are not affected by absolute errors in the value of $\Delta S^\circ_{\text{rc,std}}$ used to calculate $\Delta S^\circ_{\text{rc},1}$ and $\Delta S^\circ_{\text{rc},2}$ because the former cancels in eq 7.

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Bridging and Twist Angle Dependence of Magnetic Coupling in Doubly Bridged Copper(II) Dimers. X-ray Structure of Bis[chloro(*N*-phenyl(2-hydroxybenzylidene)aminato-*N*,*μ*-*O*)copper(II)][1]

B. Chiari, O. Piovesana,* T. Tarantelli, and P. F. Zanazzi

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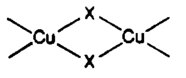
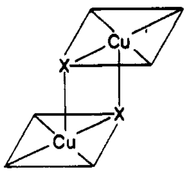
The elucidation of the structural and electronic factors that govern spin–spin coupling in magnetically condensed systems is of continuing interest.[2] Doubly bridged copper(II) dimers have proved to be well suited for such a study since, besides being conceptually simple (spin $^1/_2$ systems), they display a great variety of coordination geometries and superexchange pathways with consequent wide variations in the magnetic properties.[2]

The bridging CuXCu angle, ϕ, has been found to be of prominent importance in determining $2J$, the singlet–triplet splitting resulting from exchange coupling, in compounds with largely planar (I)[2a,b,3,4] or parallel-planar (II)[1,2a,b,5–7] geometries.



I

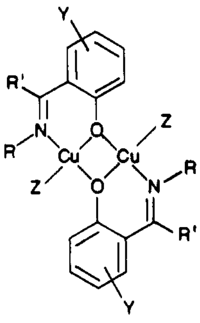


II

In particular, the remarkable linear relationship eq 1 has been established[3] for a series of type I compounds with X = OH⁻.

$$2J\ (\text{cm}^{-1}) = -74.53\phi + 7270 \tag{1}$$

It has also been demonstrated, through results on nonplanar compounds of type III[8–13] or IV,[14,15] that distortions from planar toward tetrahedral ligand environment at copper markedly affect the magnitude of $2J$. The dihedral angle, τ, between the plane of the Cu_2O_2 bridging unit and the plane of the remaining ligands (V) has been used to parametrize this tetrahedral distortion, and a direct correlation between $2J$ and τ has been proposed for these systems.[8–15]



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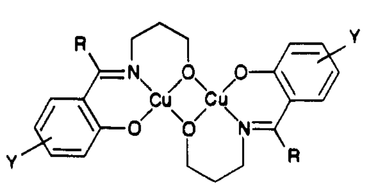

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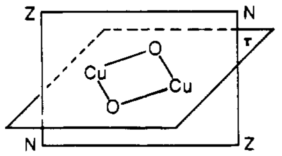

V

A seeming inconsistency between these two magnetostructural correlations is that τ differs significantly from 0° in several hydroxide-bridged dimers obeying eq 1 and that variations in ϕ in the series of nonplanar compounds do not seem to have any effect on $2J$. From an experimental viewpoint, it is not at all apparent why a single structural parameter can adequately explain the variation in $2J$ with geometry when both τ and ϕ vary.

With an aim toward obtaining some further information on the relative merit of the τ and ϕ parameters in determining the magnetic properties of dimeric complexes having nonplanar metal environments, the crystal and molecular structure of bis[chloro(*N*-phenyl(2-hydroxybenzylidene)aminato-*N*,*μ*-*O*)copper(II)], denoted $Cu_2L_2Cl_2$, is now reported and discussed in terms of the magnetic properties of the compound.

