Inorg. Chem. **1981**, *20*, 3405-3410

Contribution from the Department of Chemistry,
University of North Dakota, Grand Forks, North Dakota 58202

Substituent Effects in Bis(arene) Complexes. Structures of Bis(1,4-bis(trifluoromethyl)benzene)chromium(0), Bis(1,3-bis(trifluoromethyl)benzene)chromium(0), and Bis(1-chloro-3-(trifluoromethyl)benzene)chromium(0)

MARC W. EYRING, E. CHARLES ZUERNER, and LEWIS J. RADONOVICH*

Received March 19, 1981

$[p\text{-}C_6H_4(CF_3)_2]_2Cr^0$, $[m\text{-}C_6H_4(CF_3)_2]_2Cr^0$, and $[m\text{-}C_6H_4(CF_3)Cl]_2Cr^0$ crystallize as discrete sandwich complexes having C_2, C_1, and C_i symmetry, respectively. The structures were determined from diffractometer data and refined to respective *R* values of 6.8%, 6.7%, and 5.5%. Ring carbon atoms of the π-arene ligands are planar in each case, and opposite rings within the same complex are approximately parallel. A substantial rotation from the eclipsed orientation of ring carbon atoms, amounting to 17 and 10°, is observed for the two bis(trifluoromethyl)benzene complexes. Internal ring angles at the CF_3-substituted carbon atoms are within experimental error to the hexagonal angle of 120°. Good σ-electron-withdrawing groups are expected to open this angle. These results suggest that the CF_3 group does not behave as a strongly σ-electron-withdrawing group such as fluorine, supporting the notion that the well-established polar effect of CF_3 is a "through space" rather than a "through the bond" effect.

Introduction

As part of a continuing study of first-row transition-metal arene complexes, we are interested in determining how substituent groups affect the stereochemistry and bonding in bis(arene) complexes. Previously[1] we have reported the structure of $[p\text{-}C_6H_4F_2]_2V^0$ in which a small "boat" deformation of the carbon framework exists, with the vanadium apparently interacting to a greater extent with the more electron-rich ring carbon atoms. In order to determine if chromium displays this same sensitivity, we attempted to study the analogous chromium compound. Unfortunately, $[p\text{-}C_6H_4F_2]_2Cr^0$ would crystallize only as twins.[2] We thus sought other good electron-withdrawing candidates as substituents. Trifluoromethyl (CF_3) seemed an ideal choice on the basis of the remarkable air and thermal stability of CF_3-substituted complexes.[3] The structure determination of $[p\text{-}C_6H_4(CF_3)_2]_2Cr^0$ (**1**) and $[m\text{-}C_6H_4(CF_3)]_2Cr^0$ (**2**) revealed that planar π-arene ligands exist in these complexes; however, the average internal ring angles at the substituted carbons were not those expected for a good σ-electron-withdrawing group.[4] Nevertheless, the internal consistency of the structural parameters was less than ideal, reflecting the reluctance of the two compounds to form truly excellent quality crystals. In order to provide higher quality structural data and in order to provide a direct comparison between the CF_3 group and a σ-electron-withdrawing group, we determined the structure of $[m\text{-}C_6H_4(CF_3)Cl]_2Cr^0$ (**3**). Structural results for these three CF_3-substituted bis(arene) complexes are reported herein.

Table I. Crystal Data

	$[p\text{-}C_6H_4\text{-}(CF_3)_2]_2Cr^0$	$[m\text{-}C_6H_4\text{-}(CF_3)_2]_2Cr^0$	$[m\text{-}C_6H_4\text{-}(CF_3)Cl]_2Cr^0$
a, Å	16.53 (2)	8.076 (7)	8.879 (1)
b, Å	7.028 (8)	25.17 (1)	8.287 (1)
c, Å	16.47 (2)	9.277 (5)	10.588 (1)
β, deg	119.26 (3)	117.79 (4)	111.50 (1)
ρ_{calcd}, g/cm^3	1.91	1.92	1.889
ρ_{obsd}, g/cm^3	1.90 (1)	1.85 (2)	1.895 (8)
Z	4	4	2
space group	*C*2/*c*	*P*2$_1$/*c*	*P*2$_1$/*c*

Experimental Section

Powdered samples of **1** and **2** were supplied by H. F. Efner and K. J. Klabunde.[3] Crystals were prepared by the slow evaporation of hexane solutions at ~3 °C. Compound **3** was prepared in our laboratory by cocondensing Cr (vapor) with 1-chloro-3-(trifluoromethyl)benzene onto the walls (~77 °K) of a metal vapor reactor at 7 × 10^{-3} torr. All reagents were thoroughly degassed prior to reaction, and the metal was vaporized for 55 min. The yellow-brown matrix was warmed to room temperature and filtered under N_2, and excess ligand was stripped under high vacuum. Single crystals were obtained by sublimation. Crystals were mounted in thin-walled glass capillaries with the longest dimension parallel to the capillary walls. Crystals of **3** were mounted with the added precaution of working under a N_2 atmosphere. The crystals used for data collection had the following dimensions: 0.50 × 0.17 × 0.37 mm (**1**), 0.66 × 0.33 × 0.50 mm (**2**), and 0.47 × 0.27 × 0.27 mm (**3**). Precession photographs followed by the accurate determination of lattice constants on the diffractometer provided the crystal data listed in Table I for the three compounds.

Intensity data was collected on a Picker card-controlled diffractometer for **1** and **2** and on a FACS-1 diffractometer for **3**, using Zr-filtered Mo Kα radiation (λ = 0.7107 Å). Each peak was scanned at the rate of 1°/min, and stationary background counts were of 20-s duration at the scan limits. Scan widths of 2.12, 1.2, and 1.5° were used for compounds **1**–**3**, respectively, plus a small allowance for spectral dispersion. Crystals of the compounds provided data to a limiting 2θ of 52.87° for **1**, 56.83° for **2**, and 68.2° for **3**. The intensity of three standard reflections, monitored after every 100 data, decreased linearly by ~14% over the course of data collection for **1** and **2** but remained statistically constant for **3**. Small scaling corrections were applied to the data on **1** and **2** to account for this decrease.

The data were reduced by application of Lorentz and polarization factors, and standard deviations were calculated as described previously.[1] Values of *i* were 0.01, 0.04, and 0.01 for **1**–**3**, respectively. For **1** some 1409 data with $F_o > 3\sigma_F$ were taken as observed while for **2** and **3** some 3416 and 2500 data, respectively, with $F_o > 2\sigma_F$ were judged observed. The linear absorption coefficients[5] for **1**–**3** were 0.853, 0.855, and 1.25 mm^{-1}. Because of the crystal dimensions, the data on **1** and **3** were corrected for absorption. Transmission factors for **1** ranged from 0.861 to 0.933 while those of **3** ranged from 0.826 to 0.866.

