A Quartet–Doublet Transition in Hexacyanochromate(III) Anion

By R. Krishnamurthy and Ward B. Schaap

During the course of other studies concerned with $Cr(CN)_6{}^{3-}$ complex ion, a new weak band at $\lambda_{max} = 530$ mμ has been detected in the visible absorption spectrum of its aqueous solution. This band is hidden in the tail of the much more intense first spin-allowed absorption band, $^4A_{2g} \rightarrow {}^4T_{2g}$ (F), and has a molar extinction coefficient of 0.44. The band has been interpreted from the standpoint of the Tanabe–Sugano ligand field model, and assigned to the spin-forbidden $^4A_{2g} \rightarrow {}^2T_{2g}$ (G) transition. The significance of this transition is discussed and correlated with the nephelauxetic effect of the cyanide ligands in the complex.

The Laporte-forbidden d–d absorption spectra of chromium(III) with many ligands have been interpreted by the ligand field theory.[1-8] However, in the case of hexacyanochromate(III) ion in aqueous solution, only the first two spin-allowed bands, located at 375 and 310 mμ, have been observed.[9] These have been assigned to the $^4A_{2g} \rightarrow {}^4T_{2g}$ (F) and $^4A_{2g} \rightarrow {}^4T_{1g}$ (F) transitions, respectively (Fig. 1 and 2). There is no previous report of either the third spin-allowed band, $^4A_{2g} \rightarrow {}^4T_{1g}$ (P), or the spin-forbidden bands, $^4A_{2g} \rightarrow ({}^2E_g, {}^2T_{1g})$ (G) and $^4A_{2g} \rightarrow {}^2T_{2g}$ (G). During the course of other studies concerned with this complex ion, an additional weak and previously unreported band was observed. Therefore, we thought it of interest to study the complete spectrum, since a knowledge of these bands would enable one to calculate the Racah parameters,[10,11] B and C, of electrostatic interactions between the d electrons in the complex and permit a chemical interpretation of the "nephelauxetic"[12,13] ratios, β_{35} and β_{55}, with respect to the 'covalent' tendency of the cyanide ligands in the complex.

Using concentrated solutions, we detected at the foot of a strongly increasing absorption a distinct shoulder of very low intensity located at $\lambda_{max} = 530$

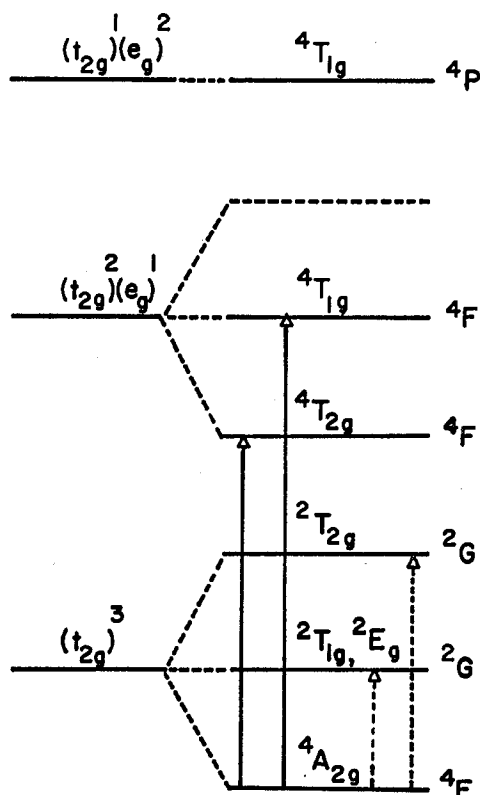(1) R. Finkelstein and J. H. Van Vleck, *J. Chem. Phys.*, **8**, 790 (1940).

(2) C. K. Jørgensen, Reports to the Tenth Solvay Conference, 1956, p. 362.

(3) C. E. Schäffer, *J. Inorg. Nucl. Chem.*, **8**, 149 (1958).

