

## Synthesis, Structure, Spectroscopy, and Magnetism of Transition-Metal Compounds with Bridging Hexafluorosilicate Groups. Crystal and Molecular Structure of *catena*-( $\mu$ -Hexafluorosilicato)tetrakis(*N*-vinylimidazole)cobalt(II)

RENÉ A. J. DRIESSEN, FRANS B. HULSBERGEN, WILLEM J. VERMIN, and JAN REEDIJK\*

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A new class of linear-chain compounds containing the  $\text{SiF}_6^{2-}$  ion as a bridging ligand is described. The compounds have the general formula  $\text{M}(\text{viz})_4\text{SiF}_6$ , with  $\text{M} = \text{Mn, Fe, Co, Ni, Cu, and Zn}$  and with  $\text{viz} = N$ -vinylimidazole. The compounds are prepared by addition of  $\text{viz}$  to alcoholic solutions containing metal(II) hexafluorosilicate in the ratio 4:1. Spectroscopic properties of the compounds agree with the chromophore  $\text{MnF}_2$ , most likely having a *trans* geometry. Detailed study of the magnetic susceptibility in the region 4–90 K shows the metal ions to be weakly antiferromagnetically coupled. Such a coupling is not observed for the Ni(II) compound, where the presence of a positive zero-field splitting of the ground-state triplet prevents the observation of any magnetic coupling. The X-ray structure of  $\text{Co}(\text{viz})_4\text{SiF}_6$  shows that Co(II) has a tetragonal coordination geometry, consisting of four equatorially coordinated *N*-vinylimidazole ligands and two F atoms belonging to different  $\text{SiF}_6^{2-}$  anions. The  $\text{SiF}_6$  groups connect the  $\text{Co}(\text{viz})_4^{2+}$  ions by forming strictly linear chains with a sequence  $-\text{F}-\text{Co}-\text{F}-\text{Si}-$ . The compound crystallizes in the tetragonal space group  $P4_2/n$ , with  $a = 12.594$  (3) Å and  $c = 7.683$  (2) Å and two formula units per unit cell. The structure was solved by standard heavy-atom techniques and refined by least-squares techniques. The residual *R* factor was 0.033 for 533 independent reflections considered as observed ( $I > 2\sigma(I)$ ). Intensities were measured on an automatic four-circle diffractometer with use of Mo  $K\alpha$  radiation. Bond distances are  $\text{Co}-\text{N} = 2.097$  (2),  $\text{Co}-\text{F} = 2.143$  (2),  $\text{Si}-\text{F}_{\text{eq}} = 1.667$  (1), and  $\text{Si}-\text{F}_{\text{ax}} = 1.699$  (2) Å. All bond angles for Co and Si are close to 90 and 180°.

### Introduction

Coordination compounds of transition-metal hexafluorosilicates have obtained little attention in the literature.<sup>1,2</sup> In fact metal(II) hydrates form the only thoroughly studied class of compounds.<sup>1</sup> These compounds with formula  $\text{M}(\text{H}_2\text{O})_6\text{SiF}_6$  form stable crystal lattices, based on the CsCl lattice, in which the cations and the anions are held together by  $\text{OH}\cdots\text{F}$  hydrogen bonds.<sup>1</sup>

In attempts to prepare fluoro-bridged Co(II) compounds in the presence of  $\text{BF}_4^-$  and *N*-vinylimidazole, it was found that crystals of approximate composition " $\text{Co}(\text{viz})_4\text{F}_6$ " separated ( $\text{viz} = N$ -vinylimidazole). The crystals were analyzed by X-ray diffraction to obtain structural information about this product.

Much larger amounts of this compound and of related compounds with Mn(II), Fe(II), Ni(II), Cu(II), and Zn(II) could be prepared when  $\text{SiF}_6^{2-}$  was added. The present paper describes the detailed synthesis of these compounds, the characterization by spectroscopic methods, the X-ray crystal structure of the Co(II) compound, and a low-temperature magnetic susceptibility study to investigate the magnetic exchange interactions in these compounds.

### Experimental Section

**Starting Materials.** Metal(II) tetrafluoroborates and  $\text{H}_2\text{SiF}_6$  were used as commercially available. *N*-Vinylimidazole (BASF, FRG) was used without further purification. Metal(II) carbonates were used as the anhydrous powders. Metal(II) hexafluorosilicates were prepared as aqueous solutions from a 30%  $\text{H}_2\text{SiF}_6$  solution, to which small amounts of  $\text{MCO}_3$  were added up to the molar ratio of 1:1. The final concentration of the metal was determined by complexometric titration.

