$$F = \sum_i (\chi_i^{\text{obsd}} - \chi_i^{\text{calcd}})^2/(\chi_i^{\text{obsd}})^2$$

Optimum values of the parameters were $J = -8.5$ cm^{-1} and $|D| = 9.6$ cm^{-1}. The solid line in Figure 5 was calculated by using these optimum parameters.

The sign of D was not determined. The evaluation of the zero-field splitting parameter from low-temperature magnetic susceptibility data for $S = {}^5/_2$ systems has been discussed by several authors.[25,26] The limitations of the practice are well-recognized, especially in the presence of magnetic exchange interactions. Calculations with various ratios of J/D confirm that it will be possible to determine the sign of D from average magnetic susceptibility data only in fortuitous circumstances.

Discussion

Consideration of the crystal packing in **1** indicates that there is little or no opportunity for π overlap between neighboring nonlinked porphyrins, and the distance between nonbridged nearest-neighbor iron atoms is large (8.97 Å). Given these facts, it is likely that a major portion of the magnetic interaction is occurring through the bridging FNT^{2-} ligand. The orientation of the FNT^{2-} ligand relative to the porphyrin plane implies that the magnetic interaction is occurring largely through the FNT^{2-} π system.

In both **1** and the related compound (TBA){[Fe(p-Cl-TPP)]$_2$[Cu(MNT)$_2$]$_2$}$\cdot$3C$_6$H$_6$[23] (hereafter **2**), the bonds between iron and sulfur are approximately perpendicular to the planes of the bridging FNT^{2-} and MNT^{2-} ligands. This is in contrast to the normal chelating mode for MNT^{2-}, in which bonding to a metal atom occurs in the plane of the ligand. The fact that the Fe-S bond distance in **1** is very similar to the Fe-S distances observed for other thiolate and thioether complexes of iron porphyrins demonstrates that the long Fe-S distances characteristic of **2** are not due to the unusual binding geometry of the MNT^{2-} ligand. Instead, these "abnormal" distances must be a consequence of the simultaneous interaction of the bridging sulfur atoms of the MNT^{2-} ligands with the copper(II) ion and with the iron(III) atoms of the porphyrin units. Since **1** contains high-spin iron(III) atoms, the influence of the copper(II) atom on the Fe-S bonding in **2** must also be responsible for the intermediate-spin ($S = {}^3/_2$) state inferred from the structural results for the five-coordinate Fe(III) atom in **2**. All other five-coordinate ferric porphyrins with axial sulfur ligand atoms are high spin, with the exception of the recently characterized low-spin (hydrosulfido)(5,10,15,20-tetrakis(4-methoxyphenyl)porphinato)iron(III) complex.[3f] Thus, the presence of the copper(II) atom in **2** is apparently responsible for both the longer Fe-S bond length *and* the unusual spin state.

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Registry No. **1**, 101248-27-5; Fe(TPP)(ClO$_4$), 57715-43-2.

Supplementary Material Available: Anisotropic thermal parameters for **2** (Table SI), calculated hydrogen atom positions (Table SII), selected least-squares planes (Table SIII), and observed and calculated structure factors (×10, Table SIV) (32 pages). Ordering information is given on any current masthead page.

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Gallium Analogues of Iron-Sulfide-Thiolate Compounds. Analysis of the Structural Parameters in Gallium(III) and Iron(III) Chalcogenide Compounds[1]

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Several gallium-sulfide-thiolate compounds that are structural analogues of the well-known Fe(III)-S^{2-}-RS$^-$ complexes have been prepared and structurally characterized. Crystalline [Ga(SR)$_4$]$^-$ complexes (SR = SMe, SEt, S-i-Pr, SPh, S-2,3,5,6-Me$_4$C$_6$H, S-2,4,6-(i-Pr)$_3$C$_6$H$_2$) have been prepared by the reaction of either GaCl$_3$ or [GaCl$_4$]$^-$ with 5 equiv of LiSR. The [Ga(SR)$_4$]$^-$ compounds were frequently isomorphous with the corresponding [Fe(SR)$_4$]$^-$ complex. The structures of [(n-Pr)$_4$N][Ga(SEt)$_4$] (**1**) and [Et$_4$N][Ga(SPh)$_4$] (**2**) were determined by X-ray crystallography. Data for **1**: tetragonal, $I\bar{4}$ space group, with $Z = 2$, $a = b = 10.643$ (3) Å, $c = 12.433$ (2) Å, and $V = 1408$ (1) Å^3. Data for **2**: orthorhombic, $P2_12_12_1$ space group, with $Z = 4$, $a = 11.449$ (3) Å, $b = 11.540$ (3) Å, $c = 24.50$ (1) Å, and $V = 3237$ (4) Å^3. The GaS$_4$ core of **1** has nearly perfect T_d symmetry, and Ga-S = 2.264 (3) Å. There are two distinctive conformations of the thiolate ligands in the [Ga(SPh)$_4$]$^-$ anion of **2**. [Et$_4$N]$_2$[Ga$_2$S$_2$(SPh)$_4$] (**3**), which is an analogue of the FeS compound [Fe$_2$S$_2$(S-p-tol)$_4$]$^{2-}$ (**4**), has been synthesized and structurally characterized. Data for **3**: monoclinic, $P2_1/n$ space group, with $Z = 2$, $a = 11.359$ (3) Å, $b = 12.745$ (2) Å, $c = 15.411$ (1) Å, $\beta = 93.56$ (2)°, and $V = 2227$ (1) Å^3. The structures of **3** and **4** and related solid-state compounds have been analyzed in the context of a general discussion of the geometric parameters of edge-sharing tetrahedra.

Introduction

Some similarities in the coordination chemistry of gallium(III) and high-spin iron(III) have long been recognized to result from their similar charges and ionic radii.[2] Because of the biological importance of iron-sulfur proteins,[3] Fe(III)-thiolate and iron-sulfide-thiolate complexes have been extensively investigated.[4] We wish to report some studies that indicate that gallium will have an analogous chemistry and that gallium-sulfide clusters will be valuable for an increased understanding of the structure/electronic structure relationships in iron-sulfur compounds. Although solid-state gallium chalcogenide compounds have come

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Table I. Summary of Crystal Data, Intensity Collection, and Final Structure Refinement

	((*n*-Pr)$_4$N)-[Ga(SEt)$_4$] (**1**)	(Et$_4$N)-[Ga(SPh)$_4$] (**2**)	(Et$_4$N)$_2$-[Ga$_2$S$_2$(SPh)$_4$] (**3**)
formula	$GaS_4NC_{20}H_{48}$	$GaS_4NC_{32}H_{40}$	$Ga_2S_6N_2C_{40}H_{60}$
fw	500.59	636.66	900.76
a, Å	10.643 (3)	11.449 (3)	11.359 (3)
b, Å	10.643 (3)	11.540 (3)	12.745 (2)
c, Å	12.433 (2)	24.50 (1)	15.411 (1)
β, deg			93.56 (2)
V, Å^3	1408 (1)	3237 (4)	2227 (1)
Z	2	4	2
space group	$I\bar{4}$ (No. 82)	$P2_12_12_1$ (No. 19)	$P2_1/n$
temp	ambient	ambient	ambient
radiation (graphite monochromator)	Mo Kα (λ = 0.710 73 Å)	Mo Kα	Mo Kα
max time per scan, s	60	60	60
linear abs coeff, cm^{-1}	13.183	11.653	15.744
scan mode	$\theta/2\theta$	$\theta/2\theta$	$\theta/2\theta$
2θ range, deg	$0 < 2\theta < 60$	$0 < 2\theta < 50$	$0 < 2\theta < 50$
reflcns			
collcd	1177	3246	4331
unique with $\lvert F_o\rvert^2 > 3\sigma\lvert F_o\rvert^2$	599	2088	2669
final no. of variables	95	314	226
$R^a = \sum[\lvert F_o\rvert - \lvert F_c\rvert]/\sum\lvert F_o\rvert$	0.0458	0.0808	0.0453
$R_w{}^a = [\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\sum wF_o{}^2]^{1/2}$	0.0539	0.1034	0.0561
std. error in observn of unit wt, e	0.787	3.361	1.931
highest e/Å^3	0.068	0.388	0.547
largest parameter shift, ESD	0.04	0.33	0.01

[a] Quantity minimized ($\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2$); weight $w = 1/(\sigma^2 + 0.0016F_o{}^2)$.

under increased investigation in the past several years,[5] the chemistry of soluble molecular compounds has not been extensively studied.[6-9] The chemistry of the chalcogenide compounds of the main-group elements has recently been reviewed.[10] The coordination chemistry of gallium is also of possible significance in medicine since gallium radionuclides have been used in clinical studies.[11]

Experimental Section

Materials and Procedures. $GaCl_3$ was obtained from AESAR, Ga_2O_3 from Aldrich. Thiols were commercially available or prepared by literature methods.[75] Lithium thiolates, LiSR, were prepared in situ by adding lithium metal to RSH in ethanol.

Ammonium tetrachlorogallate, $(NH_4)GaCl_4$, was prepared by modified procedures of Friedman and Taube[12] from Ga_2O_3 or $GaCl_3$.

(1) From Ga_2O_3. Ga_2O_3 was heated in concentrated hydrochloric acid until it dissolved completely. After the addition of excess ammonium chloride, the solution was heated to dryness. The residue was dissolved in diethyl ether and filtered to remove any insoluble solids. Vacuum removal of the ether produced a 90% yield of white $(NH_4)GaCl_4$.

