CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
COLUMBIA UNIVERSITY, NEW YORK, NEW YORK 10027, AND THE DEPARTMENT OF CHEMISTRY,
BROOKHAVEN NATIONAL LABORATORY, UPTON, NEW YORK 11973

Trigonal Prismatic Coordination. The Crystal and Molecular Structure of Tris(*cis*-1,2-diphenylethene-1,2-dithiolato)rhenium[1]

BY RICHARD EISENBERG[2a] AND JAMES A. IBERS[2b]

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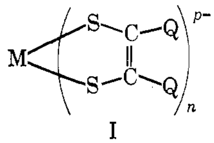
The crystal and molecular structure of tris(*cis*-1,2-diphenylethene-1,2-dithiolato)rhenium, $Re(S_2C_2(C_6H_5)_2)_3$, has been determined from three-dimensional X-ray data. The neutral complex crystallizes in space group $P\bar{1}$ of the triclinic system, with two molecules in a cell of $a = 19.73$, $b = 11.94$, $c = 9.87$ A, $\alpha = 120.1$, $\beta = 73.6$, $\gamma = 102.5°$. The crystal structure consists of the packing of discrete monomeric molecules, the closest Re–Re distance being approximately 9.5 A. In the molecule, rhenium is surrounded by six equidistant sulfur atoms in a trigonal prismatic coordination. The sides of the prism are near perfect squares with an average edge of 3.043 A. No significant differences appear between the intra- and closest interligand sulfur–sulfur distances. Hence, the ReS_6 trigonal prism is essentially perfect. The phenyl rings are twisted out of the planes of the five-membered chelate rings and appear not to be conjugated with them. While no crystallographic symmetry conditions are imposed on the molecule, the coordination geometry is clearly D_{3h} and the over-all molecular symmetry belongs nearly to the point group C_3.

Introduction

The study of bidentate sulfur ligand complexes of type I has been vigorously pursued over the past few years.[3–8] The bis systems, discovered first for Ni^{2+} and Co^{2+},[3] received primary attention because of the stabilization of the square-planar geometry[9–12] for a variety of central metal ion configurations and because of the apparent ease of oxidation and reduction of these systems with no change in coordination geometry.[4–6] These compounds make possible the study of similar complexes of transition metals in a series of formal oxidation states. The initial preparation and characterization of the tris systems opened a new area of study in the field.[13–18] As with the square-planar bis compounds, these systems readily undergo electron-transfer reactions during which the coordination remains unchanged. In interpretations of the physical properties of these systems, the complexes were assumed to have D_3 symmetry with a distorted octahedral coordination about the central metal.[15,18] However, Langford, *et al.*,[17] speculated that an "interesting possibility" for the structure might be a "trigonal prismatic, or at least a strongly trigonally distorted six-coordinate structure." Because of the activity in this field and the need for a structure determination on which to base the interpretations of other physical measurements, we have determined the structure of a typical member of the series ($Q = C_6H_5$ and $p = 0$ with $M = Re$). The powder patterns of the Re complex and its V, Cr, Mo, and W analogs have also been examined. The Re and W compounds appear to be isomorphous, as do the V, Cr, and Mo species. Owing to the changes in scattering power of the transition metal in going from the third to lower rows, it is not possible to tell whether all five complexes form a single isomorphous series, or whether the Re and W complexes possess unit cells differing from those of the Mo, Cr, and V. Since substances which are isomorphous are in general isostructural, these data lead us to the conclusion that the W analog, and possibly the V, Cr, and Mo analogs, will be found to be isostructural with the Re system. In an earlier communication[19] we reported that the neutral complex tris(*cis*-1,2-diphenylethene-1,2-dithiolato)rhenium[20] has a near perfect



$Q = CN^-, CF_3, C_6H_5, CH_3, H$

I

$n = 2$ $p = 0, 1, 2$ $M = Co, Ni, Cu, Pd, Pt, Au, Rh$
$n = 3$ $p = 0, 1, 2, 3$ $M = V, Cr, Mo, W, Re, Co$

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(2) (a) NSF predoctoral fellow, 1964–1965. (b) Department of Chemistry, Northwestern University, Evanston, Ill. 60201.