**Synthesis and Crystal Growth.** The synthesis of  $\text{Co}(\text{viz})_4\text{SiF}_6$  ( $\text{viz} = N$ -vinylimidazole) is given as a typical example. Two milliliters of an aqueous solution of  $\text{CoSiF}_6$  (containing 2.5 mmol) is dissolved in 400 mL of absolute ethanol and 20 mL of triethyl orthoformate (for dehydration) and heated to boiling. After that a solution of 0.94 g of *N*-vinylimidazole (10 mmol) in 50 mL of boiling absolute ethanol is added. The pink solution so obtained is slowly cooled, upon which pink crystals separate. The crystals are washed with ethanol and

diethyl ether and finally dried in vacuo at 40 °C; yield 80%. Similarly, the corresponding compounds with Mn(II), Fe(II), Ni(II), Cu(II), and Zn(II) were prepared.

The single crystal of  $\text{Co}(\text{viz})_4\text{SiF}_6$  used for the crystal structure determination was grown before from a solution of  $\text{Co}(\text{BF}_4)_2$  and  $\text{viz}$  in ethanol containing small amounts of  $\text{SiF}_6^{2-}$ .

**Characterization.** The compounds were characterized by chemical analysis. Metal determinations were carried out complexometrically with EDTA. Carbon, hydrogen, nitrogen and fluorine were determined by Dr. Pascher, Bonn, Federal Republic of Germany, and the formula  $\text{M}(\text{viz})_4\text{SiF}_6(\text{H}_2\text{O})_n$ ,  $n = 0-1$ , was determined. Infrared spectra were recorded on a Perkin-Elmer 580 instrument, with use of KBr disks and Nujol mulls (4000–250  $\text{cm}^{-1}$ ). Spectra in the far-IR region were obtained from pressed disks in polythene with a Beckman IR-720 interferometer (450–100  $\text{cm}^{-1}$ ). Ligand field spectra (5000–30 000  $\text{cm}^{-1}$ ) were recorded as diffuse-reflectance spectra on a Beckman DK-2A ratio-recording spectrometer, with MgO as a reference. ESR spectra were obtained on a Varian E-3 spectrometer operating at X-band frequencies. Magnetic susceptibility measurements were performed on the powdered compounds with a PAR vibrating-sample magnetometer (4–90 K).

**X-ray Data Collection.** A crystal of  $\text{Co}(\text{viz})_4\text{SiF}_6$  of approximate dimensions  $0.45 \times 0.13 \times 0.13$  mm was mounted in a thin-walled glass capillary, which was sealed with solid paraffin. Weissenberg photographs taken with Cu  $K\alpha$  radiation showed the space group to be  $P4_2/n$ . Precise lattice constants were determined by a least-squares refinement of the angular settings of 24 reflections with  $16 < \theta < 18^\circ$ . The cell dimensions are  $a = 12.594$  (3) Å and  $c = 7.683$  (2) Å, with  $V = 1219$  Å<sup>3</sup>. The calculated density of 1.573  $\text{g cm}^{-3}$  is in good agreement with the experimental value of 1.55 (2)  $\text{g cm}^{-3}$  (measured by flotation in chloroform/dibromoethane) for  $Z = 2$ . Intensity data were collected on a Nonius CAD-4 diffractometer for all reflections with  $2 < \theta < 25^\circ$  with use of graphite-monochromated Mo  $K\alpha$  radiation. The scanning rate was adjusted to the required precision of  $\sigma(I) < 0.02I$  with a maximum scan time of 240 s per reflection. Each reflection was measured in 96 steps. Sixteen steps at each end of the scan were considered as background. Intensities  $I$  and their estimated standard deviations  $\sigma(I)$  were calculated from  $I = s[P - 2(B_1 + B_2)]$  and  $\sigma(I) = s[P + 4(B_1 + B_2)]^{1/2}$ , where  $s$  is a factor to account for the variable scan speed,  $P$  is the scan count, and  $B_1$  and  $B_2$  are the low- and high-angle background counts. Three standard reflections were measured after every 5400 s of radiation time, to check for instrumental instability and crystal decomposition; a 13% decrease in intensity was observed during the data collection, and the observed intensities were corrected accordingly. Measurements of the intensities of suitable reflections at different azimuthal positions showed a transmission factor variance of 0.88–0.93, suggesting that no absorption correction was necessary ( $\mu(\text{Mo } K\alpha) = 8.1 \text{ cm}^{-1}$ ). The

