to the participation of states with a strong charge-transfer character.

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Registry No. phen, 66-71-7; $Cr(phen)_3^{3+}$, 15276-16-1; $Cr(phen)_2(OH_2)_2^{3+}$, 47667-82-3.

Contribution from the Departement de Physico-Chimie, Centre d'Etudes Nucléaires de Saclay,
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Preparation and Characterization of $Ni(BiF_6)_2$ and of the Ternary Adducts $[Ni(CH_3CN)_6](BiF_6)_2$ and $[Ni(CH_3CN)_6](SbF_6)_2$. Crystal Structure of $[Ni(CD_3CN)_6](SbF_6)_2$

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$Ni(BiF_6)_2$ was prepared from the reaction of NiF_2 with BiF_5 in anhydrous HF, followed by removal of the excess of BiF_5 by sublimation. The compound was characterized by elemental analysis, X-ray powder data, and vibrational spectroscopy. Both $Ni(BiF_6)_2$ and $Ni(SbF_6)_2$ react with acetonitrile to give ternary adducts of the formula $NiF_2{\cdot}2MF_5{\cdot}6CH_3CN$, with M = Bi or Sb. These isomorphous adducts are stable at room temperature and were characterized by elemental analyses, X-ray powder data, and infrared and electronic spectroscopy. In these ternary adducts the Ni^{2+} ion is octahedrally coordinated by six acetonitrile molecules via the nitrogen, and the counterions are MF_6^-. The $[Ni(CD_3CN)_6](SbF_6)_2$ complex was characterized by X-ray diffraction methods, crystallizing in the trigonal space group $R\bar{3}$ with $a = 11.346$ (3) Å, $c = 17.366$ (6) Å, $V = 1936$ Å^3, $Z = 3$, and $R = 0.034$. The Sb atoms lie on C_3 sites and are octahedrally coordinated by six F atoms with two nonequivalent Sb–F distances of 1.80 (1) and 1.83 (1) Å. The octahedrally coordinated Ni atoms lie on C_{3i} sites with Ni–N distances of 2.07 (1) Å. It is shown that coordination of the Ni^{2+} ions by six CH_3CN molecules lessens the strong polarizing effect of these ions on the MF_6^- counterions, which had been found for the $Ni(MF_6)_2$ salts, and reduces their distortion from octahedral symmetry.

Introduction

The preparation and characterization of $Ni(SbF_6)_2$ have been described in a recent paper,[2] and preliminary results concerning $Ni(BiF_6)_2$ and the acetonitrile adducts of both salts have been presented at a meeting.[3] This paper gives a full report on the preparation and characterization of $Ni(BiF_6)_2$ and the acetonitrile adducts. The previous formulation[2] of $NiF_2{\cdot}2SbF_5{\cdot}6CH_3CN$ as $[Ni(CH_3CN)_6]^{2+}(SbF_6^-)_2$ was confirmed by elemental analysis, vibrational and electronic spectroscopy, and a crystal structure determination. Furthermore, it was interesting to determine how coordination of the Ni^{2+} ion by CH_3CN influences its interaction with the MF_6^- counterions.

Experimental Section

Apparatus. Volatile materials were manipulated in an all-metal vacuum line equipped with Teflon or metal valves. Solid products were handled in a glovebox flushed with dry nitrogen. The high-pressure reactor used has previously been described.[4] Infrared spectra were recorded in the range 4000–200 cm^{-1} on a Perkin-Elmer Model 283 spectrophotometer. Spectra of solids were obtained by using dry powders pressed between AgCl or AgBr windows in an Econo press (Barnes Engineering Co.). The low-frequency parts of the spectra were also recorded as halocarbon (Voltalef) or Nujol mulls between silicon plates. Raman spectra were recorded on a Coderg Model T 800 spectrophotometer by using the 514.5-nm exciting line of an Ar ion Spectra Physics laser or the 647.1-nm exciting line of a Kr ion Spectra Physics laser. Sealed quartz capillaries were used as sample containers in the transverse-viewing–transverse-excitation mode. Low-temperature spectra were obtained with a Coderg liquid-nitrogen cryostat and a Coderg RC 200 regulator. The electronic absorption spectra were recorded on a Beckman UV 5240 spectrophotometer, the solution being contained in a 1 mm thick quartz cell fitted with a Teflon-TFE Rotaflo stopcock. X-ray diffraction powder patterns of the samples sealed in 0.3 mm o.d. quartz capillaries were obtained by using a Phillips camera (diameter 11.46 cm) using Ni-filtered Cu *Kα* radiation. Crystals suitable for structure determination were transferred into quartz capillaries in the drybox.