The structural problems were solved with the use of Patterson and Fourier techniques.[6] Full-matrix isotropic refinement was followed

---

(1) Radonovich, L. J.; Zuerner, E. C.; Efner, H. F.; Klabunde, K. J. *Inorg. Chem.* **1976**, *15*, 2976.

(2) We have recently determined the structure of the meta isomer ($[m\text{-}C_6H_4F_2]_2Cr^0$), which is free of the twinning problem.

(3) Klabunde, K. J.; Efner, H. F. *Inorg. Chem.* **1975**, *14*, 789.

(4) Domenicano, A.; Vaciago, A.; Coulson, C. A. *Acta Crystallogr., Sect. B* **1975**, *B31*, 221.

(5) MacGillavry, C. H., Rieck, G. D., Lonsdale, K., Eds.; "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1962; Vol. III.

0020-1669/81/1320-3405$01.25/0

Table II. Atomic Coordinates[a] in $[p\text{-}C_6H_4(CF_3)_2]_2Cr^0$

atom	10^4x	10^4y	10^4z
Cr	0.0	2787 (2)	2500
C_1	633 (5)	5064 (8)	3453 (4)
C_2	947 (5)	5089 (9)	2803 (6)
C_3	319 (6)	5105 (9)	1860 (5)
C_4	564 (6)	510 (9)	2096 (6)
C_5	951 (5)	484 (9)	3059 (6)
C_6	386 (6)	471 (9)	3463 (5)
C_7	1299 (8)	5071 (11)	4456 (6)
C_8	1178 (10)	501 (14)	1685 (10)
F_1	984 (6)	4243 (10)	4962 (4)
F_2	1521 (4)	6831 (7)	4788 (3)
F_3	2082 (5)	4266 (10)	4659 (4)
F_4	704 (7)	1254 (11)	786 (6)
F_5	1381 (5)	−1214 (8)	1533 (6)
F_6	1880 (5)	1489 (11)	2058 (7)
H_2	1532 (52)	5024 (109)	2995 (50)
H_3	456 (52)	5063 (112)	1455 (51)
H_5	1533 (53)	658 (109)	3370 (51)
H_6	606 (53)	567 (112)	4034 (51)

[a] Estimated standard deviations are given in parentheses.

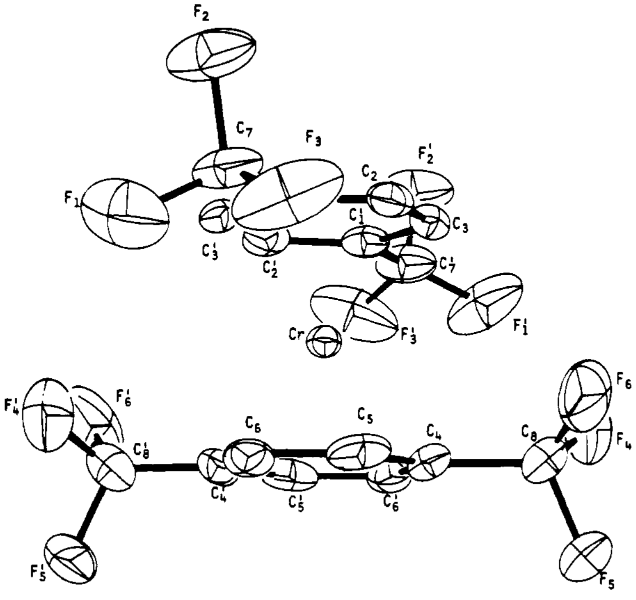


Figure 1. ORTEP drawing at 25% probability of $[p\text{-}C_6H_4(CF_3)_2]_2Cr^0$ as it exists in the crystal. Ring hydrogen atoms have been excluded for clarity. Hydrogen atoms are numbered according to the associated carbon. Prime notation is used for those atoms related by the twofold axis.

by fully anisotropic refinement,[7] using unit weights and including anomalous dispersion corrections[8] for the chromium atom. Because of the large asymmetric unit of **2**, anisotropic refinement was carried out varying the parameters of the metal and only one of the ligands in alternating cycles, thus ignoring correlations between ligands. Regions of C–H bond densities were incorporated in the final cycles of refinement with fixed thermal parameters. At this stage, punching errors were discovered on two of the data for **1**, and they were excluded in further refinement. Empirical weights ($w = 1/\sigma^2$) were then calculated as described previously[1] and used in additional cycles of refinement. None of the structures showed a sensitivity to the weighting scheme; however, the error of fit improved for **3** with use of $1/\sigma^2$ weighting. Thus the results of unit weighted refinement are reported for **1** and **2** while the results of $1/\sigma^2$ weighted refinement are reported for **3**. The final R values[9] were as follows: for **1**, R = 6.8%, R_w = 7.1%; for **2**, R = 6.7%, R_w = 6.6%; for **3**, R = 5.5%, R_w = 5.6%. The errors of fit and data to parameter ratios for the final refinements were as follows: for **1**, 2.31, 9.79; for **2**, 1.47, 11.5; for **3**, 1.39, 21.2. The atomic coordinates and associated thermal parameters from the refinements are listed in Tables II–VII. Final difference syntheses revealed residual electron densities of 0.60, 0.58, and 0.60 e/Å^3 for **1**–**3**, respectively.

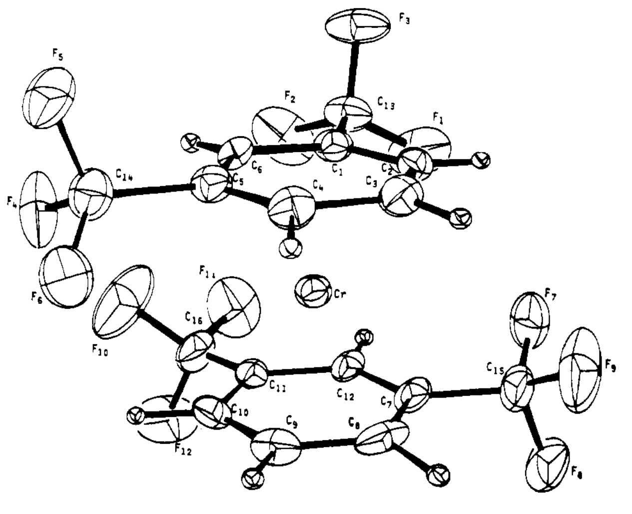


Figure 2. ORTEP drawing at 25° probability of $[m\text{-}C_6H_4(CF_3)_2]_2Cr^0$ as it exists in the crystal. Hydrogen atoms have been deliberately reduced in size for clarity and are numbered according to the associated carbon.