Experimental Section

Synthesis. $Cu_2L_2Cl_2$ has been isolated previously by Harris and Sinn.[9b] We have obtained crystals of the compound suitable for X-ray analysis by a slightly varied method. $CuCl_2{\cdot}2H_2O$ (0.17 g, 1.0 mmol) was added to a mixed-solvent solution of bis(*N*-phenyl(2-hydroxybenzylidene)aminato)copper(II)[16,17] (0.46 g, 1.0 mmol) in absolute ethanol (15 mL) and chloroform (15 mL). The addition was made over a period of 0.5 h, at 50 °C, with constant stirring. The warm solution was filtered. The filtrate was allowed to stand at room temperature for 24 h. The nonhomogeneous microcrystalline solid that formed was filtered off. After the filtrate was allowed to stand at room temperature for an additional 48 h, dark brown crystals of the compound were collected by filtration and dried under vacuum (mp 205–207 °C). Anal. Calcd for $C_{26}H_{20}N_2O_2Cl_2Cu_2$: C, 52.89; H, 3.41; N, 4.74. Found: C, 52.86; H, 3.59; N, 4.74.

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Table I. Fractional Atomic Coordinates in $Cu_2L_2Cl_2$

atom	x/a	y/b	z/c
Cu	0.12791 (4)	0.08361 (6)	0.47711 (8)
Cl	0.2661 (1)	0.0147 (2)	0.2254 (2)
O	−0.0164 (2)	0.1641 (4)	0.5944 (5)
N	0.2095 (3)	0.3127 (5)	0.6762 (5)
C(1)	−0.0294 (3)	0.3512 (5)	0.6785 (6)
C(2)	−0.1319 (4)	0.3979 (6)	0.6785 (6)
C(3)	−0.1469 (4)	0.5904 (6)	0.7683 (7)
C(4)	−0.0581 (4)	0.7396 (6)	0.8567 (7)
C(5)	0.0426 (4)	0.6964 (6)	0.8602 (7)
C(6)	0.0606 (3)	0.5026 (5)	0.7673 (6)
C(7)	0.1696 (3)	0.4724 (6)	0.7770 (6)
C(8)	0.3197 (4)	0.3072 (6)	0.7076 (7)
C(9)	0.3328 (4)	0.1462 (8)	0.7319 (8)
C(10)	0.4399 (5)	0.1336 (9)	0.7579 (9)
C(11)	0.5314 (5)	0.2867 (11)	0.7601 (9)
C(12)	0.5165 (4)	0.4438 (10)	0.7358 (9)
C(13)	0.4120 (4)	0.4596 (8)	0.7088 (8)

X-ray Data and Structure Solution. A dark brown, prismatic crystal of $Cu_2L_2Cl_2$, with dimensions $0.20 \times 0.15 \times 0.10$ mm^3, was mounted on a computer-controlled Philips PW1100 single-crystal diffractometer equipped with graphite-monochromatized Mo Kα radiation ($\lambda = 0.71069$ Å). The crystals are triclinic. The cell dimensions, determined at room temperature by a least-squares calculation based on the setting angles of 25 reflections with 2θ angles ranging between 17 and 25°, are as follows: $a = 12.236$ (3), $b = 7.658$ (3), $c = 7.312$ (3) Å; $\alpha = 114.39$ (2), $\beta = 77.04$ (2), $\gamma = 105.56$ (2)°; $V = 596.09$ Å^3. The space group is $P\bar{1}$ (from intensity statistics). The calculated density for one dimeric molecule $Cu_2C_{26}H_{20}N_2O_2Cl_2$ ($M_r = 590$) in the unit cell is 1.643 g·cm^{-3}. The absorption coefficient for Mo Kα is $\mu = 20.0$ cm^{-1}. The intensities were collected, at room temperature, up to $2\theta = 50°$; the $\omega/2\theta$ scan technique was employed, the scan range being 1.4° and the scan speed 0.05° s^{-1}. A total of 2085 independent reflections were measured, of which 562 having $I < 3\sigma(I)$ were considered as "unobserved" and excluded from the refinement. Three standard reflections, which were measured periodically, showed no apparent variation in intensity during the data collection. The data were corrected for Lorentz and polarization factors. An empirical absorption correction was applied during the refinement, according to the method of Walker and Stuart.[18] Correction factors were in the range 1.10–0.85.