(4) H. L. Schläfer, *Z. Physik. Chem.* (Frankfurt), **11**, 65 (1957).

(5) T. M. Dunn, "Modern Coördination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, New York and London, 1960.

(6) L. E. Orgel, "An Introduction to Transition-Metal Chemistry: Ligand-Field Theory," Methuen, London, 1961, p. 97.

(7) J. S. Griffith, "The Theory of Transition Metal Ions," Cambridge University Press, Cambridge, 1961, p. 301.

(8) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., New York, N. Y., 1962, pp. 235–239.

(9) H. Kuroya and R. J. Tsuchida, *J. Chem. Soc. Japan.*, **61**, 597 (1940).

(10) G. Racah, *Phys. Rev.*, **62**, 438 (1942); **63**, 367 (1943).

(11) E. U. Condon and G. H. Shortley, "The Theory of Atomic Spectra," Cambridge University Press, London, 1959. The Racah parameters, $B (= F_2 - 5F_4$ after Slater, Condon, and Shortley) and $C (= 35F_4)$, describe the energy differences between the Russell–Saunders states in the free ion.

(12) C. E. Schäffer and C. K. Jørgensen, Symposium on Coördination Compounds, Rome, 1957; *Ricerca Sci.*, **28**, 143 (1958).

(13) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, New York and London, 1962, pp. 134–145. "Nephelauxetic" is derived from the Greek words meaning "cloud expanding." The charge cloud of the d electrons expands, leading to the decrease of the interelectronic repulsion parameters in going from the free ion to the complex, and corresponds to the expanded radial function of the partly filled d-shell. The nephelauxetic ratio, β, is equal to $B_{complex}/B_{free\ ion}$. For a given metal ion, the more common ligands have been arranged in the following series in order of decreasing values of β: $F^- > H_2O > NH_3 > en > OX^{2-} > SCN^- > Cl^- > CN^-$.

Fig. 1.—Energy level diagram for octahedral chromium(III) complexes.

mμ, with a molar extinction coefficient of 0.44 (Fig. 3a). It is not surprising that this weak shoulder was not reported previously, since it is hidden in the tail of the much more intense first spin-allowed band (Fig. 2). Because of its intensity and position compared to similar bands of other Cr(III) complexes, we assign this weak band to the ground $^4A_{2g} \rightarrow {}^2T_{2g}$ (G) transition. The method of "subtraction of extrapolated background" was used to locate and separate the band.[14] The differences in optical densities of the shoulder and the extrapolated background are plotted against the wave length in mμ in the region of interest and show a parabolic shape characteristic of an absorption band (Fig. 3b). The third spin-allowed band of Cr(III) complexes, corresponding to the transition $^4A_{2g} \rightarrow {}^4T_{1g}$ (P), is predicted to lie far in the ultraviolet and could
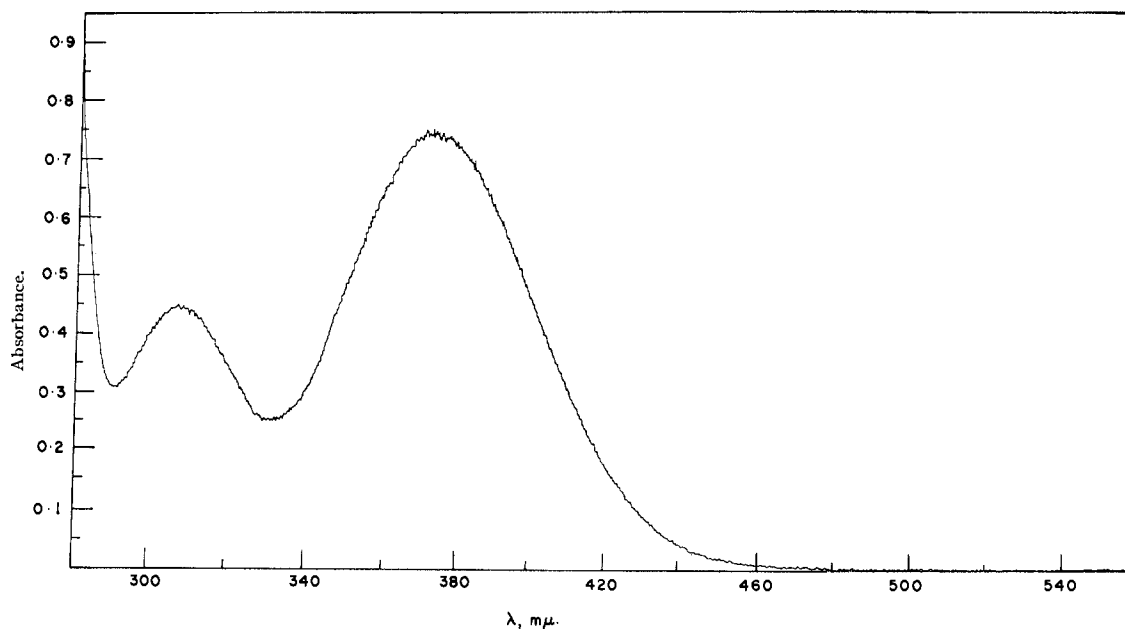
(14) Reference 13, p. 101.

