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Stereochemistry of Bis(1,4-difluorobenzene)vanadium(0)[1]

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Bis(1,4-difluorobenzene)vanadium(0) crystallizes with four molecules in a unit cell having $I2/c$ symmetry and lattice constants of a = 13.850 (6), b = 7.104 (3), c = 11.192 (4) Å, and β = 109.11 (2)°. The structure was determined from 1378 observed diffractometer data in the range $(\sin\theta)/\lambda \leq 0.707$ Å^{-1}. The molecular structure consists of a vanadium atom "sandwiched" between two 1,4-difluorobenzene ligands in a dissymmetric arrangement approximating D_2 molecular symmetry. Planes of the two ligands are parallel and the carbon atoms from the two ligands are approximately eclipsed while the dihedral angle between fluorine atoms in opposite rings is 53°. A small "boat" deformation is observed for the 1,4-difluorobenzene ligand, the fluorine-substituted carbon atoms being displaced 0.06 Å from the mean plane of the ligand. The vanadium atom is 1.67 Å from this plane and V–C bond distances are 2.187 (3) and 2.204 (2) Å.

Since the discovery of ferrocene[2] in 1951, the study of transition metal "sandwich" compounds has been an active area of chemical research. Although the synthesis of the first arene "sandwich" compound, bis(benzene)chromium, was reported[3] in 1955, the structural characterization of this compound led to a controversy concerning the equivalence of the carbon–carbon bond lengths which lasted several years.[4] With the exception of bis(benzene)chromium, however, accurate structural parameters for bis(arene) complexes of the first-row transition metals are nonexistent and little is known about the structural effects of substituent groups in these compounds. The bulk of available structural parameters deal with the arene tricarbonyl compounds which were originally studied by Bailey and Dahl[5] because they provide the advantage of localizing the hexacoordinate arrangement of metal orbitals, compared to the disordered possibility in the bis(arenes), and thus simplify the interpretation of the bonding. While similarities certainly exist between these two types of compounds, there are also substantial differences between them. Bailey and Dahl observed that the attachment of three strongly bonding CO groups significantly weakens the chromium to arene bonds as evidenced by an increase in the chromium–ring distances of ~0.1 Å[4] over the value in $(C_6H_6)_2Cr$. More recent ^{19}F NMR studies by Fletcher and McGlinchey[6] have also provided evidence that the electronic environment in substituted arenechromium tricarbonyls is considerably different from that of the corresponding bis(arene) complexes.

Recent developments in synthetic techniques[7-9] have now made it possible to prepare a variety of substituted bis(arene) complexes for a few of the transition metals. We have initiated a program to learn more about the effects of substitutent groups on the stereochemistry and bonding involved in bis(arene) systems. The present study deals with the solid-state structure of bis(1,4-difluorobenzene)vanadium(0).

Experimental Section

The compound was prepared as described previously[9] and dark amber crystals were obtained by sublimation. In order to check for air sensitivity, several crystals were mounted in thin-walled glass capillaries under argon and several were mounted under atmospheric conditions. The crystals were unaffected by brief air exposure. The crystal selected for data collection was cut from a larger crystal, under atmospheric conditions, to the approximate dimensions 0.40 mm × 0.32 mm × 0.47 mm and was secured in the capillary with a small amount of petroleum jelly.

Photographic examination with Cu Kα radiation led to an I-centered monclinic cell, chosen for the convenience of the β angle, having systematic absences consistent with a c-glide plane ($h0l$, $l = 2n + 1$) thus limiting the possible choices of space groups to $I2/c$ or Ic. Final lattice constants were determined on our Picker automatic diffractrometer using Mo Kα_1 radiation (λ 0.7093 Å) from the least-squares refinement[10] of the setting angles of 20 carefully centered reflections. The resulting lattice constants are a = 13.850 (6), b =

Table I. Atomic Coordinates[a]

Atom	Coordinates		
	10^4x	10^4y	10^4z
V	2500	183.2 (8)	0
F_1	1486 (2)	−3248 (3)	1092 (2)
F_4	943 (2)	3608 (3)	−1202 (2)
C_1	1372 (2)	−1535 (4)	514 (3)
C_2	1587 (2)	47 (5)	1272 (2)
C_3	1459 (2)	1833 (4)	683 (3)
C_4	1094 (2)	1892 (4)	−633 (3)
C_5	959 (2)	309 (4)	−1384 (2)
C_6	1113 (2)	−1480 (4)	−795 (3)
H_2	1829 (30)	−124 (46)	2163 (38)
H_3	1585 (27)	2996 (48)	1141 (34)
H_5	760 (30)	413 (44)	−2320 (37)
H_6	1049 (27)	−2699 (49)	−1267 (34)

[a] Estimated standard deviations are given in parentheses for the least significant digits.

