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Normal–Iso Rearrangement in Cyanotrialkylsilanes[1]

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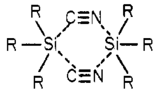
The mechanism of cyanide exchange in R_3SiCN (R = methyl, ethyl, isopropyl) has been investigated. The exchange is markedly temperature dependent and is intermolecular in the liquid phase. In dilute 1-chloronaphthalene solution, however, the *iso* form reverts to the *normal* form via intramolecular migration.

Introduction

Even since they were first reported,[2] cyanotrialkylsilanes have been a source of structural controversy. Many properties, both physical and chemical, have been attributed to the equilibrium

$$R_3SiCN \rightleftharpoons R_3SiNC \quad (1)$$

with the C-bonded ("normal") form predominating. Despite extensive investigations,[3-8] unequivocal evidence for this equilibrium came only through the spectroscopic studies of Booth and Frankiss.[9] The interconversion has been postulated to involve a bimolecular intermediate



This intermediate originally appeared in a footnote in the paper by Bither et al.[6] It has been uncritically accepted by subsequent workers, even though organic isocyanides were later found to rearrange through intramolecular migration.[10-12] As part of our research into the chemistry of organosilicon pseudohalides, we have investigated the mechanism of cyanide exchange.

Results

1. Mass Spectrometric Studies. The three compounds $(CH_3)_3SiCN$ (I), $(C_2H_5)_3SiCN$ (II), and $(i\text{-}C_3H_7)_3SiCN$ (III) gave rather involved mass spectroscopic fragmentation patterns (Table I). As the alkyl groups increase in size, C–H bond cleavage becomes enhanced. The proportion of fragments retaining Si–CN linkages also increases with alkyl group size, as does the relative quantity of molecule ion. This latter trend is exactly opposite to that found for organic nitriles, or isocyanides, as shown in Table II.[13]

Mass spectrometry, combined with gas chromatography, was used to study the exchange of cyanide groups between I and $(C_2H_5)_3Si^{13}CN$ in 1-chloronaphthalene solution. The intensities of the two peaks at *m/e* 141 and 142 ($Et_3Si^{12}CN^+$ and $Et_3Si^{13}CN^+$) were monitored over periods of time. At room temperature, exchange was slightly more than half complete after 2 days and not fully complete after 5 days (Table III). At 100 °C, exchange was complete after 30 min.

Table I. Trialkylcyanosilane Mass Spectroscopic Fragment Peaks

	CH_3-	C_2H_5-	$i\text{-}C_3H_7$-
R_3SiCN^+	2.6	18.7	71.8
R_2Si^+	4.4		
R_2SiCN^+	5.7	1.4	12.0
Rsi^+	3.8		
R_2SiHCN^+		6.6	36.5
$RSiHCN^+$		44.5	11.5
$Et_2SiC_2H_4{}^+$		18.7	
$PrMeSiCN^+$			100
$PrMeSiHCN^+$			58.7
Me_2SiCN^+			54.1

Table II. Relative Abundance of Molecule Ion

	RCN	RNC	R_3SiCN
CH_3-	100	100	2.6
C_2H_5-	12	76	18.7
$i\text{-}C_3H_7$-	3		71.8
$t\text{-}C_4H_9$-	<0.6	2.9	

Table III. Me_3SiCN–$Et_3Si^{13}CN$ Exchange Shown by 142/141 Mass Spectral Peak Ratios

Time, h	Peak ratios	Time, h	Peak ratios	Time, h	Peak ratios
0.0	4.23	1.37	3.54	49.5	2.00
0.384	3.66	5.5	3.20	120.0	1.10

Table IV. Cyanide Band Positions for R_3SiCN

R		Solvent	*E*	ν(CN), cm^{-1}	ν(NC), cm^{-1}	$\epsilon_{NC}/\epsilon_{CN}$
CH_3		C_5H_{12}	1.84	2192.5 (8.5)	2094	29
		CCl_4	2.23	2191.5 (7.4)	2096.5	24
		C_6H_6	2.27	2190.5 (6.8)	2097.5	38
		$CHCl_3$	4.81	2192.5 (3.7)	2096.5	90
		$1\text{-}ClC_{10}H_7$		2189.5 (5.7)	2098	31
		C_5H_5N	12.3	2190 (4.4)	2100	18
		CH_3CN	36.2	2191 (4.2)	2101	16
C_2H_5	^{12}CN	$1\text{-}ClC_{10}H_7$		2187	2095.5	
	^{13}CN	$1\text{-}ClC_{10}H_7$		2138	2056.5	
$i\text{-}C_3H_7$		$1\text{-}ClC_{10}H_7$		2185.5	2093.5	