Fig. 2.—Absorption spectrum of a 1.8×10^{-3} M solution of $Cr(CN)_6{}^{3-}$ at 25° with a 5-cm. cell.
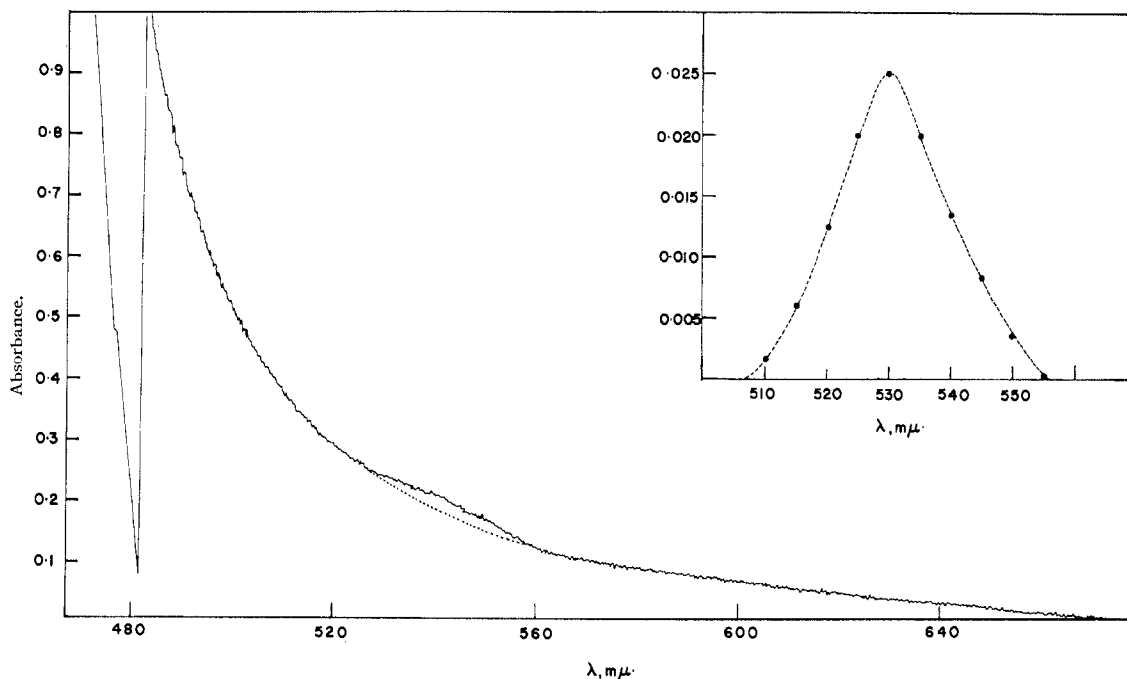