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Table I. Positional Parameters ( $\times 10^4$ ) of the Non-Hydrogen Atoms in  $\text{Co}(\text{viz})_4\text{SiF}_6$ 

atom	$x/a$	$y/b$	$z/c$
Co	2500	2500	7500
Si	2500	2500	2500
F(1)	2500	2500	4711 (3)
F(2)	3773 (1)	2138 (2)	2496 (3)
N(1)	1008 (2)	1763 (2)	7581 (5)
N(2)	-461 (2)	1113 (2)	8716 (4)
C(1)	452 (3)	1646 (2)	9021 (5)
C(2)	428 (3)	1268 (3)	6300 (4)
C(3)	-473 (3)	873 (3)	6956 (4)
C(4)	-1263 (2)	852 (2)	9945 (5)
C(5)	-1293 (3)	1222 (3)	11507 (5)

intensities were corrected for Lorentz and polarization effects. A total number of 2251 reflections was measured, which after averaging resulted in 1071 independent reflections, 533 of which were considered as significant, i.e.,  $I > 2\sigma(I)$ .

**Structure Determination and Refinement of  $\text{Co}(\text{C}_5\text{H}_6\text{N}_2)_4\text{SiF}_6$ .** The Patterson synthesis suggested the presence of two metal ions in the unit cell at positions  $1/4, 1/4, 1/4$  and  $1/4, 1/4, 3/4$ . With the assumption of these metal ions to be cobalt, Fourier maps showed the presence of all other non-hydrogen atoms, and full-matrix least-squares refinement with isotropic  $B$  values yielded  $R = 0.13$ .<sup>3</sup> Because of the large  $B$  values found for one of the metal ions and because chemical analysis only showed half of the Co(II) ions, one of the metal positions was considered to be Si, rather than Co. Subsequent full-matrix refinement resulted in  $R = 0.073$  and  $R_w = 0.076$ .<sup>3</sup> Difference Fourier maps revealed the positions of all hydrogen atoms. A final full-matrix refinement with anisotropic thermal parameters for the non-hydrogen atoms and isotropic  $B$  values for hydrogen with fixed C-H distances of 1.0 Å resulted in  $R = 0.033$  ( $R_w = 0.027$ ) for all significant reflections. A final difference Fourier synthesis did not show peaks larger than  $2\sigma(I)$ .

Scattering factors for neutral atoms were taken for all non-hydrogen atoms from ref 4 and were used with a correlation for the real part of the anomalous dispersion,  $\Delta f'$ ; those for cobalt were corrected for the imaginary part of the anomalous dispersion,  $\Delta f''$ . The scattering factors for the hydrogen atoms were taken from Stewart et al.<sup>5</sup> Final atomic parameters for the non-hydrogen atoms are given in Table I. Atomic parameters of the hydrogen atoms are given in the supplementary material, together with the thermal parameters of all atoms and a listing of observed and calculated structure factors.

## Results and Discussion

**General Considerations.** All compounds mentioned above show identical X-ray powder diagrams and very similar infrared spectra. Only the compound with Cu(II) has a different X-ray pattern but again a very similar infrared spectrum. This suggests identical coordination geometries for all metals, except for Cu(II), and this information can be used for the interpretation of the infrared and ligand field spectra of the compounds, based on the crystal structure of the Co(II) compound. The presence of small amounts of H<sub>2</sub>O in the lattice of some preparations (less than 1.0 mol) does not disturb the crystal lattice.

**Description of the Structure of  $\text{Co}(\text{viz})_4\text{SiF}_6$ .** The structure of this compound is depicted in Figure 1, showing the presence of chains built up by  $\text{Co}(\text{viz})_4^{2+}$  and  $\text{SiF}_6^{2-}$  ions, attached to each other via Co-F-Si bonds. The chains have the atomic ordering -F-Co-F-Si-. These linear chains are even better seen from the projection of the structure along the  $c$  axis, showing the packing of the isolated chains (Figure 2). From this packing picture it is further seen that the  $\text{SiF}_6^{2-}$  groups have their equatorial F atoms staggered with respect to the vinylimidazole ligands (N(1)-Co-Si-F(2) angle 42.2°).

