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Trigonal-Prismatic Coordination: The Crystal and Molecular Structure of Tris(*cis*-1,2-diphenylethene-1,2-dithiolato)vanadium

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The crystal and molecular structure of tris(*cis*-1,2-diphenylethene-1,2-dithiolato)vanadium, $V(S_2C_2(C_6H_5)_2)_3$, has been determined from three-dimensional single-crystal X-ray data collected by standard film techniques. The structure has been refined by least-squares methods to a conventional R factor of 0.077 for 1516 nonzero reflections. The neutral complex crystallizes in space group C2/c of the monoclinic system with a cell of dimensions $a = 19.25$, $b = 11.31$, $c = 18.01$ A; $\beta = 106.3°$; $V = 3763$ A^3. An experimental density of 1.36 ± 0.04 g/cm^3 is in good agreement with a calculated value of 1.37 g/cm^3 for four molecules in the unit cell ($Z = 4$). $V(S_2C_2(C_6H_5)_2)_3$ is crystallographically required to possess a twofold symmetry axis with vanadium occupying the 4(e) special positions of the space group. The six sulfur donor atoms surround the vanadium in a trigonal-prismatic coordination. As such, $V(S_2C_2(C_6H_5)_2)_3$ is the first example of trigonal-prismatic coordination in a molecular six-coordinate complex containing a first-row transition metal. The dimensions of the prism are strikingly similar to those found for complexes of second- and third-row metals. Average intra- and interligand S–S distances are approximately equal (3.058 and 3.064 A, respectively), but there is a slight distortion of the prism about the threefold axis. A detailed comparison of the molecular structures of $V(S_2C_2(C_6H_5)_2)_3$, $Re(S_2C_2(C_6H_5)_2)_3$, and $Mo(S_2C_2H_2)_3$ is presented which reinforces the previously suggested notion of interligand bonding as a stabilizing factor in trigonal-prismatic coordination.

Introduction

The discovery of trigonal-prismatic coordination has opened a new area of study in structural inorganic chemistry. The existence of this unusual coordination geometry in monomeric complexes was initially established by the structure determination of the neutral complex $Re(S_2C_2(C_6H_5)_2)_3$.[2] The subsequent structural study by Smith and co-workers[3] on $Mo(S_2C_2H_2)_3$ extended the trigonal-prismatic geometry to complexes of a second-row transition metal. In addition, spectroscopic and X-ray powder measurements strongly suggest a trigonal-prismatic coordination for the complexes M(tdt)$_3$ and M(bdt)$_3$ with M = Re, W, and Mo.[4–6] As with the square-planar bis complexes of the bidentate sulfur-donor ligand systems, the tris complexes readily undergo reversible electron-transfer reactions.[6,7] For example, the $Re(S_2C_2(C_6H_5)_2)_3$ and Re(tdt)$_3$ systems have been observed polarographically to possess four reversible oxidation–reduction waves.[6] Differences in the electronic spectra of the well-established trigonal-prismatic complexes of Re, W, and Mo and the analogous complexes of the first-row transition metals led to the conclusion that a detailed structure determination would be necessary in order to establish unequivocally the coordination geometry of the first-row complexes. This result was achieved with the structural study of the neutral complex $V(S_2C_2(C_6H_5)_2)_3$,[8] which was reported in a preliminary communication.[9] In this complex, vanadium is located at the center of a slightly distorted trigonal-prismatic array of sulfur donor atoms. On the basis of isomorphism studies and spectroscopic measurements, the trigonal-prismatic geometry was also assigned to the analogous $Cr(S_2C_2(C_6H_5)_2)_3$ complex and the $[V(S_2C_2(C_6H_5)_2)_3]^-$ monoanion. In this paper, the structure determination of $V(S_2C_2(C_6H_5)_2)_3$ is described in detail.

Collection and Reduction of the X-Ray Data

The complex $V(S_2C_2(C_6H_5)_2)_3$ was prepared in a manner similar to that described by Davison, *et al.*,[8c] and beautiful purple-black crystals were grown from methylene chloride solution. The crystals were examined by optical goniometry and Weissenberg and precession photography. On the basis of these examinations, the crystals were found to belong to the monoclinic system with a cell of dimensions: $a = 19.25 \pm 0.03$, $b = 11.31 \pm 0.02$, $c = 18.01 \pm 0.03$ A; $\beta = 106.3 \pm 0.2°$; $V = 3763$ A^3. The observed extinctions, hkl for $h + k$ odd and $h0l$ for l odd, are consistent with the two space groups C2/c and Cc. A negative piezoelectric test[10] indicated the presence of a center of symmetry, and the satisfactory agreement which was ultimately obtained between observed and calculated structure factors confirms C2/c as the correct choice. An experimental density of 1.36 ± 0.04 g/cm^3 obtained by flotation in zinc chloride solutions agrees well with a calculated value of 1.37 g/cm^3 for four molecules in the unit cell. Thus, vanadium is required to occupy one of the fourfold special positions of the space group.

Intensity data were collected at room temperature by

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[2] R. Eisenberg and J. A. Ibers, *J. Am. Chem. Soc.*, **87**, 3776 (1965); *Inorg. Chem.*, **5**, 411 (1966).

[3] A. E. Smith, G. N. Schrauzer, V. P. Mayweg, and W. Heinrich, *J. Am. Chem. Soc.*, **87**, 5798 (1965).

[4] tdt = toluene-3,4-dithiolate; bdt = benzene-1,2-dithiolate.

[5] E. I. Stiefel and H. B. Gray, *J. Am. Chem. Soc.*, **87**, 4012 (1965).

[6] E. I. Stiefel, R. Eisenberg, R. C. Rosenberg, and H. B. Gray, *ibid.*, **88**, 2956 (1966).

[7] A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *ibid.*, **86**, 2799 (1964).

[8] (a) G. N. Schrauzer, H. W. Finck, and V. P. Mayweg, *Angew. Chem.*, **76**, 715 (1964); (b) J. H. Waters, R. Williams, H. B. Gray, G. N. Schrauzer, and H. W. Finck, *J. Am. Chem. Soc.*, **86**, 4199 (1964); (c) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, **4**, 55 (1965).