2. Infrared Spectroscopic Studies. Table IV lists the C- and N-bonded cyanide band positions for I in various solvents. The latter shows a slight shift to higher frequency with increasing solvent polarity, which is consistent with the polar nature of isocyanides. Extinction coefficients for the C-bonded cyanide band tend to decrease as solvent polarity increases—just the opposite of what is observed for nitriles.[14] Acetone gave anomalous results due to cyanohydrin formation.[15] In order to test for possible hydrolysis effects, we passed

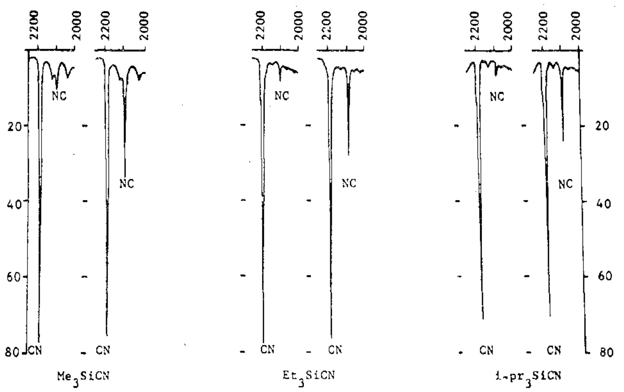


Figure 1. Temperature effect on trialkylcyanosilanes; first band at 25 °C and second band at 225 °C.

Table V. First-Order Rate Constants for Iso → Normal Conversion in R_3SiCN

R	Rate const, h^{-1}	R	Rate const, h^{-1}
CH_3	1.75 (0.02)[a]	i-C_3H_7	0.205 (0.004)
C_2H_5	0.856 (0.002)		

[a] Standard deviation in parentheses.

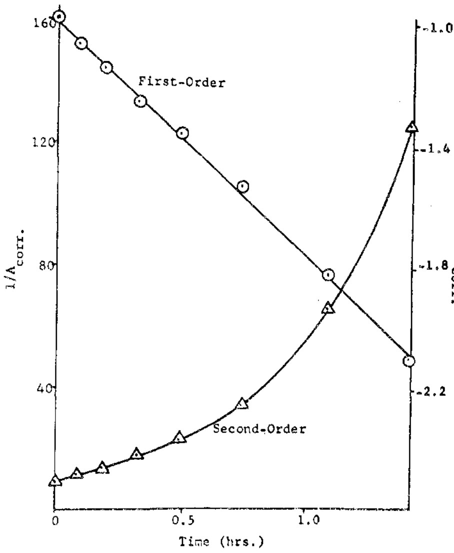


Figure 2. Rate plots for $(CH_3)_3SiNC \rightarrow (CH_3)_3SiCN$ conversion.

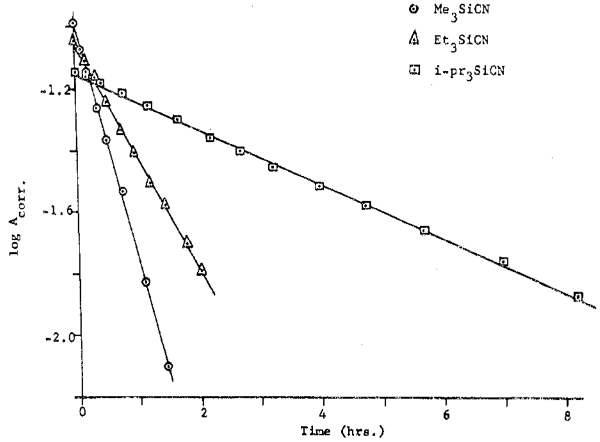


Figure 3. Rate plots of N-bonded to C-bonded cyanide conversion.