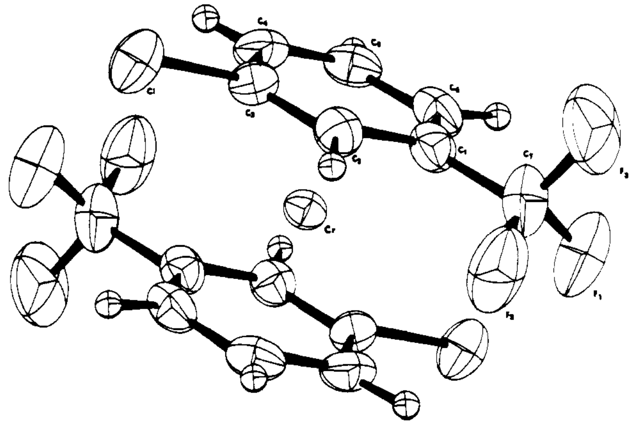


Figure 3. ORTEP drawing at 50% probability of $[m\text{-}C_6H_4(CF_3)Cl]_2Cr^0$ as it exists in the crystal. Only the asymmetric unit of structure is numbered. The molecule contains a center of inversion at the chromium. Hydrogens have been deliberately reduced in size and are numbered according to the associated carbon.

Results and Discussion

The structures of the three discrete "sandwich" molecules as they exist in the crystals are illustrated in Figures 1–3.[10] The atomic numbering scheme is shown in each case, and the hydrogen atoms have been reduced in size or eliminated for clarity. The molecular symmetry of **1** is C_2, and the 2-fold axis is coincident with the crystallographic axis perpendicular to the ring planes and passing through the chromium. Compound **2** possesses C_1 symmetry while **3** has C_i symmetry, and the center of inversion is coincident with the crystallographic inversion center. Ring carbons of the π-arene ligands are planar in the three structures with the maximum deviations being 0.016 (7) Å in **1**, 0.010 (7) Å in **2**, and 0.002 (3) Å in **3**. Planes of the two rings are parallel for **1** and **3** while a small

---

(6) Atomic form factors from Cromer and Mann (Cromer, D. T.; Mann, J. L. *Acta Crystallogr., Sect. A* **1968**, *24*, 321) and A. Zalkin's Fourier program FORDAP were used.

(7) Busing, W. R.; Martin, K. O.; Levy, H. A. Report ORNL-TM-305; Oak Ridge National Laboratory: Oak Ridge, TN, 1962. The function minimized was $w(|F_o| - |F_c|)^2$.

(8) Cromer, D. T.; Liberman, D. J. *J. Chem Phys* **1970**, *53*, 1891.

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

(10) Johnson, C. K. Report OR NL-3794; Oak Ridge National Laboratory: Oak Ridge, TN, 1965.

Table III. Thermal Parameters[a,b] in $[p\text{-}C_6H_4(CF_3)_2]_2Cr^0$

	anisotropic parameters, Å^2					
atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cr	3.60 (5)	2.43 (4)	3.83 (5)	0.0	1.88 (4)	0.0
C_1	5.6 (3)	2.7 (2)	4.7 (3)	−0.1 (2)	1.6 (3)	−0.4 (2)
C_2	4.5 (3)	3.0 (3)	7.6 (4)	−0.7 (2)	3.0 (3)	−0.3 (3)
C_3	7.9 (4)	3.0 (2)	5.9 (4)	−0.6 (3)	4.4 (3)	0.0 (2)
C_4	7.1 (4)	3.2 (3)	8.3 (5)	−0.2 (3)	5.4 (4)	−1.0 (3)
C_5	4.6 (3)	3.1 (3)	7.2 (4)	0.7 (2)	1.5 (3)	−0.0 (3)
C_6	8.6 (5)	3.4 (3)	4.7 (3)	0.9 (3)	3.3 (4)	0.8 (2)
C_7	11.3 (7)	3.8 (3)	5.9 (4)	0.2 (4)	1.7 (4)	−0.5 (3)
C_8	16 (1)	5.6 (5)	14.5 (9)	0.4 (6)	12.0 (9)	−1.1 (6)
F_1	21.6 (7)	10.9 (4)	5.4 (3)	−4.2 (5)	3.9 (4)	0.4 (3)
F_2	13.4 (4)	5.7 (2)	6.4 (2)	−0.7 (3)	1.0 (3)	−2.2 (2)
F_3	12.6 (5)	10.3 (4)	9.2 (4)	5.3 (4)	−3.3 (3)	−2.5 (3)
F_4	22.5 (8)	12.0 (5)	17.6 (6)	−0.8 (5)	16.8 (7)	−0.5 (5)
F_5	20.4 (6)	6.2 (3)	24.0 (7)	1.2 (3)	18.8 (6)	−1.5 (4)
F_6	14.6 (5)	13.8 (5)	29 (1)	−7.2 (5)	17.8 (7)	−10.6 (6)

[a] Estimated standard deviations are given in parentheses for the least significant figures. $B_{ij} = 4\beta_{ij}/a_i{}^*a_j{}^*$ where β_{ij}'s are the unitless parameters used in refinement in the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] Thermal parameters for H atoms were fixed at 7.0 Å^2.

Table IV. Atomic Coordinates in $[m\text{-}C_6H_4(CF_3)_2]_2Cr^0$

atom	10^4x	10^4y	10^4z
Cr	4395.6 (9)	3798.9 (3)	2873.0 (8)
C_1	2759 (6)	4323 (2)	3502 (5)
C_2	3756 (8)	4627 (2)	2892 (6)
C_3	5693 (8)	4573 (2)	3544 (7)
C_4	6658 (7)	4214 (2)	4822 (6)
C_5	5668 (6)	3916 (2)	5439 (5)
C_6	3720 (6)	3969 (2)	4809 (5)
C_7	3541 (7)	3711 (2)	347 (5)
C_8	5475 (9)	3605 (3)	1208 (7)
C_9	6144 (8)	3233 (3)	2406 (8)
C_{10}	4882 (9)	2959 (2)	2843 (7)
C_{11}	2937 (7)	3063 (2)	1969 (6)
C_{12}	2254 (7)	3438 (2)	696 (5)
C_{13}	720 (8)	4387 (3)	2876 (7)
C_{14}	6688 (9)	3539 (3)	6844 (6)
C_{15}	2816 (12)	4115 (3)	−1004 (7)
C_{16}	1604 (11)	2751 (3)	2301 (8)
F_1	−197 (5)	4492 (2)	1301 (5)
F_2	−103 (5)	3965 (2)	3095 (8)
F_3	314 (5)	4774 (2)	3631 (5)
F_4	5637 (7)	3159 (2)	6903 (5)
F_5	7350 (6)	3802 (2)	8264 (4)
F_6	8178 (6)	3326 (2)	6820 (5)
F_7	1226 (8)	4330 (2)	−1221 (5)
F_8	2415 (8)	3897 (2)	−2421 (4)
F_9	3964 (8)	4506 (2)	−757 (6)
F_{10}	2091 (9)	2703 (2)	3844 (6)
F_{11}	−76 (7)	2946 (2)	1662 (8)
F_{12}	1406 (9)	2269 (2)	1733 (8)
H_2	3240 (72)	4861 (21)	2053 (64)
H_3	6501 (71)	4751 (21)	3149 (61)
H_4	8026 (72)	4190 (20)	5042 (60)
H_6	2859 (70)	3758 (20)	5104 (60)
H_8	6602 (70)	3796 (20)	952 (60)
H_9	7451 (75)	3190 (21)	3009 (63)
H_{10}	5295 (70)	2681 (21)	3760 (62)
H_{12}	911 (71)	3514 (20)	211 (61)

[a] Estimated standard deviations are given in parentheses.

tilting, amounting to an interplanar angle of 2.6°, is observed for **2**.