(2) From $GaCl_3$. $GaCl_3$ was dissolved in diethyl ether in a dry ice/acetone bath. Excess ammonium chloride was stirred in the solution for several hours, and the remaining ammonium chloride that did not dissolve into the ether solution was filtered away. Complete vacuum removal of the ether and washing of the residue with chloroform produced white, powdery $(NH_4)GaCl_4$ in greater than 75% yield.

A[GaCl$_4$] [A = (Et$_4$N)$^+$, ((*n*-Pr)$_4$N)$^+$, (Et$_3$NCH$_2$Ph)$^+$, (Ph$_4$P)$^+$]. Compounds of $[GaCl_4]^-$ with various cations were isolated by the addition of an ethanolic solution of cation to a concentrated hydrochloric acid solution of $GaCl_3$ or Ga_2O_3. Filtration, followed by washing with ethanol and diethyl ether, yielded a fine white solid product, A[GaCl$_4$] in high yields.

((*n*-Pr)$_4$N)[Ga(SEt)$_4$] (1). (1) From GaCl$_3$. Gallium trichloride (0.93 g, 5.28 mmol) was reacted in 30 mL of ethanol with lithium ethanethiolate (23.3 mmol). Addition of 1.41 g (5.30 mmol) of tetra-*n*-propylammonium bromide precipitated the product immediately. This product, a white, air-stable solid, was obtained in 27% yield (0.72 g) and was recrystallized from DMF/diethyl ether.

(2) From ((*n*-Pr)$_4$N)GaCl$_4$. To a slurry of $(Pr_4N)GaCl_4$ (8.77 g, 22.0 mmol) in ethanol was added 87.8 mmol of lithium ethanethiolate in 50 mL of ethanol. All of the solid went into solution, after which a fine white solid separated from the solution. The solution was cooled to −20 °C and filtered, and the filtrate was washed with cold ethanol and the white solid dried in vacuo. A 5.11-g (46%) yield of fine white crystals was recovered. Anal. Calcd: C, 47.99; H, 9.67; N, 2.80; S, 25.62. Found: C, 47.95; H, 9.83; N, 2.81; S, 25.49.

(Et$_4$N)[Ga(SPh)$_4$] (2). The compound was prepared in a manner analogous to that used in the preparation of **1**, using 0.515 g (2.24 mmol) of $(NH_4)GaCl_4$, 10.98 mmol of lithium benzenethiolate and 0.52 g (2.50 mmol) of $(Et_4)NBr$ in 70 mL of ethanol. A 1.14-g (80%) yield of a white air-stable solid was obtained and the solid recrystallized from DMF/diethyl ether. The compound is soluble in acetonitrile, methylene chloride, DMF, and THF but insoluble in 2-propanol and diethyl ether.

The following $[Ga(SR)_4]^-$ complexes were obtained by using synthetic procedures similar to those for **1** and **2**:

(Et$_4$N)[Ga(S-2,3,5,6-Me$_4$C$_6$H)$_4$]. The white product obtained in 80% yield is recrystallized from hot DMF or hot acetonitrile.

(Et$_4$N)[Ga(SMe)$_4$]. A white crystalline solid separated from the reaction mixture upon cooling to ~−20 °C (58% yield).

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Table II. Atomic Coordinates for ((*n*-Pr)$_4$N)[Ga(SEt)$_4$] (**1**)

atom	*x*	*y*	*z*
Ga	0.0000 (0)	0.5000 (0)	0.2500 (0)
S	0.1315 (3)	0.3859 (2)	0.1453 (2)
N	0.0000 (0)	0.0000 (0)	0.0000 (0)
C1	0.180 (2)	0.503 (1)	0.0431 (12)
C1A	0.248 (4)	0.511 (4)	0.1054 (33)
C2	0.279 (2)	0.577 (2)	0.0723 (16)
C2A	0.215 (5)	0.563 (5)	−0.0018 (35)
C3	−0.099 (1)	0.069 (1)	0.0688 (13)
C3A	0.013 (2)	−0.121 (2)	−0.0685 (17)
C4	−0.164 (2)	−0.014 (2)	0.1521 (15)
C4A	−0.140 (3)	0.082 (2)	0.1484 (26)
C5	−0.259 (1)	0.055 (1)	0.2115 (9)

(Ph$_4$P)[Ga(S-*i*-Pr)$_4$]. Cooling the reaction solution at −20 °C overnight produced a very crystalline pink compound in 60% yield.

((*n*-Pr)$_4$N)[Ga(S-*i*-Pr)$_4$]. Pink crystals precipitated from the reaction mixture upon cooling overnight.

(Ph$_4$P)[Ga(S-2,4,6-*i*-Pr$_3$C$_6$H$_2$)$_4$]. The product, which is obtained in 95% yield from the reaction of NH$_4$GaCl$_4$, is recrystallized from hot acetonitrile to give colorless crystals.

(Et$_4$N)$_2$[Ga$_2$S$_2$(SPh)$_4$] (3). Reaction of 0.931 g (5.29 mmol) of GaCl$_3$ with 22.4 mmol of lithium benzenethiolate and 0.34 g (6.06 mmol) of NaSH in ethanol produced a milky white solution, which was filtered after being stirred for 3 h. Addition of 1.20 g (5.69 mmol) of (Et$_4$N)Br precipitated a fine white solid, which turned into lumps of solid in the flask. The solution was cooled for 4 days and then filtered. The lumps of solid were dried in vacuo to give 2.69 g of solid. A 0.455-g sample of this solid was recrystallized from 1–2 mL of hot acetonitrile. Some white crystals of (Et$_4$N)[Ga(SPh)$_4$] were recovered (as identified by unit cell parameters of the crystals) as well as clear, slightly pink crystals of **3**.

X-ray Crystallographic Structure Determinations

Data Collection and Reduction. An Enraf-Nonius CAD4A automated diffractometer was used for data collection for all X-ray crystal structure determinations and unit cell measurements. After the mounted crystal was centered in the X-ray beam, 25 reflections were located by an automatic search program, centered, and used to obtain cell parameters. After the cell was examined to determine the unit cell of highest symmetry, the data were examined for systematic absences to determine the space group of the unit cell. High-angle data ($2\theta > 20°$) were collected, and 25 of these reflections were centered and used to obtain more accurate cell parameters. Data were collected on this improved unit cell at ambient temperature under the control of a PDP 11/45 computing system. Data reduction and corrections for Lorentz–polarization and intensity decay were performed by using programs from the Enraf-Nonius structure determination package.

((*n*-Pr)$_4$N)[Ga(SEt)$_4$] (1). A crystal (which had been crystallized from DMF/diethyl ether) was mounted on a glass fiber for data collection. Data were collected according to the parameters in Table I. The equivalence of reflections established that the tetragonal cell had the symmetry of the Laue group $4/m$. This cell is a body-centered lattice with condition $h + k + l \neq 2n + 1$ as the only systematic absence. The volume indicates two molecules per unit cell ($Z = 2$). The symmetry necessary at the special positions and the fact that $Z = 2$ limited the choice of space group to one possibility: $I\bar{4}$. With this space group, each anion and cation is centered on a special position and possesses an S_4 axis of symmetry. The coordinates of the gallium atom were fixed at special position *c* with coordinates 0.0, 0.5, 0.25 and multiplicity = 0.25. An electron-density difference map revealed the positions of sulfur and nitrogen. The nitrogen was fixed at special position *a* and its multiplicity also set to 0.25. Successive electron density maps produced coordinates for all of the carbon atoms, showing disorder in the positions of the methyl and methylene carbons of the ethyl group and in the methylene carbons of the cation. The multiplicities of these carbons were refined and then fixed as follows: C1, 0.2; C1A, 0.8; C2, 0.8; C2A, 0.2; C3, 0.5; C3A, 0.5; C4, 0.7; C4A, 0.3.

Anisotropic refinement of all thermal parameters leads to final *R* values of $R = 0.046$ and $R_w = 0.054$. No hydrogen positions were calculated due to the large disorder in both the anion and the cation. Coordinates for the opposite enantiomer were calculated but they raised the *R* values to $R = 0.058$ and $R_w = 0.061$, which were significantly higher than those of the "correct" enantiomer. Final positional parameters are given in Table II and selected bond distance and angle parameters in Table VI.