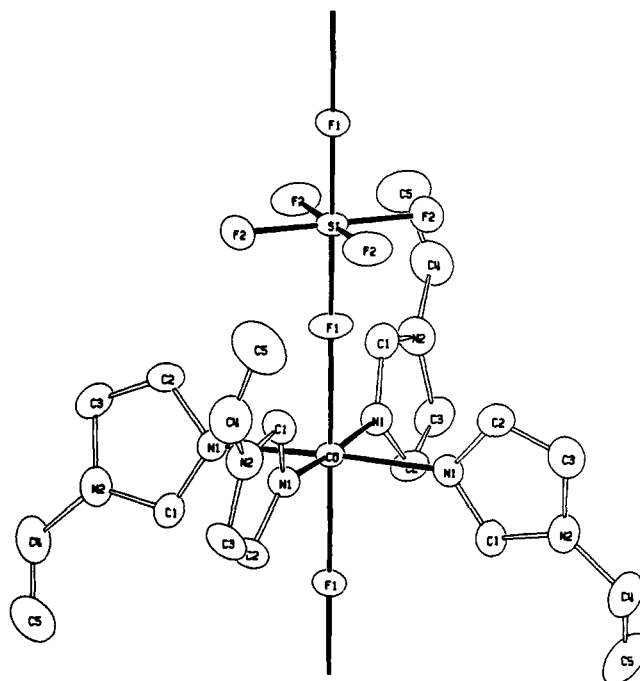


Figure 1. Drawing of one structural unit of  $\text{Co}(\text{viz})_4\text{SiF}_6$  together with the atomic labeling system. Hydrogen atoms have been omitted for clarity.

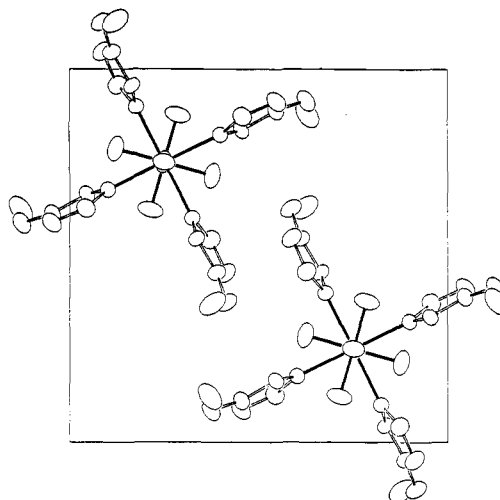


Figure 2. Projection of the structure of  $\text{Co}(\text{viz})_4\text{SiF}_6$  as seen along the  $c$  axis (direction of the chain).

Table II. Relevant Interatomic Distances (Å) and Angles (Deg) in  $\text{Co}(\text{viz})_4\text{SiF}_6$

Distances			
Co-F(1)	2.143 (2)	N(2)-C(1)	1.352 (4)
Co-N(1)	2.097 (2)	N(2)-C(3)	1.385 (4)
Si-F(1)	1.699 (2)	C(2)-C(3)	1.338 (5)
Si-F(2)	1.667 (1)	N(2)-C(4)	1.421 (4)
N(1)-C(1)	1.317 (4)	C(4)-C(5)	1.288 (4)
N(1)-C(2)	1.375 (4)		
Angles			
F(1)-Co-N(1)	91.7 (1)	C(3)-C(2)-N(1)	110.4 (3)
F(1)-Si-F(2)	90.1 (1)	N(2)-C(3)-C(2)	106.1 (3)
Si-F(1)-Co	180	C(1)-N(2)-C(3)	106.6 (3)
Co-N(1)-C(1)	123.4 (3)	C(1)-N(2)-C(4)	127.2 (3)
Co-N(1)-C(2)	130.9 (3)	C(3)-N(2)-C(4)	126.2 (3)
N(1)-C(1)-N(2)	111.2 (3)	N(2)-C(4)-C(5)	123.8 (3)
C(2)-N(1)-C(1)	105.6 (3)		

Relevant interatomic distances and angles are given in Table II. The coordination geometry around cobalt can be described as tetragonally distorted octahedral. The observed Co-N bond

(3)  $R = \sum |F_o| - |F_c| / \sum |F_o|$ ;  $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}$ .