Individual bond distances and angles[11] are listed in Tables VIII–XIII, and a comparison of some selected parameters along with those of bis(benzene)chromium[12] are given in Table XIV. The average C–C distances within the aromatic rings of 1.390 (10) Å for **1**, 1.404 (7) Å for **2**, and 1.408 (5) Å for **3** display an increasing trend, approaching the value in the low-temperature structure of bis(benzene)chromium. These results reflect the degree of thermal motion in the complexes and the overall accuracy of the structure determinations. The average Cr–C bond distance of 2.145 (6) Å for **1**, 2.147 (5) Å for **2**, and 2.137 (3) Å for **3**, as well as the perpendicular Cr–ring distances, are quite similar to the corresponding values in bis(benzene)chromium.

In order to assess the effect of a ring substituent on the stereochemistry of a bis(arene) complex, it is necessary to have some knowledge of substituent effects in the uncomplexed aromatic ring. This has been the subject of many studies; however, Domenicano[4,13] and co-workers have recently summarized the effects of a variety of substituent groups on the geometry of a benzene ring. They conclude that the internal ring angle at the unique substituent will be >120° for a σ-electron-withdrawing substituent and <120° for a σ-electron-donating substituent. Further, any π bonding to the substituent would tend to decrease this angle. Concomitant changes in the opposite direction would also be produced at the adjacent ring angles, and a small change may also occur at the position para to the substituted carbon.[4] Two substituents that are para behave independently with respect to σ effects; however, a cumulative result should occur for meta substitution.

There are, of course, required changes in the ring C–C bond distances as the angles change. Unfortunately these changes are small and are very susceptible to the effects of thermal motion in an X-ray determination. This is particularly true in bis(arene) complexes where considerable vibration is frequently observed about the axis passing through the center of the rings and the metal. We have determined the structures of several substituted bis(arene) complexes containing F and CH_3 substituents, including $[p\text{-}C_6H_4F_2]_2V^0$,[1] $[m\text{-}C_6H_4F_2]_2Cr^0$,[14] and $[p\text{-}C_6H_4(CH_3)_2]_2V^0$,[15] as well as several monoarene structures containing the CH_3 substituent.[16,17] Our results for the internal ring angles at the substituted carbons in these complexes generally agree with the bond angle pre-

---

(11) Busing, W. R.; Martin, K. D.; Levy, H. A. Report ORNL-TM-306; Oak Ridge National Laboratory: Oak Ridge, TN, 1964.

(12) Keulen, E.; Jellinek, F. *J. Organomet. Chem.* **1966**, *5*, 490.

(13) Domenicano, A.; Vaciago, A. *Acta Crystallogr., Sect. B* **1979**, *B35*, 1382.

(14) Radonovich, L. J.; Koch, F. J., to be submitted for publication.

(15) Parish, T. D.; Eyring, M. W.; Radonovich, L. J., ongoing work in our laboratory.

(16) Radonovich, L. J.; Klabunde, K. J.; Behrens, C. B.; McCollar, D. P.; Anderson, B. B. *Inorg. Chem.* **1980**, *19*, 1221.

(17) Radonovich, L. J.; Albright, T. A.; Koch, F. J. *Inorg. Chem.* **1980**, *19*, 3373.

Table V. Thermal Parameters[a,b] in $[m\text{-}C_6H_4(CF_3)_2]_2Cr^0$

	anisotropic parameters, Å²					
atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cr	3.25 (3)	3.00 (3)	2.73 (2)	−0.19 (2)	1.43 (2)	−0.26 (2)
C_1	3.9 (2)	3.9 (2)	3.2 (2)	0.5 (2)	1.4 (2)	−0.6 (1)
C_2	6.6 (3)	2.8 (2)	3.5 (2)	0.3 (2)	1.9 (2)	−0.2 (2)
C_3	5.7 (3)	3.7 (2)	4.9 (2)	−1.7 (2)	2.8 (2)	−1.0 (2)
C_4	3.7 (2)	4.7 (3)	4.0 (2)	−1.0 (2)	1.5 (2)	−1.3 (2)
C_5	3.5 (2)	4.2 (2)	2.7 (2)	−0.2 (2)	1.0 (1)	−0.4 (1)
C_6	3.7 (2)	4.3 (2)	2.9 (2)	−0.4 (2)	1.7 (2)	−0.8 (1)
C_7	5.7 (2)	3.9 (2)	2.9 (2)	−1.2 (2)	2.4 (2)	−0.9 (1)
C_8	5.9 (3)	6.2 (3)	5.9 (3)	−1.4 (3)	4.3 (3)	−2.0 (2)
C_9	4.6 (3)	5.8 (3)	6.1 (3)	0.9 (2)	2.6 (2)	−1.8 (3)
C_{10}	6.6 (3)	3.3 (2)	4.7 (2)	1.1 (2)	2.4 (2)	−0.3 (2)
C_{11}	5.2 (2)	3.0 (2)	3.6 (2)	−0.8 (2)	2.4 (2)	−0.6 (1)
C_{12}	4.4 (2)	3.5 (2)	2.8 (2)	−0.8 (2)	1.7 (2)	−0.8 (1)
C_{13}	4.4 (2)	5.7 (3)	5.6 (3)	1.3 (2)	1.6 (2)	−1.4 (2)
C_{14}	5.1 (3)	6.8 (4)	3.4 (2)	0.5 (3)	0.7 (2)	0.5 (2)
C_{15}	9.5 (5)	5.8 (3)	3.7 (2)	−1.2 (3)	3.3 (3)	0.4 (2)
C_{16}	8.2 (4)	4.6 (3)	6.0 (3)	−2.1 (3)	4.4 (3)	−0.6 (2)
F_1	6.1 (2)	15.1 (4)	5.0 (2)	4.8 (2)	0.0 (2)	−1.7 (2)
F_2	4.2 (2)	7.3 (3)	18.9 (5)	−0.4 (2)	4.2 (2)	−1.1 (3)
F_3	5.7 (2)	8.7 (3)	7.6 (2)	2.1 (2)	2.7 (2)	−2.7 (2)
F_4	9.2 (3)	8.3 (3)	7.4 (2)	−0.9 (2)	1.1 (2)	4.3 (2)
F_5	8.7 (2)	11.2 (3)	2.9 (1)	1.1 (2)	0.5 (1)	0.0 (2)
F_6	7.7 (2)	10.5 (3)	6.3 (2)	4.6 (2)	1.5 (2)	1.7 (2)
F_7	13.7 (4)	7.9 (3)	6.0 (2)	2.9 (3)	3.9 (2)	3.6 (2)
F_8	18.8 (5)	9.5 (3)	4.2 (2)	−1.3 (3)	6.3 (2)	−0.2 (2)
F_9	16.6 (4)	9.6 (3)	7.5 (3)	−7.3 (3)	3.7 (3)	2.2 (2)
F_{10}	19.5 (5)	14.1 (4)	7.5 (3)	−9.1 (4)	8.01 (3)	−0.5 (3)
F_{11}	8.3 (3)	10.2 (3)	17.9 (5)	−1.5 (3)	8.3 (3)	3.2 (3)
F_{12}	18.3 (5)	5.2 (2)	18.0 (5)	−5.7 (3)	13.5 (4)	−4.4 (3)