Table III. Atomic Coordinates for (Et$_4$N)[Ga(SPh)$_4$] (**2**)

atom	*x*	*y*	*z*	*B*(1,1), Å^2
Ga	0.1853 (1)	0.0810 (1)	0.12677 (6)	
S1	0.3709 (4)	0.1304 (4)	0.1056 (2)	
S2	0.1128 (4)	0.1739 (4)	0.1997 (2)	
S3	0.0912 (4)	0.1196 (4)	0.0473 (1)	
S4	0.1718 (5)	−0.1042 (3)	0.1556 (2)	
N	0.2214 (9)	0.969 (1)	0.3773 (5)	4.4 (2)
C11	0.433 (1)	0.129 (1)	0.1727 (7)	
C12	0.424 (2)	0.211 (2)	0.2130 (8)	
C13	0.484 (2)	0.205 (2)	0.2606 (7)	
C14	0.547 (3)	0.128 (2)	0.2736 (11)	
C15	0.554 (2)	0.049 (2)	0.2409 (9)	
C16	0.502 (2)	0.045 (2)	0.1887 (10)	
C21	0.134 (1)	0.325 (1)	0.1902 (5)	
C22	0.104 (1)	0.393 (1)	0.2334 (6)	
C23	0.122 (2)	0.516 (2)	0.2296 (7)	
C24	0.167 (1)	0.564 (2)	0.1844 (7)	
C25	0.200 (1)	0.496 (1)	0.1400 (6)	
C26	0.186 (2)	0.374 (1)	0.1454 (7)	
C31	−0.051 (1)	0.097 (1)	0.0588 (6)	
C32	−0.130 (2)	0.143 (1)	0.0183 (6)	
C33	−0.253 (1)	0.125 (2)	0.0244 (7)	
C34	−0.299 (1)	0.068 (2)	0.0691 (7)	
C35	−0.225 (1)	0.025 (2)	0.1060 (6)	
C36	−0.106 (1)	0.034 (1)	0.1028 (5)	
C41	0.228 (1)	−0.176 (1)	0.0991 (6)	
C42	0.156 (2)	−0.218 (1)	0.0568 (6)	
C43	0.202 (2)	−0.280 (2)	0.0155 (7)	
C44	0.304 (2)	−0.307 (1)	0.0131 (7)	
C45	0.398 (2)	−0.269 (2)	0.0560 (10)	
C46	0.342 (2)	−0.209 (1)	0.0953 (7)	
C1	0.344 (3)	1.015 (3)	0.3674 (15)	0.0 (10)
C2	0.437 (2)	0.922 (2)	0.3885 (8)	8.1 (5)
C3	0.173 (3)	0.848 (3)	0.3621 (13)	8.0 (8)
C4	0.219 (2)	0.812 (2)	0.3027 (7)	6.9 (4)
C5	0.179 (3)	0.983 (3)	0.4441 (11)	6.9 (7)
C6	0.072 (2)	0.978 (2)	0.4569 (8)	7.8 (5)
C7	0.134 (4)	1.048 (3)	0.3431 (17)	8.0 (10)
C8	0.153 (2)	1.178 (2)	0.3602 (8)	8.5 (5)
C1A	0.335 (5)	0.900 (5)	0.4071 (24)	13.5 (17)
C3A	0.231 (3)	0.937 (3)	0.3123 (15)	5.6 (9)
C5A	0.104 (3)	0.923 (4)	0.3955 (15)	5.7 (9)
C7A	0.258 (3)	1.102 (4)	0.3818 (15)	8.2 (10)

Table IV. Atomic Coordinates for (Et$_4$N)$_2$[Ga$_2$S$_2$(SPh)$_4$] (3)

atom	*x*	*y*	*z*
Ga	0.41447 (4)	0.43813 (4)	0.04647 (3)
S1	0.4065 (1)	0.4980 (1)	−0.09270 (7)
S2	0.4220 (1)	0.2593 (1)	0.05862 (9)
S3	0.2624 (1)	0.4823 (1)	0.12914 (9)
N	0.4002 (3)	0.1941 (3)	0.7123 (2)
C21	0.2869 (4)	0.2100 (4)	0.0139 (3)
C22	0.1984 (4)	0.2702 (4)	−0.0272 (3)
C23	0.0962 (4)	0.2262 (5)	−0.0635 (4)
C24	0.0820 (5)	0.1191 (5)	−0.0597 (4)
C25	0.1677 (6)	0.0584 (4)	−0.0189 (4)
C26	0.2689 (5)	0.1023 (4)	0.0170 (4)
C31	0.2508 (4)	0.6202 (4)	0.1324 (3)
C32	0.2940 (4)	0.6874 (4)	0.0709 (3)
C33	0.2814 (5)	0.7933 (4)	0.0788 (3)
C34	0.2271 (5)	0.8363 (4)	0.1473 (4)
C35	0.1841 (5)	0.7721 (4)	0.2081 (3)
C36	0.1954 (4)	0.6659 (4)	0.2018 (3)
C1	0.4690 (5)	0.2833 (4)	0.7579 (3)
C2	0.5063 (6)	0.3689 (5)	0.7002 (4)
C3	0.3579 (5)	0.1206 (5)	0.7802 (4)
C4	0.4527 (6)	0.0639 (5)	0.8340 (4)
C5	0.4797 (5)	0.1381 (5)	0.6534 (4)
C6	0.4318 (5)	0.0409 (5)	0.6103 (4)
C7	0.2929 (5)	0.2349 (5)	0.6596 (3)
C8	0.2107 (6)	0.2986 (6)	0.7090 (5)

(Et$_4$N)[Ga(SPh)$_4$] (2). A crystal (which was obtained from slow evaporation of an ethanolic solution) was mounted on a glass fiber for data collection. The unit cell parameters indicated an orthorhombic cell with the value of the cell parameter *a* only slightly different from *b* (30 σ). Intensity data were collected for reflections that would be equivalent in a tetragonal unit cell. The inequivalence of these reflections ruled out a tetragonal cell. The systematic reflections were only consistent with

Table V. Unit Cell Parameters for Iron and Gallium Tetrathiolates and Tetraphenolates

compd	space group	Z	a, Å	b, Å	c, Å	angles, deg
$(Et_4N)[Ga(SMe)_4]$	$I\bar{4}$	2	9.807 (7)	9.807 (7)	10.738 (9)	
$(Et_4N)[Fe(SMe)_4]$	$I\bar{4}$	2	9.780 (3)	9.780 (3)	10.801 (3)	
$((n\text{-}Pr)_4N)[Ga(SEt)_4]$	$I\bar{4}$	2	10.641 (6)	10.641 (6)	12.439 (4)	
$((n\text{-}Pr)_4N)[Fe(SEt)_4]$	$I\bar{4}$	2	10.598 (2)	10.598 (2)	12.588 (2)	
$((n\text{-}Pr)_4N)[Ga(S\text{-}i\text{-}Pr)_4]$	$I\bar{4}$	2	10.80 (1)	10.80 (1)	14.20 (1)	
$((n\text{-}Pr)_4N)[Fe(S\text{-}i\text{-}Pr)_4]$	$I\bar{4}$	2	10.787 (5)	10.787 (5)	14.239 (7)	
$(Et_4N)[Ga(SPh)_4]$	$P2_12_12_1$	4	11.479 (2)	11.567 (1)	24.461 (5)	
$(Et_4N)[Fe(SPh)_4]$	$P2_1/n$	4	9.194 (2)	8.892 (2)	40.779 (8)	92.69 (1)[a]
$(Et_4N)[Ga(S\text{-}2,3,5,6\text{-}Me_4C_6H)_4]$	$I\bar{4}$	2	12.341 (8)	12.341 (8)	16.30 (2)	
$(Et_4N)[Fe(S\text{-}2,3,5,6\text{-}Me_4C_6H)_4]$	$I\bar{4}$	2	12.366 (2)	12.366 (2)	16.352 (4)	
$(Ph_4P)[Ga(S\text{-}2,4,6\text{-}i\text{-}Pr_3C_6H_2)_4]$	$P\bar{1}$	2	14.71 (2)	21.08 (2)	13.94 (2)	91.43 (9), 106.9 (1), 77.7 (1)[b]
$(Ph_4P)[Fe(S\text{-}2,4,6\text{-}i\text{-}Pr_3C_6H_2)_4]$	$P\bar{1}$	2	14.709 (2)	20.928 (5)	13.901 (2)	90.97 (3), 105.43 (3), 78.13 (3)[b]
$(Et_4N)[Ga(O\text{-}2,6\text{-}Me_2C_6H_3)_4]$	$I\bar{4}$	2	11.122 (3)	11.122 (3)	15.711 (8)	
$(Et_4N)[Al(O\text{-}2,6\text{-}Me_2C_6H_3)_4]$	$I\bar{4}$	2	11.071 (2)	11.071 (2)	15.797 (4)	
$(Et_4N)[Fe(O\text{-}2,6\text{-}Me_2C_6H_3)_4]$	$I\bar{4}$	2	11.145 (3)	11.145 (3)	15.788 (7)	

[a] β. [b] α, β, and γ, respectively.