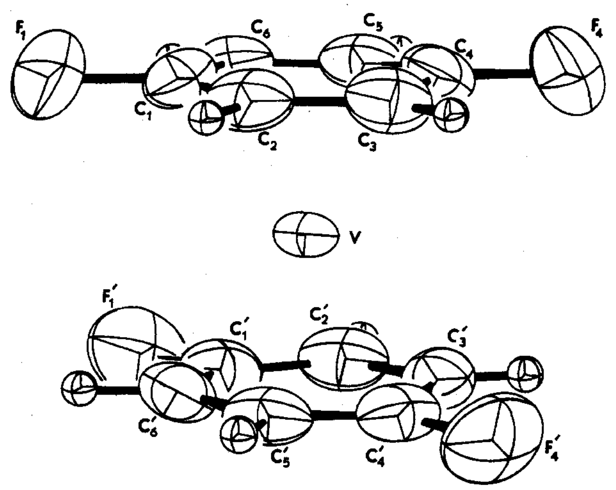


Figure 1. ORTEP drawing of $(C_6H_4F_2)_2V^0$ showing the anisotropic ellipsoids listed in Table II at 50% probability and the numbering scheme employed. The size of the hydrogen atoms has been deliberately reduced for clarity.

7.104 (3), $c = 11.192$ (4) Å, and $\beta = 109.11$ (2)°. This cell containing four molecules of $(C_6H_4F_2)_2V^0$ provides a calculated density of 1.78 g/ml.

Intensity data were collected on the Picker diffractometer using zirconium-filtered Mo Kα radiation with a takeoff angle of ~3°. Using a scan rate of 1°/min each peak was symmetrically scanned 2° in 2θ plus an increment allowing for spectral dispersion. Stationary-background counts of 20 s were taken at the scan limits and attenuators were inserted automatically when a count rate of ~9000 counts/s was exceeded. In this manner 1560 independent data in the quadrant $\pm h,k,l$ were scanned to a limiting 2θ of 60.40°.

Evidence for a small amount of crystal deterioration with exposure time was provided by three standard reflections which were monitored after every 100 data. These standards displayed a decrease in intensity amounting to 13% over the course of data collection. Statistical analysis of the standards was handled by scaling each standard relative to its initial magnitude and the average value of each set was fit to an equation of a straight line by the method of least squares. The 18 sets of standards showed only trivial fluctuation from this line, the average deviation being <1%, indicating that the linear approximation was indeed valid. Minor scaling corrections calculated from this equation were applied to the data.

The linear absorption coefficient for Mo Kα radiation is 1.04 mm^{-1} and for the described crystal the maximum error introduced on F by ignoring adsorption effects is estimated at ~5%.

The intensity data were reduced to a set of $|F_o|$'s by application of Lorentz and polarization corrections (Lp) and standard deviations were calculated according to the formula

$$\sigma_F = [(C + k^2B)/4|F_o|^2(Lp)^2]^{1/2} + 0.04|F_o|$$

where C and B are the counts of the scan and backgrounds, respectively, and k is the ratio of scan to background counting time. Those 1378 data having $F_o > 2\sigma_F$ were taken as observed and utilized in the structure determination.

A Patterson synthesis provided coordinates for the vanadium atom and subsequent electron density maps[11] led to the positioning of all atoms in the asymmetric unit of structure except hydrogens. Isotropic refinement[12] of the parameters, in which the function $w(|R_o| - |F_c|)^2$ was minimized, produced an R value of 12.7% where $R = \sum||F_o| - |F_c||/\sum|F_o|$. Further isotropic refinement followed by fully anisotropic refinement, employing unit weights and adding anomalous dispersion corrections[13] for the vanadium atom, produced an R value of 6.0% and an R_w of 5.9%, where $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$. Attempts to fit the model structure to the noncentrosymmetric space group (Ic) were unsuccessful leading us to conclude that the centrosymmetric space group was the correct one and that the molecule had full twofold symmetry.