Fig. 3.—(a) Absorption spectrum of a 0.10 M solution of $Cr(CN)_6{}^{3-}$ at 25° with a 5-cm. cell. (b) Insert: An enlarged plot of the difference between observed spectrum and extrapolated background in the region 510–550 mμ.

not be observed in our spectrum. In addition, Schäffer[15] has demonstrated that this band often deviates from the predicted position due to electron-transfer interactions. The other low energy transition, $^4A_{2g} \rightarrow$ $(^2E_g, {}^2T_{1g})$ (G), could not be detected.

Experimental

"Electronic Grade," yellow, crystalline potassium hexacyanochromate(III) was purchased from the City Chemical Corporation, New York, N. Y. There was no noticeable change in its absorption spectrum upon recrystallization from water. $K_3Cr(CN)_6$ was synthesized in this Laboratory by a method described

previously.[16] Its spectrum was identical with that of the "Electronic Grade" sample, both exhibiting the weak shoulder band at 530 mμ. The molar extinction coefficients of the 375 and 310 mμ bands are in excellent agreement with those reported previously.[9]

Near-infrared, visible, and ultraviolet absorption spectra were obtained with a Cary Model 14 recording spectrophotometer. The aqueous solutions were clear, yellow, and quite transparent. The spectra were immediately measured in matched silica cells of 5.0 cm. path length, against water as a reference, from 700 mμ to shorter wave lengths until intense absorption set in.

Calculations

The strong field electrostatic matrix elements have

(15) Reference 12, p. 149.

(16) W. C. Fernelius, *Inorg. Syn.*, **2**, 203 (1946).

been calculated for d^n systems in cubic field (O_h) symmetry by Tanabe and Sugano.[17] The diagonal elements of energy of the lowest states springing from the sub-shell configuration $(T_{2g})^3$ (Fig. 1), in terms of Racah parameters, B and C, and the ligand field perturbation parameter, $10Dq$ (denoted also $(E_1 - E_2)$ or Δ), are

$$
\begin{aligned}
{}^4A_{2g}\ (F)&: \quad -12Dq \\
{}^2E_g\ (G)&: \quad -12Dq + 9B + 3C \\
{}^2T_{1g}\ (G)&: \quad -12Dq + 9B + 3C \\
{}^2T_{2g}\ (G)&: \quad -12Dq + 15B + 5C
\end{aligned}
$$

The energies of these terms are not corrected for configurational interactions. Using the average value of $C = 4B$ in the non-diagonal elements and applying the second order perturbation theory, Schäffer[18] has calculated from the Tanabe and Sugano determinants the corrections due to the effects of intermixing of the other sub-shell configurations. The energy differences above the ground state of the doublet terms[19, 20] then turn out to be

$$
\begin{aligned}
{}^2E_g&: \quad 9B + 3C - 90B^2/10Dq \\
{}^2T_{1g}&: \quad 9B + 3C - 24B^2/10Dq \\
{}^2T_{2g}&: \quad 15B + 5C - 176B^2/10Dq
\end{aligned}
$$

The energy of the first spin-allowed absorption band, observed at 26,700 cm.$^{-1}$, gives directly the value of $10Dq$. Using this Dq value and making the second spin-allowed band fit the eigenvalues of the determinants assuming intermixing of the $^4T_{1g}$ states,[21] the Racah parameter, $B_{complex}$, can be shown to be equal to 530 cm.$^{-1}$, as Schäffer and Jørgensen have shown.[12] This gives a value of 0.58 for β_{35}. From the $^4A_{2g} \rightarrow {}^2T_{2g}$ (G) transition, which occurs at 18,870 cm.$^{-1}$, the Racah parameter, $B_{complex}$, turns out to be 590 cm.$^{-1}$. This leads to another nephelauxetic ratio, β_{55}, of 0.64. The value of $15B$ corresponding to the $(^4P - {}^4F)$ interval for the free Cr^{3+} ion used for the calculation of β values is taken to be 13,770 cm.$^{-1}$. β_{35} is a measure of the interaction between one electron in each of the two sub-shells, e_g (or γ_3) and t_{2g} (or γ_5). β_{55} refers to the interaction between electrons in the lowest sub-shell, t_{2g}, in which spin-forbidden transitions take place.[20,22]