Materials. Anhydrous nickel difluoride[5] was obtained by the treatment of nickel acetate with HF at 270 °C followed by fluorination with F_2 at 200 °C. Bismuth and antimony trifluorides were from Ozark Mahoning Co., and their purities were checked by infrared spectroscopy and X-ray diffraction. Fluorine (Union Carbide Co.) was passed over NaF pellets to remove HF. Bismuth pentafluoride was prepaed by the reaction of BiF_3 with F_2 at 350 °C at a pressure of 20 atm. Acetonitrile (Prolabo) and acetonitrile-d_3 (CEA) were refluxed over P_2O_5 followed by treatment and storage on 5A molecular sieves. The adduct $Ni(SbF_6)_2$ was prepared as described previously[2] except that NiF_2 and SbF_3 were used instead of Ni and SbF_5, respectively. Microanalyses were by Analytische Laboratorien, Elbach, West Germany.

Preparation of $Ni(BiF_6)_2$. A mixture of NiF_2 (2.57 mmol) and BiF_5 (5.15 mmol) was loaded in the drybox into half of a prepassivated Teflon double-U metathesis apparatus.[6] Dry HF (≈10 mL) was added on the vacuum line to the half containing NiF_2–BiF_5, and the resulting mixture was stirred for 6 h at 25 °C. The metathesis apparatus was inverted, and the resulting solution, pressurized by 2 atm of dry nitrogen, was filtered into the other half of the apparatus. The HF solvent was pumped off for 12 h at 25 °C, leaving 1.4749 g of a pale yellow solid. The X-ray powder diffraction patterns indicated that this solid consisted of a mixture of $Ni(BiF_6)_2$ and BiF_5 and that the filter cake contained NiF_2 and $Ni(BiF_6)_2$. The solid residue obtained from the evaporation of the solution was ground and loaded in the drybox into a prepassivated 30 cm long sapphire tube, which was connected to an aluminum valve by a Swagelock compression fitting using Teflon ferrules. The lower part of the tube was

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(1) (a) Centre d'Etudes Nucléaires de Saclay. (b) Rocketdyne.

(2) Christe, K. O.; Wilson, W. W.; Bougon, R.; Charpin, P. *J. Fluorine Chem.* **1987**, *34*, 287.

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(4) Hagenmuller, P. *Preparative Methods in Solid State Chemistry*: Academic: New York and London, 1972; p 423.

(5) Sample kindly supplied to us by M. Bergez, CEA/IRDI.

(6) Christe, K. O.; Schack, C. J.; Wilson, R. D. *Inorg. Chem.* **1977**, *16*, 849.

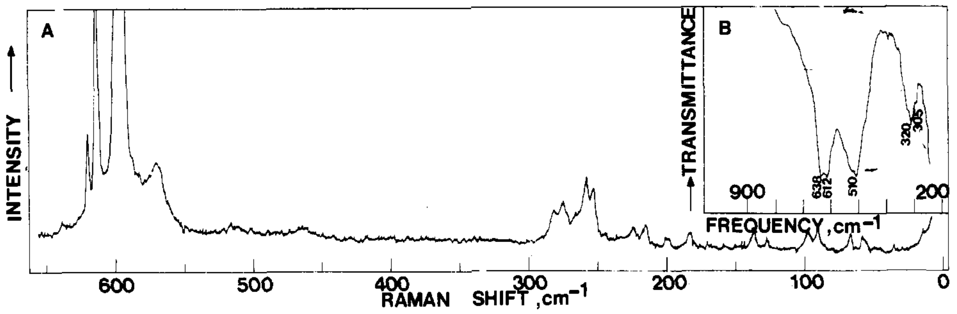

Figure 1. Vibrational spectra of $Ni(BiF_6)_2$.