A Fourier difference synthesis at this stage revealed that the four largest residual electron densities were in the regions expected for C–H bond densities. The coordinates of these hydrogen atoms,[14] with fixed isotropic thermal parameters, were varied in further unit-weighted refinement which converged with an R value of 4.8% and an R_w of 4.9%. In order to check the sensitivity of the structural model on the weighting scheme employed during refinement, empirical weights ($w = 1/\sigma^2$) were calculated as described previously.[15]

Several cycles of full-matrix refinement of the 90 structural parameters using this weighting scheme produced an R value of 4.7% and a R_w of 4.4%. The error of fit, defined as $[\sum w(|F_o| - |F_c|)^2/(n - v)]^{1/2}$ where n is the number of independent data and v is the number of structural parameters varied in refinement, was 1.288 and the data:parameter ratio was 15.3. Switching to the $1/\sigma^2$ weighting scheme improved one of the C–H bond distances but the range of observed C_a–C_b distances, which showed remarkable internal consistency using unit weights, increased somewhat. The average C_a–C_b distance changed by only 0.004 Å however, and the other structural parameters were rather insensitive to this change. The atomic coordinates obtained from this final refinement are listed in Table I and the associated anisotropic thermal parameters are listed in Table II.[16]

A final electron density difference synthesis revealed that the largest residual had a magnitude of 0.41 e/Å^3 in the vicinity of the metal atom, confirming the correctness of the structure.

Table II. Thermal Parameters of the Atoms[a]

Atom[b]	Anisotropic parameters, Å^2					
	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
V	2.01 (2)	3.61 (2)	2.46 (2)	0.0 (0)	0.67 (1)	0.0 (0)
F_1	8.5 (1)	6.8 (1)	9.0 (1)	−1.11 (9)	3.0 (1)	2.93 (9)
F_4	7.2 (1)	6.8 (1)	8.5 (1)	2.15 (8)	1.83 (9)	2.77 (9)
C_1	3.8 (1)	5.4 (1)	5.7 (1)	−0.51 (9)	1.9 (1)	1.2 (1)
C_2	3.87 (9)	7.3 (2)	3.71 (9)	−0.1 (1)	1.81 (7)	0.5 (1)
C_3	4.0 (1)	5.7 (1)	4.7 (1)	0.4 (1)	1.8 (1)	−0.8 (1)
C_4	3.19 (9)	5.4 (1)	5.3 (1)	0.93 (9)	1.19 (9)	1.1 (1)
C_5	2.82 (7)	7.1 (2)	3.57 (9)	−0.01 (9)	0.31 (6)	0.2 (1)
C_6	3.4 (1)	5.7 (1)	4.9 (1)	−1.05 (9)	0.98 (9)	−0.7 (1)

[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 Å^2.

Table III. Bond Distances (Å) in $(C_6H_4F_2)_2V^0$

1,4-Difluorobenzene ligand				Coordination sphere	
Bond	Length	Bond	Length	Bond	Length
C_1-C_2	1.380 (4)	C_1-F_1	1.363 (3)	V-C_1	2.203 (2)
C_1-C_6	1.390 (4)	C_4-F_4	1.360 (3)	V-C_2	2.194 (2)
C_4-C_3	1.393 (4)	C_2-H_2	0.95 (4)	V-C_3	2.182 (3)
C_4-C_5	1.379 (4)	C_3-H_3	0.96 (3)	V-C_4	2.205 (2)
C_2-C_3	1.414 (4)	C_5-H_5	1.00 (4)	V-C_5	2.191 (2)
C_5-C_6	1.416 (4)	C_6-H_6	1.00 (3)	V-C_6	2.181 (2)

Table IV. Bond Angles (deg) in the Coordination Sphere and the 1,4-Difluorobenzene Ligand of $(C_6H_4F_2)_2V^0$

Angle	Value	Angle	Value	Angle	Value
$C_2C_1C_6$	123.6 (3)	$C_5C_4F_4$	118.4 (3)	$C_1C_2H_2$	118 (2)
$C_3C_2C_1$	118.4 (2)	$C_3C_4F_4$	118.0 (3)	$C_3C_2H_2$	123 (2)
$C_4C_3C_2$	117.8 (3)	C_1VC_6	37.0 (1)	$C_2C_3H_3$	124 (2)
$C_5C_4C_3$	123.4 (3)	C_2VC_1	36.6 (1)	$C_4C_3H_3$	119 (2)
$C_6C_5C_4$	118.6 (2)	C_3VC_2	37.7 (1)	$C_4C_5H_5$	121 (2)
$C_1C_6C_5$	117.6 (3)	C_4VC_3	37.0 (1)	$C_6C_5H_5$	120 (2)
$C_2C_1F_1$	117.8 (3)	C_5VC_4	36.6 (1)	$C_1C_6H_6$	119 (2)
$C_6C_1F_1$	118.4 (3)	C_6VC_5	37.8 (1)	$C_5C_6H_6$	124 (2)

Results and Discussion

A traced computer drawing of the bis(arene) complex as it exists in the crystal is shown in Figure 1.[17] The thermal parameters listed in Table II are represented by ellipsoids for all atoms except the hydrogen atoms which were deliberately reduced in size for clarity. The atomic numbering scheme for the asymmetric unit of structure is also indicated and the prime notation is used for those atoms related by the crystallographic twofold axis of symmetry.