Discussion

If one uses the values of Dq and B derived from the quartet–quartet transitions and assumes that B is constant and that $C = 4B$, the calculated value for the $^2T_{2g}$ transition lies around 570 mμ (17,600 cm.$^{-1}$), which is close to the experimentally observed band at 530 mμ (18,870 cm.$^{-1}$), making this assignment reasonable. On the other hand, use of these same values of

(17) Y. Tanabe and S. Sugano, *J. Phys. Soc. Japan*, **9**, 766 (1954).

(18) C. E. Schäffer, unpublished results.

(19) C. K. Jørgensen, private communications.

(20) C. K. Jørgensen, "Orbitals in Atoms and Molecules," Academic Press, New York, N. Y., 1962, p. 57.

(21) The only two states of the same symmetry designation arising from the different configurations $(t_{2g})^2(e_g)^1$ and $(t_{2g})^1(e_g)^2$ are $^4T_{1g}(F)$ and $^4T_{1g}(P)$, respectively. They interact and give rise to the non-diagonal element, $6B$ in this symmetry, which perturbs the two levels, depressing the former and raising the latter by equal amounts of energy relative to the non-interacting case. This interaction causes the hyperbolic shape in the Orgel or the Tanabe–Sugano diagrams.

(22) C. K. Jørgensen, *Progr. Inorg. Chem.*, **4**, 73 (1962).

Dq, B, and C to calculate the energy of the lower, spin-forbidden transitions to the $^2T_{1g}$ and ^2E_g states predicts the absorption to be around 740 mμ (13,500 cm.$^{-1}$). The validity of the assignment to $^2T_{2g}$ can be justified further by comparison with experimental values for other Cr(III) complexes. In the cases of $Cr(ox)_3^{3-}$, $Cr(H_2O)_6^{3+}$, and ruby (Cr^{3+}, Al_2O_3), whose spectra are well understood, the $(^2T_{1g}, {}^2E_g)$ lie at 700 mμ (14,350 cm.$^{-1}$), 670 mμ (15,000 cm.$^{-1}$), and 692 mμ (14,450 cm.$^{-1}$), respectively. It is very unlikely that this transition would shift to 530 mμ (18,870 cm.$^{-1}$) in $Cr(CN)_6^{3-}$ because, as can be seen from the Tanabe–Sugano diagram, the transitions between the ground state and the $^2T_{1g}$ and ^2E_g states should be almost independent of the ligand field strength. Also, $(9B + 3C)$ would be larger than this quantity, and hence $B > 900$ cm.$^{-1}$ and $\beta_{55} > 0.98$ if the transition were $^2T_{1g}$, ^2E_g. Actually, β_{55} would be greater than 1 after the correction for sub-shell configuration interactions in this case and it would be unrealistic for β_{35} to be so much smaller than β_{55}. On the other hand, if the observed weak band is fitted to the $^2T_{2g}$ energy level, $(15B + 5C)$ gives a B value of 540 cm.$^{-1}$, which after correction for sub-shell configuration intermixing, $-176B^2/10Dq$ for $^2T_{2g}$, leads to 590 cm.$^{-1}$ for B and 0.64 for β_{55}, which are reasonable.