The structure was solved by Patterson and Fourier methods and refined by the full-matrix least-squares method, with use of the SHELX-76 set of programs.[19] The function minimized was $\sum w^{1/2}\Delta F$. Anisotropic thermal parameters were refined for all the non-hydrogen atoms. The contribution of hydrogen atoms at their calculated positions (C–H = 1.08 Å), with overall isotropic thermal parameter $U = 0.08$ Å^2, was included. The final R was 0.033 ($R_w = 0.038$, $w = 1/\sigma^2(F)$), for 1523 observations and 155 parameters. The atomic scattering factors were taken from ref 19 for Cl, C, O, N, and H and from ref 20 for Cu. A correction for the anomalous dispersion was included.

Results and Discussion

The crystal structure of $Cu_2L_2Cl_2$ consists of centrosymmetric dimeric units that are well separated from one another. Final positional parameters are listed in Table I, and the more important interatomic distances and bond angles are compiled in Table II. The structure of the compound is presented in Figure 1. The two copper atoms are doubly bridged by phenoxide groups. The Cu_2O_2 bridging unit is exactly planar because of the crystallographic center of inversion at its center. The Cu–O separations of 1.924 (2) and 1.961 (3) Å and the phenolic C–O distance of 1.344 (4) Å are normal for compounds of type III.[8,10-12] Also, the Cu–Cl distance of 2.192 (1) Å compares well with corresponding values (in the range 2.202 (1)–2.209 (1) Å) in the analogous compounds of type III with Z = Cl whose structures have so far been determined.[8,11] The bridging angle at oxygen is 103.3 (1)°. The copper environment, CuO_2NCl, is distorted from planar toward tetrahedral, the dihedral angle, τ, between the planes CuOCu′O′ and CuNClCu′N′Cl′ being 37.3°. The bond lengths and angles in the Schiff base ligands have their usual values within error limits.

Table II. Bond Lengths (Å) and Angles (deg) in $Cu_2L_2Cl_2$

Cu–Cl	2.192 (1)	C(3)–C(4)	1.394 (5)
Cu–O	1.924 (2)	C(4)–C(5)	1.367 (5)
Cu–N	1.949 (2)	C(5)–C(6)	1.410 (5)
Cu–O′	1.961 (3)	C(6)–C(7)	1.435 (4)
O–C(1)	1.344 (4)	C(8)–C(9)	1.370 (7)
N–C(7)	1.301 (4)	C(8)–C(13)	1.388 (7)
N–C(8)	1.432 (4)	C(9)–C(10)	1.399 (5)
C(1)–C(2)	1.393 (5)	C(10)–C(11)	1.384 (9)
C(1)–C(6)	1.412 (4)	C(11)–C(12)	1.349 (10)
C(2)–C(3)	1.389 (6)	C(12)–C(13)	1.380 (8)
Cl–Cu–O	151.6 (1)	C(2)–C(3)–C(4)	119.9 (3)
Cl–Cu–N	100.5 (1)	C(3)–C(4)–C(5)	120.2 (3)
Cl–Cu–O′	101.7 (1)	C(4)–C(5)–C(6)	121.0 (3)
O–Cu–N	92.2 (1)	C(1)–C(6)–C(5)	118.9 (3)
O–Cu–O′	76.7 (1)	C(1)–C(6)–C(7)	124.3 (2)
N–Cu–O′	151.0 (1)	C(5)–C(6)–C(7)	116.8 (3)
Cu–O–C(1)	124.3 (2)	N–C(7)–C(6)	126.2 (2)
Cu–O–Cu′	103.3 (1)	N–C(8)–C(9)	118.6 (3)
C(1)–O–Cu′	131.8 (2)	N–C(8)–C(13)	120.8 (3)
Cu–N–C(7)	122.7 (2)	C(9)–C(8)–C(13)	120.6 (3)
Cu–N–C(8)	118.6 (2)	C(8)–C(9)–C(10)	120.2 (3)
C(7)–N–C(8)	118.7 (3)	C(9)–C(10)–C(11)	118.9 (4)
O–C(1)–C(2)	120.3 (3)	C(10)–C(11)–C(12)	119.9 (4)
O–C(1)–C(6)	120.5 (2)	C(11)–C(12)–C(13)	122.4 (3)
C(2)–C(1)–C(6)	119.2 (3)	C(8)–C(13)–C(12)	118.0 (3)
C(1)–C(2)–C(3)	120.7 (3)		