The molecule has quasi-D_2 (222) symmetry, a rarely encountered point group in chemistry, but only one of the twofold axes is a real crystallographic axis. Figure 2, a projection of the molecule down the $-a$ axis, shows the position of this twofold axis relative to the molecular framework. One of the two quasi-twofold axes passes through the center of the two rings and the vanadium atom while the other one passes through the vanadium atom in the horizontal plane of Figure 2. The dihedral angle between the plane containing atoms F_4, C_4, and V and the plane containing atoms F_4', C_4', and V is 53°. Thus the carbon atoms of the two rings are closer to the eclipsed orientation than the staggered orientation although precise alignment of the carbon atoms is precluded because of the nonequivalence of the C–C bond lengths. Individual bond lengths in the structure are listed in Table III and the bond angles are listed in Table IV.[18] Standard deviations, estimated from the full variance–covariance matrix, are listed in parentheses for the least significant digits.

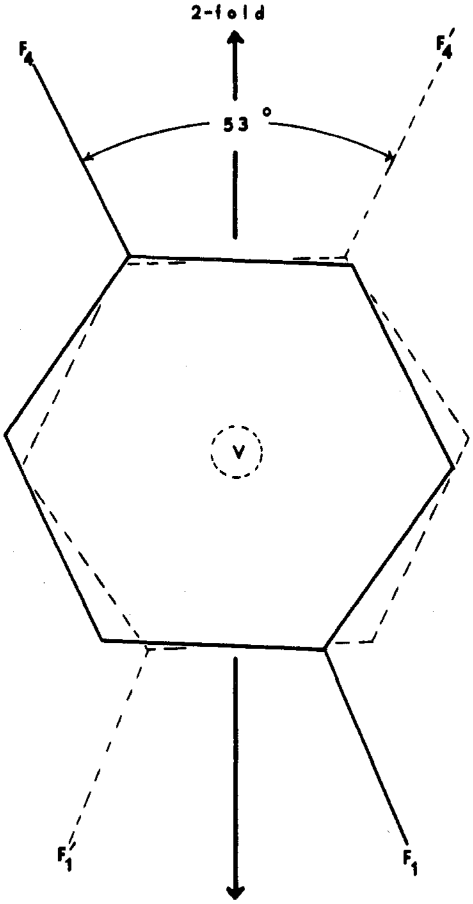


Figure 2. Projection of the molecule down the $-a$ axis showing the relationship of the molecular framework to the twofold crystallographic axis.

The thermal parameters listed in Table II and depicted in Figure 1 are consistent with some libration of the aromatic ligands about the quasi-twofold axis passing through the vanadium atom and the center of the ring. Thermal motion of this type, which is not uncommon in π-bonded complexes,[19] would cause an apparent shortening of the bonds in the arene ligands although these effects would be relatively small in this structure. The fluorine atoms show the largest individual thermal parameters with a large component perpendicular to the C–F bonds.

Two distinct types of C–C bonds exist in the complex. Referring to the carbons that are bonded to fluorine atoms as C_a and the remaining carbons as C_b, we have averaged the results in Table V according the maximum C_{2v} symmetry of the ligand in its observed conformation. It should be noted that the idealized (D_2) symmetry of the entire complex requires only the parallel C_a–C_b bonds to be equivalent. This fact combined with the observed difference between the two sets of parallel C_a–C_b bond lengths could lead to the view that all of the C_a–C_b bond lengths may not be equivalent. Opposing this view however were the results of unit-weighted refinement,

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

Type	$(C_4H_4F_2)V^0$ [b]	C_6H_5F[c] (microwave)	$(C_6H_6)_2V^0$ [d]	$(C_6H_6)_2Cr^0$ [e] (at 100 K)	$(C_6H_6)Cr(CO)_3$ [f] (at 78 K)	$(H_3C)_6C_6Cr(CO)_3$[g]
C-C	1.386 (4)	1.383			1.402 (2)	
	1.415 (4)	1.396		1.417 (3)	1.420 (2)	1.42 (1)
C-F	1.362 (3)	1.354				
C-H	0.98 (4)	1.082		0.93 (3)	0.91 (2)	
M-C	2.204 (2)					
	2.187 (3)		2.17	2.142 (2)	2.221 (2)	2.23 (1)
M-ring	1.671		1.66	1.609 (1)		1.73
CCC	123.5 (3)	123.4			120.00 (7)	120 (1)