The nephelauxetic effect has been correlated with the reduction in term distance and with the covalency or polarizability of the ligands.[12] In other words, the effect is to delocalize the d electron cloud over the entire complex, thus increasing the mean distance between the d electrons and thereby decreasing the interelectronic repulsions. If both the sub-shells, t_{2g} and e_g, are expanded to the same extent, it may be assumed that there is one nephelauxetic ratio.[22] If β_{35} is significantly lower than β_{55}, the e_g sub-shell, being σ antibonding, carries most of the nephelauxetic effect caused by 'symmetry-restricted' covalency, while the t_{2g} sub-shell, which alone can be affected by π-bonding, is closer to "electrostatic behavior." In most chromium(III) complexes where π-bonding is much less important than σ-bonding, β_{55} shows a much less drastic variation than β_{35} (Table I).

However, in the case of $Cr(CN)_6^{3-}$, the value of β_{55} is significantly different from the corresponding values found for the other Cr(III) complexes. We do not have a further independent check on this

TABLE I

NEPHELAUXETIC RATIOS IN OCTAHEDRAL d^3 CHROMIUM COMPLEXES

Complex	Environment (donor atoms)	$\beta_{55}{}^a$	$\beta_{35}{}^a$
$Cr(H_2O)_6^{3+}$	6 O	0.91	0.79
$Cr(urea)_6^{3+}$	6 O	.88	.72
$Cr(ox)_3^{3-}$	6 O	.88	.68
$CrCl_3$ (solid)	6 Cl	.83	.56
$Cr(dtp)_3{}^b$	6 S	.80	.45
$Cr(CN)_6^{3-}$	6 C	$.64^c$	.58

^{a} β_{55} calculated from spin-forbidden and β_{35} from spin-allowed transitions.[19,22]　^{b} dtp$^-$ = diethyldithiophosphate anion.　^{c} β_{55} = 0.64 obtained from this work.

parameter since the $^4A_{2g} \rightarrow (^2E_g, \, ^2T_{1g})$ transition could not be detected in our work. The value of β_{55} is close to that of β_{35}. This demonstrates that the π^*-antibonding delocalization is more or less of equal importance as σ^*-antibonding delocalization, presumably because the orbitals of the lower triplet have the correct symmetry to overlap with the empty π^*-antibonding orbitals of the cyanide ligands. This results in a further depression of the triplet with respect to the upper doublet, which accounts for the relatively higher value

of $10Dq$, and also argues against applying to cyano complexes the simple "electrostatic crystal field" approach in which π-bonding is ignored.

The Preparation and Properties of Some New Nitrogen and Fluorine Derivatives of Disilane[1a]

By MANSOUR ABEDINI and ALAN G. MacDIARMID[1b]

Disilanyl bromide, H_3SiSiH_2Br, has been found to react with $(CH_3)_2NH$ to yield the new compounds $H_3SiSiH_2N(CH_3)_2$ and $H_3SiSiH[N(CH_3)_2]_2$. Boron trifluoride underwent reaction with $(H_3SiSiH_2)_3N$ at low temperatures to give the addition compound $(H_3SiSiH_2)_3N \cdot BF_3$, which then decomposed to yield the new species, H_3SiSiH_2F. A number of physical properties of the above new compounds have been examined and the significance of certain properties of analogous silyl, disilanyl, methyl, and ethyl compounds are discussed.

As a continuation of a study of the Si–Si bond as reflected in the properties of compounds containing this linkage,[2-5] it was considered desirable to investigate further the properties of disilanylamines since only one nitrogen derivative of disilane, $(H_3SiSiH_2)_3N$, had previously been described.[3] Although the silylamines $(H_3Si)_3N$, $(H_3Si)_2NCH_3$, and $H_3SiN(CH_3)_2$ have all been isolated,[6-8] $H_3SiN(CH_3)_2$ is reported to be unstable thermally and it decomposes at a measurable rate at 3–4°.[8] It was therefore of interest to attempt to prepare $H_3SiSiH_2N(CH_3)_2$ to see what effect the substitution of an Si–H bond in $H_3SiN(CH_3)_2$ by a SiH_3 group would have on the stability of the amine. A second purpose of the investigation was to ascertain whether BF_3 would cleave the Si–N bond in $(H_3SiSiH_2)_3N$ to give H_3SiSiH_2F in an analogous reaction to that between BF_3 and $(H_3Si)_3N$,[9,10] *viz.*

$$(H_3Si)_3N + BF_3 \longrightarrow H_3SiF + (H_3Si)_2NBF_2 \quad (1)$$

or whether cleavage would occur preferentially at the Si–Si bond.