Table VI. Bond Lengths (Å) and Bond Angles (deg) for $((n\text{-}Pr)_4N)[Ga(SEt)_4]$ (**1**)

Ga–S	2.264 (3)	S–Ga–S	109.8 (2) (×2)
S–C1	1.85 (3)		109.3 (1) (×4)
S–C1A	1.89 (9)	Ga–S–C1	101.9 (6)
C1–C2	1.37 (4)	Ga–S–C1A	100 (2)
C1A–C2A	1.49 (8)	S–C1–C2	115 (4)
S–S′	3.705 (4)	S–C1A–C2A	110 (9)
S–S″	3.693 (4)		
N–C3	1.55 (2)		
N–C3A	1.55 (3)	C3–N–C3	113 (2) (×2)
C3–C4	1.52 (3)		107.9 (8) (×4)
C3A–C4A	1.43 (5)	C3A–N–C3A	113 (2) (×2)
C4–C5	1.46 (3)		108 (1) (×4)
C4A–C5	1.52 (5)	N–C3–C4	114 (2)
		N–C3A–C4A	116 (3)
		C3–C4–C5	111 (2)
		C3A–C4A–C5	110 (3)

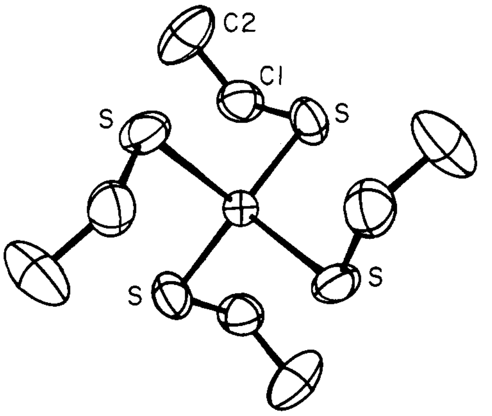

Figure 1. ORTEP diagram of the anion of $[(n\text{-}Pr)_4N][Ga(SEt)_4]$ (**1**) as viewed down the crystallographic S_4 axis.

the space group $P2_12_12_1$. Data were collected according to the parameters in Table I and were corrected for absorption. The orthorhombic space group $P2_12_12_1$ with $Z = 4$ does not impose any crystallographic symmetry on the compound. An origin-removed Patterson map allowed the position of the gallium atom to be determined. Successive difference Fourier electron-density maps produced coordinates for the anion and the cation including those of disordered methylene carbons in the cation. The multiplicities of these disordered carbons were refined and then fixed at values of 0.6 and 0.4 or 0.5 and 0.5. The atoms in the anion were allowed to refine anisotropically, and hydrogens were calculated on the phenyl rings but were not refined. Coordinates for the opposite enantiomer were refined but the R values increased. Final R values are $R = 0.0808$ and $R_w = 0.1034$. Final positional parameters are given in Table III and selected bond distance and angle parameters in Table VII.

$(Et_4N)_2[Ga_2S_2(SPh)_4]$ (3). A crystal was obtained by hot acetonitrile recrystallization of the product of a reaction solution of $GaCl_3$ + 2LiSPh + NaHS in ethanol. The crystal was mounted on a glass fiber, and data were collected according to the parameters in Table I. This compound crystallizes in the space group $P2_1/n$ with $Z = 2$. Therefore, the compound has a crystallographically imposed center of symmetry, and only half of the atoms in the formula unit are independent. An origin-removed Patterson map allowed the gallium atom to be located. Subsequent difference Fourier maps produced the coordinates for the remaining atoms. The hydrogens on the phenyl carbons and on the cation were calculated (C–H = 0.95Å) but were not refined. The final R values were $R = 0.0453$ and $R_w = 0.0561$. Final positional parameters are given in Table IV and selected bond distance and angle parameters in Table VIII.

Results and Discussion

Synthesis and Properties of $[Ga(SR)_4]^-$ Complexes. White crystalline $[Ga(SR)_4]^-$ complexes can be readily prepared with a wide range of thiolate ligands (SR = SMe, SEt, S-*i*-Pr, SPh, $S\text{-}2,3,5,6\text{-}Me_4\text{-}C_6H$, $S\text{-}2,4,6\text{-}(i\text{-}Pr)_3C_6H_2$) by the reaction of either $GaCl_3$ or $[GaCl_4]^-$ with 5 equiv of lithium thiolate in alcohol followed by the addition of suitable $[R_4N]^+$ or $[R_4P]^+$ cations. In the majority of cases the $[Ga(SR)_4]^-$ complexes are isomorphous with their $[Fe(SR)_4]^-$ counterparts (Table V). $[NEt_4][Ga(S\text{-}2,3,5,6\text{-}Me_4C_6H)_4]$ and $[Ph_4P][Ga(S\text{-}2,4,6\text{-}(i\text{-}Pr)_3C_6H_2)_4]$ are isomorphous and presumably isostructural with iron analogues whose X-ray crystal structures have been reported.[13,14] The majority of the $[NR_4][Ga(SR)_4]$ and related $[NR_4][Fe(SR)_4]$ complexes also crystallize in the tetragonal space group $I\bar{4}$, which imposes S_4 point group symmetry on the cations and anions. The isomorphous relationship between the gallium and iron complexes has proven valuable in several aspects. First, it has been possible to prepare mixed single crystals with varying amounts of the colored, paramagnetic iron complex doped into the colorless and diamagnetic gallium complex. The optically and magnetically dilute materials are being studied by single-crystal electronic spectroscopy and ESR measurements. Because of the inaccessibility of the +2 oxidation state of gallium, gallium thiolate complexes do not undergo the auto redox reaction ($M^{3+} + RS^- = M^{2+} + {}^1/_2RSSR$) that is responsible for the instability of many Fe(III) thiolate complexes. Due to the great sensitivity of $[Fe(SR)_4]^-$ complexes, we have found it advantageous to first prepare the gallium complex and then apply the information learned concerning cations of crystallization, solvents, and methods of crystallization toward the synthesis of the isomorphous iron complex. Using this approach, we were able, for the first time, to synthesize and isolate the $[Fe(SR)_4]^-$ complexes with sterically unhindered thiolate ligands (e.g. R = Me, Et, *i*-Pr).[15]

Crystal Structures of $[Ga(SEt)_4]^-$ and $[Ga(SPh)_4]^-$. $[(n\text{-}Pr)_4N][Ga(SEt)_4]$ (**1**) and $[NEt_4][Ga(SPh)_4]$ (**2**) were structurally characterized by X-ray crystallography. Compound **1** is isomorphous and isostructural with its iron analogue, $[(n\text{-}$

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(14) Millar, M.; Koch, S. A.; Fikar, R. *Inorg. Chim. Acta* **1984**, *88*, L15–L16.

(15) Koch, S. A.; Maelia, L. E.; Millar, M. *J. Am. Chem. Soc.* **1983**, *105*, 5944–5945.

Table VII. Bond Lengths (Å) and Bond Angles (deg) for $(Et_4N)[Ga(SPh)_4]$ (**2**)

Ga–S1	2.260 (3)	S4–C41	1.74 (1)
Ga–S2	2.242 (3)	C41–C42	1.42 (1)
Ga–S3	2.270 (2)	C41–C46	1.37 (2)
Fe–S4	2.257 (3)	C42–C43	1.35 (2)
		C43–C44	1.20 (2)
S1–C11	1.79 (1)	C44–C45	1.57 (3)
C11–C12	1.37 (2)	C45–C46	1.35 (2)
C11–C16	1.31 (2)		
C12–C13	1.36 (2)	N–C1	1.51 (2)
C13–C14	1.19 (2)	N–C3	1.55 (2)
C14–C15	1.22 (2)	N–C5	1.71 (2)
C15–C16	1.41 (2)	N–C7	1.59 (3)
		N–C1A	1.70 (4)
S2–C21	1.778 (8)	N–C3A	1.64 (2)
C21–C22	1.36 (1)	N–C5A	1.52 (3)
C21–C26	1.37 (1)	N–C7A	1.59 (3)
C22–C23	1.43 (1)		
C23–C24	1.34 (2)	C1–C2	1.60 (3)
C24–C25	1.40 (1)	C3–C4	1.60 (2)
C25–C26	1.42 (1)	C5–C6	1.26 (2)
		C7–C8	1.57 (3)
S3–C31	1.68 (1)	C1A–C2	1.27 (4)
C31–C32	1.50 (1)	C3A–C4	1.48 (3)
C31–C36	1.44 (1)	C5A–C6	1.67 (3)
C32–C33	1.35 (2)	C7A–C8	1.58 (3)
C33–C34	1.38 (2)		
C34–C35	1.34 (1)		
C35–C36	1.37 (1)		
S1··S2	3.780 (3)	S1··S3	3.509 (3)
S1··S4	3.780 (4)	S2··S3	3.793 (3)
S2··S4	3.452 (4)	S3··S4	3.817 (4)
S1–Ga–S2	114.2 (1)	S4–C41–C42	122.1 (8)
S1–Ga–S3	101.6 (1)	S4–C41–C46	122.8 (8)
S1–Ga–S4	112.0 (1)	C42–C41–C46	115 (1)
S2–Ga–S3	114.5 (1)	C41–C42–C43	120 (1)
S2–Ga–S4	100.2 (1)	C42–C43–C44	124 (2)
S3–Ga–S4	115.0 (1)	C43–C44–C45	124 (1)
		C44–C45–C46	108 (1)
Ga–S1–C11	99.2 (3)	C41–C46–C45	130 (1)
Ga–S2–C21	108.3 (3)		
Ga–S3–C31	106.7 (3)	C1–N–C3	127 (1)
Ga–S4–C41	100.1 (3)	C1–N–C5	113 (1)
		C1–N–C7	107 (1)
S1–C11–C12	129 (1)	C3–N–C5	102 (1)
S1–C11–C16	121 (1)	C3–N–C7	99 (1)
C12–C11–C16	110 (1)	C5–N–C7	106 (1)
C11–C12–C13	123 (1)	C1A–N–C3A	105 (2)
C12–C13–C14	125 (2)	C1A–N–C5A	113 (2)
C13–C14–C15	115 (2)	C1A–N–C7A	103 (2)
C14–C15–C16	126 (2)	C3A–N–C5A	105 (1)
C11–C16–C15	120 (2)	C3A–N–C7A	106 (1)
		C5A–N–C7A	124 (1)
S2–C21–C22	115.3 (6)		
S2–C21–C26	124.8 (7)	N–C1–C2	109 (2)
C22–C21–C26	119.7 (8)	N–C3–C4	110 (1)
C21–C22–C23	118.7 (9)	N–C5–C6	121 (1)
C22–C23–C24	121 (1)	N–C7–C8	109 (2)
C23–C24–C25	121 (1)	N–C1A–C2	117 (3)
C24–C25–C26	117 (1)	N–C3A–C4	112 (2)
C21–C26–C25	122.3 (9)	N–C5A–C6	109 (2)
		N–C7A–C8	108 (1)
S3–C31–C32	118.7 (8)		
S3–C31–C36	128.6 (7)		
C32–C31–C36	112.7 (9)		
C31–C32–C33	121 (1)		
C32–C33–C34	122.5 (9)		
C33–C34–C35	118.0 (8)		
C34–C35–C36	124 (1)		
C31–C36–C35	120.9 (9)		