(4) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1968; Vol. 4.

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**Table III.** Far-Infrared Spectra ( $\text{cm}^{-1}$ ) of Compounds with Formula  $\text{M}(\text{viz})_4\text{SiF}_6$  ( $350\text{--}100\text{ cm}^{-1}$ )

	band max with some assigns				
	M-F str	M-N str	other bands		
$\text{Mn}(\text{viz})_4\text{SiF}_6$	285	258, 244	221	196	154 107
$\text{Fe}(\text{viz})_4\text{SiF}_6$	292	260, 250	232	199	170 sh 153 110
$\text{Zn}(\text{viz})_4\text{SiF}_6$	296	263, 254	228 sh	211	173 153 114
$\text{Co}(\text{viz})_4\text{SiF}_6$	306	267, 260	242	213	180 161 117
$\text{Ni}(\text{viz})_4\text{SiF}_6$	313	279	247	223	189 sh 167 121
$\text{Cu}(\text{viz})_4\text{SiF}_6^a$	<i>b</i>	313, 302,	252	205 sh	196 140 114
		282			

<sup>a</sup> The copper compound has a slightly different X-ray powder pattern. <sup>b</sup> This absorption most likely falls between the M-N stretches (see text).

length of 2.097 Å is significantly shorter than those found for other Co-N(imidazole) compounds, where distances from 2.15–2.19 Å were found.<sup>6</sup> On the other hand, the distance is significantly longer than tetrahedral Co-N(imidazole) distances (2.01 Å<sup>7</sup>) and five-coordinate Co-N(azole) distances (2.03–2.04 Å<sup>8</sup>). The Co-F distance of 2.143 Å is identical with that found in the cubane-type<sup>6c</sup> cluster  $\text{Co}_4\text{F}_4(\text{L})_{12}^{4+}$ , which is much longer than the values occurring in lattice compounds such as  $\text{KCoF}_3$  and  $\text{K}_2\text{CoF}_4$ , where values of about 2.00–2.04 Å are found.<sup>9</sup> The coordination around Si is almost undistorted octahedral. The Si-F distances in the chain direction are slightly longer than those in the equatorial ligands. This difference of 0.03 Å (Table III) can be ascribed to the coordination of the axial fluoride to the cobalt ion.

The bond distances and bond angles within the vinyl-imidazole can be considered as normal.<sup>6–8</sup> The bond length N(2)–C(4) is somewhat shorter than a normal C–N single bond, which is an indication for some conjugation between the vinyl group and the imidazole ring. This effect is further seen from the orientation of the vinyl groups, which are very close to the imidazole plane (the angle with the plane is only 8.6°). The orientation of the imidazole ligands with respect to the equatorial plane is almost perpendicular (angle of 100.9°) to minimize steric interactions with the  $\text{SiF}_6$  groups. All intermolecular contacts between the chains appear to be normal van der Waals contacts. Within the chain the shortest contacts are between H(1) and F(1) and between H(2) and F(1)' (2.41 and 2.68 Å, respectively).

**Spectroscopic Measurements.** The infrared spectra of the compounds mentioned above appear to be simple additions of vinylimidazole peaks and peaks that can be ascribed to  $\text{SiF}_6^{2-}$  ions. In addition several new peaks are observed in the far-IR region, which have to be ascribed to M–N and M–F vibrations. The bands due to coordinated *N*-vinylimidazole are very close to those reported before for other compounds of this ligand.<sup>10</sup> Uncoordinated  $\text{SiF}_6^{2-}$  is known<sup>11</sup> to have two IR-active vibrations which are observed at about 740 and 480  $\text{cm}^{-1}$ . The present compounds exhibit a clear splitting of the band at 740  $\text{cm}^{-1}$  into two components at 735 and 755  $\text{cm}^{-1}$ . This splitting is apparently due to the lowering of the symmetry of the  $\text{SiF}_6^{2-}$