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(20) Two alternative names which have been proposed for the complex are tris(dithiobenzil)rhenium(0) and tris(*cis*-stilbenedithiolato)rhenium(VI). We recommend the present name because we feel it is more descriptive of the ligand system and because the other names imply certain incorrect features about the electronic structure of the molecule. We do not wish to imply that we know the formal charge on the metal atom.

trigonal prismatic coordination. In this paper we describe in detail that structure determination.

Collection and Reduction of the X-Ray Data

Green crystals of $Re(S_2C_2(C_6H_5)_2)_3$, kindly supplied by G. N. Schrauzer, were examined optically and by precession and Weissenberg photography. On the basis of the examinations, the crystals were assigned to the triclinic system. A Delaunay reduction failed to suggest the presence of hidden symmetry. The cell chosen is a primitive one of dimensions $a = 19.73 \pm 0.04$, $b = 11.94 \pm 0.03$, $c = 9.87 \pm 0.03$ A, $\alpha = 120.1 \pm 0.1°$, $\beta = 73.6 \pm 0.1°$, $\gamma = 102.5 \pm 0.1°$, $V = 1922$ A^3. The assumption of a center of symmetry (space group $P\bar{1}$) appears justified by the satisfactory agreement ultimately obtained between observed and calculated structure factors. An experimental density of 1.53 ± 0.05 g/cm^3, determined by flotation in zinc chloride solutions, agrees well with a calculated value of 1.57 g/cm^3 for two molecules in the unit cell. Thus, all atoms are in general positions and no crystallographic symmetry conditions are imposed on the molecule.

Intensity data were collected at room temperature from a single crystal with the G.E. XRD-5 goniostat. The crystal was mounted with a^* parallel to the spindle or ϕ axis. Niobium-filtered Mo Kα radiation was employed. The intensities of 2041 independent reflections accessible within the angular range $\theta_{Mo} \leqslant 16.5°$ were measured by the stationary crystal–stationary counter technique. A general background correction and the usual Lorentz-polarization factor were applied to each of these intensities to yield F_o^2 values (where F_o is the observed structure amplitude), and these were then corrected for absorption. In order to carry out the absorption correction the six crystal faces were identified by optical goniometry and their dimensions carefully measured. The volume of the crystal used is approximately 0.0014 mm^3 and has a calculated weight of only 2.2 μg. However, using an absorption coefficient of 37.1 cm^{-1}, we find the resultant transmission coefficients to range from 0.59 to 0.85.[21]

Solution and Refinement of the Structure

The positions of the rhenium and the six sulfur atoms were readily determined from a three-dimensional Patterson function. These positional parameters, along with variable isotropic temperature factors assigned to each of the atoms and a single over-all scale factor, 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 complete trial structure was refined by a least-squares procedure. The function minimized was $\Sigma w(F_o - F_c)^2$, with w equal to $1/\sigma^2$ and the standard deviation of each reflection, σ, estimated by the function $(TLp)^{-1}(CT + CB + (0.03(CT - CB)^2)^{1/2}/2F_o$ (CT is the total count, CB is the background count, Lp is the appropriate Lorentz-polarization factor, and T is the transmission factor for the particular reflection).[22] The atomic scattering factors for the neutral light atoms tabulated by Ibers[23a] were used. The Re scattering factor was that of Cromer and Waber.[23b] The anomalous parts of the Re and S scattering factors were obtained from Cromer's tabulation[24] and were included in the calculated structure factors.[25]