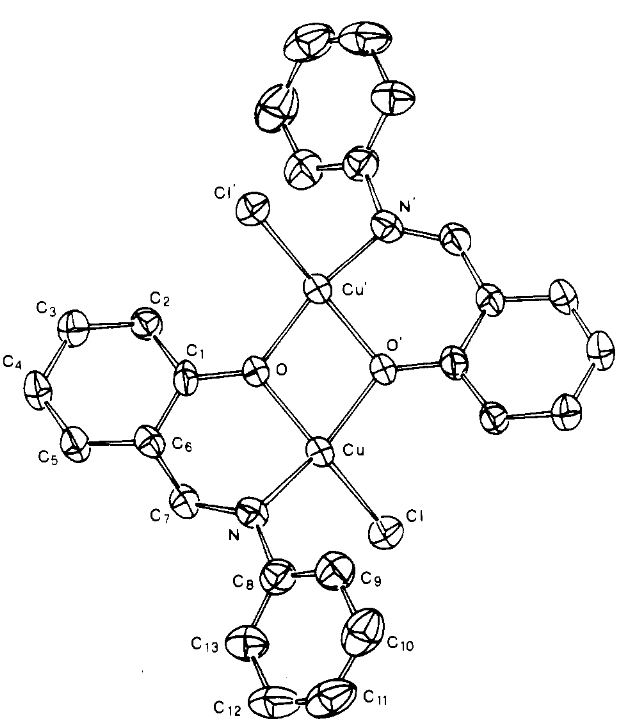

Figure 1. View of the molecular structure of the binuclear units in $Cu_2L_2Cl_2$. Hydrogen atoms have been omitted for clarity. Unlabeled atoms are related to labeled atoms by the inversion center.

The combined magnetic[9] and structural data for $Cu_2L_2Cl_2$ fully conform to the view, first proposed by Sinn et al.,[8-13] that a direct correlation between $2J$ and τ exists in compounds of type III. Structural and magnetic data for the seven such compounds that have been completely characterized so far are collected in Table III and plotted in Figure 2, where it may be seen that the singlet–triplet splittings for compounds A–F fall on or near a straight line. Data for compounds of type IV[14,15] have not been considered for the purpose of the present discussion since these compounds have, with respect to those of type III, shorter bridging Cu–O distances (the average value is 1.91 Å) and higher electron density at the bridging oxygens. This complicates an analysis of the

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Table III. Structural and Magnetic Properties of Copper(II) Compounds of Type III

compd[a]	substituents Z	R	R′	Y	Cu–O, Å		ϕ, deg	τ, deg	$-2J$, cm^{-1}	ref
A	Cl	C_2H_5	H	H	1.923 (3)	1.966 (3)	103.3 (2)	33.1	480	8, 9
B	Br	C_4H_9	C_6H_5	5-Cl	1.95 (2)	1.96 (2)	101.1 (8)	35.6	440	10
C	Br	C_2H_5	H	H	1.89 (1)	1.96 (1)	104.6 (2)	35.7	410	8
D	Cl	C_6H_5	H	H	1.924 (2)	1.961 (3)	103.3 (1)	37.3	360	9, *b*
E	Cl	CH_3	H	H	1.915 (7)	1.992 (7)	102.2 (2)	39.3	292	8, 9
F	Cl	$CH(CH_3)_2$	H	H	1.928 (1)	1.976 (1)	103.56 (4)	40.1	290	9, 11
G	ONO_2	C_2H_5	H	H	1.926 (3)	1.968 (3)	101.1 (1)	27.4	166	12, 13

[a] The Cu_2O_2 bridging units are strictly planar in all of the compounds owing to crystallographic inversion symmetry. [b] Present work.