**Table IV.** Ligand Field and EPR Spectra of  $\text{M}(\text{viz})_4\text{SiF}_6$  Compounds and Some  $\text{M}(\text{viz})_4\text{Cl}_2$  Compounds (Assignments Based upon ref 14)

compd	band max, $\text{cm}^{-1}$ , and assigns	
$\text{Fe}(\text{viz})_4\text{SiF}_6$	12 500, <sup>a</sup>	8000 w <sup>a</sup>
$\text{Fe}(\text{viz})_4\text{Cl}_2$	11 300, <sup>a</sup>	7500 m <sup>a</sup>
$\text{Co}(\text{viz})_4\text{SiF}_6$	24 800, <sup>b</sup>	20 200, <sup>c</sup> 19 200, <sup>c</sup> 9500, <sup>d</sup> 5000 w, br <sup>e</sup>
$\text{Co}(\text{viz})_4\text{Cl}_2$	21 200, <sup>b</sup>	19 700, <sup>c</sup> 18 200, <sup>c</sup> 9100, <sup>d</sup> 7000 w, vbr <sup>e</sup>
$\text{Ni}(\text{viz})_4\text{SiF}_6$	28 500, <sup>f</sup>	17 300, <sup>g</sup> 14 500 sh, <sup>h</sup> 12 500, <sup>i</sup> 8000 w, br <sup>j</sup>
$\text{Ni}(\text{viz})_4\text{Cl}_2$	26 400, <sup>f</sup>	16 200, <sup>g</sup> 13 500 w, <sup>h</sup> 11 300, <sup>i</sup> 7800 <sup>j</sup>
$\text{Cu}(\text{viz})_4\text{SiF}_6$	17 400, <sup>k</sup>	14 300 sh <sup>k</sup>

<sup>a</sup> Components of the  ${}^5\text{E}_g \leftarrow {}^5\text{T}_{2g}$  transition (no assignment based upon  $D_{4h}$  symmetry appeared to be possible). <sup>b</sup>  ${}^4\text{A}_{2g} \leftarrow {}^4\text{A}_{2g}$ . <sup>c</sup> Components of  ${}^4\text{E}_g \leftarrow {}^4\text{A}_{2g}$ ; in addition a weak shoulder at about  $15.8 \times 10^3\text{ cm}^{-1}$  is tentatively assigned to the  ${}^4\text{B}_{1g} \leftarrow {}^4\text{A}_{2g}$  transition. <sup>d</sup>  ${}^4\text{E}_g(\text{F}) \leftarrow {}^4\text{A}_{2g}$ . <sup>e</sup>  ${}^4\text{B}_{2g} \leftarrow {}^4\text{A}_{2g}$ . <sup>f</sup>  ${}^3\text{E}_g \leftarrow {}^3\text{B}_{1g}$ . <sup>g</sup>  ${}^3\text{E}_g(\text{F}) \leftarrow {}^3\text{B}_{2g}$ . <sup>h</sup>  ${}^3\text{A}_{2g} \leftarrow {}^3\text{B}_{1g}$ . <sup>i</sup>  ${}^3\text{B}_{2g} \leftarrow {}^3\text{B}_{1g}$ . <sup>j</sup>  ${}^3\text{E}_g \leftarrow {}^3\text{B}_{1g}$ . <sup>k</sup> Components of  ${}^2\text{E}_g$ ,  ${}^2\text{B}_{2g}$ ,  ${}^2\text{A}_{1g} \leftarrow {}^2\text{B}_{1g}$ . <sup>l</sup> EPR spectrum:  $g_{\parallel} = 2.27$ ;  $g_{\perp} = 2.06$ ;  $A_{\parallel} = 180\text{ G}$ .  $A_{\parallel}$  is hardly resolved and accurate to  $\pm 10\text{ G}$ .

from  $O_h$  to  $D_{4h}$ .<sup>11</sup> The precise location of this doublet is difficult to determine, because the coordinated viz ligand has some absorptions in this region too.<sup>10</sup> The other splitting expected for a  $D_{4h}$   $\text{SiF}_6^{2-}$  ion is the asymmetric bending at about 480  $\text{cm}^{-1}$ . In fact such a clear, strong doublet splitting is observed only for the nonisomorphous Cu(II) compound (476 and 492  $\text{cm}^{-1}$ ). For the other compounds for which a  $D_{4h}$  symmetry is shown by the X-ray structure of the Co(II) compound, a strong band is observed at 470  $\text{cm}^{-1}$ , accompanied by a weaker doublet at 488 and 504  $\text{cm}^{-1}$ . The band at 504  $\text{cm}^{-1}$  is assigned to a free-ligand band.<sup>10</sup> The band at 488  $\text{cm}^{-1}$  may indeed be the other component of the asymmetric Si–F bending. Other possible assignments are the  $\nu_2$  stretching (Raman active and known to occur at 477  $\text{cm}^{-1}$ ) of  $\text{SiF}_6^{2-}$  or a splitting of the free-ligand band at about 500  $\text{cm}^{-1}$ .