[9] R. Eisenberg, E. I. Stiefel, R. C. Rosenberg, and H. B. Gray, *J. Am. Chem. Soc.*, **88**, 2874 (1966).

[10] The authors are grateful to Dr. J. A. Ibers for performing this measurement.

the equiinclination Weissenberg technique using Zr-filtered Mo Kα radiation. A spherical crystal of radius 0.21 mm was mounted along the *b* axis and the layers $h0l$ to $h10l$ were recorded on multiple films. The intensities of 2146 independent reflections accessible within the angular range $\theta_{\mathrm{Mo}} \leqslant 22°$ were estimated visually using a calibrated intensity strip. The usual Lorentz-polarization factors were then applied to these intensities to yield F_o^2 values where F_o is the observed structure amplitude. Absorption effects were constant for all reflections ($\mu R = 0.13$).[11] The F_o values were subsequently brought to an approximate absolute scale through a modification of Wilson's procedure.[12]

Solution and Refinement of the Structure

The positions of the V and S atoms were readily determined from a three-dimensional Patterson function. We find vanadium to be located in the 4(e) special positions of the space group $[(0, y, {}^1/_4;\ 0, \bar{y}, {}^3/_4) + (0, 0, 0;\ {}^1/_2, {}^1/_2, 0)]$[13] and thus the molecule possesses a twofold axis of symmetry. The positional parameters of the V and three independent S atoms, along with variable isotropic temperature factors assigned to them, were refined through several cycles of least squares. All carbon atoms were then located in a difference Fourier based on phases obtained from the heavy atoms.

The structure was refined by a least-squares procedure. The function minimized was $\Sigma w(F_o - F_c)^2$ where the weights w were assigned in the following way: $I < 5$, $w = (I/5)^2$; $5 \leqslant I \leqslant 180$, $w = 1$; $I > 180$, $w = (180/I)^2$, where I is the average raw intensity of the reflection. The neutral atom scattering factors which have been tabulated by Ibers[14] were used. The anomalous parts of the V and S scattering factors were obtained from Templeton's tabulation[15] and included in the calculated structure factors.[16]

In the initial round of calculations, all atoms were assigned individual isotropic temperature factors. This refinement of 109 positional, scale, and thermal parameters rapidly converged to a conventional R factor ($R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$) of 0.093 and a weighted R factor R' ($R' = (\Sigma w(F_o - F_c)^2/\Sigma w F_o^2)^{1/2}$) of 0.106. A difference Fourier based on this refinement provided evidence for anisotropic thermal motion of the heavy atoms.

After correction of several indexing errors, a further refinement was carried out in which the V and S atoms were allowed to vibrate anisotropically, while all other atoms were restricted to isotropic vibration. This refinement, in which the individual level scale factors were not varied, converged to a conventional R factor of 0.083 and a weighted R factor R' of 0.079 for 1516 independent nonzero reflections. In a difference Fourier based on this refinement, reasonable positions for 14 of the 15 independent phenyl hydrogen atoms were determined. In the last cycles of least squares, fixed hydrogen atom contributions were added to the calculated structure factors. The anisotropic thermal parameters and the individual level scale factors were refined on alternate cycles of the least squares. In this refinement, no anisotropic thermal parameter changed by more than one standard deviation. The final refinement for 116 positional and thermal parameters converged to conventional and weighted R factors of 0.077 and 0.070, respectively. A final difference Fourier showed no peaks higher than 0.27 e/A^3 (about 15% the height of a C atom).

The parameters obtained in this final round of calculations are taken as the final parameters of the structure and are given in Table I. Standard deviations, as obtained from the inverse matrix, are also given. In Table II, the values of F_o and $|F_c|$ (in electrons × 10) are given for the 1516 observed reflections. The $|F_c|$ values for the unobserved reflections are omitted from Table II, since none of the intensities calculated for the unobserved but accessible reflections exceeds the minimum observable intensity value.

The anisotropic thermal parameters can be interpreted in terms of the real amplitudes of vibration since they are essentially uncorrelated with the scale factors. It should be noted that in the partial anisotropic refinement, 21 carbon atoms representing a reasonable fraction of the scattering power in the asymmetric unit were restricted to isotropic vibration. In Table III the principal values of the root-mean-square amplitudes of vibration are listed. The orientations of the thermal ellipsoids which may be derived from the parameters in Table I are not given.

Description of the Structure

The structure described by the parameters of Table I, the unit cell constants, and the symmetry operations of the space group consists of the packing of discrete molecules of the neutral $V(S_2C_2(C_6H_5)_2)_3$ complex. The vanadium atoms are well separated with nearest neighbors being over 10 A apart. The closest intermolecular approaches to vanadium are made by phenyl hydrogens from adjacent molecules. However, all intermolecular contacts appear normal.

The crystallographically required twofold symmetry axis of the molecule bisects one of the five-membered metal–chelate rings. The six sulfur donor atoms of the complex are equidistant from vanadium and surround the central metal in a trigonal-prismatic coordination. The average V–S bond length is 2.338 A and the average S–V–S bond angle is 81.7°. All principal intramolecular distances and angles are tabulated in Table IV. In addition, a perspective drawing of an isolated molecule of the complex is shown in Figure 1. The S_6 trigonal prism is slightly but significantly

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[11] "International Tables for X-ray Crystallography," Kynoch Press, Birmingham, England, 1965, Vol. 2, Table 5.3 6B.

[12] The computing for this structure determination was carried out on Columbia's IBM 7094 computer. The main programs used in this work were Brookhaven modifications of Zalkin's FORDAPER Fourier program, the Busing–Levy ORFLS least-squares program, and the Busing–Martin–Levy ORFFE function and error program. Other programs from the Brookhaven Crystallographic Library were also employed.

[13] Reference 11, Vol. 1, p 101.

[14] J. A. Ibers, ref 11, Vol. 3, Table 3.3.1A.