Table I. X-ray Powder Data for $Ni(BiF_6)_2$

d, Å	intens	*d*, Å	intens
4.67	m	1.883	m
4.21	s	1.854	vw
		1.826	w
3.75	s		
3.68	m	1.742	w
		1.734	ms
2.77	w	1.717	vw
2.74	m		
		1.661	m
2.55	m	1.630	m
2.387	mw		
2.357	w	1.515	mw
		1.504	w
2.252	m	1.475	m
2.241	m	1.445	w
		1.411	w
2.189	mw	1.376	w
2.109	m	1.343	mw

heated for 17 h at 100 °C with pumping. The solid that had sublimed onto the wall of the tube was identified as BiF_5 whereas the X-ray pattern and the vibrational spectra showed that the solid residue in the bottom of the tube (0.757 g) contained only $Ni(BiF_6)_2$.

Anal. Calcd for $Ni(BiF_6)_2$: Ni, 8.33; Bi, 59.32; F, 32.35. Found: Ni, 8.27; Bi, 60.65; F, 30.41.

Preparation of $[Ni(CH_3CN)_6]^{2+}(MF_6^-)_2$ (M = Sb or Bi). The $Ni(MF_6)_2$ salts, typically on a 1–5 mmol scale, were loaded in the drybox into the Teflon double-U metathesis apparatus.[6] Approximately 10 mL of CH_3CN or CD_3CN was condensed at −196 °C onto the $Ni(MF_6)_2$; the mixture was warmed to 20 °C and stirred for 2 h. The blue solutions were filtered into the second half of the apparatus. Upon solvent removal in vacuo, the solutions yielded purple crystals of $[Ni(CH_3CN)_6](MF_6)_2$.

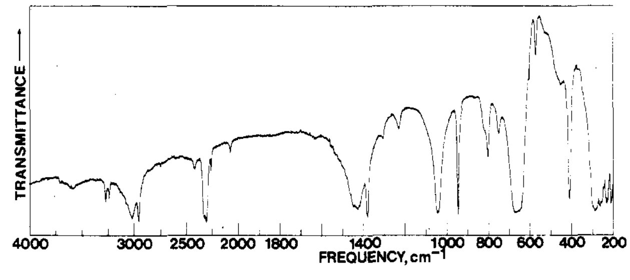

Figure 2. Infrared spectrum of $[Ni(CH_3CN)_6](SbF_6)_2$.

Single crystals of $[Ni(CD_3CN)_6](SbF_6)_2$ were grown from these solutions by slow evaporation of some of the solvent.

Anal. Calcd for $Ni(CH_3CN)_6(SbF_6)_2$: C, 18.56; H, 2.34; N, 10.82; F, 29.36; Sb, 31.36; Ni, 7.56. Found: C, 18.53; H, 2.32; N, 10.79; F, 29.31; Sb, 31.67; Ni, 7.59.

Anal. Calcd for $Ni(CH_3CN)_6(BiF_6)_2$: C, 15.16; H, 1.91; N, 8.84; F, 23.97; Bi, 43.95; Ni, 6.17. Found: C, 15.15; H, 1.86; N, 8.80; F, 22.85; Bi, 44.55; Ni, 6.20.

Results and Discussion

Synthesis of $Ni(BiF_6)_2$. The combination of NiF_2 with an excess of either BiF_5 at 160 °C in a Teflon FEP tube or $BiF_3 + F_2$ at 240 °C in an alumina crucible, contained in a Monel reactor, did not produce pure $Ni(BiF_6)_2$. The solid products were always contaminated with excess BiF_5 and to some extent NiF_2 and/or BiF_3. The NiF_2 impurity was removed by anhydrous HF in which NiF_2 is insoluble. Any excess of BiF_5 was removed by vacuum sublimation at 100 °C. In this manner pure $Ni(BiF_6)_2$ was obtained.