some dried HCN gas through rigorously dried I. The original bands at 2191.5 and 2096.5 cm^{-1} did not change. Two additional bands at 3280 and 2089 cm^{-1} appeared; these arise from the C—H and C≡N stretching vibrations, respectively, of HCN.[16a] Our observations confirm the conclusion of Booth and Frankiss that the 2096.5-cm^{-1} band is not due to HCN.[9]

In $(C_2H_5)_3Si^{13}CN$, the C-bonded cyanide stretching band shows an isotopic shift of 49 cm^{-1}, which is close to the values of 51 and 50.5 cm^{-1} reported for $(CH_3)_3Si^{13}CN$ by Booth and Frankiss[9] and Linton and Nixon,[5] respectively. The N-bonded cyanide stretching band shows a shift of 39 cm^{-1}, again very close to the 40 cm^{-1} shift found by Booth and Frankiss.[9]

3. Rearrangement Studies. Solutions of 0.2 *m* R_3SiCN in 1-chloronaphthalene were heated to 225 °C. Ten minutes at this temperature sharply enhanced the N-bonded form and slightly reduced the C-bonded form (Figure 1). This enhancement enabled more precise measurement of band intensities. From Beer's law the following equation can be derived

$$[CN]_T = \frac{A_{CN}}{l\epsilon_{CN}} + \frac{A_{NC}}{l\epsilon_{NC}}$$

where $[CN]_T$ is the total concentration of cyanosilane and l is the cell length. Determination of absorbances at different concentrations made it possible to calculate values for the extinction coefficients. I (bp 117.8 °C) and II (bp 182 °C) showed some tendency to vaporize from solution, but this was negligible for III (bp 227 °C (743 Torr)). For III, ϵ_{CN} was 5.43 kg/(mol mm) and ϵ_{NC} was 80 ± 30 kg/(mol mm). Their ratio is 15 ± 6, in reasonable agreement with the ratio of 27 ± 15 reported by Booth and Frankiss[9] for pure liquid I. From these values, the concentrations of the "normal" and "iso" forms in "0.2 *m*" solution were calculated as 0.199 and 0.003 *m*, respectively. This gives a mole fraction of 0.0015 ± 0.0006, in excellent agreement with the value of Booth and Frankiss.[9]

When heated solutions were quenched in an ethanol slush bath, they reverted to room temperature within 30 s. Upon standing of the solutions, the N-bonded cyanide band slowly diminished, indicating conversion to the C-bonded form. The rate of conversion for this process could be followed by infrared spectroscopy, using the cell in–cell out method.[16b] When ΔA (difference between observed absorbance and equilibrium absorbance) was plotted against time, a curve resulted (Figure 2); however, a plot of log ΔA against reciprocal time gave a straight line (Figure 3) for all three compounds. The rate constants are listed in Table V.

Discussion

Although first-order rate plots were obtained in the quenching reequilibration experiment, this need not necessarily imply a first-order mechanism, especially if perturbation from the equilibrium concentration is small. For a bimolecular exchange mechanism, the rate equation would be

$$d[SiNC]/dt = k_1[SiCN]^2 - k_{-1}[SiNC]^2$$

If the deviation from equilibrium, Δc, is defined as

$$\Delta c = [SiNC] - [SiNC]_{eq} = [SiCN]_{eq} - [SiCN]$$

and substituted for the concentrations, the rate equation now becomes

$$d[SiNC]/dt = (k_{-1} - k_1)(\Delta c)^2 + 2(k_1[SiCN]_{eq} + k_{-1}[SiNC]_{eq})\Delta c + k_{-1}[SiNC]_{eq}{}^2 - k_1[SiCN]^2$$

However, $k_{-1} >> k_1$ and $k_1[SiCN]_{eq} = k_{-1}[SiNC]_{eq}{}^2/[SiCN]$. The rate equation thereby simplifies to

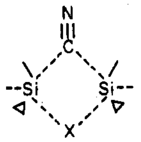
$$d[SiNC]/dt = k_1\left\{(\Delta c)^2 + 2[SiNC]_{eq}\left(\frac{[SiNC]_{eq}}{[SiCN]_{eq}} + 1\right)\Delta c\right\}$$