The phenyl rings were constrained to their well-known geometry (D_{6h} symmetry, C–C = 1.392 A, C–H = 1.08 A) by means of the least-squares group-refinement procedure previously described.[26,27] In this procedure, each ring is described by a single variable isotropic thermal parameter and six variable positional parameters. These are the fractional coordinates of the ring center, x_c, y_c, z_c, and the three angles δ, ϵ, and η, which are successive counterclockwise rotations about $\mathbf{a}_2'$, $\mathbf{a}_1'$, and $\mathbf{a}_3'$ orthogonal internal axes that bring about alignment, except for translation, of this coordinate system with an orthogonal, external coordinate system $\mathbf{A}$. The origin of the internal coordinate system is taken at the ring center, and $\mathbf{a}_3'$ is normal to the plane of the ring while $\mathbf{a}_1'$ intersects a vertex. The orthogonal external coordinate system $\mathbf{A}$ is formed from the triclinic coordinate system in the following way: $\mathbf{A}_2$ is parallel to $\mathbf{a}_2$; $\mathbf{A}_1$ is parallel to $\mathbf{a}_2 \times \mathbf{a}_3$; $\mathbf{A}_3$ is parallel to $\mathbf{A}_1 \times \mathbf{A}_2$. The initial refinement of the rings together with the 13 nongroup atoms, each of which had a variable isotropic temperature factor, converged to a conventional R factor ($R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$) of 0.145 for the 95 positional, scale, and thermal parameters.

In the preliminary X-ray examinations, the Re crystals were observed to have unusually large mosaic spreads. Because no other crystals of the complex were available at that time, a complete set of intensity data was collected, but with the apprehension that an overlap problem might exist. Although the resultant structure seemed correct, the agreement between observed and calculated structure factors was extremely poor for higher angle reflections along the a^* direction. In almost every case, the magnitude of the observed structure factor was greater than the calculated value and we concluded that an overlap problem did indeed exist for these reflections. This was readily verified photographically. The use of Mo radiation, and the magnitude of the a axis, together with the unusually large mosaic spread all contributed to this problem. Although correction of the overlapping reflections was feasible, we decided instead to formulate an objective basis on which such data could be rejected. The derived function, which is described completely in a

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(21) In addition to various local programs, the programs for the IBM 7094 used in this work were Hamilton's GONO9 absorption program, local modifications of Zalkin's FORDAP Fourier program and the Busing–Levy ORFLS least-squares program, and the ORFFE error function program.

(22) W. R. Busing and H. A. Levy, *J. Chem. Phys.*, **26**, 563 (1957).

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TABLE I

POSITIONAL, THERMAL, AND GROUP PARAMETERS FOR $Re(S_2C_2(C_6H_5)_2)_3$

Atom	x	y	z	B, A^2			
Re	0.2486 (1)[a]	0.0169 (1)	0.0239 (1)	2.68 (6)			
S_1	0.2477 (6)	0.1561 (6)	0.2939 (8)	2.9 (2)			
S_2	0.1545 (6)	−0.0831 (6)	0.1363 (8)	3.0 (2)			
S_3	0.3197 (6)	−0.0852 (6)	0.0740 (8)	3.0 (2)			
S_4	0.3354 (6)	−0.0406 (6)	−0.2090 (8)	2.9 (2)			
S_5	0.1765 (7)	−0.0526 (7)	−0.1599 (9)	3.5 (2)			
S_6	0.2577 (6)	0.2133 (6)	0.0199 (8)	2.7 (2)			
C_1[b]	0.256 (2)	0.317 (2)	0.329 (3)	2.3 (7)			
C_2	0.090 (2)	−0.137 (2)	0.026 (3)	3.1 (7)			
C_3	0.385 (2)	−0.145 (2)	−0.077 (3)	1.5 (6)			
C_4	0.391 (2)	−0.130 (2)	−0.206 (3)	2.0 (6)			
C_5	0.105 (2)	−0.131 (2)	−0.110 (3)	1.5 (6)			
C_6	0.256 (2)	0.339 (2)	0.208 (3)	2.2 (6)			
Group	x_c[c]	y_c	z_c	δ	ϵ	η	B, A^2
R_1	0.253 (1)	0.501 (1)	0.663 (2)	0.81 (1)	6.14 (1)	1.68 (1)	3.6 (4)
R_2	−0.042 (1)	−0.242 (1)	0.165 (2)	0.18 (2)	0.93 (1)	0.37 (3)	5.7 (5)
R_3	0.490 (1)	−0.262 (1)	−0.038 (1)	5.36 (2)	6.01 (1)	2.86 (1)	3.8 (4)
R_4	0.503 (1)	−0.231 (2)	−0.493 (2)	2.73 (2)	6.03 (2)	5.51 (2)	7.1 (5)
R_5	0.005 (1)	−0.238 (1)	−0.325 (2)	4.55 (1)	5.62 (2)	4.70 (1)	5.3 (4)
R_6	0.258 (1)	0.606 (1)	0.274 (1)	1.42 (2)	5.65 (1)	2.83 (1)	3.9 (4)