[a] All of the parameters listed are uncorrected for thermal motion. Distances are in angstroms; angles are in degrees. [b] This work. [c] C–C lengths other than those involving C_1 have been averaged.[20] [d] Not a complete structure determination.[28] [e] Reference 25. [f] Reference 27. [g] A twofold distortion was observed in this molecule. The results listed have been averaged.[26]

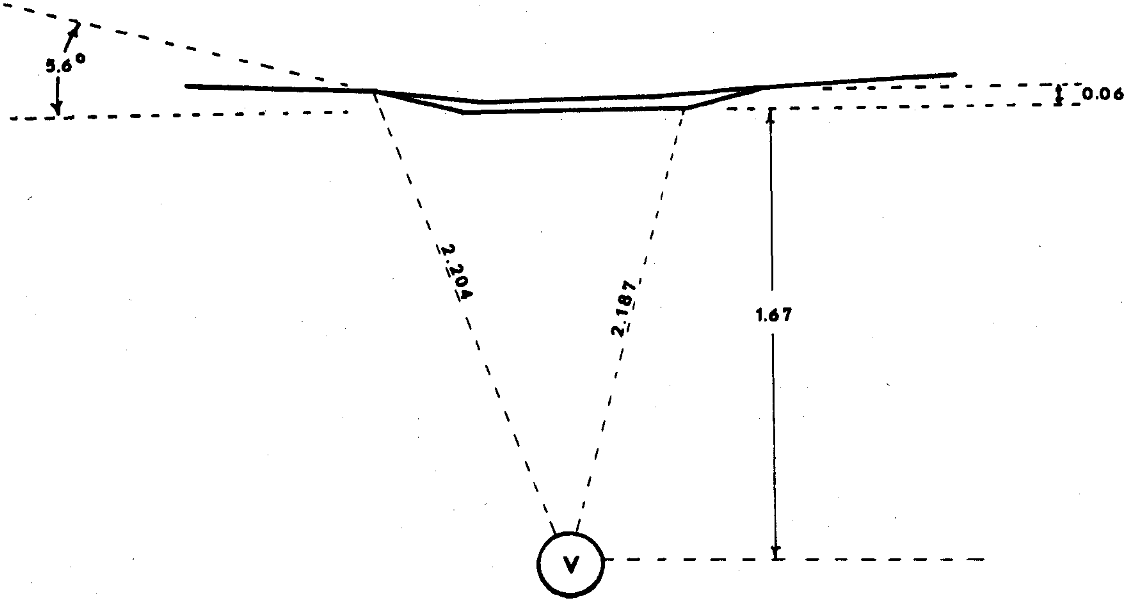


Figure 3. Side view of the asymmetric unit of structure excluding hydrogen atoms and showing the average bond parameters in the coordination sphere. Distances are in angstroms and angles in degrees.

which showed the four experimentally determined C_a–C_b distances to be equivalent at 1.382 (3) Å. The C_a–C_b distances are thus averaged and a value of 1.386 (4) Å is obtained. This distance is shorter by $\sim 5\sigma$ than the average C_b–C_b distance of 1.415 (4) Å which was independent of the weighting scheme employed. An even larger difference is found for the bond angles at the C_a and C_b carbon atoms. The angles at C_a average 123.5 (3)°, more than 5° different from the average angle at C_b of 118.1 (3)°.

The observed C_a–C_b distance and the angle at C_a correspond within experimental error to the results found for the structure of the planar fluorobenzene molecule from microwave data.[20] These results are summarized in Table V. This increase in the internal bond angle at the fluorine-substituted carbon atom has also been observed in the solid-state structure determinations of 1,5- and 1,8-difluoronaphthalene where the average value is 123.8°[21] and appears to be a general phenomenon for electron-withdrawing substituents.[22] The average C_b–H distance of 0.98 (4) Å is also in agreement allowing for the approximate contraction of ~ 0.1 Å for C–H bond distances crudely determined from x-ray diffraction.