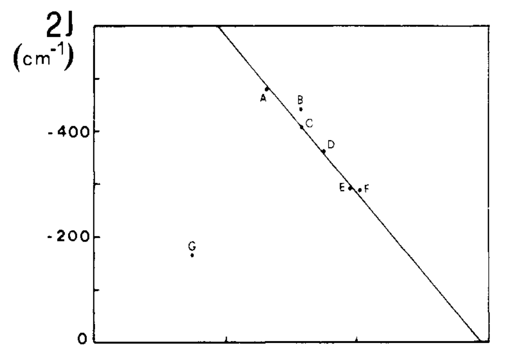

Figure 2. $2J$ vs. dihedral twist angle (τ) for copper(II) dimers of type III. The data points are keyed by capital letter to the data in Table III. The straight line was calculated from $2J$ (cm^{-1}) = $29.7\tau - 1473.4$.

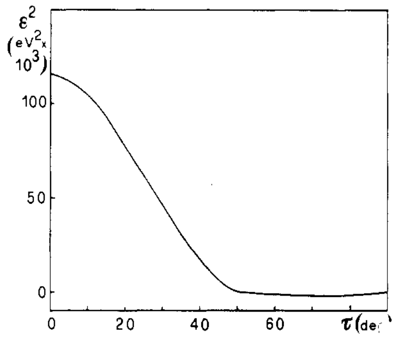

Figure 3. ϵ^2 as a function of dihedral twist angle (τ). ϵ^2 is the difference between Δ^2 at a constant bridge angle of 105° and Δ^2 at a constant bridge angle of 101°, where Δ is the energy difference between the two highest occupied energy levels of the dimer.

magnetic data in terms of τ and ϕ since both the bond lengths in the superexchange pathway[2a,e,21,22] and the electron density at the bridging atoms[23,24] have been shown to be relevant factors in determining the extent of exchange coupling.

The data for compound G in Table III represent a serious deviation from the apparent correlation, seemingly as a reflection of the different structure of this compound, the only one in the series that shows distorted (4 + 1) square-pyramidal geometry at copper. If true, this is interesting since it indicates that the superexchange interaction in systems of type III is much more sensitive to the presence of a fifth weak apical bond than the interaction in e.g. the hydroxo-bridged compounds of type I, in which there is no perturbing influence of such bonds.[2e] Neglecting the data for compound G, the best least-squares line through the data is found to be

$$2J \text{ (cm}^{-1}\text{)} = 29.7\tau - 1473.4 \qquad (2)$$

with a linear correlation coefficient of −0.983 96. The standard error of estimate is 9 cm^{-1}, which is likely to be smaller than the uncertainty in the measurements of the $2J$ values.

That variations in ϕ have a negligible effect on $2J$ in the present selection of compounds is clearly apparent from the relative magnetic coupling in B and C, which show identical τ angles (35.6 and 35.7°) but different ϕ angles of 101.2 and 104.6°, respectively. $2J$ changes by only 30 cm^{-1} on going from compound B to compound C. For the purpose of comparison, the change in $2J$ predicted by eq 1 for the same variation in ϕ is 253 cm^{-1} and is in the opposite direction.

A qualitative explanation of the observed dependence of $2J$ on τ and ϕ in the compounds under discussion can be found with use of semiempirical MO theory. In the orbital model for superexchange developed by Hoffmann et al.[23] the exchange energy, $2J$, for the interaction of two spin $^1/_2$ ions can be expressed by the combination of a ferromagnetic term ($2J_F > 0$) and an antiferromagnetic contribution ($2J_{AF} < 0$):