Table II. Vibrational Frequencies and Assignments for $Ni(BiF_6)_2$

obsd freq, cm⁻¹ (rel intens[a])			assignment	
	Raman			
IR	28 °C	−196 °C		
638 vs	639 (0+)	639 (2)	$\nu_{as}(BiF_3)$ out of phase	nonbridging BiF_3 stretching modes
612 vs	619 sh	621 (11)	$\nu_{as}(BiF_3)$ in phase	
	613 (33)	615 (33)	$\nu_{sym}(BiF_3)$ out of phase	
	596 (100)	596 (100)	$\nu_{sym}(BiF_3)$ in phase	
	569 sh	571 (10)	$\nu_{sym}(BiF_3)$ out of phase	bridging BiF_3 stretching modes
510 vs		517 (1)	$\nu_{as}(BiF_3)$ out of phase	
305 sh			Ni···FBi stretching	
320 ms				
		283 (4)	Bi–F deformations	
	275 sh	276 (5)		
	261 (6)	259 (8)		
		254 (6)		
	225 (3)	225 (2)		
215 ms		216 (2)		
		201 (0+)		
	181 (0+)	184 (3)		
		138 (3)		
	123 (1)	128 (1)		
	95 (3)	99 (3)	Ni···F deformations or lattice modes	
		91 (3)		
	64 (3)	68 (2)		
	59 (3)	59 (2)		

[a] Uncorrected Raman intensities based on relative peak heights.

Table III. Electronic Absorption Data for $[Ni(CH_3CN)_6](SbF_6)_2$ in CH_3CN Solution

band max, cm^{-1}	ϵ_{max}, L mol^{-1} cm^{-1}	assignment
10430	40	$\Gamma_5(^3F) \leftarrow \Gamma_2(^3F)$
13910	9	$\Gamma_3(^1D) \leftarrow \Gamma_2(^3F)$
17120	35.4	$\Gamma_4(^3F) \leftarrow \Gamma_2(^3F)$
22990	weak sh	$\Gamma_5(^1D) \leftarrow \Gamma_2(^3F)$
27400	52.6	$\Gamma_4(^3P) \leftarrow \Gamma_2(^3F)$

X-ray Diffraction Data. The X-ray power diffraction data for $Ni(BiF_6)_2$, which are listed in Table I, indicate that the structure of this compound is very similar to that[2] of $Ni(SbF_6)_2$. Nevertheless, a splitting of some of the lines indicate that the symmetry is probably lowered, so that not all lines could be assigned in the hexagonal system proposed[2] for $Ni(SbF_6)_2$.

Vibrational Spectra. The observed infrared and Raman spectra of $Ni(BiF_6)_2$ are shown in Figure 1, and the frequencies are summarized in Table II. As discussed[2] for $Ni(SbF_6)_2$, the spectra clearly indicate that the MF_6^- anion is not octahedral but is strongly distorted, and that both bridging and nonbridging fluorines are present. The assignments given in Table II are based on those[2] previously proposed for $Ni(SbF_6)_2$.

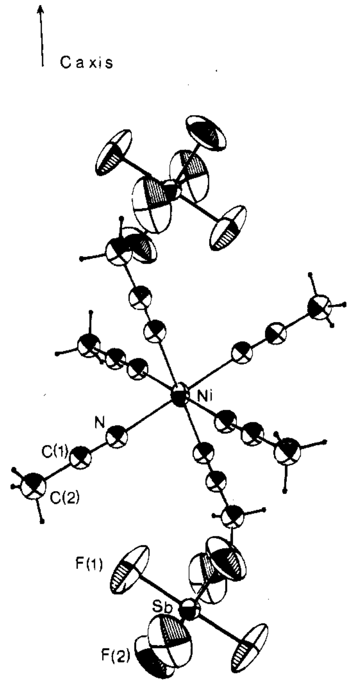

Figure 3. ORTEP[13] drawing of the molecular unit $[Ni(CD_3CN)_6](SbF_6)_2$.

Syntheses and Properties of the $[Ni(CH_3CN)_6](MF_6)_2$ Adducts. The $Ni(MF_6)_2$ salts, where M = Sb or Bi, are very soluble in CH_3CN and form bright blue solutions containing the $[Ni(CH_3CN)_6](MF_6)_2$ adducts. The electronic absorption spectra of these solutions are characteristic of an octahedrally coordinated Ni^{2+} ion and are quite comparable to those reported[7,8] for $[Ni(CH_3CN)_6]^{2+}(BF_4^-)_2$. The data obtained from the spectrum of $[Ni(CH_3CN)_6]^{2+}(SbF_6^-)_2$ are summarized in Table III. A strong