The most striking feature of the molecule is the small but apparently significant nonplanar distortion of the ligand shown in Figure 3. The four C_b carbon atoms form a plane, plane A in Table VI, at a distance of 1.67 Å from the vanadium atom and the two C_a carbon atoms are displaced out of this plane by 0.06 Å away from the metal atom. The average V–C_a distance is 2.204 (3) Å and the average V–C_b distance is 2.187 (3) Å. Plane B defined by atoms C_1, C_2, and C_6 and plane C defined by atoms C_3, C_4, and C_5 are rotated 5.4 and 5.7°, respectively, from plane A. The fluorine atoms are rotated by only half this amount, F_1 by 2.7° and F_4 by 2.5°. This resulting small "boat" deformation of the carbon skelton is the first reported distortion of this type in a bis(arene) complex. A larger but different type of distortion amounting to a >40° folding of an arene ligand has been observed in π-cyclopentadienylhexakis(trifluoromethyl)benzenerhodium[23] and in bis(hexamethylbenzene)ruthenium(0).[24] The distortion in the ruthenium complex has been attributed to the electronic effect of the metal. However, the influence of the substituents in the rhodium complex is considered more important.[24]

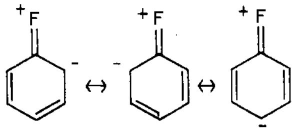
Table VI. Results of Mean-Planes Calculations and Deviations (Å) of Individual Atoms[a,b]

Atom	Dev	Atom	Dev
	Plane A		
C_2*	−0.009 (3)	F_1	−0.094 (3)
C_3*	0.009 (3)	F_4	−0.087 (3)
C_5*	−0.009 (3)	H_2	0.03 (4)
C_6*	0.009 (3)	H_3	0.03 (4)
V	1.671 (1)	H_5	0.02 (4)
C_1	−0.062 (3)	H_6	0.07 (4)
C_4	−0.065 (3)		
	Plane B		
C_6*	0.000 (3)	C_5	−0.151 (3)
C_1*	0.000 (3)	F_1	0.096 (3)
C_2*	0.000 (3)	F_4	−0.408 (3)
C_3	−0.115 (3)	V	1.597 (1)
C_4	−0.259 (3)		
	Plane C		
C_3*	0.000 (3)	C_6	0.123 (3)
C_4*	0.000 (3)	F_1	0.434 (3)
C_5*	0.000 (3)	F_4	−0.114 (3)
C_1	0.266 (3)	V	−1.593 (1)
C_2	0.158 (3)		

[a] The equations are derived from the equally weighted refinement of those atoms indicated by an asterisk and are based upon an orthonormal coordinate system where X, Y, Z are in Å and their directions are related to the unit cell as follows: $b' = b$, $c' = a \times b$, and $a' = b \times (a \times b)$. [b] Equations for the planes: A, $-0.999\,32X - 0.001\,93Y - 0.036\,69Z = -1.789\,53$; B, $-0.993\,26X + 0.079\,07Y - 0.084\,76Z = -1.832\,07$; C, $0.996\,06X + 0.087\,63Y - 0.013\,99Z = 1.867\,62$.

The average C_b–C_b bond length in Table V is similar to the average C–C distances found in bis(benzene)chromium[25] and hexamethylbenzenechromium tricarbonyl[26] which are remarkably similar in spite of the difference in experimental temperatures. This distance is slightly longer than the distance in fluorobenzene, in agreement with the normal lengthening observed when a metal atom is bonded to an olefin.[27] The average C_a–C_b distance remains within experimental error equal to the value observed in uncomplexed fluorobenzene. Although our results are not accurate enough to detect any significant effects on these C_a–C_b distances, the results do suggest that the effects of complexation on the C_a–C_b distance are smaller than the effects on the C_b–C_b distance.

One can attempt to rationalize these structural parameters in terms of resonance effects using a simple valence-bond model for the 1,4-difluorobenzene ligand. The addition of a fluorine substituent to benzene results in an increase in electron density at the ortho and para positions because of contributions from resonance forms of the type



The addition of two fluorine atoms in para positions will tend to cancel the electron density in the positions para to the fluorines resulting in the four C_b carbon atoms being the most electron rich. These four carbons are then the preferred sites for bonding to the vanadium atom. This view could be criticized for several reasons, however. First, one would not expect resonance forms that have a net positive charge on the electronegative fluorine atoms to be very important. Second, conjugation of this type would tend to decrease the internal bond angles at the C_a carbons.[22] Finally, the observed nonplanarity of the ligand does not lend support to this rationalization. An alternative view utilizing simply the electron-withdrawing (inductive) power of fluorine would also predict the C_b carbons to be the most electron rich. Whichever view is taken, the experimental results reported herein indicate that the vanadium atom is more strongly bonded to the C_b carbons than to the C_a carbons.

The V–C_b distances are larger than the Cr–C distances in bis(benzene)chromium[25] but shorter than the corresponding distances in the tricarbonyl compounds. The V–C_b distance and the perpendicular vanadium to ring distance are similar to those in bis(benzene)vanadium.[28] The results for bis(benzene)vanadium are not accurate enough, however, for detailed comparison to determine if the bonding to the metal is weakened by the fluorine substitutents. Accurate structural parameters from a complete structure determination on bis(benzene)vanadium would facilitate this comparison.