[a] Numbers in parentheses here and in succeeding tables are standard deviations in the least significant digits. [b] C_1 is the carbon bonded to S_1 and R_1 is the phenyl ring attached to C_1, etc. [c] x_c, y_c, and z_c are the fractional coordinates of the ring centers. The angles δ, ϵ, and η (in radians) are defined in the text.

separate paper,[28] considers the finite height of the counter aperture, the spectral range of the radiation employed, and the angular separation between the reflections in question. While the overlap problem appeared specific to the a^* direction, the mosaic spread was relatively isotropic and therefore not considered in the derived function. On the basis of these calculations, 676 data, including most of the reflections for higher orders of h, were rejected. A further refinement through two more cycles of least squares in which only the 1365 nonoverlapping data (of which 1260 were nonzero) were considered converged to a conventional R factor of 0.069 and a weighted R factor R' ($R' = (\Sigma w(F_o - F_c)^2/\Sigma wF_o^2)^{1/2}$) of 0.079. A difference Fourier based on this refinement exhibited electron density as high as 1.2 e/A^3 in the vicinity of the Re position. While this and other regions of electron density suggested anisotropic vibration of the heavy atoms, the rejection of the overlapping data along the a^* axis prevented an unbiased anisotropic thermal refinement of the molecule. After correction of several indexing errors, a final cycle of least squares for the 95 positional, scale, and thermal parameters was run in which the hydrogen atom contributions were added to the calculated structure factors. The conventional and weighted R factors for the remaining 1256 nonzero reflections converged to final values of 0.064 and 0.071, respectively. The estimate of the standard deviation of an observation of unit weight has the value 2.40.

The parameters obtained in this final round of calculations are taken as the final parameters for the structure and are given in Table I. Standard deviations, as obtained from the inverse matrix, are also given. Table II lists the fractional coordinates for the ring carbon atoms which can be derived from the data of Table I. In Table III the values of F_o and $|F_c|$ (in electrons) are given for the 1256 observed reflections. The $|F_c|$ values for the unobserved reflections are omitted from Table III, since none of the intensities calculated for the unobserved but accessible reflections exceeds the minimum observable intensity value.

Description of the Structure

The crystal structure described by the space group, the parameters of Table I, and the cell parameters consists of the packing of individual monomeric molecules. The rhenium atoms are well separated, nearest neighbors being over 9 A apart. The closest intermolecular approaches to the rhenium are made by phenyl hydrogens at about 3.2 A. No intermolecular contacts appear closer than those predicted from van der Waal's radii. Figure 1 is a perspective drawing of an isolated molecule of the complex.

In the molecule, rhenium is surrounded by the six equidistant sulfur atoms in a trigonal prismatic coordination. The average Re–S bond distance is 2.325 A and the average S–Re–S bond angle is 81.4°. Principal intramolecular distances and angles are given in Table IV. Since all intermolecular contacts appear normal they are not listed. The sides of the prism are near-perfect squares with an average edge of 3.043 A. Intra- and interligand S–S distances lie within experimental limits of each other, the average intraligand value being 3.032 A and the nearest neighbor's interligand value being 3.050 A. The estimated standard deviations for these distances are 0.010 and 0.008 A, respectively. Although D_{3h} symmetry allows elongation or compression along the 3-fold axis, the ReS_6 trigonal prism found here is essentially perfect. A perspective drawing of the coordination geometry is shown in Figure 2. The metal–ligand planes de-

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(28) R. Eisenberg, to be published.