Table IV. Infrared Data (cm^{-1}) for $[Ni(CH_3CN)_6]^{2+}(SbF_6^-)_2$, $[Ni(CH_3CN)_6]^{2+}(BiF_6^-)_2$, and $[Ni(CD_3CN)_6]^{2+}(SbF_6^-)_2$

Fundamental Modes of Free[a] and Coordinated CH_3CN (CD_3CN)

CH_3CN[a]	$[Ni(CH_3CN)_6]^{2+}$-$(SbF_6^-)_2$	$[Ni(CH_3CN)_6]^{2+}$-$(BiF_6^-)_2$	CD_3CN[a]	$[Ni(CD_3CN)_6]^{2+}$-$(SbF_6^-)_2$	assignment
2942	2946	2949	2115	2114	$\nu_1(A_1)$ sym $CH_3(D_3)$ str
2252	2299	2299	2259	2308	$\nu_2(A_1)$ C≡N str
1374	1373	1374	1102	1104	$\nu_3(A_1)$ sym $CH_3(D_3)$ def
919	942	945	832	858	$\nu_4(A_1)$ C—C str
3001	3012	3012	overlapped with ν_2	2257	$\nu_5(E)$ asym $CH_3(D_3)$ str
1415	1422	1429	1036	1034	$\nu_6(E)$ asym $CH_3(D_3)$ def
1039	1040	1039	848	overlapped with ν_4	$\nu_7(E)$ $CH_3(D_3)$ rock
378	412	412	347	382	$\nu_8(E)$ C—C≡N bend

Combination Modes of Coordinated $CH_3CN(CD_3CN)$

$[Ni(CH_3CN)_6]^{2+}$-$(SbF_6^-)_2$	$[Ni(CH_3CN)_6]^{2+}$-$(BiF_6^-)_2$	assignment	$[Ni(CD_3CN)_6]^{2+}$-$(SbF_6^-)_2$	assignment
3268	3267	$2\nu_4 + \nu_3$	3420	$\nu_2 + \nu_3$
3232	3239	$\nu_2 + \nu_4$	3282	$\nu_5 + \nu_6$
2740	2738	$2\nu_3$	3167	$\nu_1 + \nu_6$, $\nu_2 + \nu_4$, $\nu_2 + \nu_7$
			3120	$\nu_5 + \nu_7$, $\nu_4 + \nu_5$
			2957	$\nu_1 + \nu_4$, $\nu_1 + \nu_7$
2412	2420	$\nu_3 + \nu_7$, $\nu_6 + \nu_7$	2917	$2\nu_6 + \nu_4$
2320	2321	$\nu_3 + \nu_4$	1949	$\nu_3 + \nu_4$, $\nu_3 + \nu_7$
2252	2254	$2\nu_8 + \nu_6$	1880	$\nu_4 + \nu_6$, $\nu_6 + \nu_7$
2072	2070	$2\nu_7$	1725	$2\nu_4$, $2\nu_7$, $\nu_4 + \nu_7$
			1460	$\nu_3 + \nu_8$
819	820	$2\nu_8$		
800	799	?	743	$2\nu_8$

XF_6^- Modes (X = Sb, Bi)

$[Ni(CH_3CN)_6]^{2+}(SbF_6^-)_2$	$[Ni(CH_3CN)_6]^{2+}(BiF_6^-)_2$	$[Ni(CD_3CN)_6]^{2+}(SbF_6^-)_2$	assignment[b]
1306	1150	1304	$\nu_1 + \nu_3$
1228	1100	1226	$\nu_2 + \nu_3$
750	659		$\nu_2 + \nu_6$
			$\nu_1(A_{1g})$
665	570	668 sh 654	$\nu_3(F_{1u})$
570		568	$\nu_2(E_g)$
450			$\nu_5 + \nu_6$?
288	215	288	$\nu_4(F_{1u})$
270			$\nu_5(F_{2g})$

[a] Liquid at 35 °C.[10] [b] Assignment based on space group O_h. See text.