Table VIII. Bond Lengths (Å) and Bond Angles (deg) for $(Et_4N)_2[Ga_2S_2(SPh)_4]$ (**3**)

Ga··Ga′	2.943 (1)	S3–C31	1.764 (4)
Ga–S1	2.273 (1)	C31–C32	1.391 (5)
Ga–S1′	2.264 (1)	C31–C36	1.400 (5)
Ga–S2	2.288 (1)	C32–C33	1.363 (5)
Ga–S3	2.279 (1)	C33–C34	1.371 (6)
S1··S1′	3.453 (2)	C34–C35	1.357 (6)
S1··S2	3.831 (3)	C35–C36	1.363 (6)
S1··S2′	3.676 (3)	N–C1	1.525 (5)
S1··S3	3.886 (3)	N–C3	1.506 (5)
S1··S3′	3.844 (3)	N–C5	1.501 (5)
S2··S3	3.576 (3)	N–C7	1.514 (4)
S2–C21	1.759 (3)	C1–C2	1.486 (6)
C21–C22	1.386 (5)	C3–C4	1.503 (6)
C21–C26	1.388 (5)	C5–C6	1.493 (6)
C22–C23	1.377 (5)	C7–C8	1.482 (7)
C23–C24	1.376 (7)		
C24–C25	1.365 (6)		
C25–C26	1.364 (6)		
Ga–S1–Ga′	80.88 (3)	S3–C31–C32	124.4 (3)
S1–Ga–S1′	99.12 (3)	S3–C31–C36	118.3 (3)
S1–Ga–S2	114.25 (4)	C31–C32–C33	120.4 (3)
S1′–Ga–S2	107.71 (3)	C32–C33–C34	121.3 (4)
S1–Ga–S3	117.22 (4)	C33–C34–C35	119.3 (4)
S1′–Ga–S3	115.61 (4)	C34–C35–C36	120.7 (4)
S2–Ga–S3	103.05 (4)	C31–C36–C35	121.1 (4)
Ga–S2–C21	107.3 (1)	C1–N–C3	108.6 (3)
Ga–S3–C31	108.8 (1)	C1–N–C5	108.8 (3)
		C1–N–C7	111.3 (3)
S2–C21–C22	124.8 (3)	C3–N–C5	110.8 (3)
S2–C21–C26	117.8 (3)	C3–N–C7	107.8 (3)
C21–C22–C23	121.9 (4)	C5–N–C7	109.5 (3)
C22–C23–C24	119.0 (4)		
C23–C24–C25	119.9 (4)	N–C1–C2	115.4 (3)
C24–C25–C26	120.9 (4)	N–C3–C4	115.7 (3)
C21–C26–C25	120.9 (4)	N–C5–C6	116.6 (3)
		N–C7–C8	115.1 (3)

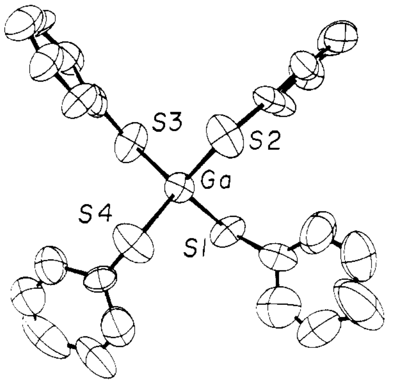

Figure 2. ORTEP diagram of the anion of $[Et_4N][Ga(SPh)_4]$ (**2**).

Pr)$_4$N][Fe(SEt)$_4$].[15] The ORTEP diagram of the anion of **1** displayed in Figure 1, shows a view directed down the crystallographically imposed S_4 axis. The crystallographic symmetry enforces S_4 point group symmetry on the entire anion. The $[GaS_4]$ unit has required D_{2d} symmetry with the result that there are only two independent S–Ga–S angles. The two S–Ga–S angles bisected by the S_4 axis are 109.8 (2)° and the four other S–Ga–S angles are 109.3 (1)°. As a result of the near equivalence of the two sets of angles, the $[GaS_4]$ core has T_d symmetry. The Ga–S distance in **1** is 2.264 (3) Å; it is not statistically different from the Fe–S distance [2.269 (1) Å] in $[(n\text{-}Pr)_4N][Fe(SEt)_4]$. In fact, there are only very slight differences between the gallium and iron structures.

$[NEt_4][Ga(SPh)_4]$ (**2**) is not isomorphous with its $[Fe(SPh)_4]^-$ analogue,[15] and its crystal structure shows distinct differences in the conformation of the SPh ligands. Although there is no crystallographic required symmetry in the anion (Figure 2), the $[Ga(SPh)_4]^-$ has a pseudo C_2 axis that bisects the S2–Ga–S3 [114.5 (1)°] and the S1–Ga–S4 [112.0 (1)°] angles. The four other S–Ga–S angles are divided by the C_2 axis into two groups of two: S1–Ga–S3 [101.6 (1)°] ≅ S2–Ga–S4 [100.2 (1)°] and S1–Ga–S2 [114.2 (1)°] ≅ S3–Ga–S4 [115.0 (1)°]. The structure shows two distinct conformations of the thiolate ligands. In the thiolate ligands of S1 and S4, the Ga–S bonds are approximately

Table IX. Distances (Å) and Angles (deg) in Selected Edge-Sharing Tetrahedral Dimers and Extended Systems of Ga(III) and Fe(III)

compd	M–M	M–X_b	M–X_t	M–X_{av}	X_b–X_b	M–X_b–M	X_b–M–X_b	X_t–M–X_t	X_b–M–X_t	ref
$[Ga_2S_2(SPh)_4]^{2-}$	2.943 (1)	2.269 (5)	2.284 (5)	2.276	3.45	80.88 (3)	99.12 (3)	103.05 (4)	113.7	*a*
$[Fe_2S_2(S\text{-}p\text{-tol})_4]^{2-}$	2.691 (1)	2.201 (1)	2.312 (1)	2.257	3.48	75.39 (4)	104.61 (4)	111.2	110.3	21
$[Fe_2S_2(Cl)_4]^{2-}$	2.716 (1)	2.201 (1)	2.252 (9)		3.46	76.21 (3)	103.79 (3)	105.37 (4)	112.0	24
$Ba_3Ga_2S_6$	3.096	2.34 (3)	2.243 (2)	2.290	3.50	82.9	97.1 (1)	118.1 (1)	109.8	25
$Na_6Fe_2S_6$	2.877 (2)	2.28 (2)	2.251 (1)	2.265	3.54	78.3	101.7	111.1	110.9	26
$[Fe_2Se_2(Se_5)_2]^{2-}$	2.787 (2)	2.323 (6)	2.425 (4)	2.374	3.72	73.73 (7)	106.27 (8)	108.61 (7)	110.2	27
$Cs_6Ga_2Se_6$	3.427 (3)	2.49 (2)	2.40 (1)	2.442	3.59	87.1 (1)	92.9 (1)	110.6 (1)	113.1	28
$Na_6Fe_2Se_6$	2.974 (6)	2.39 (2)	2.369 (2)	2.383	3.75	76.8	103.2	110.8	110.6	29
$K_6Ga_2O_6$	2.72	1.94	1.84	1.89	2.77	88.5	91.5	110.4	113.4	30
$K_6Fe_2O_6$	2.72	1.95	1.86	1.90	2.79	88.5	91.5	110.4	113.4	31, 32
$CsGaS_2$	2.953 (3)	2.274 (11)		2.274	3.46	80.8	99.2		114.8[b]	33
$CsFeS_2$	2.71 (1)	2.231 (3)		2.231	3.54	74.8	105.2		111.6[b]	33
Ga_2Cl_6	3.12	2.29 (9)	2.06 (3)	2.18	3.35	86 (2)	94 (2)	123 (2)	109 (2)	34
Fe_2Cl_6	3.17	2.28 (3)	2.11 (3)	2.20	3.28	88	92 (3)	128 (3)	*c*	35

[a] This work. [b] External. [c] Not given.

perpendicular to the phenyl rings. In the thiolate ligands of S2 and S3, the phenyl rings lie in the same plane as the Ga–S bonds. All the thiolate ligands in the structure of $[Fe(SPh)_4]^-$ have the latter thiolate conformation.[15] In fact this latter thiolate conformation, in which the sulfur 3p lone-pair orbital is in conjugation with the phenyl ring, is the prevalent conformation found for benzenethiolate ligands coordinated to tetrahedral MS_4 cores.[15–17] Although the difference in the conformation of the thiolate ligands has no apparent effect on Ga–S bond distances, it has an effect on the Ga–S–C angles, which differ by about 7°. The Ga–S–C angles of thiolates of S2 and S3 (108.3°, 106.7°) compare favorably to the Fe–S–C angles in $[Fe(SPh)_4]^-$ [112 (2)° average] while the Ga–S–C angles of thiolates of S1 and S4 (99.2 (3)°, 100.1 (3)°] can be compared to the Fe–S–C angles [102.4 (2)°] in $[Fe(S\text{-}2,3,5,6\text{-}Me_4C_6H)_4]^-$ in which the presence of *o*-methyl groups enforces a similar thiolate conformation.[13] The increase in Ga–S–C angle for thiolates of S2 and S3 results from steric interaction of the ortho hydrogen of the phenyl ring with the $[GaS_4]$ core. The effect of this type of interaction on the S–M–S angles of $[M(SPh)_4]$ compounds has been previously described in detail.[15–17] The observed S–Ga–S angles in **2** are consistent with that type of analysis.