Table II

Derived Parameters for Group Carbon Atoms

Group atom[a]	x	y	z
R_1C_1	0.255 (1)	0.413 (2)	0.502 (2)
R_1C_2	0.208 (1)	0.509 (2)	0.583 (2)
R_1C_3	0.206 (1)	0.597 (2)	0.744 (2)
R_1C_4	0.251 (1)	0.588 (2)	0.825 (2)
R_1C_5	0.298 (1)	0.492 (2)	0.743 (2)
R_1C_6	0.300 (1)	0.405 (2)	0.582 (2)
R_2C_1	0.022 (1)	−0.193 (2)	0.101 (3)
R_2C_2	−0.017 (2)	−0.113 (2)	0.250 (3)
R_2C_3	−0.081 (2)	−0.162 (2)	0.314 (2)
R_2C_4	−0.106 (1)	−0.291 (2)	0.230 (3)
R_2C_5	−0.067 (2)	−0.372 (2)	0.080 (3)
R_2C_6	−0.003 (2)	−0.323 (2)	0.016 (2)
R_3C_1	0.442 (1)	−0.203 (2)	−0.060 (2)
R_3C_2	0.515 (2)	−0.182 (1)	−0.111 (2)
R_3C_3	0.563 (1)	−0.240 (2)	−0.089 (2)
R_3C_4	0.537 (1)	−0.320 (2)	−0.017 (2)
R_3C_5	0.464 (2)	−0.341 (2)	0.034 (2)
R_3C_6	0.417 (1)	−0.283 (2)	0.013 (2)
R_4C_1	0.449 (2)	−0.179 (3)	−0.358 (3)
R_4C_2	0.451 (2)	−0.313 (2)	−0.449 (3)
R_4C_3	0.505 (2)	−0.365 (2)	−0.585 (3)
R_4C_4	0.556 (2)	−0.282 (3)	−0.629 (3)
R_4C_5	0.554 (2)	−0.148 (2)	−0.538 (3)
R_4C_6	0.501 (2)	−0.096 (2)	−0.402 (3)
R_5C_1	0.050 (2)	−0.188 (2)	−0.218 (3)
R_5C_2	0.077 (1)	−0.254 (2)	−0.382 (3)
R_5C_3	0.032 (2)	−0.304 (2)	−0.489 (2)
R_5C_4	−0.040 (2)	−0.289 (2)	−0.433 (3)
R_5C_5	−0.067 (1)	−0.223 (2)	−0.269 (3)
R_5C_6	−0.022 (2)	−0.172 (2)	−0.161 (2)
R_6C_1	0.261 (1)	0.477 (1)	0.233 (2)
R_6C_2	0.208 (1)	0.511 (2)	0.193 (2)
R_6C_3	0.206 (1)	0.640 (2)	0.234 (2)
R_6C_4	0.255 (1)	0.736 (1)	0.315 (2)
R_6C_5	0.308 (1)	0.702 (2)	0.355 (2)
R_6C_6	0.310 (1)	0.573 (2)	0.313 (2)

[a] C_1 is attached to the ethylene carbon of the ligand; other C atoms are numbered in succession so that C_4 is *para* to C_1. The errors are derived from estimated standard deviations in the group parameters and are meant to be used in error analyses on inter-ring distances. Intra-ring distances, of course, are fixed (C–C = 1.392 A).