Table V. Crystal Data

formula	$C_{12}D_{18}F_{12}N_6NiSb_2$
fw	794.6
crystn solvent	acetonitrile-d_3
cryst syst	trigonal
space group	$R\bar{3}$
cryst dimens, mm	0.300 × 0.200 × 0.050
cryst color	purple
lattice params	
a, Å	11.346 (3)
c, Å	17.366 (6)
Z	3
V, Å^3	1936
d_{calcd}, g cm^{-3}	2.045
radiation	Mo Kα (λ = 0.7107 Å), graphite monochromator
μ(Mo Kα), cm^{-1}	29.1
temp, K	295
instrument	Enraf-Nonius CAD 4
ω range, deg	2–40
octants	h,k,l (0 to +10, 0 to +10, 0 to +16)
no. of collcd data	256
no. of data with $\sigma(I)/I < 0.33$	148
no. of params	45
data/variable ratio	5.7
resolution programs	SDP 80 program package, Enraf-Nonius, Delft, The Netherlands
scattering factor (f', f'') sources	a
structure soln	heavy-atom method
$R(F)$	(0.035)
$R_w(F)$	(0.042)
w	$4F_o^2/\sigma(I_o)^2 + (pF_o^2)$ with $p = 0.04$
function used in the least-squares refinement	$\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
deuterium atoms	in calcd positions, riding on their C atoms, with thermal param $B_H = 15B_c$

[a] *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Tables 2-2B and 2-3-1.

Table VI. Positional and Thermal Parameters for $[Ni(CD_3CN)_6](SbF_6)_2$

atom	x	y	z	B,[a] Å^2
Sb	0.000	0.000	0.3293 (1)	4.01 (3)*
F(1)	−0.131 (1)	−0.002 (2)	0.3891 (7)	14.1 (5)*
F(2)	−0.131 (1)	−0.129 (1)	0.2669 (7)	13.3 (5)*
Ni	0.000	0.000	0.000	2.38 (8)*
N	0.149 (1)	0.151 (1)	−0.0675 (6)	3.9 (3)
C(1)	0.241 (1)	0.243 (1)	−0.1012 (9)	4.1 (4)
C(2)	0.349 (1)	0.348 (1)	−0.1419 (9)	4.5 (4)
D(1)	0.317	0.387	−0.179	6.8
D(2)	0.407	0.416	−0.107	6.8
D(3)	0.398	0.311	−0.167	6.8

[a] Starred values denote anisotropically refined atoms for which $B_{equiv} = {}^4/_3\sum_{ij}\beta_{ij}\bar{a}_i\bar{a}_j$.

Table VII. Interatomic Distances (Å) and Angles (deg)

	$[Ni(NCCD_3)_6]^{2+}$ Octahedron		
Ni–N	2.07 (1)	C(1)–C(2)	1.40 (2)
N–C(1)	1.20 (2)		
Ni–N–C(1)	175 (2)	N–C(1)–C(2)	179 (2)
	SbF_6^- Octahedron		
Sb–F(1)	1.80 (1)	Sb–F(2)	1.83 (1)
F(1)–Sb–F(1)	90.2 (6)	F(1)–Sb–F(2)	91.7 (7)
F(1)–Sb–F(2)	89.7 (6)	F(1)–Sb–F(2)	178.2 (7)
F(2)–Sb–F(2)	88.5 (7)		

band at 46 510 cm^{-1}, which is not included in Table III, is assigned to a charge transfer. The value of the ligand field splitting (10*Dq*)[9] was found from the $\Gamma_5(^3F) \leftarrow \Gamma_2(^3F)$ transition to be equal to 10 430 cm^{-1}.

The acetonitrile adducts and their solutions are stable at room temperature. Owing to their absorption range, which includes the wavelengths of the laser exciting lines used for Raman spectroscopy, no Raman spectra of these adducts were obtained. However, information regarding the molecular arrangement could be obtained from the infrared spectra alone since they displayed sharp and well-defined bands (see Figure 2 and Table IV).