[a] Estimated standard deviations are given in parentheses for the least significant figures. $B_{ij} = 4\beta_{ij}/a_i{}^*a_j{}^*$ where β_{ij} are the unitless parameters used in refinement in the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] Thermal parameters for H atoms were fixed at 5.0 Å².

Table VI. Atomic Coordinates[a] in $[m\text{-}C_6H_4(CF_3)Cl]_2Cr^0$

atom	10^4x	10^4y	10^4z
Cr	0	0	0
C_1	1878 (3)	1582 (3)	18 (3)
C_2	−607 (3)	2502 (3)	−116 (3)
C_3	962 (3)	2286 (3)	822 (3)
C_4	1300 (4)	1168 (4)	1897 (3)
C_5	31 (4)	269 (4)	2021 (3)
C_6	−1564 (4)	460 (4)	1094 (3)
C_7	3564 (4)	1810 (5)	988 (4)
Cl	2525.8 (9)	3442 (1)	676.0 (9)
F_1	−4438 (2)	472 (3)	−1190 (3)
F_2	−3588 (3)	2304 (3)	−2177 (2)
F_3	−4346 (3)	2925 (4)	−567 (3)
H_2	−823 (51)	3172 (54)	−844 (45)
H_4	2497 (53)	982 (52)	2488 (43)
H_5	264 (56)	−556 (56)	2652 (47)
H_6	−2388 (55)	−163 (53)	1158 (46)

[a] Estimated standard deviations are given in parentheses.

dictions[4,13] for substituted benzenes. Thus, it appears that π complexation of a substituted arene to a transition metal does not significantly change these angles when the structure is free of unusual packing constraints. If the CF_3 group were a strongly σ-electron-withdrawing substituent, as it is commonly considered, then one would expect the ring angle at the substituted carbon to be >120°, approaching the angle of ~123° observed for F substituents.[1] The two independently determined ring angles at the CF_3 substituted carbons in **1** of 120.0 (6) and 119.3 (6)° are within two esd's of 120°. Of the four independently determined angles in **2**, two are 120.0 (4)° and two are opened slightly to 121.4 (4)°. The average value of 120.7 (4)°, however, is within two esd's of the hexagonal angle. The more definitive results of **3** reveal that the angle at the CF_3-substituted carbon is 120.4 (3)°, well within experimental error to 120°. Comparatively, the ring angle at the Cl-substituted carbon is 121.3 (3)°, consistent with the values observed in uncomplexed aromatics and consistent with the

Table VII. Anisotropic Thermal Parameters[a,b] in $[m\text{-}C_6H_4(CF_3)Cl]_2Cr^0$

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cr	2.66 (2)	2.55 (2)	2.03 (2)	0.06 (2)	0.93 (1)	0.06 (2)
C_1	3.14 (10)	3.19 (10)	3.76 (11)	0.40 (8)	1.61 (8)	−0.19 (9)
C_2	3.39 (10)	2.71 (9)	3.40 (10)	0.30 (8)	1.33 (8)	0.03 (8)
C_3	3.34 (10)	2.84 (9)	3.06 (9)	−0.33 (8)	1.07 (8)	−0.50 (8)
C_4	4.13 (12)	3.89 (12)	2.24 (8)	0.12 (10)	0.70 (8)	−0.50 (8)
C_5	5.33 (14)	3.79 (13)	2.40 (8)	0.14 (10)	1.85 (9)	0.02 (8)
C_6	4.25 (12)	3.81 (12)	3.85 (11)	−0.05 (10)	2.60 (10)	−0.12 (9)
C_7	2.88 (11)	5.09 (17)	6.65 (19)	0.00 (47)	1.85 (12)	0.58 (14)
Cl	3.67 (3)	4.21 (3)	5.42 (4)	−1.18 (3)	1.04 (3)	−0.09 (3)
F_1	3.48 (8)	6.87 (13)	8 81 (15)	−1.14 (9)	0.79 (9)	1.06 (11)
F_2	3.83 (8)	9.52 (16)	5.86 (12)	0.24 (10)	0.22 (8)	2.81 (11)
F_3	4.74 (11)	8.57 (17)	11.50 (20)	2.78 (11)	3.10 (12)	−0.37 (15)

[a] Estimated standard deviations are given in parentheses for the least significant digits. $B_{ij} = 4\beta_{ij}/a_i{}^*a_j{}^*$, where β_{ij} are the unitless parameters used in refinement in the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] Isotropic thermal parameters of the hydrogen atoms are fixed at 7 Å².

Table VIII. Bond Distances (Å) in $[p\text{-}C_6H_4(CF_3)_2]_2Cr^0$

		Coordination Sphere			
$Cr\text{–}C_1$	2.126 (6)	$Cr\text{–}C_3$	2.143 (6)	$Cr\text{–}C_5$	2.130 (6)
$Cr\text{–}C_2$	2.137 (6)	$Cr\text{–}C_4$	2.188 (6)	$Cr\text{–}C_6$	1.143 (6)
		Within the Ligands			
$C_1\text{–}C_2$	1.400 (9)	$C_1\text{–}C_7$	1.47 (1)	$C_8\text{–}F_5$	1.31 (1)
$C_2\text{–}C_3$	1.38 (1)	$C_4\text{–}C_8$	1.47 (1)	$C_8\text{–}F_6$	1.23 (1)
$C_3\text{–}C_1'$	1.40 (1)	$C_7\text{–}F_1$	1.31 (1)	$C_2\text{–}H_2$	0.86 (7)
$C_4\text{–}C_5$	1.39 (1)	$C_7\text{–}F_2$	1.331 (8)	$C_3\text{–}H_3$	0.80 (7)
$C_5\text{–}C_6$	1.39 (1)	$C_7\text{–}F_3$	1.30 (1)	$C_5\text{–}H_5$	0.85 (7)
$C_6\text{–}C_4'$	1.38 (1)	$C_8\text{–}F_4$	1.40 (1)	$C_6\text{–}H_6$	0.83 (7)