This equation indicates that, if Δc is small, the rate will appear to be first order, regardless of the actual mechanism. Under our experimental conditions, $[\mathrm{SiCN}]_{\mathrm{eq}} = 0.199\ m$ and $[\mathrm{SiNC}]_{\mathrm{eq}} = 0.0003\ m$. Substitution of these values into the rate equation gives

$$\mathrm{d}[\mathrm{SiNC}]/\mathrm{d}t = k_{-1}[(\Delta c)^2 + 0.00060\Delta c]$$

In order for any second-order contribution to be negligible, Δc would have to be less than $5 \times 10^{-5}\ m$. The observed Δc was $2.5 \times 10^{-3}\ m$ (the concentration of N-bonded cyanide was much higher than the equilibrium value). Therefore, we conclude that the rearrangement actually is first order. The Si–NC linkage is considerably more labile than the C–NC linkage in organic isocyanides, and migration of N-bonded organosilicon groups is well known.[17] Hence, intramolecular migration of triorganosilyl groups from the nitrogen to the carbon of a cyanide group seems quite plausible as a possible mechanism.

However, some exchanges involving cyanides must proceed through intermolecular transfer. The compound $(CH_3)_2Si(CN)_2$ undergoes ready exchange with dimethylsilyl halides and isothiocyanates[18] to form mixed species $(CH_3)_2Si(CN)X$. Similar reactions are known for the trialkylsilyl series.[3,8] It does not necessarily follow, however, that such exchange must proceed through the bridging intermediate proposed by Bither et al.[6] An alternative possibility is the C-bonded intermediate



Since C-bonded forms predominate so greatly, such an intermediate may well be important for exchange in the pure cyanides.

All available evidence indicates that the relative position of the "normal–iso" equilibrium will depend on (i) the nature of the groups on silicon, (ii) the temperature, (iii) the phase conditions, and (iv) the solvation and surface effects. The first of these factors has been the most studied. Neither infrared spectroscopy[19] nor microwave spectroscopy[20] gave any evidence for the presence of silyl isocyanide in H_3SiCN. Cyanotriphenylsilane also showed no infrared peak near 2100 cm^{-1}, though it may simply have been too feeble for observation, as the 2195-cm^{-1} peak was also weak[3]. Pentamethylcyanodisilane shows both isomers, with more C-bonded form than I;[21] this is also observed in the Ge analogues.[22] Permethylcyanopolysilanes with three or more silicon atoms also show both isomers; apparently the proportion of N-bonded form increases irregularly as the number of Si atoms increases.[21] In the series we have investigated, the proportion of N-bonded isomer seems to decrease as the size of the alkyl group increases. In the mixed species CH_3SiH_2CN[23] and $(CH_3)_2SiHCN$[24] the Si–H infrared bands obscure the cyanide bands; the latter, but not the former, did have a band at 2085 cm^{-1}, possibly due to the N-bonded isomer. Cl_3SiCN also had a very weak band at 2086 cm^{-1}, along with the strong 2207-cm^{-1} C-bonded band.[25] F_3SiCN showed no bands at 2000–2200 cm^{-1}, but this was primarily due to the conditions under which this highly unstable compound was studied.[26] While the available data are extremely scanty, it at least suggests that electron-withdrawing groups tend to favor the C-bonded form and that steric effects are probably secondary.

Phase effects are also important. Recently Durig et al. did a microwave study on gaseous I, from which they estimated that the N-bonded form was present to the extent of 5.3%.[27] This contrasts sharply with the much lower value found by Booth and Frankiss in the liquid state.[9] Also, the increase in N-bonded form with temperature and the related thermodynamic parameters differed appreciably.

While the intermolecular exchange mechanism originally proposed by Bither et al.[6] does occur, it is not the only possible mechanism and may occur only under certain conditions. Exchange and isomerization seemingly proceed by several routes, perhaps even simultaneously. Further investigation into these possible mechanisms seems to be needed.