[15] D. H. Templeton, ref 11, Vol. 3, Table 3.3.2.B.

[16] J. A. Ibers and W. C. Hamilton, *Acta Cryst.*, **17**, 781 (1964).

TABLE I

FINAL PARAMETERS FOR $V(S_2C_2(C_6H_5)_2)_3$

Positional and Isotropic Thermal Parameters

Atom	*x*	*y*	*z*	*B*, A^2
V	0.0000	0.2196 (2)[a]	0.2500	...
S_1	−0.0445 (1)	0.3762 (2)	0.1647 (2)	...
S_2	−0.1145 (1)	0.1520 (2)	0.1814 (1)	...
S_3	−0.0336 (1)	0.1345 (2)	0.3531 (1)	...
C_1[b]	−0.0220 (5)	0.5069 (9)	0.2098 (5)	3.6 (2)
R_1C_1	−0.0483 (6)	0.6148 (9)	0.1660 (6)	4.2 (2)
R_1C_2	−0.0435 (5)	0.6290 (9)	0.0921 (6)	4.4 (2)
R_1C_3	−0.0670 (7)	0.733 (1)	0.0510 (7)	6.1 (3)
R_1C_4	−0.0973 (7)	0.821 (1)	0.0851 (8)	7.2 (3)
R_1C_5	−0.1060 (8)	0.809 (1)	0.1573 (8)	7.5 (3)
R_1C_6	−0.0806 (6)	0.703 (1)	0.2019 (7)	5.7 (3)
C_2	−0.1557 (5)	0.0910 (8)	0.2433 (5)	3.4 (2)
R_2C_1	−0.2310 (5)	0.0503 (8)	0.2071 (5)	3.3 (2)
R_2C_2	−0.2803 (5)	0.1232 (8)	0.1578 (6)	3.8 (2)
R_2C_3	−0.3493 (6)	0.0825 (9)	0.1209 (6)	4.9 (2)
R_2C_4	−0.3697 (6)	−0.033 (1)	0.1343 (7)	5.6 (3)
R_2C_5	−0.3229 (6)	−0.102 (1)	0.1843 (7)	5.3 (3)
R_2C_6	−0.2531 (6)	−0.0624 (9)	0.2226 (6)	4.1 (2)
C_3	−0.1194 (5)	0.0815 (8)	0.3210 (5)	3.2 (2)
R_3C_1	−0.1510 (5)	0.0268 (8)	0.3791 (5)	3.5 (2)
R_3C_2	−0.2173 (6)	0.069 (1)	0.3850 (7)	5.3 (3)
R_3C_3	−0.2499 (7)	0.014 (1)	0.4392 (8)	6.8 (3)
R_3C_4	−0.2148 (7)	−0.081 (1)	0.4790 (7)	5.6 (3)
R_3C_5	−0.1516 (7)	−0.119 (1)	0.4763 (7)	5.7 (3)
R_3C_6	−0.1181 (6)	−0.0639 (9)	0.4241 (6)	4.2 (2)

Anisotropic Thermal Parameters

Atom	β_{11}[c]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
V	0.00244 (8)	0.0053 (2)	0.00243 (9)	0.0000	0.00074 (7)	0.0000
S_1	0.00291 (9)	0.0061 (2)	0.0030 (1)	0.0001 (1)	0.00039 (8)	0.0004 (1)
S_2	0.00248 (9)	0.0080 (2)	0.0024 (1)	−0.0011 (1)	0.00068 (8)	−0.0001 (1)
S_3	0.00264 (9)	0.0077 (2)	0.0026 (1)	−0.0000 (1)	0.00080 (8)	0.0005 (1)

[a] Numbers in parentheses here and in succeeding tables are estimated standard deviations in the least significant digit. [b] C_1 refers to the carbon bonded to S_1, R_1C_1 refers to the phenyl carbon bonded to C_1, etc. [c] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

distorted about the threefold axis with independent interligand S–S values of 2.927, 3.088, and 3.178 A. It should be noted, however, that despite the distortion, the average inter- and intraligand S–S distances are approximately equal with values of 3.064 and 3.058 A, respectively.[17]

The one crystallographically independent metal–chelate ring does show significant deviations from planarity in the ethylene carbons of the ligand. These deviations, though significant, are still quite small. The best weighted least-square plane[18] through the five-membered metal–chelate ring is given by the equation $8.800x - 9.885y - 5.159z = 3.455$ in monoclinic coordinates. The deviations of atoms V, S_2, S_3, C_2, and C_3 from this plane are −0.006 (2), 0.009 (3), 0.009 (3), −0.070 (9), and −0.058 (9), respectively. The three intraligand VS_2 planes of the complex coincide with the dihedral mirrors about the threefold axis in D_{3h} symmetry. The independent dihedral angles between the VS_2 planes are calculated to be 119.5° (between the VS_1S_1' and VS_2S_3 planes) and 120.9° (between the VS_2S_3 and $VS_2'S_3'$ planes).

The four-atom S–C–C–S ligand unit is definitely planar. The average S–C and C–C bond lengths of 1.69 and 1.41 A, respectively, indicate multiple-bond character and extensive π delocalization over the ligand unit. However, the phenyl rings are twisted out of the planes of the chelate rings and are not conjugated with the inner π-bonding network of the complex. The calculated dihedral angles between phenyl rings 1, 2, and 3 and their respective chelate rings are 46.2, 46.7, and 57.0° with estimated standard deviations of 0.4° for the three values. The orientation of the phenyl rings with respect to the inner coordination geometry is clearly illustrated in Figure 1. The C–C bond lengths in the phenyl rings exhibit a normal distribution with an average value of 1.387 A. The C–C ring distances are presented in Table V.