$$2J = 2J_F + 2J_{AF} \qquad (3)$$

J_F is assumed to be small and virtually constant in a series of chemically related compounds, and J_{AF} is related to the square of the energy separation, Δ, between the two highest occupied molecular orbitals containing the unpaired electrons. The larger Δ^2, the stronger the antiferromagnetic interaction. Since Δ^2 can be easily calculated, by means of semiempirical MO techniques, as a function of various molecular parameters, it is possible to predict qualitatively the effect that changes in molecular geometry will have on the strength of exchange coupling. Calculations by both Hoffmann et al.,[23] using the extended Hückel approach, and Bencini and Gatteschi,[25] using the angular overlap approach, have shown that for a planar dimer of type I (i.e. $\tau = 0°$) Δ, and hence $|J_{AF}|$, is enhanced as ϕ increases from a critical value near 90° and that, at a fixed ϕ angle of 95°, Δ is decreased as τ increases from 0°. With orbital energies obtained from the angular overlap approach, we have calculated the difference, denoted ϵ^2, between Δ^2 at a constant ϕ angle of 105° and Δ^2 at a constant ϕ angle of 101°, as a function of τ. The values of 105 and 101° were selected since ϕ varies between these limits in the compounds under discussion. The results of the calculations[26] are shown graphically in Figure 3 and lead to the following predictions: (i) When τ is small (less than ca. 10–20°), ϵ^2 is large and varies slowly with τ. This suggests that, in this region, ϕ should play the key role in determining $2J$, in agreement with the results on the hydroxo-bridged series. (ii) For τ values larger than ca. 50°, ϵ^2 is

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(26) The calculations were performed as described in ref 25. The values of e_σ = 0.7439 eV (6000 cm^{-1}) and e_σ/e_π = 5.5, which compare well with the values suggested for nitrogen and oxygen ligands in ref 25, were used. For τ = 0° and ϕ in the range 101–105°, the level ordering of the two highest orbitals (metal d_{xy} like) is found to be the same as that predicted in ref 23 for the same values of the τ and ϕ angles. As described in the text, when τ increases, a level crossing occurs near τ = 50°. The origin of this crossing is of the same nature as that very clearly discussed in ref 23, p 4890.

virtually 0 and, therefore, variations in ϕ should have almost no effect on the antiferromagnetic coupling. (iii) For intermediate values of τ, ϵ^2 decreases very rapidly as τ increases. Consequently, for increasing τ values, the effect of ϕ is expected to become progressively less important and τ assumes the leading role. Finally, it may be noticed that eq 2 predicts the presence of a triplet ground state ($2J > 0$) for a τ angle near 50° or larger. The calculations lead to a similar expectation since Δ^2, and hence J_{AF}, turns out to be 0 for $\tau \sim 50°$ and ϕ in the range 101–105°. Although no complexes of type III or IV have been reported with $\tau \geq 50°$, it might be of some interest that $[Ph_4P]CuCl_3$,[27] $[Ph_4As]CuCl_3$,[28] $[Ph_4Sb]CuCl_3$,[29] $[Ph_4P]CuBr_3$,[30] and $[Ph_4As]CuBr_3$[31] exhibit τ angles in the range 45–50° and all have a triplet ground state.[30-32]

In conclusion, although it would be inappropriate to ascribe much significance to the actual computed τ and ϕ angles since they are dependent on the choice of parameters, the trends that emerge from the calculations are in agreement with the experimental results and provide a reasonable basis for a qualitative understanding of the relative merit of the τ and ϕ parameters in determining the extent of magnetic coupling in doubly bridged, nonplanar copper(II) dimers.

Registry No. $Cu_2L_2Cl_2$, 21448-43-1.

Supplementary Material Available: Listings of thermal parameters and hydrogen atom coordinates (2 pages); a table of calculated and observed structure factors (9 pages). Ordering information is given on any current masthead page.

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Gas-Phase Molecular Structure of Ethynylsulfur Pentafluoride, $F_5SC{\equiv}CH$, by Electron Diffraction

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Six-coordinate sulfur compounds of the types F_5SX and $(F_5S)_2Y$ have structural interest arising from the effect of the odd ligands on the relative lengths of the axial and equatorial S–F bonds and on the bond angles in the SF_5 groups. There are experimental structural data for the molecules with X = Cl,[3,4] Br,[5] F_2N,[6] OCN,[7] F_3C,[8,9] and FO[10] and for those with Y = HN,[11] FN,[11] and O.[12] Ab initio calculations (double-ζ or lower quality) for X = Cl have been done;[4] others involving polarization functions are in progress.[13] For the molecules with the ligands Br, FO, and OCN it was not possible to determine which of the S–F bond types was longer nor whether the F_a–S–F_e angle was different from 90°. For the molecules with the ligands F_2N, HN, FN, and O, the axial S–F bond was determined to be longer than the equatorial one and, except for F_5SNF_2 (where it was measured to be 90.0 (9)°), the F_a–S–F_e angles were found to be slightly less than 90°. In the case of F_5SCl the two types of S–F bonds were found to be insignificantly different, but the F_a–S–F_e angle at 89.63 (10)° is surely less than 90°. It is only for F_5SCF_3 that the axial bond is found to be shorter than the equatorial one (by 0.010 (7) Å), and in this case, too, the F_a–S–F_e angle at 89.5 (2)° appears to be slightly less than 90°. These data are summarized in Table I.