Results and Discussion

Disilanyl bromide, H_3SiSiH_2Br, and $(CH_3)_2NH$ were found to undergo reaction at low temperatures to yield the new compound N-disilanyldimethylamine, $H_3SiSiH_2N(CH_3)_2$.

$$H_3SiSiH_2Br + 2(CH_3)_2NH \longrightarrow H_3SiSiH_2N(CH_3)_2 + \\ (CH_3)_2NH \cdot HBr \quad (2)$$
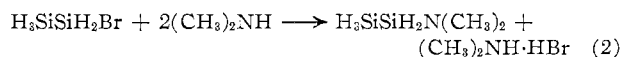
The presence of the H_3SiSiH_2 group in the compound appeared, if anything, to make the material more stable thermally than the silyl analog, $H_3SiN(CH_3)_2$, since 80% of a sample of $H_3SiSiH_2N(CH_3)_2$ could be recovered unchanged after standing for 47 hr. at 0°.

Also formed in the above reaction was the new compound, 1,1-bis-(dimethylamino)-disilane, $H_3SiSiH[N(CH_3)_2]_2$. It appears that this may have been formed by the decomposition of some of the $H_3SiSiH_2N(CH_3)_2$ before it could be isolated and purified since a considerable quantity of Si_2H_6 also was found among the reaction products, *viz.*

$$2H_3SiSiH_2N(CH_3)_2 \longrightarrow H_3SiSiH[N(CH_3)_2]_2 + Si_2H_6 \quad (3)$$
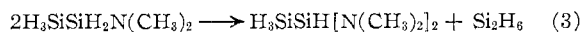
The fact that CH_3NH_2, $(CH_3)_3N$, and NH_3 catalyze the decomposition of $(H_3Si)_3N$,[11] *viz.*

$$3(H_3Si)_3N \longrightarrow (SiH_2NSiH_3)_3 + 3SiH_4 \quad (4)$$

(1) (a) This report is based on portions of a thesis to be submitted by Mansour Abedini to the Graduate School of the University of Pennsylvania in partial fulfillment of the requirements for the degree of Doctor of Philosophy. It is in part a contribution from the Laboratory for Research on the Structure of Matter, University of Pennsylvania, supported by the Advanced Research Projects Agency, Office of the Secretary of Defense. Reproduction in whole or in part is permitted for any purpose of the United States Government. (b) Alfred P. Sloan Research Fellow.
(2) L. G. L. Ward and A. G. MacDiarmid, *J. Am. Chem. Soc.*, **82**, 2151 (1960).
(3) L. G. L. Ward and A. G. MacDiarmid, *J. Inorg. Nucl. Chem.*, **21**, 287 (1961).
(4) L. G. L. Ward and A. G. MacDiarmid, *ibid.*, **20**, 345 (1961).
(5) A. D. Craig, J. V. Urenovitch, and A. G. MacDiarmid, *J. Chem. Soc.*, 548 (1962).
(6) A. Stock and K. Somieski, *Ber.*, **54**, 740 (1921).
(7) H. J. Emeléus and N. Miller, *J. Chem. Soc.*, 819 (1939).
(8) S. Sujishi and S. Witz, *J. Am. Chem. Soc.*, **76**, 4631 (1954).
(9) S. Sujishi and S. Witz, *ibid.*, **79**, 2447 (1957).
(10) A. B. Burg and E. S. Kuljian, *ibid.*, **72**, 3103 (1950).

(11) R. Schaeffer, L. Ross, M. Thompson, and R. Wells, Report No. 2, Office of Naval Research, Contract Nonr-908(14), Task NR 052-410, Aug. 31, 1960.