The average Ga–S distance [2.26 (1) Å] in **2** is equal to the distance in **1** [2.264 (1) Å]. The similarity of these two distances should be contrasted to the small but significant difference in the Fe–S distances of 2.269 (1) Å for $[(n\text{-}Pr)_4N][Fe(SEt)_4]$ and 2.297 (6) Å for $[Et_4N][Fe(SPh)_4]$.[15] Ga–S(R) bond distances are essentially independent of thiolate substituents, while Fe(III)–S(R) distances are inversely proportionate to the electron donating capacity of the thiolate ligand. The Shannon–Prewitt crystal radii for tetrahedral Fe(III) and Ga(III) are 0.63 and 0.61 Å, respectively.[18,19] These radii, taken with the radius of S^{2-} (1.70 Å), predict distances of 2.33 Å for Fe(III)–S and 2.31 Å for Ga(III)–S bonds. The shorter M–S distances observed in the $[Fe(SR)_4]^-$ and $[Ga(SR)_4]^-$ complexes are examples of a general phenomena in M–S compounds. The values of the Shannon–Prewitt empirical radii for Fe(III) and Ga(III) are based on structural data from metal oxides and fluorides. Ga–S and Fe–S bonds as well as many other M–S bonds are shorter than the predicted distances based on the oxide radii values.[18–20] Shannon has recently discussed the problems associated with metal sulfide distances and has presented a preliminary table of empirical sulfide crystal radii.[20] Shannon has assigned a sulfide crystal radius of 0.58 Å to tetrahedral $[Ga^{III}S_4]$, which predicts a Ga–S distance of 2.28 Å. Recent structure reports[5] and the structures presented in this paper are in good agreement with a narrow range of 2.26–2.30 Å for Ga(III)–S_{av} distances in GaS_4 units. Fe(III)–S_{av} bonds in $[Fe(III)S_4]$ units show a substantially wider range of distances and a distinct dependence on the identity of the sulfur ligands (vide infra).

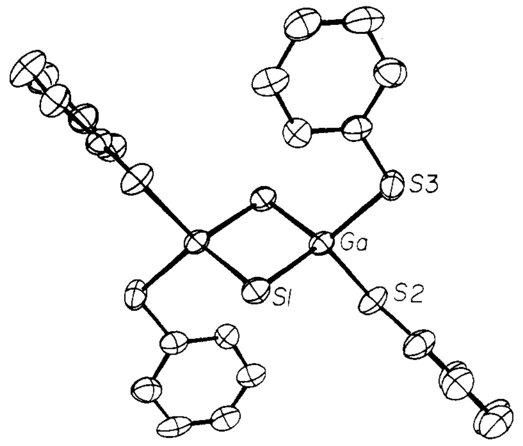

Figure 3. ORTEP diagram of the anion of $[Et_4N]_2[Ga_2S_2(SPh)_4]$ (**3**).

Structure of the $[Ga_2S_2(SPh)_4]^{2-}$ Anion. We attempted the synthesis of gallium–sulfur compounds of higher nuclearity to see if the close structural analogy exhibited by the gallium and iron tetrathiolates could be extended to cluster compounds. The reaction of $GaCl_3$ with NaSH (1 equiv) and LiSPh (4 equiv) in ethanol followed by the addition of $(NEt_4)Br$ gave $(NEt_4)_2[Ga_2S_2(SPh)_4]$ (**3**). The overall structure of this centrosymmetric dimer (Figure 3) is similar to that reported for $(NEt_4)_2[Fe_2S_2(S\text{-}p\text{-tol})_4]$ (**4**).[21] An immediate conclusion is that the $[MS_2M]$ unit, which is the basic structural unit of FeS clusters, can be reproduced in a molecular non-transition-metal complex. Compound **3** is not, however, isomorphous with **4**[21] (or with $(NEt_4)_2[Fe_2S_2(SPh)_4]$).[22] Although the thiolate ligands in both **3** and **4** have the conformation in which the M–S bond is in the same plane as the phenyl ring, the overall geometric arrangement by which the four phenyl rings interact with the $[M_2S_6]$ cores is different. In **3** the phenyl ring of thiolate ligand of S3 is approximately perpendicular to the $[GaS_2Ga]$ plane. A similar conformation has been previously observed in the structures of $(NEt_4)_3[Fe_3S_4(SPh)_4]$[23] and $(Et_4N)_2[S_2WS_2Fe(SPh)_2]$.[17] The

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variation and the relative values of the S_b–M–S(R) angles in **3** and **4** can be understood in terms of the steric interaction of the phenyl groups of the thiolate ligands with the $[M_2S_6]$ core. This interaction is analogous to that of the benzenethiolate ligands in $[M(SPh)_4]^{n-}$ complexes which was previously discussed.

Analysis of the Structures of M_2X_6 Compounds. The structural parameters of **3** and **4** and related structural units in molecular compounds and in solid-state materials (Table IX) provide a database for an attempt to understand the relationship between bonding and structure in metal chalcogenide $[MX_2M]$ dimers. We would like to understand the differences in the structural parameters of **3** and **4** (e.g., why the Ga–Ga distance in **3** [2.943 (1) Å] is longer than the corresponding Fe–Fe distance in **4** [2.691 (1) Å]. Any analysis of the structural distortions in a series of edge-bridged tetrahedral dimers is complicated by the interrelationship between the various structural parameters. The change of one structural parameter in a MX_2M unit, by necessity, results in a change in at least one other distance or angle. The bonding in edge-sharing dimers, which was first discussed by Pauling[38] in 1929, has been the subject on many subsequent studies.[39–46]

The structures of Ga_2Cl_6 (solid)[34] and Fe_2Cl_6 (gas phase)[35] display bond distance and angle parameters (Table IX) that are prototypical of simple M_2X_6 dimers. In the dimers, the M–Cl_b distance is increased and the M–Cl_t distance is decreased in comparison to the distance in the monomeric $[MCl_4]^-$ complex. However, the average of all the metal chloride distances in the dimers is close to the distance in the monomer. In Fe_2Cl_6, the average of Fe–Cl_b (2.28 Å) and Fe–Cl_t (2.11 Å) is 2.20 Å, while in $[FeCl_4]^-$,[47,48] Fe–Cl is 2.18 Å. In Ga_2Cl_6, the average of Ga–Cl_b (2.29 Å) and Ga–Cl_t (2.11 Å) is 2.18 Å, while in $[GaCl_4]^-$,[49,50] Ga–Cl is 2.17–2.18 Å. Similar relationships are seen in the structures of $[Zn_2Cl_6]^{2-}$ and $[ZnCl_4]^{2-}$,[51,52] $[Co_2Cl_6]^{2-}$ and $[CoCl_4]^{2-}$,[53,54] and $[Fe_2(SEt)_6]^{2-}$ and $[Fe(S_2\text{-}o\text{-xyl})_2]^{2-}$.[55,56]

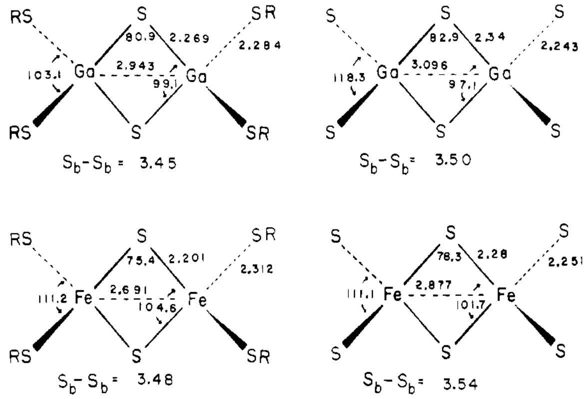

Figure 4. Structural diagrams showing bonding parameters for $[Ga_2S_2(SPh)_4]^{2-}$, $[Fe_2S_2(S\text{-}p\text{-tol})_4]^{2-}$, $[Ga_2S_2(S)_4]^{6-}$, and $[Fe_2S_2(S)_4]^{6-}$.

In a geometrically idealized dimer, the X_b–M–X_b and M–X_b–M angles would be 109.5 and 70.5°, respectively. From these angles and the experimentally determined Fe–Cl_b distance of 2.28 Å, an idealized Fe_2Cl_6 structure would have Fe–Fe and Cl_b–Cl_b distances of 2.63 and 3.72 Å, respectively. The deviations from this idealized structure are substantial (Table IX). A simple bonding picture can explain the observed distortions. The structure of the $[MCl_2M]$ ring in Fe_2Cl_6 and Ga_2Cl_6 results from an increase in the M–M distance, which is due to metal–metal repulsion, with the increase limited by the intraring Cl_b–Cl_b repulsion. This simple structural explanation is related to the third of Pauling's electrostatic valence rules.[38] The Fe–Cl_b distance together with a constant Cl_b–Cl_b distance determines the other distance and angle parameters in the $[FeCl_2Fe]$ ring. Thus, the similarity of M–M distances in Fe_2Cl_6 and Ga_2Cl_6 results from the similarity in their M–Cl_b distances.