Below 400  $\text{cm}^{-1}$  the present compounds show<sup>2</sup> many absorptions, most of which can be assigned to M–F and M–N(imidazole) vibrations. Bands down to 100  $\text{cm}^{-1}$  are summarized in Table III, together with some tentative assignments. The band that varies from 285 to 313  $\text{cm}^{-1}$  on going from Mn to Ni is at much higher frequency than observed before in transition-metal pyrazole and imidazole compounds<sup>11,12</sup> and is therefore assigned to the asymmetric M–F stretching vibration. The bands at lower frequency are most likely due to M–N vibrations in view of earlier findings.<sup>12</sup> For a tetragonal species  $\text{MN}_4\text{F}_2$  with  $D_{4h}$  symmetry, one would expect 15 normal vibrations, but only two  $a_{2u}$  (M–F stretch and  $\text{MN}_4$  out-of-plane bend) and three  $e_1$  (M–N stretch,  $\text{MN}_4$  in-plane bend, and F–M–F bend) are IR active.<sup>11,12a</sup> As seen from Table III, all these vibrations are at least observed, although apart from the M–F and M–N stretching no assignments are allowed. In fact the small splitting in this vibration (except for M = Ni) might well be due to the fact that the actual symmetry for the metal ions is  $D_{2d}$  rather than  $D_{4h}$ . Further evidence for the assignment of the M–F and M–N vibrations comes from a comparison with the spectra of the corresponding compounds  $\text{M}(\text{viz})_4\text{Cl}_2$ , which contain the species *trans*- $\text{MN}_4\text{Cl}_2$ . These compounds have M–N vibrations in the 260–280- $\text{cm}^{-1}$  region and have no bands above 285  $\text{cm}^{-1}$ .<sup>10a,13</sup> The assignment of the bands for the Cu(II) compound is more difficult because the structure is not isomorphous. Moreover, if a Cu–F axial bond would exist, it would certainly be rather

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Table V. Magnetic Information of Compounds M(viz)<sub>4</sub>SiF<sub>6</sub>

compd	$\mu_{\text{eff}}^a$		parameters obtained	
	90 K	4 K	$\Theta$ , K	other
Mn(viz) <sub>4</sub> SiF <sub>6</sub>	5.60 (8)	5.05 (8)	-3 (1) <sup>b</sup>	
Fe(viz) <sub>4</sub> SiF <sub>6</sub>	5.32 (5)	4.40 (6)	-6 (1) <sup>c</sup>	
Co(viz) <sub>4</sub> SiF <sub>6</sub>	4.90 (5)	3.98 (5)	-17 (2) <sup>d</sup>	
Ni(viz) <sub>4</sub> SiF <sub>6</sub>	3.10 (4)	2.30 (4)		$D = 11 (1) \text{ cm}^{-1}$ , $g_{\parallel} = 2.20 (3)$ , $g_{\perp} = 2.25 (3)$
Cu(viz) <sub>4</sub> SiF <sub>6</sub>	2.10 (9)	2.04 (9)	-0.5 (4) <sup>c</sup>	

<sup>a</sup> Magnetic moments are in  $\mu_{\text{B}}$ . <sup>b</sup> Determined in the region from 10 to 80 K. <sup>c</sup> Determined in the region from 20 to 80 K.

<sup>d</sup> Determined in the region from 40 to 80 K.

weak. The band at 313  $\text{cm}^{-1}$  could then be assigned to a Cu-N vibration, as such a band is also found in the corresponding perchlorate and tetrafluoroborate compounds.<sup>10b</sup> It is finally noticed that the Irving-Williams sequence of metal ions<sup>11</sup> holds nicely among the series Mn < Fe < Co < Ni < Cu > Zn.