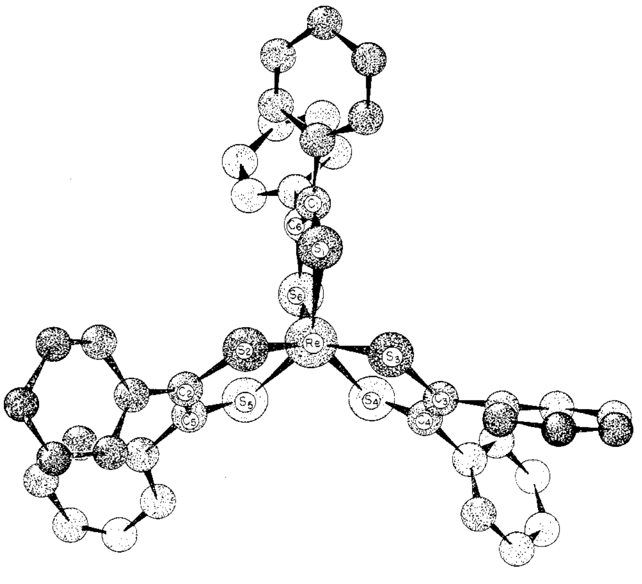

Figure 1.—A perspective drawing of a single molecule of the complex. Phenyl hydrogens are not shown.

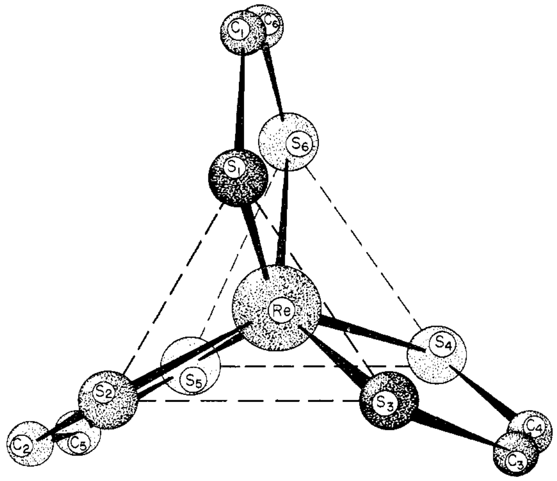

Figure 2.—A perspective drawing of the coordination geometry excluding the phenyl rings.

fined by the five-membered chelate rings radiate out from the 3-fold symmetry axis in a "paddle wheel" fashion. The equations of the best least-squares planes[29] through the chelate rings (in triclinic coordinates) and the distances of the atoms from their respective planes are given in Table V. Only one atom, C_4, shows a possibly significant deviation from its plane. The carbon–carbon double bond appears to be a true one with an average distance of 1.34 A. Surprisingly, the S–C bond lengths exhibit the greatest variation, ranging from a minimum value of 1.62 A to a maximum of 1.75 A with estimated errors for these values of 0.03 A. These differences do not appear regular or systematic. The phenyl rings, shown in Figure 1, are twisted out of the ligand planes. Calculated values for the dihedral angles between the chelate and phenyl rings, given in Table VI, range from 38.2 to 65.2°. In addition, the phenyl rings are skewed with respect to each other. The carbon–carbon bond connecting the rings to the ethylene carbons of the ligand has an average value of 1.53 A, in agreement with the accepted single bond value. It is thus clear that the phenyls are not conjugated with the inner network of the molecule.

Although the over-all molecular symmetry is approximately C_3, the coordination geometry is clearly trigonal prismatic. A complete molecular orbital calculation has been completed to describe the bonding in such D_{3h} systems.[30] The contributions of the phenyl rings to the π_v bonding are justifiably ignored and the system treated is similar to the one pictured in Figure 2. The ground state of the complex is found to be $\ldots(a_1')^1 = {}^2A_1'$ with the highest filled m.o. composed primarily of the $5d_{z^2}$. This result is consistent with the electron

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

(30) R. Eisenberg and H. B. Gray, to be published.

