$ kK, $\beta = 0.75$ for comparison purposes. Relaxing of the B_2/B_4 ratio and the Dq_{ax}/Dq_{eq} ratio significantly affects the order of the ^{3}A$_2$′ and ^{3}A$_1$″ + ^{3}A$_2$″ energy levels. Since the latter, accidentally degenerate levels are below and well separated from the former level, a low B_2/B_4 ratio, as well as a Dq_{ax}/Dq_{eq} ratio of *ca.* 1, is suggested for this complex. Such a Dq_{ax}/Dq_{eq} ratio fully agrees with the relative positions of isothiocyanate and tertiary nitrogen in the spectrochemical series.[8] The weak intensity of the band at 13.2 kK agrees with the nonallowed nature of this transition. From Figure 3 it appears that the effect of a C_{3v} perturbation causes the splitting of the previously degenerate ^{3}A$_1$″ and ^{3}A$_2$″ levels and a larger separation between the latter levels and the ^{3}A$_2$′ level. Such effects could improve the previous fitting. In fact, the band with a maximum at 13.2 kK is unsymmetrical in the single-crystal spectra whereas the reflectance spectra of both the NCS and Br derivatives show that at least two transitions are present under the band envelope. This might well be due to the splitting of the accidentally degenerate ^{3}A$_1$″ and ^{3}A$_2$″ levels or to

TABLE IV

PROPOSED ASSIGNMENT OF THE TRANSITIONS OF THE NiNCS(Me$_6$tren)(SCN)·H$_2$O COMPLEX

Freq, kK		
Calcd[a]	Found	Transition
6.9	7.7	^{3}E′ $\rightarrow$ ^{3}E″
11.9	13.2	^{3}A$_1$″ + ^{3}A$_2$″
13.1	16.2	^{3}A$_2$′
20.2	~21	^{3}E″
22.7	24.6	^{3}A$_2$′

[a] See text.

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(6) M. Ciampolini, *Struct. Bonding (Berlin)*, **6**, 52 (1969).

(7) S. T. Spees, Jr., J. R. Perumareddi, and A. W. Adamson, *J. Phys. Chem.*, **72**, 1822 (1968).

(8) S. F. Pavkovic and D. W. Meek, *Inorg. Chem.*, **4**, 20 (1965); C. K. Jørgensen, "Inorganic Complexes," Academic Press, London, 1963.