In light of the discussion of the structures of Ga_2Cl_6 and Fe_2Cl_6, the structures of $[Ga_2S_2(SPh)_4]^{2-}$ (**3**) and $[Fe_2S_2(S\text{-}p\text{-tol})_4]^{2-}$ (**4**) show some structural anomalies. The Fe–Fe 2.691 (1) Å] and Ga–Ga [2.943 (1) Å] distances in **3** and **4** are significantly different, and in both cases they are shorter than the distances in Fe_2Cl_6 (3.17 Å) and Ga_2Cl_6 (3.12 Å). The Ga–S_b bonds (2.269 Å) in **3** are shorter than the Ga–S_t bonds (2.284 Å), and the Fe–S_b distance (2.201 Å) in **4** is considerably shorter than the Fe–S_t distances (2.312 Å). The Fe–S(R) bond distance in **4** is also longer than the corresponding distance in monomeric $[Fe(SR)_4]^-$ complexes. In spite of this opposite trend in the M–S_t and M–S_b bond distances, the average values of M–S_b and M–S_t are still comparable to the M–S distance in the monomeric $[M(SR)_4]^-$. The Ga–S_{av} bond distance (2.276 Å) in **3** is longer than the Fe–S_{av} distance (2.257 Å) in **4**. It is important to note that the bridging and terminal ligands in **3** and in **4** are not the same.

Considerable insight into the structures of **3** and **4** can be obtained through a comparison (Figure 4) with the structures of the $[Ga_2S_2(S)_4]^{6-}$ and $[Fe_2S_2(S)_4]^{6-}$ ions.[25,26] These are two members of the complete series of discrete $[M_2X_6]^{6-}$ (M = Ga, Fe; X = O, S, Se) anions which have been structurally characterized in solid-state materials (Table IX).[25,26,28–32] The structure of $[Fe_2S_2(S)_4]^{6-}$ is quite important because it is a $[Fe_2S_2]^{2+}$ compound whose Fe–Fe distance (2.877 Å) is far outside the small range of Fe–Fe distances (2.68–2.70 Å) found for all other

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Table X. Trends in the Bonding Parameters of $[M_2X_6]^{6-}$, Discrete Iron(III) and Gallium(III) Chalcogenide Dimers

	diff, Å		
	$[M_2O_6]^{6-}$	$[M_2S_6]^{6-}$	$[M_2Se_6]^{6-}$
(Ga–Ga) – (Fe–Fe)	0.0	0.22	0.45
($Ga–X_b$) – ($Fe–X_b$)	0.0	0.06	0.10
($Ga–X_{av}$) – ($Fe–X_{av}$)	0.01	0.03	0.06
($Ga–X_b$) – ($Ga–X_t$)	0.10	0.10	0.095
($Fe–X_b$) – ($Fe–X_t$)	0.09	0.03	0.02

$[Fe_2S_2(L)_4]^{2-}$ compounds (L = SPh, Cl, NC_4H_4, L_2 = S_2-*o*-xyl, S_5, *o,o'*-biphenolate).[21,24,36,37] The Ga–Ga distance in $[Ga_2S_2(S)_4]^{6-}$ is 3.096 Å and is also measurably longer than in **3**. $[Ga_2S_2(S)_4]^{6-}$ and $[Fe_2S_2(S)_4]^{6-}$ have structures that follow the normal pattern found for M_2X_6 dimers; the $M–S_b$ bonds are longer than the $M–S_t$ bonds. Again, the average of the $M–S_t$ and $M–S_b$ bonds distances are nearly equal to the M–S distance in the monomers. In both pairs ($[M_2S_2(SR)_4]^{2-}$ and $[M_2S_2(S)_4]^{6-}$; M = Fe, Ga), replacement of the terminal thiolate ligands with a terminal sulfido ligand gives a decrease in the $M–S_t$, which causes an increase in the $M–S_b$ distance and a concomitant increase in the distance between the metals. A quite analogous structural difference is displayed by the $[Fe_2Se_2(Se_5)_2]^{2-}$ and the $[Fe_2Se_2(Se)_4]^{6-}$ ions.[27,29]

The factors governing the geometry of $[MS_2M]$ units are the same as in the $[MCl_2M]$ unit of M_2Cl_6. The M–M distance is due to metal–metal repulsion, which in turn is limited by the nonbonded repulsion of the bridging atoms. For a given set of bridging atoms, the $X_b–X_b$ distance should be constant. The $S_b–S_b$ distance in **3** is 3.45 Å, which is only slightly different from the $S_b–S_b$ distance in **4** (3.48 Å). Similar $S_b–S_b$ distances are present in $[Ga_2S_6]^{6-}$ (3.50 Å) and $[Fe_2S_6]^{6-}$ (3.54 Å). If one assumes a model with a constant $S_b–S_b$ distance, then the difference in the M–M distance in **3** and **4** is geometrically accounted for by the 0.07-Å difference in the $Ga–S_b$ and $Fe–S_b$ bond lengths. The difference in the M–M distances in $[Ga_2S_6]^{6-}$ and $[Fe_2S_6]^{6-}$ is likewise explained by the 0.06-Å difference in their $M–S_b$ bond lengths. The differences between the iron and the gallium structures can be explained by the increased covalency in Fe–S vs. Ga–S bonds in the $[MS_2M]$ unit rather than by a difference in the M–M metal bonding. The extent of the covalency of the metal–chalcogenide bonds and its distribution between terminal and bridging ligands appears to be a controlling factor. This factor together with metal–metal repulsion and the nonbonded interaction between the two bridging ligands provides a satisfactory explanation for the parameters in the $[MX_2M]$ units. Other factors such as metal–metal bonding and interionic interactions would seem to be less important.

Further support for this analysis comes from consideration of corresponding oxide and selenide complexes. The structural parameters of the $[M_2O_2(O)_4]^{6-}$ anions are particularly interesting.[30-32] Both the iron and gallium anions have nearly identical metrical values; both have M–M bonds of 2.72 Å. The equivalence of the M–M distance in both compounds would argue against Fe–Fe bonding in the anion. The related structure of $K_6Mn_2O_6$ has a Mn–Mn distance of 2.80 Å and an $O_b–O_b$ distance of 2.69 Å.[32]

Several interesting trends in iron and gallium chalcogenide bonding can be observed in the structural parameters of the $[M_2X_6]^{6-}$ anions (Table X). The difference in the M–M distances between the gallium and iron analogues increases as a periodic function of the chalcogenide ligand. The parallel increase in the difference in the $M–X_b$ distances for the analogous compounds is the determining factor for the trend in the M–M distances. The differences in the $M–X_{av}$ distances also depend upon the chalcogenide. This trend has been discussed by Shannon in his analysis of empirical crystal radii for metal sulfides.[20] Fe(III)–S bonds have been observed to be shorter than predicted from the value of the crystal radius of Fe(III) on the basis of data obtained from Fe–O and Fe–F bonds. Ga–S bond distances, on the other hand, agree more closely with extrapolation from the crystal radius of Ga(III) based on Ga–O bond length data. The data shown in Table X support Shannon's observations and indicate that the trend toward increased covalency in Fe(III)–S bonds continues in Fe(III)–Se bonds.

Structures of Extended Chains of Edge-Shared Ga and Fe Tetrahedra. $[Ga_4Se_{10}]^{8-}$ and $[Ga_6Se_{14}]^{10-}$, two anions with linear, oligomeric chains of edge-shared $[GaSe_4]$ tetrahedra, have recently been synthesized and structurally characterized.[57] The Ga–Ga distances in these ions become gradually shorter as one moves toward the center of the chains. The metrical values in these structures can be explained in detail by using our structural model. In these two centrosymmetric anions, there are a total of five independent intraring $Se_b–Se_b$ distances. These distances vary only by 0.02 Å. The terminal selenides cause a skewed distribution in the Ga–Se bonds in the $[GaSe_4]$ tetrahedra on the end on the chains. This effect is transmitted toward the center of the chains by the bridging selenides. Both the skewed distribution in the Ga–Se distances and the dissymmetry in the selenide bridges are dissipated on moving from the ends toward the middle of the chains. The observed values in the Ga–Ga distance follow from the $Ga–Se_b$ bond lengths and the constant intraring $Se_b–Se_b$ distance.

Holm and co-workers have characterized a linear trimer of formula $[Fe_3S_4(SPh)_4]^{3-}$;[23,58] this unit can also be produced in the enzyme aconitase, under nonphysiological conditions.[59] The intraring $S_b–S_b$ distances of 3.48 Å are similar to the values in the dimers. The Fe–S(R) distances are considerably longer than the distance in $[Fe(SPh)_4]^{-}$, but again this longer distance is offset by the short $Fe–S_b$ distances in the $[(RS)_2Fe(S)_2]$ units. The $Fe–S_{av}$ distance in the central $[Fe(S_b)_4]$ unit (2.235 Å) is shorter than the $Fe–S_{av}$ distance in the $[Fe(S_b)_2(SPh)_2]$ units (2.264 Å). If a linear oligomer with terminal sulfido ligands were synthesized (e.g., $[Fe_3S_8]^{7-}$) we would predict that the Fe–Fe distances would be substantially longer than those in $[Fe_3S_4(SPh)_4]^{3-}$ (2.714 Å).