TABLE III

OBSERVED AND CALCULATED STRUCTURE FACTOR AMPLITUDES (IN ELECTRONS) FOR TRIS(*cis*-1,2-DIPHENYLETHENE-1,2-DITHIOLATO)RHENIUM

K	L	OBS	CAL
*****H= 0*****			
0	0		905
0	-1	248	239
0	-2	106	107
0	-3	104	106
0	-4	103	104
0	-5	81	77
0	-6	53	50
1	0	207	192
1	-1	295	294
1	-2	136	139
1	-3	71	72
1	-4	41	43
1	-5	65	65
1	-6	63	63
1	-7	48	50
2	0	58	58
2	-1	195	203
2	-2	41	47
2	-4	83	83
2	-5	88	91
2	-6	73	68
2	-7	39	44
3	0	89	92
3	1	77	84
3	-1	99	103
3	-2	135	149
3	-3	23	27
3	-4	61	64
3	-5	90	95
3	-6	100	96
3	-7	43	43
4	0	65	67
4	1	97	101
4	-1	57	64
4	-2	61	69
4	-3	97	107
4	-4	48	52
4	-5	98	107
4	-6	81	87
4	-7	64	68
5	0	63	56
5	1	72	78
5	-1	89	103
5	-2	100	110
5	-3	104	118
5	-4	67	72
5	-5	97	103
5	-6	109	112
5	-7	66	71
6	0	78	79
6	1	22	23
6	-1	97	102
6	-2	90	99
6	-3	94	96
6	-4	113	129
6	-5	86	92
6	-7	82	83
7	0	37	38
7	-1	64	62
7	-2	78	86
7	-3	96	104
7	-4	75	81
7	-5	50	57
7	-6	79	82
7	-7	71	73
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-2	-3	61	56
-2	-4	36	36
-3	3	56	50
-3	4	9	9
-3	5	19	22
-3	6	63	62
-3	7	59	56
-3	-2	46	46
-3	-3	43	35
-4	0	77	71
-4	2	52	43
-4	3	106	104
-4	4	56	62
-4	5	22	23
-4	6	31	31
-4	7	44	54
-4	-1	68	65
-4	-2	57	56
-4	-3	14	12
-5	0	108	99
-5	1	112	104
-5	2	16	12
-5	3	64	65
-5	4	20	24
-5	5	34	31
-5	6	26	34
-5	7	31	41
-5	-1	86	86
-5	-2	73	67
-6	0	121	111
-6	1	77	73
-6	2	63	59
-6	3	23	22
-6	4	24	24
-6	7	11	15
-6	-1	122	115
-7	0	93	88
-7	1	64	64
-7	2	31	31
-7	6	31	39
-8	1	34	35
-8	2	10	18
-8	6	37	43
-9	4	28	29
-9	5	31	35
*****H= 8*****			
0	4	121	119
0	5	67	73
0	6	69	71
1	3	102	94
1	4	49	51
1	5	36	36
1	-5	35	31
2	3	55	49
3	2	93	82
3	3	58	53
4	2	106	103
4	3	44	44
5	1	122	115
5	2	83	82
6	0	86	73
6	1	91	88
-1	4	146	139
-1	5	92	94
-1	6	42	40
-2	4	152	139
-2	5	113	111
-2	6	34	36
-2	7	22	27
-2	-4	23	18
-3	4	195	178
-3	5	114	108
-3	6	32	33
-3	-3	29	27
-4	3	153	142
-4	4	152	140
-4	5	58	60
-4	6	39	41
-4	-1	107	96
-4	-2	69	63
-4	-3	42	43
-5	0	99	88
-5	1	53	42
-5	2	109	100
-5	3	134	127
-5	4	96	88
-5	5	91	89
-5	6	69	71
-5	7	27	29
-5	-1	103	92
-5	-2	78	71
-6	0	103	95
-6	1	82	71
-6	2	84	78
-6	3	117	110
-6	4	117	113
-6	5	88	92
-6	6	65	67
-6	7	42	46
-6	-1	84	77
-7	0	84	69