The ligand field and (some) EPR spectra of the compounds have been listed in Table IV together with some spectra of the related compounds M(viz)<sub>4</sub>Cl<sub>2</sub>. All ligand field spectra of the compounds with M = Fe, Co, Ni, and Cu agree with strongly distorted octahedral coordination, as deduced from the clear tetragonal splittings. No attempts were undertaken to evaluate the tetragonal parameters<sup>14</sup>  $D_s$  and  $D_t$  from these spectra. It is however clear that the in-plane ligand field strength is relatively high compared with those of other azole compounds containing the MN<sub>4</sub>X<sub>2</sub> chromophore<sup>14</sup> and with those of the corresponding chlorides listed also in Table IV. This further confirms the weak axial binding of the F atoms, as already seen from the Co-F distance and the relatively short Co-N distances. The ESR spectrum of the Cu(II) compound appears to be normal for tetragonal copper species<sup>12d,15</sup> or azole ligands. The absence of clearly resolved hyperfine splitting suggests the occurrence of magnetic exchange narrowing.

**Magnetic Susceptibility.** For the investigation of the possible magnetic exchange interaction between the metal ions within the chain, magnetic susceptibility measurements were performed on the powdered compounds in the temperature range 4–90 K. The results have been summarized in Table V.

The magnetic exchange in all compounds appears to be relatively small, compared to that in other types of chain compounds. The Ni(II) compound appeared to behave differently. As Ni(II) ions in tetragonal fields are known to exhibit significant zero-field splittings,<sup>15</sup> which can be larger than the magnetic exchange in the present chain, the sus-

ceptibility was analyzed in terms of single-ion zero-field splitting, as is known for other compounds. The obtained parameters are listed also in Table V; the values are as expected<sup>15</sup> for tetragonal NiN<sub>4</sub>X<sub>2</sub> species. The small magnetic interactions in the other compounds are in agreement with the long M-M distances along the chain (equal to the  $c$  axis, viz., 6.8 Å), as ligands such as SiF<sub>6</sub><sup>2-</sup> are not expected to induce strong couplings. For a detailed study of the magnetic exchange, measurements at very low temperatures would be required. Even in that case it would be difficult to detect the details of the exchange interaction. The values of the Curie constants in Table V have been determined from the linear part of the inverse susceptibility vs. temperature plot. For Fe(II) and Co(II) compounds the low-temperature behavior can also be influenced significantly by single-ion anisotropies,<sup>8,16,17</sup> therefore, only the high-temperature linear part (Table V) was used for the determination of  $\Theta$ .

**Concluding Remarks.** The new compounds described in the present paper form a very interesting group of new chain compounds, in which the SiF<sub>6</sub><sup>2-</sup> ion acts as a very weakly coordinating, bridging ligand. It seems likely that the vinylimidazole ligands can be replaced by other ligands, resulting in basically the same structure.

The magnetic exchange through the SiF<sub>6</sub><sup>2-</sup> group seems to be rather weak but significant. Unfortunately, the single-ion anisotropies in the case of Co(II) and Fe(II) and the large zero-field splitting in the case of Ni(II) hamper the detailed study of the magnetic exchange coupling in these cases. The study of the Cu(II) compound is hampered by the fact that the structure is not isomorphous with the compounds containing the other metals.

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**Registry No.** Mn(viz)<sub>4</sub>SiF<sub>6</sub>, 82374-11-6; Fe(viz)<sub>4</sub>SiF<sub>6</sub>, 82374-13-8; Zn(viz)<sub>4</sub>SiF<sub>6</sub>, 82374-15-0; Co(viz)<sub>4</sub>SiF<sub>6</sub>, 82374-17-2; Ni(viz)<sub>4</sub>SiF<sub>6</sub>, 82374-19-4; Cu(viz)<sub>4</sub>SiF<sub>6</sub>, 82374-21-8; Fe(viz)<sub>4</sub>Cl<sub>2</sub>, 82390-14-5; Co(viz)<sub>4</sub>Cl<sub>2</sub>, 67069-49-2; Ni(viz)<sub>4</sub>Cl<sub>2</sub>, 82399-51-7.

**Supplementary Material Available:** Listings of observed and calculated structure factors, calculated positions for hydrogen atoms, and anisotropic thermal parameters for the non-hydrogen atoms and a plot of the inverse magnetic susceptibility of Co(viz)<sub>4</sub>SiF<sub>6</sub> as a function of temperature (Figure 3) (7 pages). Ordering information is given on any current masthead page.

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