Experimental Section

General Data. Because of the extreme sensitivity of organosilicon cyanides to moisture and the toxicity of the hydrolysis product hydrogen cyanide, rigorous precautions were needed to exclude water. Chemicals and glassware were thoroughly dried before use. Whenever possible, reactions were carried out under nitrogen in a drybox.

Cyanosilane Preparation. Trimethyl-, triethyl-, and triisopropylcyanosilanes were prepared by previously described methods.[8] A 0.500-g sample of $KC^{13}N$ (Merck Sharp and Dohme of Canada; listed as 89.2 atom % ^{13}C) was dissolved in water and added dropwise to a 0.14 M solution of $AgNO_3$ at 0 °C. The resulting precipitate was filtered and washed repeatedly with water and ether. After drying, 0.995 g of $Ag^{13}CN$ was recovered (97.4% yield). This was used to prepare $Me_3Si^{13}CN$ and $Et_3Si^{13}CN$.

Mass Spectra. The mass spectra of the cyanosilanes were recorded on a differentially pumped Hitachi Perkin-Elmer RMU-7 mass spectrometer with the following settings: ion source temperature 200 °C, ion source pressure 3×10^{-6} Torr, accelerating voltage 3.6 kV, trap current 40 μA, electron energies 20, 45, 70, eV. Spectra using 20 eV had the greatest wealth of detail and received the most attention. The instrument was flushed out with trimethylcyanosilane to remove both siloxane impurities and fluorosilanes formed from perfluorokerosene standard.

Intermolecular Exchange Studies. Stock solutions containing 0.20 m $(CH_3)_3SiCN$ and $(C_2H_5)_3Si^{13}CN$ in 1-chloronaphthalene were prepared. Aliquots (100-μl) of each were mixed in a Pierce Chemical Co. Reacti-vial at room temperature. After mixing, 2-μl aliquots were added successively to a LKB–900 gas chromatograph–mass spectrometer which used a 10% OV-17 on gas chrom-Q (100–120 mesh) in a 1.80 m × 2 mm Pyrex glass column. Exchange was monitored by using the two m/e peaks at 141 and 142. Various experimental problems, such as pen response time and injection and column temperature effects, prevented accurate quantitative measurements.[1] A typical series of room-temperature results is shown in Table III.

Intramolecular Exchange Studies. The 0.20 m stock solutions were placed in sealed Pyrex vessels and heated to 225 °C. Quenching in an ethanol–liquid nitrogen slush bath brought the temperature back to 25 °C within 20 s. Aliquots were transferred to 0.5-mm solution cells, and infrared spectra run on a Beckman IR-12. Running a stream of nitrogen gas over the cell kept the temperature at 25 °C; without such a stream, the temperature rose to 42 °C. In an alternate method, samples were withdrawn from the heated solution using a long thin glass capillary, put into the cell, and studied directly. Results obtained in this fashion proved virtually identical with those from the first method. The spectral region between 2200 and 2250 cm^{-1} was used as baseline for comparative quantitative studies.

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Registry No. $(CH_3)_3SiCN$, 7677-24-9; $(C_2H_5)_3SiCN$, 18301-88-7; $(i\text{-}C_3H_7)_3SiCN$, 35856-38-3; $(C_2H_5)_3Si^{13}CN$, 57652-44-5; $(CH_3)_3SiNC$, 18169-72-7; $(C_2H_5)_3SiNC$, 18301-43-4; $(C_2H_5)_3SiN^{13}C$, 57652-45-6; $(i\text{-}C_3H_7)_3SiNC$, 57652-46-7.

References and Notes

(1) Taken from the doctoral dissertation of J. A. Seckar, University of Cincinnati, 1973.
(2) (a) C. Eaborn, *J. Chem. Soc.*, 2755 (1949); (b) *ibid.*, 3077 (1950).
(3) J. S. Thayer and R. West, *Adv. Organomet. Chem.*, **5**, 169 (1967).
(4) J. J. McBride and H. C. Beachell, *J. Am. Chem. Soc.*, **74**, 5247 (1952).
(5) H. R. Linton and E. R. Nixon, *J. Chem. Phys.*, **28**, 990 (1958).
(6) T. A. Bither, W. H. Knoth, R. V. Lindsay, and W. H. Sharkey, *J. Am. Chem. Soc.*, **80**, 4151 (1958).
(7) J. S. Thayer, *Inorg. Chem.*, **7**, 2599 (1968).