As Rees and Coppens[29] have noted, ligand hydrogen atoms in metal "sandwich" complexes are frequently bent slightly toward the metal atom. They attribute this to a slight bending of the p_π orbitals of carbon toward the metal.[29] The four hydrogen atoms in this structure are consistently displaced toward the vanadium atom by 0.02–0.07 Å. Although the average displacement is within 1σ, the fact that it is systematic and the fact that it was observed in the accurate neutron diffraction study[29] lead us to believe that it is probably real. This tilting of the C_b carbons to achieve better overlap with the metal orbitals stands in sharp contrast to the displacement of the C_a carbons above the plane which would reduce their interaction with the metal.

This dissymmetric molecule crystallizes as a racemic compound[30] with pairs of enantiomers related by a center of inversion in a centrosymmetric unit cell. As shown in Figure 4 planes of the ligands from enantiomeric pairs are approximately parallel. No severe intermolecular contact distances are observed. The shortest C---C intermolecular contact is 3.47 Å, occurring between C_4 and C_1^{I} where I is the center of inversion symmetry operator. This intermolecular contact distance would not favor an out-of-plane deformation, however, but rather would favor a planar configuration since a movement of these atoms into the plane of the C_b carbons would increase the contact distance by $\sim$0.12 Å.

The observed deformation of the 1,4-difluorobenzene ligand is also not attributable to intramolecular repulsion forces since no unusually short interactions are present. Plane A defined by the four C_b carbons is parallel, within experimental error, to plane A′ and the intramolecular perpendicular spacing is 3.34 Å. This separation is considerably larger than the normal van der Waals contact distance for fluorine of 2.94 Å[31] and, consequently, the fluorine atoms could easily be accommodated even in an eclipsed orientation considering this interaction alone. Although the carbon atoms have somewhat more stringent packing requirements, the closest C---C contact between these planes of 3.36 Å, occurring between C_2 and C_5', is not short for an intramolecular interaction.

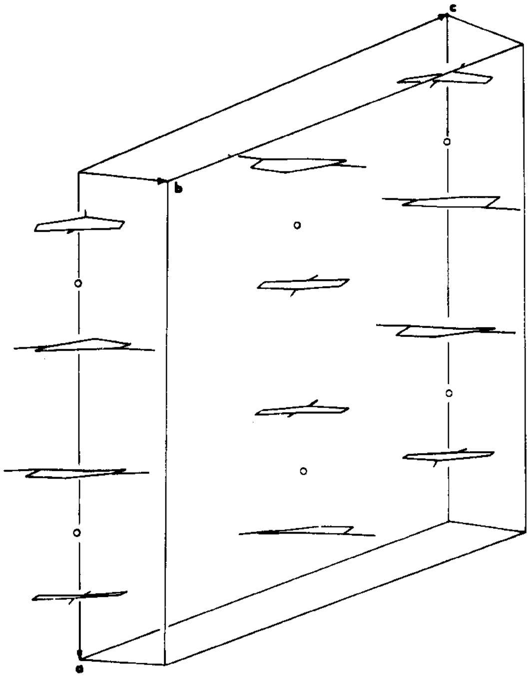


Figure 4. Packing diagram of $(C_6H_4F_2)_2V^0$.

Further studies are under way to determine to what extent the observed results are a function of the electronic configuration of the metal atom and to elucidate the effects of a variety of substitutent groups.

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Registry No. $(C_6H_4F_2)_2V$, 53966-04-4.

Supplementary Material Available: Listing of structure factor amplitudes (7 pages). Ordering information is given on any current masthead page.

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Nickel(II), Palladium(II), Platinum(II), and Platinum(IV) Complexes of the Dithiolate Ligand, $C_5H_4CS_2^{2-}$. Crystal Structure and Molecular Geometry of $[(C_2H_5)_4N]_2[Ni(C_5H_4CS_2)_2]$