Discussion

The structure of $V(S_2C_2(C_6H_5)_2)_3$ clearly establishes the existence of trigonal-prismatic coordination in the complexes containing first-row transition metals. Furthermore, on the basis of previously reported isomorphism measurements,[2,3] the $Cr(S_2C_2(C_6H_5)_2)_3$ complex is

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(17) The exact nature of the distortion in the coordination prism of the $V(S_2C_2(C_6H_5)_2)_3$ complex is rather unclear at this time. Calculated values of the intermolecular distances in the crystal indicate no unusual intermolecular contacts or packing effects. Although it is possible to attribute the distortion to electronic effects such as a static Jahn–Teller distortion, such an assignment would certainly be premature. For the comparison of the three structures, we believe an averaging of the interligand S–S values in $V(S_2C_2(C_6H_5)_2)_3$ to be valid despite the fact that these distances are significantly different in the structure.

(18) W. C. Hamilton, *Acta Cryst.*, **14**, 185 (1961).

Table II

Observed and Calculated Structure Factor Amplitudes (in electrons × 10) for $V(S_2C_2(C_6H_5)_2)_3$

H	L	OBS	CAL
******K= 0******			
6	0	212	164
8	0	773	736
10	0	391	365
12	0	441	452
14	0	290	297
18	0	214	210
4	2	983	929
6	2	195	166
8	2	697	679
10	2	298	326
12	2	100	99
14	2	109	77
16	2	334	328
18	2	127	141
-4	2	1835	1857
-6	2	483	496
-8	2	155	218
-10	2	85	78
-12	2	189	180
-14	2	367	390
-16	2	159	165
-18	2	172	161
0	4	865	911
2	4	1056	1078
4	4	99	118
6	4	419	425
8	4	365	382
10	4	166	111
12	4	593	590
14	4	425	445
16	4	402	401
-4	4	1034	957
-8	4	167	175
-10	4	874	814
-12	4	799	793
-14	4	213	267
-16	4	112	99
-20	4	183	187
0	6	826	820
2	6	974	889
6	6	87	94
8	6	133	152
12	6	629	633
14	6	273	283
16	6	127	126
-2	6	499	468
-4	6	639	644
-6	6	488	503
-8	6	436	485
-10	6	656	712
-12	6	798	812
-14	6	696	669
-16	6	232	241
-20	6	129	136
0	8	204	178
4	8	615	625
6	8	411	414
10	8	190	202
12	8	166	191
14	8	125	93
-4	8	253	277
-6	8	1182	1158
-8	8	189	206
-10	8	160	155
-12	8	372	380
-14	8	767	819
0	10	473	467
2	10	1066	1027
4	10	651	661
6	10	294	304
8	10	110	109
-4	10	234	251
-6	10	175	258
-8	10	132	141
-10	10	428	435
-14	10	110	137
-16	10	117	136
-18	10	176	209
0	12	532	488
2	12	567	602
4	12	362	339
10	12	259	270
-2	12	368	395
-4	12	314	305
-6	12	99	94
-10	12	182	210
-12	12	445	471
-16	12	310	273
-18	12	264	254
0	14	227	221
4	14	299	305
-2	14	153	157
-4	14	214	185
-6	14	215	221
-8	14	410	433
-10	14	159	164
-16	14	126	130
2	16	238	252
4	16	347	414
-2	16	166	138
-6	16	202	262
-8	16	499	525
-10	16	404	437
-12	16	327	286
-2	18	127	119
-6	18	126	143
-8	18	179	147
-10	18	257	284
******K= 1******			
5	0	340	319
7	0	250	268
9	0	696	689
15	0	108	85
5	1	979	1000
7	1	815	811
9	1	157	166
13	1	100	106
17	1	204	201
-5	1	82	66
-7	1	437	433
-9	1	292	327
-13	1	338	309
-17	1	115	137
-19	1	124	143
5	2	695	675
7	2	948	913
9	2	559	554
11	2	186	158
-5	2	1298	1260
-7	2	582	575
-9	2	290	238
-17	2	198	211
-19	2	174	178
3	3	59	25
7	3	565	569
9	3	288	300
11	3	135	121
13	3	282	287
15	3	295	268
17	3	248	234
-5	3	60	80
-9	3	255	258
-11	3	237	235
-17	3	114	129
-19	3	245	260
1	4	810	756
3	4	345	360
5	4	434	464
7	4	641	643
13	4	107	83
15	4	115	106
-3	4	1103	1095
-5	4	716	280
-7	4	716	742
-9	4	238	245
-11	4	238	218
-13	4	215	216
-17	4	160	111
-19	4	244	252
1	5	917	872
3	5	155	168
5	5	221	234
7	5	313	327
9	5	185	155
11	5	175	171
13	5	493	484
15	5	319	291
17	5	178	193
-1	5	320	313
-3	5	165	202
-5	5	554	556
-7	5	242	250
-9	5	524	546
-11	5	736	729
-13	5	513	493
-15	5	182	170
-19	5	122	146
3	6	132	170
7	6	153	158
9	6	251	274
-1	6	208	212
-3	6	167	191
-5	6	474	515
-9	6	267	213
-13	6	255	231
-17	6	114	102
3	7	112	145
5	7	476	496
13	7	312	340
15	7	123	173
-1	7	215	194
-3	7	296	346
-5	7	412	424
-7	7	157	141
-9	7	290	339
-11	7	528	547
-13	7	656	690
-15	7	230	223
3	8	172	196
5	8	160	135
7	8	320	302
9	8	466	490
-1	8	394	363
-3	8	332	346
-5	8	1175	1123
-7	8	142	158
-9	8	151	150
-11	8	162	151
-13	8	100	161
-15	8	215	171
-17	8	323	313
-19	8	123	127
1	9	467	494
3	9	631	635
5	9	390	406
11	9	114	147
-1	9	344	329
-3	9	622	664
-5	9	261	239
-7	9	306	294
-9	9	128	98
-13	9	209	196
-15	9	154	151
3	10	94	148
7	10	105	130
9	10	227	236
11	10	204	193
-1	10	123	146
-3	10	359	341
-5	10	396	425
-7	10	251	246
-15	10	301	265
-19	10	177	157
1	11	504	564
3	11	564	541
5	11	342	310
7	11	154	133
11	11	122	142
-1	11	284	337
-3	11	91	150
-5	11	158	150
-7	11	352	357
-9	11	272	259
-11	11	207	207
-15	11	160	170
7	12	244	278
9	12	238	218
11	12	257	256
-3	12	317	346
-5	12	339	328
-7	12	246	218
-11	12	105	74
-13	12	190	159
-15	12	249	234
1	13	282	294
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-10	8	87	97
2	9	204	197
4	9	88	72
6	9	347	358
8	9	316	349
10	9	184	192
-4	9	243	229
-6	9	197	200
-8	9	119	87
-10	9	126	105
-12	9	212	225
-14	9	176	166
-16	9	187	184
0	10	85	80
2	10	124	109
4	10	92	101
6	10	265	289
8	10	103	102
-2	10	382	386
-6	10	222	211
-10	10	206	190
-12	10	218	217
-16	10	110	68
0	11	89	57
2	11	92	50
-2	11	356	373