The positions of the ligand bands are as expected[7] for coordinated acetonitrile. Compared to those for free acetonitrile,[10] the bands assigned to the C—C≡N skeletal modes, ν_2, ν_4, and ν_8, show the expected[7,11] frequency increase while the remaining modes are essentially unshifted. The remaining bands in the infrared spectra can be assigned to the MF_6^- anions.[12] According to the crystal structure (see below), the site symmetry of the SbF_6^- anion is C_3, which implies that the modes coresponding to $\nu_3(F_{1u})$, $\nu_4(F_{1u})$, $\nu_5(F_{2g})$, and $\nu_6(F_{2u})$ of O_h symmetry each might be split into two components of symmetry A and E, which are active in both the Raman and infrared.[2] The number of infrared bands, their contours, and relative intensities indicate that the octahedral symmetry of the MF_6^- anions is indeed lower than O_h in these adducts but that the distortion is considerably less than that observed for the $Ni(MF_6)_2$ salts. This is not surprising in view of the fact that the polarizing strength and hardness of the Ni^{2+} acid is greatly diminished by surrounding it with six bulky CH_3CN ligands, which isolate the Ni^{2+} cations from the MF_6^- anions.

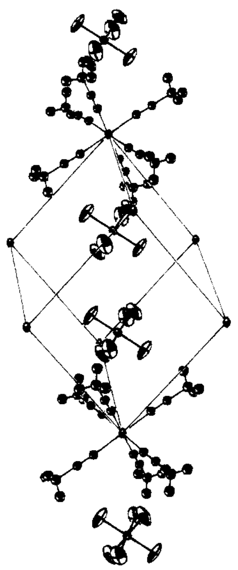

Figure 4. View of the molecular packing of $[Ni(CD_3CN)_6](SbF_6)_2$.

Crystal Structure. The molecular stereochemistry of the ternary adducts was established by a single-crystal study of the adduct $[Ni(CD_3CN)_6]^{2+}(SbF_6^-)_2$. Crystal data are given in Table V. Final positional and thermal parameters are given in Table VI with their estimated standard deviations. The relevant distances and angles are given in Table VII. Figure 3 shows the molecular unit and atomic labeling scheme, and Figure 4 gives a view of the molecular packing.[13] Both ions have octahedral geometry. In $[Ni(CD_3CN)_6]^{2+}$, the Ni atom lies on a C_{3i} symmetry and the six nitrogen atoms form a slightly compressed octahedron with

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(7) Reedijk, J.; Groeneveld, W. L. *Recl. Trav. Chim. Pays-Bas* **1967**, *86*, 1103.

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(10) Shimanouchi, T. *Natl. Stand. Ref. Data Ser.* (*U.S., Natl. Bur. Stand.*) *NSRDS-NBS 39*, 84. Pace, E. L.; Noe, L. W. *J. Chem. Phys.* **1968**, *49*, 5317.

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(12) Reedijk, J.; Zuur, A. P.; Groeneveld, W. L. *Recl. Trav. Chim. Pays-Bas* **1967**, *86*, 1127 and references therein.

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the two N–N distances being significantly different: 2.95 (2) Å and 2.89 (2) Å. The SbF_6^- anion has only a C_3 symmetry and hence two independent F atoms: Sb–F(1) = 1.80 (1) Å; Sb–F(2) = 1.83 (1) Å. The F–F distances are equal: F(1)–F(1) = 2.55 (2) Å; F(2)–F(2) = 2.56 (2) Å; F(1)–F(2) = 2.57 (2) Å. Thus, in spite of the two nonequivalent F atoms, Sb lies in a nearly regular octahedron.

Conclusion. The results of this study show that the corrosion products formed in high-temperature fluorination reactions involving BiF_5 in nickel or Monel reactors are analogous to those[2] found for SbF_5. In the formed $Ni(MF_6)_2$ products the MF_6^- anions are strongly distorted by the strong polarizing effect of the small, doubly charged Ni^{2+} cations and the resulting strong fluorine bridging. Basic ligands with good donor properties, such as CH_3CN, can add to the Ni^{2+} cations and form ternary adducts of the composition $[Ni(CH_3CN)_6](MF_6)_2$. The increased size and softness of the new cations diminishes the strong polarizing effect of the Ni^{2+} cations on the MF_6^- anions in the $Ni(MF_6)_2$ type compounds.

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Note Added in Proof. After submission of this paper, the results of an independent crystal structure determination of $[Ni(CH_3CN)_6](SbF_6)_2$ have been published by: Leban, Gantar, Frlec, Russell, and Holloway, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1987**, *43*, 1888.