Table I. Values of Parameters for the SF_5 Group in F_5SX and $(F_5S)_2Y$ Molecules[a]

substituent		parameter			
X	Y	$\langle r(S{-}F)\rangle$	$\Delta r(S{-}F)$	$\angle F_a{-}S{-}F_e$	ref
F		1.5623 (4)	0.0	90.0	26
Cl[b]		1.5702 (10)	0.001 (8)	89.63 (10)	4
Br[c]		1.5970 (25)	0.0[d]	88.8[d]	5
F_2N		1.549 (4)	0.014 (27)[e]	90.0 (9)	6
OCN		1.567 (2)	0.0[d]	90.0[d]	7
C≡CH		1.574 (2)	0.001 (14)	88.9 (2)	this work
F_3C		1.570 (2)	−0.010 (7)	89.5 (2)	9
FO		1.530 (10)	0.0[d]	90.0[d]	10
	HN	1.568 (3)	0.015 (26)[e]	88.4 (5)	11
	FN	1.557 (4)	0.026 (28)[e]	88.1 (9)	11
	O	1.560 (4)	0.014 (42)[e]	87.9 (9)	12

[a] Distances (r) in angstroms, angles ($\angle$) in degrees. If not otherwise noted, distances refer to r_a and angles to $\angle_a$. [b] Joint electron diffraction and microwave spectroscopic analysis; r_g distances and $\angle_\alpha$ angle. [c] From microwave spectroscopy. [d] Value fixed during structure refinement. [e] Error limit not reported. Value estimated from $\epsilon(\Delta r(S{-}F)) = \epsilon(r(S{-}F_e)) + \epsilon(r(S{-}F_a))$.

An interesting additional example of this type of molecule is ethynylsulfur pentafluoride, $F_5SC{\equiv}CH$. The interest lies in the combined effect of the spatial and electron-donating properties of the acetylenic group on the structure of the SF_5 group. In view of what had been found for the molecules discussed above, distortions of this group were expected to be small and difficult to measure accurately by electron diffraction. However, the prospects for success clearly would be improved if data at high scattering angles, which increases the resolution of some of the interatomic distances, were obtained. We decided to carry out an investigation that included high-angle data. After our work was well along, we learned that a parallel study of $F_5SC{\equiv}CH$ was also being carried out in Professor H. Oberhammer's laboratory;[14] we understand publication of that work is also planned.

Experimental Section

Preparation of F_5SC_2H. A 118-mmol amount of F_5SBr and 104 mmol of HC≡CH were placed in a 300-mL Hoke stainless steel vessel equipped with a Whitey stainless steel valve. The reaction mixture was heated at 57 ± 2 °C for 2.5 h. The $F_5SCH{=}CHBr$ adduct was distilled, and the fraction boiling at 80–91 °C was collected, washed with water, dried over $MgSO_4$ (12 h), and redistilled. The fraction boiling at 86–89 °C was collected in 45% yield for subsequent dehydrobromination.

The $F_5SCH{=}CHBr$ was dehydrobrominated according to a literature method.[15] $F_5SC{\equiv}CH$ was purified by trap-to-trap distillation using traps cooled to −78, −98, and −196 °C. The pure product was found in the −98 and −196 °C traps; yield 50%. The infrared spectrum agreed with the literature spectrum,[15] and the molecular weight was found to be 151.4 g/mol (theoretical value 152.1 g/mol).

Conditions of Experiments. The electron diffraction data were obtained with the Oregon State apparatus. Conditions of the experiments

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