Table IX. Bond Distances (Å) in $[m\text{-}C_6H_4(CF_3)_2]_2Cr^0$

		Coordination Sphere			
$Cr\text{–}C_1$	2.132 (5)	$Cr\text{–}C_5$	2.128 (4)	$Cr\text{–}C_9$	2.162 (5)
$Cr\text{–}C_2$	2.148 (5)	$Cr\text{–}C_6$	2.149 (5)	$Cr\text{–}C_{10}$	2.154 (5)
$Cr\text{–}C_3$	2.161 (5)	$Cr\text{–}C_7$	2.124 (4)	$Cr\text{–}C_{11}$	2.146 (5)
$Cr\text{–}C_4$	2.150 (5)	$Cr\text{–}C_8$	2.154 (5)	$Cr\text{–}C_{12}$	2.154 (4)
		Within the Ligands			
$C_1\text{–}C_2$	1.407 (7)	$C_1\text{–}C_{13}$	1.478 (7)	$C_{15}\text{–}F_9$	1.297 (7)
$C_1\text{–}C_6$	1.410 (6)	$C_5\text{–}C_{14}$	1.509 (7)	$C_{16}\text{–}F_{10}$	1.301 (7)
$C_2\text{–}C_3$	1.396 (8)	$C_7\text{–}C_{15}$	1.504 (8)	$C_{16}\text{–}F_{11}$	1.297 (8)
$C_3\text{–}C_4$	1.402 (8)	$C_{11}\text{–}C_{16}$	1.476 (7)	$C_{16}\text{–}C_{12}$	1.304 (7)
$C_4\text{–}C_5$	1.399 (7)	$C_{13}\text{–}F_1$	1.321 (7)	$C_2\text{–}H_2$	0.91 (5)
$C_5\text{–}C_6$	1.405 (6)	$C_{13}\text{–}F_2$	1.317 (8)	$C_3\text{–}H_3$	0.99 (5)
$C_7\text{–}C_8$	1.409 (8)	$C_{13}\text{–}F_3$	1.327 (6)	$C_4\text{–}H_4$	1.03 (5)
$C_7\text{–}C_{12}$	1.404 (6)	$C_{14}\text{–}F_4$	1.296 (7)	$C_6\text{–}H_6$	1.01 (5)
$C_8\text{–}C_9$	1.390 (9)	$C_{14}\text{–}F_5$	1.343 (7)	$C_8\text{–}H_8$	1.15 (5)
$C_9\text{–}C_{10}$	1.407 (9)	$C_{14}\text{–}F_6$	1.326 (7)	$C_9\text{–}H_9$	0.94 (5)
$C_{10}\text{–}C_{11}$	1.416 (8)	$C_{15}\text{–}F_7$	1.321 (8)	$C_{10}\text{–}H_{10}$	1.03 (5)
$C_{11}\text{–}C_{12}$	1.408 (6)	$C_{15}\text{–}F_8$	1.318 (7)	$C_{12}\text{–}H_{12}$	0.98 (5)

Table X. Bond Distances (Å) in $[m\text{-}C_6H_4(CF_3)Cl]_2Cr^0$

		Coordination Sphere			
$Cr\text{–}C_1$	2.127 (3)	$Cr\text{–}C_3$	2.129 (3)	$Cr\text{–}C_5$	2.142 (3)
$Cr\text{–}C_2$	2.135 (3)	$Cr\text{–}C_4$	2.146 (3)	$Cr\text{–}C_6$	2.143 (3)
		Within the Ligands			
$C_1\text{–}C_2$	1.412 (4)	$C_6\text{–}C_1$	1.417 (4)	$C_7\text{–}F_3$	1.327 (4)
$C_2\text{–}C_3$	1.394 (4)	$C_1\text{–}C_7$	1.497 (4)	$C_2\text{–}H_2$	0.91 (4)
$C_3\text{–}C_4$	1.412 (4)	$C_3\text{–}Cl$	1.740 (3)	$C_4\text{–}H_4$	1.03 (4)
$C_4\text{–}C_5$	1.397 (4)	$C_7\text{–}F_1$	1.325 (4)	$C_5\text{–}H_5$	0.93 (5)
$C_5\text{–}C_6$	1.405 (4)	$C_7\text{–}F_2$	1.317 (4)	$C_6\text{–}H_6$	0.92 (4)

Table XI. Bond Angles (Deg) in $[p\text{-}C_6H_4(CF_3)_2]_2Cr^0$

$C_3'C_1C_2$	119.3 (6)	$C_6'C_4C_8$	120.7 (9)
$C_1C_2C_3$	120.1 (6)	$C_5C_4C_8$	119.2 (9)
$C_2C_3C_1'$	120.5 (6)	$F_3C_7F_2$	104.9 (9)
$C_3'C_1C_7$	120.3 (8)	$F_3C_7F_1$	107.3 (8)
$C_2C_1C_7$	120.3 (8)	$F_2C_7F_1$	105.6 (9)
$C_4'C_6C_5$	119.7 (6)	$F_6C_8F_5$	110.4 (12)
$C_6C_5C_4$	120.2 (6)	$F_6C_8F_4$	102.7 (10)
$C_5C_4C_6$	120.0 (6)	$F_4C_8F_5$	102.2 (10)

Table XII. Bond Angles (Deg) in $[m\text{-}C_6H_4(CF_3)_2]_2Cr^0$

$C_1C_2C_3$	120.6 (5)	$C_8C_7C_{15}$	119.9 (5)
$C_2C_3C_4$	119.8 (5)	$C_{12}C_7C_{15}$	118.7 (5)
$C_3C_4C_5$	119.5 (5)	$C_{10}C_{11}C_{16}$	120.3 (5)
$C_4C_5C_6$	121.4 (4)	$C_{12}C_{11}C_{16}$	119.5 (5)
$C_5C_6C_1$	118.6 (4)	$F_1C_{13}F_2$	105.6 (6)
$C_6C_1C_2$	120.0 (4)	$F_1C_{13}F_3$	106.8 (5)
$C_7C_8C_9$	119.8 (5)	$F_2C_{13}F_3$	104.1 (5)
$C_8C_9C_{10}$	119.8 (5)	$F_4C_{14}F_5$	106.9 (5)
$C_9C_{10}C_{11}$	120.4 (5)	$F_4C_{14}F_6$	108.7 (6)
$C_{10}C_{11}C_{12}$	120.0 (5)	$F_5C_{14}F_6$	105.5 (5)
$C_{11}C_{12}C_7$	118.6 (5)	$F_7C_{15}C_8$	104.4 (6)
$C_{12}C_7C_8$	121.4 (5)	$F_7C_{15}F_9$	106.3 (7)
$C_2C_1C_{13}$	121.7 (5)	$F_8C_{15}F_9$	108.4 (6)
$C_6C_1C_{13}$	118.2 (5)	$F_{10}C_{16}F_{11}$	104.6 (6)
$C_4C_5C_{14}$	120.3 (5)	$F_{10}C_{16}F_{12}$	106.0 (6)
$C_6C_5C_{14}$	118.3 (5)	$F_{11}C_{16}F_{12}$	105.2 (6)