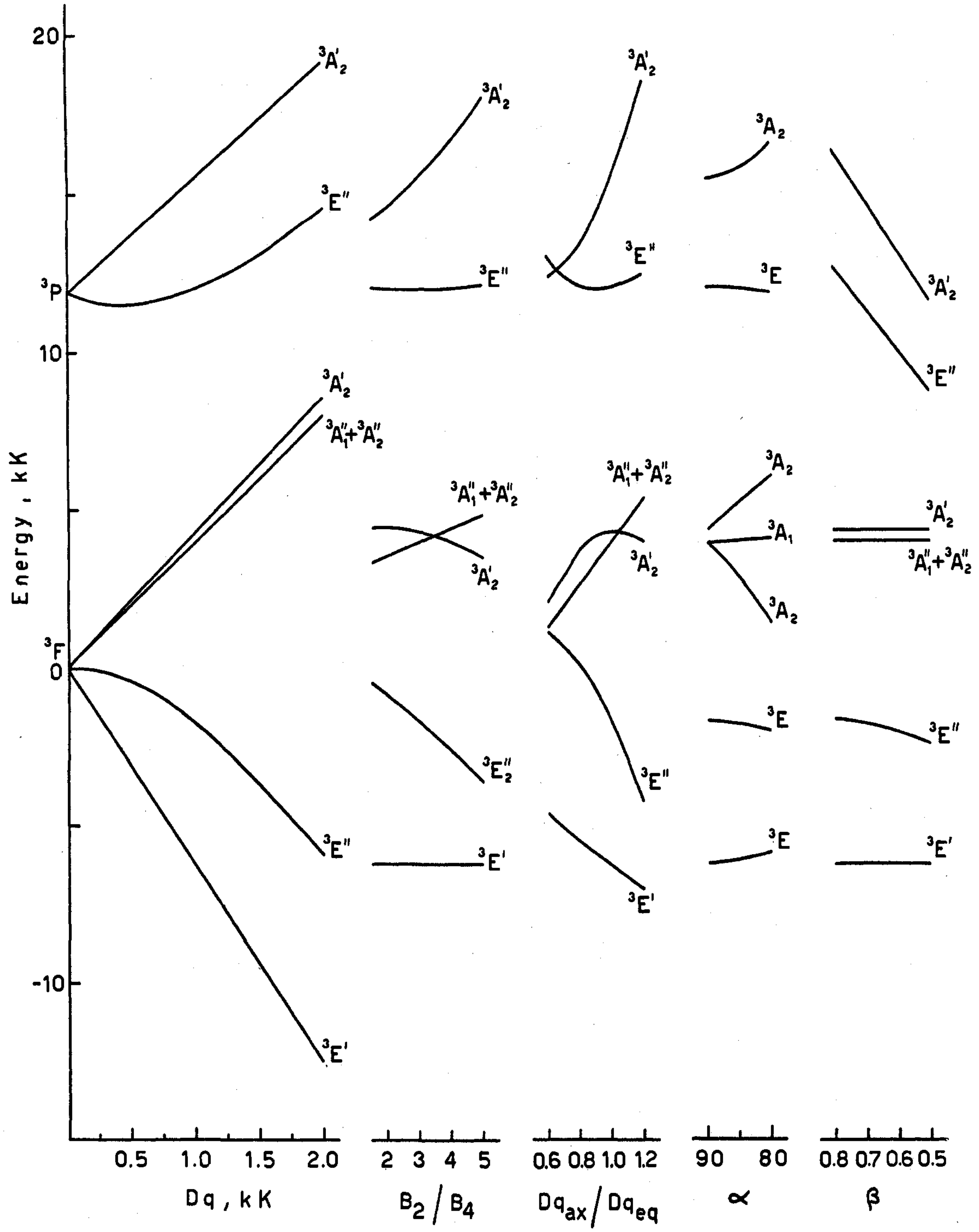

Figure 3.—Energy-level diagrams for a nickel(II) ion in D_{3h} trigonal-bipyramidal symmetry, $B_2/B_4 = 3.0$, $\beta = 0.75$, $Dq_{ax} = Dq_{eq}$. From the left to the right the effect of changing the B_2/B_4 ratio, the Dq_{ax}/Dq_{eq} ratio, the apical angle α and the nephelauxetic β parameter is shown for a $Dq_{eq} = 1.0$ kK.

spin-forbidden transitions as they are expected to fall in this region. The present assignment confirms the previous assignment of the bands of the [Ni(Me$_6$tren)Br]-Br complex.[9,10]

The magnetic moment value of 3.3 BM deserves some comments. This value is quite low for a double degenerate ground level and is much lower than expected.[10] For comparison purposes it is recalled that square-pyramidal nickel complexes which have a $^3B_1$ ground level with an excited ^3E level at about 5 kK have magnetic moment values of 3.40–3.70 BM.[11] Quenching of the orbital contribution to the magnetic moment in the present case presumably arises from distortions from both D_{3h} and C_{3v} symmetries. Although the effects of distortion are drastic on the magnetic properties, as expected from the Van Vleck equa-

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(9) M. Ciampolini, N. Nardi, and G. P. Speroni, *Coord. Chem. Rev.*, **1**, 222 (1966).

(10) J. S. Wood, *Inorg. Chem.*, **7**, 853 (1968).

(11) M. Gerloch, J. Kohl, J. Lewis, and W. Urland, *J. Chem. Soc. A*, 3269 (1970); A. M. Brodie, S. H. Hunter, G. A. Rodley, and C. J. Wilkins, *Inorg. Chim. Acta*, **2**, 195 (1968).

tion,[12] they may be only slightly operative on the polarization properties as in the present case.

It should be recalled, however, that also the [Ni(Me$_6$tren)Br]Br complex, in which the nickel ion is in a C_3 site symmetry, has a value of only 3.4 BM.[2] This has not been explained although a dynamical Jahn–Teller distorsion, as so often invoked for copper complexes,[13] could account for it.

Acknowledgments.—Thanks are expressed to Professor L. Sacconi for interest and to D. Masi for X-ray technical assistance.

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[12] J. H. Van Vleck, "Theory of Electric and Magnetic Susceptibilities," Oxford University Press, London, 1932, p 182.

[13] B. J. Hathaway and D. E. Billing, *Coord. Chem. Rev.*, **5**, 143 (1970).

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Reactions of Hexachlorocyclotriphosphazene with Triphenylstannyl- and Tri-*n*-butylstannyllithium