(8) J. A. Seckar and J. S. Thayer, *Inorg. Chem.*, **14**, 573 (1975).
(9) M. R. Booth and S. G. Frankiss, *Spectrochim. Acta, Part A*, **26**, 859 (1970).
(10) F. W. Schneider and B. S. Rabinovitch, *J. Am. Chem. Soc.*, **85**, 2365 (1963).
(11) J. Casanova, N. D. Werner, and R. E. Schuster, *J. Org. Chem.*, **31**, 3473 (1966).
(12) G. W. Van Dine and R. Hoffmann, *J. Am. Chem. Soc.*, **90**, 3229 (1968).
(13) F. W. McLafferty, *Anal. Chem.*, **34**, 26 (1962).
(14) N. S. Bayliss, A. R. H. Cole, and L. H. Little, *Spectrochim. Acta*, **15**, 12 (1959).
(15) (a) D. A. Evans and L. K. Truesdale, *Tetrahedron Lett.*, 4929 (1973); (b) W. Lidy and W. Sundermeyer, *Chem. Ber.*, **106**, 587 (1973).
(16) (a) W. J. Potts, "Chemical Infrared Spectroscopy", Wiley, New York, N.Y., 1963, p 27; (b) *ibid.*, p 161.
(17) R. West, M. Ishikawa, and R. E. Bailey, *J. Am. Chem. Soc.*, **89**, 4068 (1967).
(18) K. Moedritzer and J. R. Van Wazer, *J. Organomet. Chem.*, **6**, 242 (1966).
(19) H. R. Linton and E. R. Nixon, *Spectrochim. Acta*, **10**, 299 (1958).
(20) A. J. Careless and H. W. Kroto, *J. Mol. Spectrosc.*, **57**, 198 (1975).
(21) J. V. Urenovitch, A. G. MacDiarmid, and E. R. Nixon, *Appl. Sectrosc.*, **19**, 80 (1965).
(22) A. J. Andy and J. S. Thayer, *J. Organomet. Chem.*, **76**, 339 (1974).
(23) H. Emeleus, M. Onyszchuk, and W. Kuchen, *Z. Anorg. Allg. Chem.*, **283**, 75 (1956).
(24) W. Kuchen, *Z. Anorg. Allg. Chem.*, **288**, 101 (1956).
(25) F. A. Miller and D. H. Lemmon, *Spectrochim. Acta, Part A*, **25**, 1799 (1969).
(26) B. J. Aylett, I. A. Ellis, and J. R. R. Richmond, *J. Chem. Soc., Dalton Trans.*, 981 (1973).
(27) J. R. Durig, W. O. George, Y. S. Li, and R. O. Carter, *J. Mol. Struct.*, **16**, 47 (1973).

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Emission Spectra of $Cs_2NaEuCl_6$ and $Cs_2Na(Eu,Y)Cl_6$

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The emission spectra of $Cs_2NaEuCl_6$ and $Cs_2Na(Eu_xY_{1-x})Cl_6$ ($x = 0.01$ and 0.10) have been determined at room temperature and at 77 K. These compounds have a face-centered cubic structure and the rare earth ion lies on a site of perfect octahedral symmetry surrounded by six chloride ions. The emission spectrum of the europium(III) ion confirms this symmetry and is dominated by those transitions which obey magnetic dipole selection rules. Weak, broad vibronic transitions are observed in place of the electric dipole transitions which are forbidden by the selection rules for octahedral symmetry. In $Cs_2NaEuCl_6$ transitions are found between 4900 and 6500 Å and arise from the $^5D_0$, $^5D_1$, and $^5D_2$ excited states. In the doped compounds transitions are observed between 4500 and 6500 Å and arise from the $^5D_3$ excited state as well as from $^5D_0$, $^5D_1$, and $^5D_2$.