Table XIII. Bond Angles (Deg) in $[m\text{-}C_6H_4(CF_3)Cl]_2Cr^0$

$C_6C_1C_2$	120.4 (3)	C_2C_3Cl	119.2 (2)
$C_1C_2C_3$	119.1 (3)	C_4C_3Cl	119.5 (2)
$C_2C_3C_4$	121.3 (3)	$C_1C_7F_1$	112.5 (3)
$C_3C_4C_5$	119.0 (3)	$C_1C_7F_2$	112.4 (3)
$C_4C_5C_6$	121.1 (3)	$C_1C_7F_3$	111.0 (3)
$C_5C_6C_1$	119.1 (3)	$F_1C_7F_2$	107.6 (3)
$C_6C_1C_7$	120.4 (3)	$F_2C_7F_3$	106.1 (3)
$C_2C_1C_7$	119.2 (3)	$F_1C_7F_3$	106.9 (3)

Table XIV. Comparison of Some Selected Bond Parameters[a]

type	$[p\text{-}C_6H_4\text{-}(CF_3)_2]_2Cr$	$[m\text{-}C_6H_4\text{-}(CF_3)_2]_2Cr$	$[m\text{-}C_6H_4\text{-}(CF_3)Cl]_2Cr$	$(C_6H_6)_2Cr$[b] (100 K)
$Cr\text{–}C_{av}$	2.145 (6)	2.147 (5)	2.137 (3)	2.142 (2)
⊥M-ring	1.626	1.624	1.609	1.609
$C\text{–}C_{av}$	1.390 (10)	1.404 (7)	1.408 (5)	1.417 (3)
$C\text{–}CF_3$	1.472 (11)	1.492 (7)	1.497 (4)	
$C\text{–}C_T\text{–}C$[c]	119.7 (6)	120.7 (4)	120.4 (4)	
ϕ[d]	17	10	0	0
θ[e]	0	2.6	0	0

[a] All of the parameters listed are uncorrected for thermal motion motion. Distances are in Å and angle in degrees. [b] Reference 12. [c] Angle at C_T is the internal ring angle at the CF_3-substituted carbon atom. [d] ϕ is the angle of rotation between carbons in opposite rings. $\phi = 0°$ for an eclipsed orientation. [e] θ is the dihedral angle between planes of the two π-arene ligands. $\theta = 0°$ when the two planes are parallel.

σ-electron-withdrawing ability of Cl.[18,19] Thus it appears that the internal ring angle at CF_3-substituted carbons is within experimental error to 120°. In addition, the most reliable value from the present study for the $C\text{–}CF_3$ distance is 1.497 (4) Å, which does not lend support to any large amount of conjugation to the substituent.

It is of interest to note that Holmes and Thomas[20] have done a point-charge analysis of the core-binding energy shifts for CF_3-substituted benzenes. They conclude that the CF_3 group does not withdraw electron density from the adjacent ring carbons but, rather, it donates electron density to the ring. They attribute the well-established polar effect of CF_3 to a "through space" dipole effect rather than a "through the bond" electron withdrawal. If one accepts the bond angle deformation arguments[4] cited above, then our results are consistent with their conclusion that the CF_3 group does not withdraw electron density from the ring carbon to which it is bonded. We find no evidence, however, that it is substantially electron releasing.

A general feature of other bis(arene) complexes that we have studied is that carbon atoms in opposite rings tend toward an eclipsed orientation ($\phi = 0°$). This, of course, is also true in equally substituted complexes studied by others.[12,21] The two ditrifluoromethyl-substituted complexes in this study, however, display a relatively large rotation of 10° in **2** and 17° in **1**. The rotation in **1** is more than half way toward the staggered orientation ($\phi = 30°$). This is probably due to the interactions

---

(18) Domenicano, A.; Vaciago, A.; Coulson, C. A. *Acta Crystallogr., Sect. B* **1975**, *B31*, 1630.

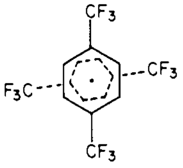
(19) On the basis of the effects of a Cl substituent on electrophilic substitution reactions, one would classify it as a relatively strong σ-electron-withdrawing group. On this basis one might expect an even larger internal ring angle at the Cl-substituted carbon, closer to the 123° angle observed for an F substituent. A possible rationalization for the observed angle could be made by considering that Cl could conjugate (π donate) somewhat to the ring, thus canceling some of the σ-withdrawing effect on the bond angle. Alternatively, the average value for the internal ring angle of several chloro-substituted benzene derivatives of 121.4 (1)° is considered by Domenicano and co-workers[18] to correlate well with the nominal electronegativity of Cl when essentially a σ bond is assumed.

(20) Holmes, S. A.; Thomas, T. O. *J. Am. Chem. Soc.* **1975**, *97*, 2337.

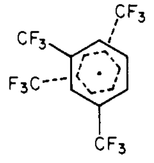
(21) Thompson, M. R.; Day, C. S.; Day, V. W.; Menk, R. I.; Muetterties, E. L. *J. Am. Chem. Soc.* **1980**, *102*, 2979.

Inorg. Chem. **1981**, *20*, 3410–3420

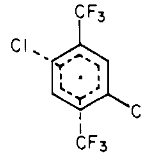
of the CF_3 substituents in opposite rings. The orientation of the two π-arene rings with respect to one another are illustrated in **1**–**3**. In **1** the rotation of 17° results in F---F intramolecular contacts that are all greater than normal estimates of van der Waal distances.[22] However, in the meta-substituted case, **2**, simple rotation cannot alleviate all of these interactions, and one interaction distance (F_2---F_{11}) is 2.89 Å. This is close to the estimated van der Waals contact of 2.94 Å considering that the large thermal ellipsoids observed for the fluorines would result in an underestimation of these distances. Further, C_{16} is displaced from the mean plane of the ring by ~0.08 Å away from the chromium while displacement of the CF_3 carbon in **1** and **3** is 0.01 Å or less. The absence of a second CF_3 group in **3** allows the carbons of the two rings to eclipse, with all intramolecular contacts of the substituents being greater than van der Waals distances.