-4	11	284	281
-6	11	153	141
-10	11	233	219
-12	11	205	213
0	12	94	62
2	12	137	106
6	12	183	166
-2	12	368	354
-4	12	92	99
-6	12	131	119
-10	12	139	135
-12	12	103	109
0	13	139	128
4	13	105	83
-2	13	404	401
-4	13	261	276
-6	13	346	366
-8	13	197	187
-10	13	176	166
4	14	155	138
-2	14	101	119
-4	14	174	164
-6	14	143	142
-12	14	109	83
0	15	186	192
2	15	156	149
-2	15	106	111
-4	15	257	239
-6	15	210	220
-6	16	154	168
******K= 7******			
3	0	202	231
5	0	379	399
9	0	167	149
15	0	142	136
3	1	218	272
5	1	140	136
9	1	171	175
11	1	190	150
13	1	93	66
15	1	144	130
-3	1	191	213
-9	1	128	104
-13	1	91	101
3	2	184	190
5	2	60	75
7	2	351	328
9	2	315	317
11	2	174	172
13	2	134	135
15	2	103	69
-5	2	655	720
-7	2	725	768
-9	2	378	317
-13	2	264	287
-15	2	98	117
1	3	146	166
3	3	150	133
7	3	72	48
9	3	114	94
11	3	89	72
13	3	137	141
-1	3	103	120
-5	3	179	193
-7	3	177	189
-9	3	104	128
-15	3	98	102
1	4	286	316
3	4	274	242
7	4	76	56
11	4	204	156
13	4	99	84
-1	4	235	258
-3	4	167	182
-5	4	674	639
-7	4	731	735
-9	4	287	273
-13	4	155	104
3	5	202	206
5	5	183	205
9	5	173	146
13	5	102	119
-1	5	232	211
-3	5	191	214
-5	5	150	146
-7	5	339	315
-9	5	164	166
-13	5	156	142
-15	5	138	129
1	6	410	369
3	6	406	437
7	6	320	324
9	6	246	241
11	6	237	237
-1	6	274	265
-3	6	287	273
-5	6	65	92
-7	6	298	271
-9	6	225	217
-11	6	84	42
-15	6	98	67
1	7	69	72
3	7	74	57
9	7	161	168
-1	7	183	184
-3	7	94	87
-9	7	158	148
-13	7	226	222
-15	7	99	81
3	8	201	197
5	8	118	139
7	8	309	295
9	8	324	285
11	8	230	204
-1	8	176	172
-3	8	258	229
-5	8	126	134
-7	8	171	188
-9	8	200	199
-11	8	195	198
-13	8	162	132
-15	8	174	173
3	9	83	73
5	9	215	216
-1	9	108	106
-3	9	244	224
-5	9	139	143
1	10	84	80
3	10	123	152
5	10	130	143
7	10	275	279
-1	10	230	244
-3	10	80	95
-5	10	230	236
-7	10	84	103
-9	10	255	254
-11	10	309	299
-13	10	258	240
1	11	88	86
5	11	192	183
7	11	101	133
-1	11	288	314
-5	11	85	115
-11	11	95	91
1	12	92	68
-1	12	420	403
-3	12	293	268
-5	12	219	221
-11	12	195	190
-13	12	144	153
-1	13	95	124
-7	13	95	53
1	14	101	91
-1	14	140	154
-3	14	419	396
-5	14	386	366
-7	14	139	134
-5	15	144	158
******K= 8******			
4	0	274	311
6	0	170	154
8	0	270	253
10	0	254	269
12	0	281	237
14	0	172	188
4	1	119	124
10	1	145	136
12	1	226	229
14	1	202	170
-4	1	165	175
-6	1	328	344
-8	1	124	118
-12	1	201	167
-14	1	312	289
4	2	57	76
8	2	171	131
12	2	94	101
-4	2	191	205
-6	2	150	139
-12	2	242	218
-14	2	218	225
2	3	316	364
4	3	162	167
8	3	79	82
10	3	215	202
12	3	167	158
-4	3	173	215
-6	3	474	470
-8	3	311	306
-10	3	139	145
-12	3	89	110
-14	3	194	198
0	4	247	258
2	4	207	209
4	4	372	378
10	4	157	180
12	4	139	102
-2	4	104	137
-4	4	98	108
-6	4	64	50
-10	4	197	175
-12	4	178	188
0	5	324	321
2	5	359	397
4	5	141	155
10	5	245	227
-2	5	141	152
-6	5	395	359
-8	5	208	190
-10	5	82	60
0	6	397	420
2	6	229	246
4	6	244	241
-2	6	178	177
-8	6	186	169
-10	6	277	275
-12	6	336	324
-14	6	170	159
0	7	376	371
2	7	74	79
6	7	233	227
8	7	252	250
10	7	223	211
-2	7	69	83
-8	7	193	180
-10	7	85	66
-4	8	166	135
-8	8	163	137
-10	8	151	161
-12	8	93	92
-14	8	100	106
0	9	225	232
6	9	230	235
8	9	223	202
-2	9	192	174
-6	9	81	55
-8	9	147	155
-10	9	201	192
-12	9	165	139
0	10	270	277
2	10	240	222
4	10	294	316
-6	10	85	106
-8	10	216	192
-10	10	207	185
-12	10	98	134
0	11	155	151
2	11	93	102
-2	11	231	222
-4	11	215	196
-6	11	89	70
-8	11	92	113
-10	11	191	210
-12	11	201	186
0	12	163	190
2	12	97	111
-4	12	92	84
-6	12	161	170
-8	12	165	140
-10	12	278	278
-2	13	168	190
-4	13	255	261
-6	13	97	109
-8	13	99	65
******K= 9******			
5	0	171	174
7	0	295	264
11	0	228	243
3	1	45	69
5	1	80	84
7	1	95	109
9	1	76	80
11	1	146	130
-5	1	152	155
-7	1	176	140
-9	1	73	132
-11	1	82	85
-13	1	202	164
3	2	347	352
5	2	307	307
7	2	222	202
9	2	221	239
11	2	193	192
-5	2	108	89
-9	2	73	75
-11	2	141	136
-13	2	155	149
3	3	77	24
5	3	63	95
9	3	139	145
-7	3	357	387
-9	3	126	105
1	4	310	341
3	4	270	271
5	4	284	253
7	4	75	78
9	4	220	215
-3	4	89	88
-7	4	93	97
-9	4	104	95
-11	4	81	109
-13	4	89	85
1	5	511	542
3	5	338	323
-1	5	157	185
-3	5	57	71
-7	5	165	171
-9	5	212	244
-11	5	164	167
-13	5	127	120
1	6	387	403
3	6	119	83
5	6	184	178
9	6	126	99
-1	6	162	157
-3	6	169	170
-5	6	65	50
-7	6	140	179
1	7	227	203
3	7	104	132
-1	7	133	114
-3	7	66	53
-7	7	103	115
1	8	343	322
3	8	110	117
-1	8	359	335
-3	8	275	269
-5	8	73	61
-7	8	256	275
-9	8	162	178
-11	8	87	51
1	9	189	189
3	9	298	236
-5	9	203	198
-9	9	169	158
-11	9	199	181
1	10	118	112
3	10	87	82
-1	10	161	153
-3	10	227	214
-5	10	176	187
-7	10	220	196
-9	10	229	191
1	11	740	223
-9	11	156	158
-3	12	153	142
******K=10******			
6	0	128	149
8	0	105	102
4	1	239	275
6	1	175	192
8	1	196	186
10	1	228	206
8	2	193	173
-4	2	127	122
-6	2	228	276
2	3	148	145
4	3	267	296
6	3	306	313
8	3	306	287
-6	3	90	119
-8	3	104	96
0	4	143	148
2	4	216	222
8	4	84	94
-4	4	116	113
-6	4	316	295
-10	4	83	53
0	5	177	187
2	5	160	143
4	5	102	100
6	5	80	109
-2	5	133	103
-6	5	69	108
-8	5	76	99
0	6	94	109
2	6	158	160
-8	6	135	146
0	7	205	183
2	7	107	132
4	7	81	90
-2	7	274	279
-4	7	203	203
-6	7	352	340
-8	7	229	213
-4	8	171	149
-6	8	112	102
-8	8	119	92
-2	9	198	183
-4	9	288	265
-6	9	281	271