Introduction

There are very few compounds of the trivalent rare earth ions which have sixfold, octahedral coordination.[2] As a result, most spectroscopic work has been done with compounds in which the symmetry of the environment around the rare earth ion is lower than octahedral, a fact which introduces complicating factors. In previous studies of the rare earth ions in cubic sites, such as the eightfold coordination of the ions doped in CaF_2[3] or the sixfold, octahedral, coordination in CaO,[4] there are the additional problems of charge compensation and multiple-site occupancy. These arise because of the difference in charge between the trivalent rare earth ion and the divalent calcium ion. For example, in the case of Er^{3+} in CaF_2, in addition to the cubic sites, trigonal sites (C_{3v}), tetragonal sites (C_{4v}), and 16 other sites having more than one Er^{3+} ion have also been observed.[3]

There have been two recent detailed spectroscopic studies of rare earth ions in sixfold, octahedral, environments. Gruber, Mendel, and Ryan[5] have examined the absorption spectrum of $[(C_6H_5)_3PH]_3NdCl_6$ and found that the neodymium ion occupies two slightly inequivalent sites having essentially octahedral symmetry with a slight distortion along one of the axes. Butter and Seifert[6] have investigated the emission spectra of $(pyH)_3EuCl_6$ and $(pyH)_3EuBr_6$ and interpreted their results in terms of a weakly distorted octahedral symmetry about the europium ion. The emission spectrum of europium(III) doped into the compound Ba_2GdNbO_6[7] has also been studied. The rare earth ion in this compound is in a site of octahedral symmetry which was demonstrated by the appearance of the magnetic dipole transition $^5D_0 \rightarrow {}^7F_1$ and the vibronic transition $^5D_0 \rightarrow {}^7F_2$.

As part of a project to investigate the emission spectrum of europium(III) in compounds in which the ion has discrete octahedral symmetry but does not suffer from the disadvantages mentioned above, we have measured the spectra of $Cs_2NaEuCl_6$ and $Cs_2Na(Eu_xY_{1-x})Cl_6$ ($x = 0.01$ and 0.10). These compounds were first prepared by Morss[8] and belong to a broad class of compounds of the trivalent metal ions which have been shown to have the face-centered cubic structure. All of the rare earth ions can exist in this lattice and the ESR spectra and magnetic susceptibilities have been reported for some of the ions.[9-11] In all cases the results which have been obtained are in agreement with the rare earth ion occupying a site of essentially perfect octahedral symmetry. In addition the absorption and magnetic circular dichroism spectra have been reported for the Ce^{3+} ion doped into Cs_2NaYCl_6[12] and the transitions and vibronic analysis were found to be indicative of the octahedral symmetry around the Ce^{3+} ion. The fluorescence emission of the Nd^{3+} compound[13] has also been determined and the long fluorescence lifetime is in accord with the suggestion made previously by Dieke.[14]

Because the rare earth ion in these compounds lies on a site which has inversion symmetry, this is an ideal system in which to check the degree to which the selection rules for the various optical transitions in europium(III) are obeyed. In principle, only those electronic transitions allowed under the magnetic dipole selection rules should be permitted and the electric dipole transitions will be replaced by vibronic transitions.[15] After our initial emission measurements were made, we became aware of the work carried out by Schwartz on the visible absorption spectrum and magnetic circular dichroism spectrum of $Cs_2NaEuCl_6$.[16] The results of these measurements complement the emission results reported here.

Experimental Section

Preparation of $Cs_2NaLnCl_6$. The compound $Cs_2NaEuCl_6$ was prepared by dissolving 2 mmol of CsCl, 1 mmol of NaCl, and 0.5 mmol of Eu_2O_3 in 6 M HCl and evaporating the resulting solution to dryness (preparation E).[7] Analysis of the resulting microcrystalline material for europium by EDTA titration was in agreement with the expected formula. The x-ray diffraction pattern agreed well with that previously reported and gave no evidence for significant amounts of NaCl or CsCl. The doped compounds, $Cs_2Na(Eu_xY_{1-x})Cl_6$ ($x = 0.01$ or 0.10), were made by the same procedure with the exception that the Eu_2O_3 was replaced by sufficient Y_2O_3 to yield the desired formulation. Samples of large crystals of $Cs_2NaEuCl_6$ were also