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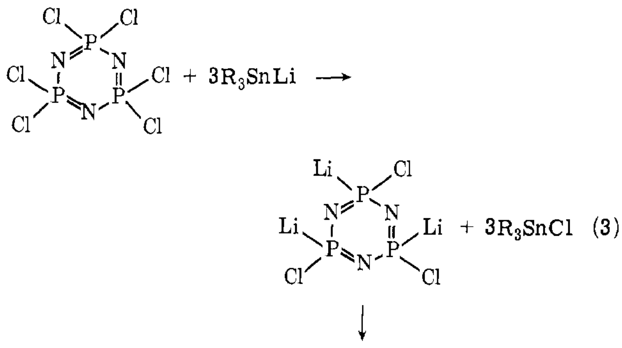
Hexachlorocyclotriphosphazene has been previously shown to undergo nucleophilic substitution reactions with hydroxides, alkoxides, phenoxides, alcohols, many sulfur-containing organic compounds, primary or secondary amines, ammonia, hydrazine, organometallic reagents, and metal salts to give the corresponding partially or fully substituted derivatives. We now wish to report the results of the reactions of hexachlorocyclotriphosphazene with triphenylstannyllithium and tri-*n*-butylstannyllithium, aimed at the synthesis of fully substituted phosphazene derivatives of the type $[NP(SnR_3)_2]_3$, where R = C_6H_5 or n-C_4H_9. We had thought that the chlorine atoms on the chlorophosphazene would undergo simple nucleophilic substitution by triphenylstannyl or tri-*n*-butylstannyl groups to yield the corresponding phosphazene derivatives in accordance with the equations

$$[PNCl_2]_3 + 6(C_6H_5)_3SnLi \longrightarrow [NP(Sn(C_6H_5)_3)_2]_3 + 6LiCl \quad (1)$$

$$[PNCl_2]_3 + 6(n\text{-}C_4H_9)_3SnLi \longrightarrow [NP(Sn(n\text{-}C_4H_9)_3)_2]_3 + 6LiCl \quad (2)$$

Instead we have found that the chlorophosphazene reacts with $(C_6H_5)_3SnLi$ and $(n\text{-}C_4H_9)_3SnLi$ in an unusual manner which involves breaking the phosphazene ring with the production of hexaphenyldistannane and hexa-*n*-butyldistannane, respectively, in good yields. Lithium chloride and a complex solid containing carbon, hydrogen, tin, phosphorus, and nitrogen are also obtained. This solid which appears to be impure has not been identified. No partially or fully substituted phosphazene derivatives containing $(C_6H_5)_3Sn$ or $(n\text{-}C_4H_9)_3Sn$ groups were obtained from the products of these reactions.

A reasonable reaction scheme which would account for the formation of the distannanes involves the following sequence of reactions



3LiCl + unidentified products

$$3R_3SnLi + 3R_3SnCl \longrightarrow 3R_3SnSnR_3 + 3LiCl$$

where R = C_6H_5 or n-C_4H_9. This reaction sequence must, of course, be regarded as tentative. A comparison, however, of the bond dissociation energies of P–Sn (44 kcal/mmol) and P–Li (64 kcal/mmol) would support the postulation of reaction 3.[1] The possibility that R_3SnSnR_3 may be present as a contaminant in the starting materials (R_3SnCl) and/or results as a by-product from the reaction of R_3SnCl and lithium due to incomplete formation of R_3SnLi has been considered. If so, it can only be present in trace amounts since the conversion to R_3SnLi is usually nearly quantitative. However, it is well known that the Sn–Sn bond in both hexa-*n*-butyldistannane and hexaphenyldistannane is readily cleaved by lithium metal in tetrahydrofuran.[2,3]

The fact that high yields of R_3SnSnR_3 compound are obtained and that an excess of lithium metal was used to ensure complete conversion of R_3SnCl to R_3SnLi should make very improbable the formation of R_3SnSnR_3 from R_3SnCl and lithium in the absence of hexachlorocyclotriphosphazene. Furthermore, the fact that all the chlorophosphazene was consumed would also support the reaction path proposed since it is very improbable that R_3SnSnR_3 would react with the phosphazene trimer.

The results obtained in this study are in general agreement with some earlier observations of anomalous results from attempted arylations or alkylations of chlorocyclophosphazenes. Reactions with some metal organic compounds have been shown to result in ring cleavage of the chlorocyclophosphazenes at rates which are comparable with, or faster than, rates of alkylation of the cyclic compounds. Bezman and Reed[4] studied the reactions of hexachlorocyclotriphosphazene with sodium salts of some carboxylic acids. They have shown that the reaction with the sodium salt of benzoic acid results in the production of benzonitrile, benzoic anhydride, sodium chloride, and some phosphorus-containing compounds whose identity could not be established conclusively. The P–N ring probably undergoes rupture.[4] In contrast to hexachlorocyclotriphosphazene, hexafluorocyclotriphosphazene has been reported to undergo smooth reactions with the

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[1] The bond energies were calculated using the equation $D_{A-B} = \frac{1}{2}(D_{A-A} + D_{B-B}) + 23.06(X_A - X_A)^2$.

[2] C. Tamborski, F. E. Ford, and E. J. Soloski, *J. Org. Chem.*, **28**, 237 (1963).

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[4] I. I. Bezman and W. R. Reed, *J. Amer. Chem. Soc.*, **82**, 2167 (1960).