also definitely trigonal prismatic. The electronic spectra of these complexes have been measured in both $CHCl_3$ solution and the solid,[9] and have been found to be essentially identical in the two states. It is thus possible to propose a trigonal-prismatic coordination for the $[V(S_2C_2(C_6H_5)_2)_3]^-$ anion from the great similarity of its electronic spectrum with that of the isoelectronic $Cr(S_2C_2(C_6H_5)_2)_3$ complex.

A comparison of the molecular structures of $V(S_2C_2(C_6H_5)_2)_3$, $Re(S_2C_2(C_6H_5)_2)_3$, and $Mo(S_2C_2H_2)_3$ appears quite relevant to a discussion of trigonal-prismatic coordination and suggests at least one factor which is important in stabilizing the coordination geometry. The salient feature of the comparison is that the average dimensions of the prism are strikingly similar in all three structures. In particular, a near

Table III

Root-Mean-Square Amplitudes of Vibration (in A)

Atom	Minimum	Intermediate	Maximum
V	0.185 (4)	0.190 (4)	0.205 (4)
S_1	0.192 (4)	0.211 (4)	0.242 (4)
S_2	0.185 (4)	0.190 (4)	0.246 (3)
S_3	0.193 (4)	0.214 (4)	0.228 (4)

Table IV

Principal Intramolecular Distances and Angles

Distances, A		Angles, deg	
$V-S_1$	2.343 (4)	S_1-V-S_1'	81.8 (2)
$V-S_2$	2.331 (4)	S_2-V-S_3	81.6 (1)
$V-S_3$	2.338 (4)	$V-S_1-C_1$	110.5 (4)
S_1-S_1'[a]	3.069 (7)	$V-S_2-C_2$	109.5 (4)
S_2-S_3	3.052 (6)	$V-S_3-C_3$	109.6 (3)
S_1-S_2	2.927 (5)	$S_1-C_1-C_1'$	118.6 (3)
S_1-S_3'	3.178 (5)	$S_2-C_2-C_3$	120.2 (7)
S_2-S_3'	3.089 (5)	$S_3-C_3-C_2$	119.0 (7)
S_1-C_1	1.68 (1)	$S_1-C_1-R_1C_1$	118.0 (7)
S_2-C_2	1.69 (1)	$S_2-C_2-R_2C_1$	114.7 (7)
S_3-C_3	1.70 (1)	$S_3-C_3-R_3C_1$	117.4 (7)
C_1-C_1'	1.46 (2)		
C_2-C_3	1.38 (1)		
$C_1-R_1C_1$	1.46 (1)		
$C_2-R_2C_1$	1.49 (1)		
$C_3-R_3C_1$	1.49 (1)		

[a] S_1' refers to the sulfur which is related to S_1 by the twofold symmetry axis, etc.