1



2



3

An analysis of the intermolecular packing interactions reveals normal contact distances in **3**. In **1**, an F---F interaction of 2.80 Å, occurring at F_3---F_3^{I} where I = $^1/_2 - x, {}^1/_2 - y, 1 - z$, is shorter than the normal[22] 2.94 Å distance. Similarily an F---H contact of 2.51 Å occurs between F_2---H_8^{II} and F_8---H_6^{III} where II = $-1 + x, y, z$ and III = $x, y, -1 + z$. Comparatively, the estimated F---H van der Waals distance is 2.67 Å.[22] Of course, the large thermal motion of the F atoms combined with the crude determination of hydrogen atomic positions produces a relatively large error in these distances.

Acknowledgment. Support of this work from the Research Corp. is acknowledged with gratitude. Acknowledgment is also made to the University of North Dakota for computer time.

Registry No. **1**, 53966-06-6; **2**, 53966-05-5; **3**, 78166-85-5.

Supplementary Material Available: Listings of the structure factor amplitudes (35 pages). Ordering information is given on any current masthead page.

---

[22] Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

Contribution from the Department of Chemistry,
McMaster University, Hamilton, Ontario, Canada L8S 4M1

Preparation, X-ray Crystal Structures, and Vibrational Spectra of Some Salts of the $As_3S_4^+$ and $As_3Se_4^+$ Cations

BEVERLEY H. CHRISTIAN, RONALD J. GILLESPIE,* and JEFFERY F. SAWYER

Received July 28, 1980

The reactions of α- and β-As_4S_4 and some arsenic–selenium melts with various oxidants in SO_2 as solvent are reported. It is shown by X-ray crystallography that the reactions of As_4S_4 and a 1:1 As–Se melt with the Lewis acids AsF_5 and SbF_5 in a 1:3 molar ratio in SO_2 give the hexafluoroarsenate and hexafluoroantimonate salts of the novel arsenic chalcogen cations $As_3S_4^+$ and $As_3Se_4^+$. Crystals of $(As_3S_4)(SbF_6)$ are yellow plates which crystallize in the orthorhombic space group *Pcam* with $a = 20.453$ (4) Å, $b = 5.990$ (1) Å, $c = 9.609$ (2) Å, $U = 1177.3$ (4) Å^3, and $d_c = 3.32$ g cm^{-3} for $Z = 4$. Crystals of the isomorphous $(As_3S_4)(AsF_6)$ are dark yellow prisms and rhombs with cell dimensions $a = 19.962$ (4) Å, $b = 5.930$ (1) Å, $c = 9.441$ (3) Å, $U = 1115.8$ (5) Å^3, and $d_c = 3.22$ g cm^{-3} for $Z = 4$. The compound $(As_3Se_4)(SbF_6)$ forms orange diamond-shaped plates which crystallize in the monoclinic space group $P2_1/m$ with $a = 6.224$ (3) Å, $b = 9.564$ (5) Å, $c = 10.643$ (5) Å, $\beta = 92.65$ (4)°, $U = 632.9$ (5) Å^3, and $d_c = 4.07$ g cm^{-3} for $Z = 2$. The structure of the compound $(As_3S_4)(SbF_6)$ was solved by using the Patterson function and refined by least-squares methods to final agreement indices $R_1 = 0.036$ and $R_2 = 0.043$ for 699 observed data. The isomorphous compound $(As_3S_4)(AsF_6)$ has similarly been refined by least-squares methods to final agreement indices $R_1 = 0.043$ and $R_2 = 0.052$ for 546 observed data. The structure of the compound $(As_3Se_4)(SbF_6)$ was solved by using direct methods and has been refined by least-squares to final agreement indices $R_1 = 0.064$ and $R_2 = 0.082$ for 620 observed reflections. The two cations $As_3S_4^+$ and $As_3Se_4^+$ are isostructural with crystallographic mirror symmetry and an overall symmetry of C_s. The cage structure of the two cations can be derived by bridging three edges of a tetrahedron of three arsenic and one sulfur or selenium atoms by the remaining sulfur or selenium atoms. Bond distances, bond angles and some significant interionic contact distances in these compounds are discussed. In addition, the Raman and IR spectra of these cations as well as the Raman spectrum of As_4S_3 and an improved Raman spectrum of the compound α-As_4S_4 are reported.

Introduction

Although the reactions of S_4N_4 and related compounds with various oxidizing agents and Lewis acids and the reactions of S_4N_4 in reducing media such as potassium/liquid ammonia solutions have been observed to give various new cations and anions,[1–6] the analogous reactions of the structurally related compounds As_4S_4[7–10] and As_4Se_4[11–14] have previously not been studied in any depth. The only ionic derivative of As_4S_4 that has been definitely characterized is the $As_4S_6^{2-}$ anion which

---

[1] Gillespie, R. J.; Ireland, P. R.; Vekris, J. E. *Can. J. Chem.*, **1975**, *53*, 3147.

[2] Gillespie, R. J.; Kent, J. P.; Sawyer, J. F. *Inorg. Chem.*, in press.

[3] Gillespie, R. J.; Slim, D. R.; Tyrer, J. D. *J. Chem. Soc., Chem. Commun.* **1977**, 253. Gillespie, R. J.; Kent, J. P.; Sawyer, J. F.; Slim, D. R.; Tyrer, J. D. *Inorg. Chem.*, in press.

[4] Bojes, J.; Chivers, T.; Drummond, I.; MacLean, G. *Inorg. Chem.* **1978**, *17*, 3668.

[5] Bojes, J.; Chivers, T. *J. Chem. Soc., Chem. Commun.* **1978**, 391.

[6] Wolmershauser, G.; Street, G. B.; Smith, R. D. *Inorg. Chem.* **1979**, *18*, 383.

[7] Ito, T.; Morimoto, N.; Sadanaga, R. *Acta Crystallogr.* **1952**, *5*, 775.

[8] Porter, E. J.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1972**, 1347.

[9] Mullen, D. J. E.; Nowacki, W. *Z. Kristallogr.* **1972**, *136*, 48. This paper also reports the crystal structure of As_2S_3 which is isostructural with that of As_2Se_3.[11,16] More recently, structures of the mixed $As_2(S,Se)_3$ compounds have also been published.[16]

[10] It should be noted, however, that an isomeric form of As_4S_4 has been found, the structure of which is based on an edge-bridged cube with one vertex missing. Kutoglu, A. *Z. Anorg. Allg. Chem.* **1976**, *419*, 176.

[11] Renninger, A. L.; Averbach, B. L. *Acta Crystallogr., Sect. B* **1973**, *B29*, 1583.

[12] Bastow, T. J.; Whitfield, H. J. *J. Chem. Soc., Dalton Trans.* **1973**, 1739.

[13] Smail, E. J.; Sheldrick, G. M. *Acta Crystallogr., Sect. B* **1973**, *B29*, 2014.

[14] Goldstein, P.; Paton, A. *Acta Crystallogr., Sect. B* **1974**, *B30*, 915.