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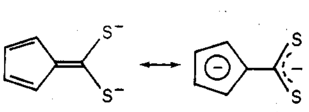
The preparations of tetraethylammonium salts of bis(cyclopentadienedithiocarboxylato)metalate(II) where the metal is Ni, Pd, and Pt are reported as well as that of the tetraethylammonium salt of tris(cyclopentadienedithiocarboxylato)-platinate(IV). The complexes are diamagnetic. The Ni(II) complex has been examined by a single-crystal x-ray diffraction study at 3.0 ± 1.0 °C. This complex crystallizes in the centrosymmetric triclinic space group $P\bar{1}$ with $a = 6.990$ (2) Å, $b = 8.437$ (3) Å, $c = 14.475$ (6) Å, $\alpha = 96.89$ (3)°, $\beta = 90.39$ (3)°, $\gamma = 111.47$ (3)°, and $V = 787.5$ (5) Å^3. The calculated density was 1.264 g/cm^3 for a molecular weight of 599.7 with one molecule per unit cell. X-ray diffraction data (Cu Kα radiation) were collected with a Syntex $P\bar{1}$ automatic diffractometer and the structure was solved by the Patterson method. All nonhydrogen atoms other than the carbon atoms of the $(C_2H_5)_4N$ unit were refined anisotropically to convergence. Least-squares refinement resulted in final agreement factors of $R_1 = 0.091$ and $R_2 = 0.107$ for the 808 independent reflections. The molecular geometry thus determined shows the $(C_5H_4CS_2)_2Ni^{2-}$ ion to be planar, the cis S–Ni–S angles being 101.5 (1)°. The two independent Ni–S distances are 2.203 (4) and 2.198 (4) Å. The formally C–C double bonds in the C_5 ring are 1.42 (2) and 1.38 (2) Å, while the formally single bonds are 1.43 (2), 1.44 (2), and 1.50 (2) Å. The optical spectrum of the Ni(II) system is reported and interpreted in terms of this geometry. Spectroscopic data for the Pd(II), Pt(II), and Pt(IV) complexes are also reported.

Introduction

With the great deal of recent interest in metal–sulfur coordination complexes,[1-3] it is not surprising that a new dithiolate ligand type which promised to add a new dimension to the overall picture of coordination complexes has received a great deal of attention in our laboratories.[4-9] Previously, we have demonstrated that metal complexes of the $C_5H_4CS_2^{2-}$ moiety induce unique electronic properties at metal centers because of the specific out-of-plane π-accepting ability of ligand.

The exact extent of this π-bonding ability or rather the importance of the resonance structure Ib of the ligand when



Ia Ib

bound to a metal can be estimated from electron spin resonance studies,[3-5] the coupling constants of the ring protons,[6-8] and Mössbauer data.[7,8] In all previous cases, it has not been possible to obtain single crystals of the metal complexes for a definitive study of the nature of the carbon backbone in the five-membered ring. Recently, however, a Ni(II) complex has been isolated as small platelets which were *marginally* suitable for a single-crystal x-ray analysis. Those results as well as a spectroscopic characterization of the Ni(II), Pd(II), Pt(II), and Pt(IV) complexes are reported here.

Experimental Section

Materials. Anhydrous solvents were prepared as before[4-9] except tetrahydrofuran which was distilled from Na–K amalgam. $NiBr_2$, $PdCl_2$, $PtCl_2$, and $PtCl_4$ were obtained from Research Organic/Inorganic Chemical Corp.

$Na_2C_5H_4CS_2 \cdot C_4H_8O$. This complex was prepared as previously reported.[6]

$[(C_2H_5)_4N]_2Ni(C_5H_4CS_2)_2$. This complex was prepared in a manner similar to that previously reported for other transition metal complexes.[4-9] Typically, 1.07 g (4.14 × 10^{-3} mol) of $Na_2C_5H_4CS_2 \cdot C_4H_8O$ and 0.454 g (2.07 × 10^{-3} mol) of $NiBr_2$ were added to 150 ml of CH_3CN. After stirring of this solution for 1 h at room temperature, 0.687 g (4.14 × 10^{-3} mol) of $(C_2H_5)_4NCl$ was added to the red solution. The mixture was filtered to remove NaX (X = Cl, Br). The resulting filtrate was reduced in volume several times and filtered again at each stage. A relatively small yield was obtained as red-orange platelets. Anal. Calcd for $[(C_2H_5)_4N]_2Ni(C_5H_4CS_2)_2$: C, 56.08; H, 8.07; N, 4.67; S, 21.39. Found: C, 55.98; H, 8.00; N, 4.68; S, 21.30.

$[(C_2H_5)_4N]_2Pd(C_5H_4CS_2)_2$. This orange-brown product ultimately crystallized as small platelets. Anal. Calcd: C, 51.95; H, 7.47; N, 4.33. Found: C, 52.03; H, 7.40; N, 4.39.

$[(C_2H_2)_4N]_2Pt(C_5H_4CS_2)_2$. Careful fractional cystallization is required during the isolation. The first few fractions of an apparently pure bright red product were considerably contaminated with NaX.