Table V

Carbon–Carbon Phenyl Ring Distances, A

$R_1C_1-R_1C_2$	1.37 (1)[a]
$R_1C_2-R_1C_3$	1.39 (2)
$R_1C_3-R_1C_4$	1.38 (2)
$R_1C_4-R_1C_5$	1.37 (2)
$R_1C_5-R_1C_6$	1.45 (2)
$R_1C_6-R_1C_1$	1.42 (1)
Average value for ring 1	1.397
$R_2C_1-R_2C_2$	1.38 (1)
$R_2C_2-R_2C_3$	1.39 (1)
$R_2C_3-R_2C_4$	1.40 (2)
$R_2C_4-R_2C_5$	1.34 (1)
$R_2C_5-R_2C_6$	1.40 (1)
$R_2C_6-R_2C_1$	1.40 (1)
Average value for ring 2	1.385
$R_3C_1-R_3C_2$	1.40 (1)
$R_3C_2-R_3C_3$	1.44 (2)
$R_3C_3-R_3C_4$	1.36 (2)
$R_3C_4-R_3C_5$	1.30 (1)
$R_3C_5-R_3C_6$	1.43 (1)
$R_3C_6-R_3C_1$	1.35 (1)
Average value for ring 3	1.380

[a] As is quite commonplace in least-squares refinements, the estimated standard deviations of the C–C bond lengths may be slightly optimistic. A detailed statistical analysis in order to establish confidence intervals for these values can be easily carried out. See, for example, W. C. Hamilton, "Statistics in Physical Science," Ronald Press, New York, N. Y., Chapter 3.

constancy is observed in the average interligand S–S distance around 3.07 A [3.064 A in $V(S_2C_2(C_6H_5)_2)_3$, 3.050 A in $Re(S_2C_2(C_6H_5)_2)_3$, and 3.11 A in $Mo(S_2C_2H_2)_3$]. This average S–S value is relatively short for distances between nonbonded ligands and is taken as an indication of inter-donor atom bonding forces which help stabilize the trigonal-prismatic coordination in these complexes. In addition, a similar average S–S value has been observed in the structures of the bis-planar complexes involving related ligand systems.[19–23]

A second rather remarkable feature of the three structures can be viewed as a direct consequence of the phenomenon of interligand S–S bonding. We observe in these complexes that there is no significant difference between the V–S bond length of 2.338 A and the Re–S and Mo–S distances of 2.325 and 2.33 A, respectively, despite the fact that both the covalent and ionic radii of vanadium are at least 0.07 A shorter than the corresponding radii for rhenium and molybdenum.[24]

We now direct our attention to the electronic structure of the $V(S_2C_2(C_6H_5)_2)_3$ complex and propose a tentative assignment of its ground-state configuration. We have previously suggested[6] a level scheme for second- and third-row trigonal-prismatic complexes in which the ordering of molecular orbitals of interest for the assignment of ground and low excited states is $4e' < 2a_2' < 3a_1' < 5e' < 4e''$. The ground state suggested for $Re(S_2C_2(C_6H_5)_2)_3$ is thus $(4e')^4(2a_2')^2(3a_1')^1 = {}^2A_1'$. This energy level scheme in some respects differs significantly from the one recently proposed by Schrauzer and Mayweg[25] for $V(S_2C_2H_2)_3$, primarily because of differences in the estimation of starting ligand orbital energies.[26] The energy level ordering that we have proposed for second- and third-row trigonal-prismatic complexes may be used with only slight modification as the basis for describing the electronic structures of the first-row complexes. In suggesting a modification of the $Re(S_2C_2(C_6H_5)_2)_3$ molecular orbital ordering, we take cognizance of the fact that antibonding levels of d symmetry and character are more stable in first-row complexes than in analogous second- and third-row situations. For example, the ordering $WO_4^{2-} > MoO_4^{2-} > CrO_4^{2-}$ is observed in the position of the lowest L→M charge transfer in the absorption spectra of these oxyanions.[30]

Thus it is reasonable to suggest that an inversion of the $2a_2'-3a_1'$ order occurs in going to the first-row

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(19) R. Eisenberg, J. A. Ibers, R. J. H. Clark, and H. B. Gray, *J. Am. Chem. Soc.*, **86**, 113 (1964); R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **4**, 605 (1965).

(20) J. D. Forrester, A. Zalkin, and D. H. Templeton, *ibid.*, **3**, 1500 (1964).

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(22) C. J. Fritchie, *Acta Cryst.*, **20**, 107 (1966).

(23) D. Sartain and M. R. Truter, *Chem. Commun.*, 382 (1966).

(24) See L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, Chapters 7 and 13.

(25) G. N. Schrauzer and V. P. Mayweg, *J. Am. Chem. Soc.*, **88**, 3235 (1966).

(26) The main difference in the two calculations appears to be the value of diagonal Hamiltonian matrix elements chosen for the ligands. Schrauzer and Mayweg use $-82{,}000$ cm^{-1} for the energy of an sp^2 hybrid orbital on sulfur, whereas we take $-110{,}000$ cm^{-1} for this quantity. Both methods claim to include some consideration of interatomic Coulomb terms which stabilize the ligand orbitals with respect to the metal diagonal elements. The need for this correction in simple MO methods has been pointed out by several investigators.[27–29] We believe our estimates for the diagonal Hamiltonian matrix elements of the ligand orbitals to be more realistic relative to the metal orbital energies.

(27) H. Basch and H. B. Gray, *Inorg. Chem.*, **6**, 639 (1967).

(28) R. F. Fenske, K. G. Caulton, D. D. Radtke, and C. C. Sweeney, *ibid.*, **5**, 951, 960 (1966).

(29) C. K. Jørgensen, "Orbitals in Atoms and Molecules," Academic Press, New York and London, 1964.