Solid-state compounds with an infinite linear chain of edge-shared $[MS_4]$ tetrahedra have been structurally characterized in SiS_2,[60] $AFeS_2$ (A = Na, K, Rb, Cs, $Ba_{0.5}$),[33,61-63] $CsGaS_2$,[33,64] and in the mixed-valence chain compounds, $Ba_{1+x}Fe_2S_4$[65] and $Na_3Fe_2S_4$.[62,66] Interestingly, the M–M distances in $CsGaS_2$ and $CsFeS_2$ are in closer agreement with the parameters in **3** and **4** rather than those of the $[M_2S_6]^{6-}$ anions. This result simply reflects the fact that the "terminal" sulfido ligands in $S_2MS_2MS_2$ units of the extended chain systems are also bridging ligands. In this regard, the monovalent thiolate ligand rather than the terminal divalent sulfido ligand more closely approximates the valence of the "terminal" sulfido ligands in the extended-chain systems. The Ga–S distance in $CsGaS_2$ is quite similar to the $Ga–S_{av}$ distance in **3** and $[Ga_2S_6]^{6-}$. However, the Fe–S distance in $CsFeS_2$ is considerably shorter than the $Fe–S_{av}$ distances in either **4** or $[Fe_2S_6]^{6-}$, but it is equal to the Fe–S distance in the $[Fe^{III}(S_b)_4]$ center metal in the linear $[Fe_3S_4(SR)_4]^{3-}$ trimer.[23,58]

Summary and Conclusions

$[Ga(SR)_4]^{-}$ and $[Ga_2S_2(SPh)_4]^{2-}$ complexes, which are close structural analogues to the biologically important iron–sulfur compounds, have been synthesized and structurally characterized. In the case of several of the $[Ga(SR)_4]^{-}$ complexes, their synthesis

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predated and aided in the synthesis of the corresponding $[Fe(SR)_4]^-$ analogues. The structures of $[Ga_2S_2(SR)_4]^{2-}$ and its iron analogue have been analyzed in the context of a general discussion of the geometric parameters of edge-sharing tetrahedral dimers. Many of the structural effects found in iron(III) chalcogenide compounds are also found in the gallium(III) chalcogenide systems. There are some important differences in the observed trends in the lengths of Ga(III)–S and Fe(III)–S bonds. The $Ga-S_{av}$ bond lengths in $[GaS_4]$ centers are not greatly affected by the nature of the sulfur ligands; $Ga-S_{av}$ distances are approximately the same in $[Ga(SR)_4]^-$, $[(S_b)_2Ga(SR)_2]$, and $[Ga(S_b)_4]$ units. In the case of Fe(III)–S bonds, there is a definite trend such that the $Fe-S_{av}$ bond length decreases in the series $[Fe^{III}(SR)_4]$ (2.267–2.30 Å) > $[(S_b)_2Fe(SR)_2]$ (2.25–2.26 Å) > $[Fe^{III}(S_b)_4]$ (2.23 Å). A major feature in the structure of $Fe(III)-S^{2-}-RS^-$ compounds is the strong tendency of Fe(III) to form short bonds to S^{2-}.[69] This tendency is displayed in several ways. The Fe–S bond distances in $[Fe(S_b)_4]$ centers are considerably shorter than Fe–S distances in $[Fe(SR)_4]^-$ compounds. The very short $Fe-S_b$ distance in $[Fe_2S_2(SR)_4]^{2-}$ complexes causes a reversal in normal behavior for edge-shared tetrahedra where $M-X_b$ is usually longer than $M-X_t$. In $[FeS_2Fe]^{2+}$ dimers the Fe–Fe distance is controlled by the $Fe-S_b$ bond distance, and the $Fe-S_b$ distance can affect (or be affected by) the $Fe-X_t$ bonds. Changes in the length of individual Fe–S bonds in an $[Fe^{III}S_4]$ unit in a cluster are counterbalanced by an opposite change in the length of another Fe–S bond in that unit. Detailed molecular orbital calculations of the $[Fe^{III}(SR)_4]^-$ and $[Fe_2S_2(SR)_4]^{2-}$ centers (performed by using the crystallographic values of Fe–S bond distances) have indicated that bridge S–Fe bonding is stronger than terminal S–Fe bonding.[70–72] Quantum mechanical calculations of gallium chalcogenide compounds would be valuable.

Although our analysis has been limited to Fe(III) centers, some of these structural observations will also be found in the structures of mixed-valence Fe–S clusters. For example, our analysis of M–S bond distances gives us a possible explanation of an anomaly that has been found in the structure of iron–sulfur model compounds. The $M-S_t$ bonds in $[Fe_2S_2(SR)_4]^{2-}$ (2.312 Å, R = *p*-tol)[21] are longer than the $M-S_t$ bonds in $[Fe_4S_4(SR)_4]^{2-}$ (2.263 Å, R = Ph) clusters[73] in spite of the fact that the average oxidation state of the iron atoms in the latter compound is +2.5 while in the former it is +3. This anomaly is removed if one considers all the ligands about each $[FeS_4]$ unit in these complexes. In $[Fe_2S_2(S\text{-}p\text{-tol})_4]^{2-}$ the average of the terminal and bridging Fe–S bonds is 2.257 Å while in $[Fe_4S_4(SPh)_4]^{2-}$ the average Fe–S bond distance is 2.281 Å. In a similar manner, the difference in the Fe–O bonds in $[Fe_4S_4(OPh)_4]^{2-}$ [1.865 (8) Å][74] and $[Fe_2S_2(o,o'\text{-biphenolate})_2]^{2-}$ [1.893 (3) Å][36] and the difference in the Fe–Cl bonds in $[Fe_4S_4Cl_4]^{2-}$ (2.216 Å), and $[Fe_2S_2Cl_4]^{2-}$ (2.252 Å) can be explained.[24]

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Registry No. **1**, 101165-29-1; **2**, 101165-31-5; **3**, 101165-33-7; $(Et_4N)[Ga(S\text{-}2,3,5,6\text{-}Me_4C_6H)_4]$, 101165-35-9; $(Et_4N)[Ga(SMe)_4]$, 101198-38-3; $(Ph_4P)[Ga(S\text{-}i\text{-}Pr)_4]$, 101165-37-1; $((n\text{-}Pr)_4N)[Ga(S\text{-}i\text{-}Pr)_4]$, 101165-38-2; $(Ph_4P)[Ga(S\text{-}2,4,6\text{-}i\text{-}PrC_6H_2)_4]$, 101165-40-6; $((n\text{-}Pr)_4N)GaCl_4$, 18430-55-2; NH_4GaCl_4, 15636-60-9.

Supplementary Material Available: Tables of hydrogen coordinates and thermal parameters (5 pages). Ordering information is given on any current masthead page. According to policy instituted Jan 1, 1986, the tables of calculated and observed structure factors (24 pages) are being retained in the editorial office for a period of 1 year following the appearance of this work in print. Inquiries for copies of these materials should be directed to the Editor.

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Notes

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Synthesis and Characterization of $NF_4^+BrF_4^-$ and $NF_4^+BrF_4O^-$

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Although the NF_4^+ cation is known to form salts with a large variety of anions, such as XF_2^- (X = H), XF_4^- (X = B, Al), XF_5^- (X = Ge, Sn, Ti), XF_6^- (X = P, As, Sb, Bi, Pt, Cr), $X_2F_{11}^-$ (X = Sb, Bi, Pt), XF_6^{2-} (X = Si, Ge, Sn, Ti, Mn, Ni), XF_7^- (X = W, U, Xe), XF_8^{2-} (X = Xe), XF_5O^- (X = W, U), XO_3F^- (X = S), and XO_4^- (X = Cl),[1] no salts are presently known in which the anion is derived from a halogen fluoride or oxyfluoride. Previous attempts[2] have been unsuccessful to prepare and isolate, for example, $NF_4^+XF_4O^-$ (X = Br, Cl), by metathesis according to

$$NF_4SbF_6 + CsXF_4O \overset{HF}{\nrightarrow} CsSbF_6\downarrow + NF_4XF_4O \quad (1)$$

When HF was used as a solvent, solvolysis of $CsXF_4O$ occurred according to

$$CsXF_4O + HF \rightarrow CsHF_2 + XF_3O \quad (2)$$

For $CsClF_4O$, substitution of HF by BrF_5 also resulted in a displacement reaction:

$$CsClF_4O + BrF_5 \rightarrow CsBrF_6 + ClF_3O \quad (3)$$

For $CsBrF_4O$ the analogous displacement by BrF_5 was not observed, and the observation of the correct amounts of $CsSbF_6$, NF_3, F_2, and BrF_3O for reaction 1 indicated the possible formation of $NF_4^+BrF_4O^-$ as an unstable intermediate. These results encouraged us to attempt the isolation and characterization of $NF_4^+BrF_4O^-$ and possibly $NF_4^+BrF_4^-$.

Experimental Section

Materials. Literature methods were used for the syntheses of NF_4SbF_6,[1] $CsBrF_4O$,[3] and $CsBrF_4$.[4] The BrF_5 (Matheson) was treated with

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