Registry No. $Ni(BiF_6)_2$, 112817-17-1; NiF_2, 10028-18-9; BiF_5, 7787-62-4; $[Ni(CH_3CN)_6]^{2+}(SbF_6^-)_2$, 69102-75-6; $[Ni(CH_3CN)_6]^{2+}(BiF_6^-)_2$, 112817-18-2; $[Ni(CD_3CN)_6](SbF_6)_2$, 112839-66-4.

Supplementary Material Available: Tables of bond distances, bond angles, atomic positional parameters, anisotropic thermal parameters, and lattice constants and space group (7 pages); a table of calculated and observed structure factors (2 pages). Ordering information is given on any current masthead page.

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Luminescence Spectra and Lifetimes of Cerium(III) Compounds as Indicators of Solution Behavior and Radiative Efficiency

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The luminescence spectra and radiative lifetimes of a number of cerium(III) organometallics and halide compounds have been obtained by using a picosecond laser single-photon-counting system. These spectra, which can be determined for solids or solutions, are very useful for determining the exact nature of organocerium species in solution. Herein we report the solution behavior of some bis(pentamethylcyclopentadienyl)cerium compounds, including the tendency of $[K(THF)_2][(C_5Me_5)_2CeI_2]$ (**1**) to adopt a $(C_5Me_5)_2CeIL_n$ solution structure in either THF (n = 1) or CH_3CN (n = 2). While crystallization from THF regenerates the salt adduct **1**, the salt-free material $(C_5Me_5)_2Ce(I)(NCCH_3)_2$ (**3**) crystallizes from CH_3CN in high yield. A crystallographic study of **3** shows that the compound adopts a highly distorted trigonal bipyramidal solid-state geometry with axial nitrile ligands; the steric bulk of the C_5Me_5 rings causes the nitriles to bend toward the iodide. Crystal data: space group *Pnab*, $a = 13.952$ (3) Å, $b = 14.768$ (3) Å, $c = 12.831$ (3) Å, $V = 2643.59$ Å^3, $Z = 4$ (−150 °C). Lastly, the study of lifetimes has revealed a correlation between luminescence energy and lifetime, in accord with theoretical predictions. This correlation holds for a wide range of compounds, indicating that most of them have a high radiative efficiency (ca. 1); a noteworthy exception is **3**, which has a radiative efficiency of ca. 0.02. The presence of nonradiative decay channels resulting from the structural characteristics of **3** is considered.

Introduction

Recently we reported the luminescence spectra of a series of cerium(III) organometallic and halide compounds.[1] All of the cerium(III) compounds we have studied to date exhibit such emissions, and we noted a strong dependence of luminescent wavelength on the nature of the ligand sphere. As such, halide complexes such as $CeX_3(THF)_x$ (X = Cl, I; x = 3, 4) emit at higher energies (ca. 350 nm) while bis(pentamethylcyclopentadienyl)cerium(III) species (e.g. $[Li(Et_2O)_2][(C_5Me_5)_2CeX_2]$) were found to emit at lower energies (ca. 550–600 nm). The compounds typically show two broad bands in their emission spectra, which are assigned to emission from the lowest ^2D excited-state component to the two spin–orbit components of the ground state, $^2F_{5/2}$ and $^2F_{7/2}$.[2] The energetic separation of these emission bands (ca. 2000 cm^{-1}) reflects the magnitude of the ground-state splitting; the relative constancy from one compound to another indicates that the f orbitals are largely unaffected by the nature of the ligand sphere. However, the wide range of emission energies exhibited across the series of compounds (ca. 350–600 nm) illustrates that the energies of the excited ^2D states vary considerably as a function of ligand sphere. In this regard cerium(III) is very different from other trivalent lanthanides that are known to luminesce as a result of f–f transitions;[3] the latter are considerably less sensitive to the nature of the ligand sphere.

The cerium(III) emissions can also be used empirically to gather information regarding the nature of the medium in which the compound is located. This can be highly useful since most of the trivalent lanthanides are paramagnetic,[4] and thus NMR studies are of limited utility. Moreover, the luminescence method operates in a time regime which is considerably shorter than that of the NMR experiment. As such, we presented data in our previous paper[1] regarding the spectra of compounds such as $[Li][(C_5Me_5)_2CeCl_2]$ and $(C_5Me_5)CeI_2(THF)_3$ in various solvents as well as the solid state; substantial differences were noted as a

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