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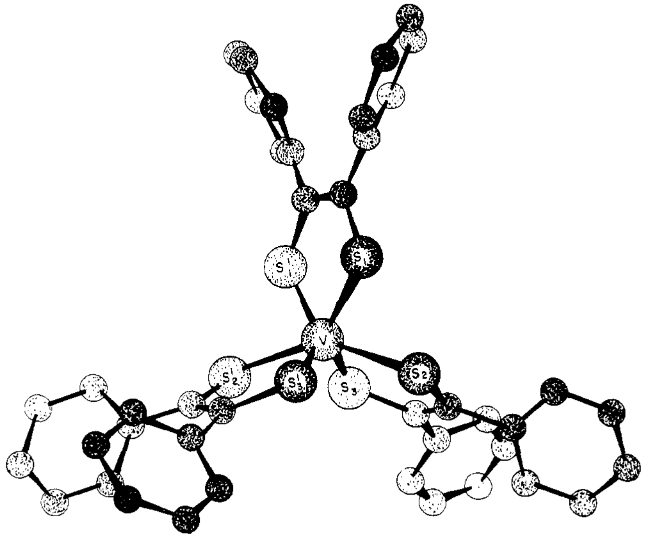

Figure 1.—A perspective drawing of an isolated molecule of the $V(S_2C_2(C_6H_5)_2)_3$ complex. Phenyl hydrogens are not shown.

$M(S_2C_2R_2)_3$ systems, such that we have $4e' < 3a_1' < 2a_2' < 5e' < 4e''$. The proposed ground state for $V(S_2C_2(C_6H_5)_2$ is therefore . . . $(4e')^4(3a_1')^1 = {}^2A_1$.[31] This means that if the 4e′ level is assigned to the ligand (as is traditional), the complex is formally a d^1 complex of V(IV) and $[(S_2C_2(C_6H_5)_2)_3{}^{4-}]$ and the ligand system is fully oxidized by two electrons from its classical trisdithiolate state. A second, equally arbitrary formalism for the complex may be derived by assigning the filled 4e′ level to the metal. In this formulation $V(S_2C_2(C_6H_5)_2)_3$ is a d^5 V(0) complex with an uncharged $[(S_2C_2(C_6H_5)_2)_3]$ ligand unit. Although the V(IV)–$[L_3{}^{4-}]$ formulation may seem more appealing in view of the average C–C distance of 1.41 A, the average C–S distance of 1.69 A suggests C=S and thus is more compatible with a V(0) $[L_3]$ model. However, in either case it is clear that the ligand system is at least partially oxidized and the 4e′ level is strongly delocalized over the MS_2C_2 chelate ring.

It is also worth noting that the assignment of the unpaired electron to $3a_1'$ $(s + z^2)$ is not in conflict with the esr data which show a nearly isotropic *g* value of 1.99 and a substantial isotropic ^{51}V hyperfine splitting of 61.6 gauss.[8b,8c] In this respect the proposed electronic structure is superior to . . . $(4e')^4(2a_2')^1 = {}^2A_2'$, in which the unpaired electron would be entirely out on the ligands. In any event, further studies are needed to help elucidate the electronic structures of the first-row systems.[31,32]

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(31) According to the Schrauzer–Mayweg scheme, the ground state for the undistorted $V(S_2C_2(C_6H_5)_2)_3$ complex should be $^2E'$. If this assignment is correct, the observed distortions in the coordination geometry can be accommodated from Jahn–Teller considerations. However, it is on the strength of the available solution esr data that we suggest the $^2A_1'$ ground state, as discussed in the text. More detailed studies including a single crystal esr investigation of the $V(S_2C_2(C_6H_5)_2)_3$ complex doped into the isomorphous $Cr(S_2C_2(C_6H_5)_2)_3$ complex and the calculation of spin Hamiltonian parameters appear necessary in order to establish firmly the ground-state configuration of $V(S_2C_2(C_6H_5)_2)_3$.

(32) In a preliminary communication of their work on the trisdithioglyoxa complexes [G. N. Schrauzer, V. P. Mayweg, and W. Heinrich, *Chem. Ind.* (London), 1464 (1965)], Schrauzer, *et al.*, suggested the energy level ordering $4e' < 3a_1' < 2a_2' < 5e'$ for the neutral third row complex $Re(S_2C_2H_2)_3$. This ordering agrees qualitatively with our proposed energy-level scheme for the first-row $V(S_2C_2(C_6H_5)_2)_3$ complex. However, Schrauzer and Wayweg[25] now suggest $^2E'$ ground states for the neutral V and Re complexes on the basis of their subsequent calculations.

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Reactions of Potassium Hexacyanochromate(III) and Some Transition Metal Cyanonitrosyls with Molecular Hydrogen at Elevated Temperatures

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The reactions of potassium hexacyanochromate(III) and a number of pentacyanonitrosyl complexes with molecular hydrogen at moderately elevated temperatures have been investigated. At 400°, potassium hexacyanochromate(III) is reduced to a compound of the empirical formula $K_3Cr(CN)_4$. The same substance is formed when potassium pentacyanonitrosylchromate(I) is treated with hydrogen at the same temperature. Reaction of hydrogen and potassium pentacyanonitrosylferrate(II) monohydrate at 230° yields a substance of the composition $K_2Fe(CN)_4$. From the interaction of potassium pentacyanonitrosylmanganate(I) with hydrogen at 330° there is isolated a material of the approximate composition $Mn(CN)_{2.1}$. At 200°, potassium pentacyanonitrosylvanadate(−I) monohydrate is converted by hydrogen to a compound corresponding to the composition $K_5V(CN)_5$. Infrared spectra and magnetic moments indicate the presence of bridging cyanide groups in all of the products. All but the vanadium-containing product are water insoluble.

In a previous report from our laboratory[1] the reduction of some transition metal cyano complexes by molecular hydrogen at moderately elevated temperatures was described. This technique yielded, by removal of one or two cyanide ligands as hydrogen cyanide, complexes containing the transition metals in low oxidation states. The current paper extends the previous

(1) J. S. Yoo, E. Griswold, and J. Kleinberg, *Inorg. Chem.*, **4**, 365 (1965).