-7	1	73	70
-7	2	27	22
-7	3	35	36
-7	4	92	93
-7	5	54	56
-7	6	41	44
-7	7	35	43
-8	1	63	54
-8	2	22	26
-8	3	22	24
-8	4	56	53
-8	5	66	66
-8	6	43	49
-9	4	52	50
*****H= 9*****			
0	4	25	28
0	5	36	39
0	6	48	48
1	4	41	46
1	5	22	25
2	3	24	30
2	4	14	17
2	5	10	17
3	3	30	33
3	4	10	17
4	2	51	54
4	3	55	54
5	1	52	52
5	2	85	87
6	0	23	22
-1	4	15	13
-1	5	16	14
-1	6	51	49
-2	4	24	22
-2	5	49	48
-2	6	55	52
-2	7	42	35
-3	4	29	28
-3	5	49	44
-3	6	82	77
-3	7	86	84
-3	-3	68	62
-4	4	73	66
-4	6	74	67
-4	7	71	67
-4	-2	47	39
-5	0	42	34
-5	3	36	34
-5	4	46	47
-5	7	44	42
-5	-1	50	42
-5	-2	55	54
-6	0	60	53
-6	1	38	39
-6	2	39	40
-6	3	16	8
-6	4	30	28
-6	5	21	22
-6	6	60	53
-6	-1	63	58
-7	0	73	70
-7	1	51	49
-7	2	21	21
-7	3	21	27
-7	5	25	19
-7	6	58	60
-7	7	47	44
-8	2	32	39
-8	6	39	38
*****H=10*****			
0	5	39	37
1	4	49	51
1	5	32	36
2	4	22	27
3	3	59	57
5	1	74	67
-1	5	94	88
-1	6	60	61
-2	5	100	90
-2	6	53	50
-3	5	90	77
-3	6	35	35
-4	5	111	100
-4	6	44	48
-4	7	11	13
-4	-2	64	64
-5	4	137	123
-5	5	115	110
-5	6	67	67
-5	7	20	25
-5	-1	93	80
-6	0	78	63
-6	1	71	56
-6	2	71	64
-6	3	109	98
-6	4	99	97
-6	5	78	80
-6	6	50	50
-6	7	35	41
-7	1	50	42
-7	2	28	29
-7	3	48	45
-7	4	82	84
-7	5	76	70
-7	6	65	63
-8	3	57	56
-8	4	60	55
-8	5	47	47
*****H=11*****			
0	5	71	69
1	5	31	31
2	4	43	37
3	3	45	43
-1	5	55	46
-1	6	45	46
-2	5	17	25
-2	6	38	37
-3	6	34	31
-4	5	15	13
-5	5	11	5
-5	6	20	24
-5	-1	27	25
-6	0	18	16
-6	3	40	38
-6	4	17	27
-7	2	46	39
-7	3	69	66
-7	4	23	19
-8	4	18	20
*****H=12*****			
0	5	44	41
-1	5	76	73
-2	6	36	28
-3	6	65	65
-4	5	63	57
-4	6	90	81
-5	5	78	65
-5	6	96	92
-6	4	95	78
-6	5	83	74
-6	6	99	92
-7	2	46	37
-7	3	61	57
-7	4	97	87
-7	5	68	69
*****H=13*****			
-1	5	57	49
-4	6	46	39
-5	6	21	27
-6	5	11	8
*****H=-1*****			
0	-3	97	98
0	-4	134	138
0	-5	76	76
0	-6	33	37
1	-2	66	65
1	-3	57	56
1	-4	79	82
1	-5	79	84
1	-6	10	12
2	-3	5	17
2	-4	28	37
2	-5	47	51
2	-6	24	30
3	-2	90	93
3	-5	61	61
3	-6	68	69
3	-7	40	40
4	-1	38	40
4	-2	17	24
4	-3	37	42
4	-5	21	22
4	-6	60	62
4	-7	56	59
5	-1	87	90
5	-2	76	78
5	-3	53	61
5	-4	37	35
5	-5	16	19
5	-6	45	45
5	-7	51	52
6	0	49	44
6	-1	47	50
6	-2	100	111
6	-3	75	81
6	-4	9	17
6	-5	14	4
6	-6	23	23
6	-7	31	36
7	0	60	61
7	-1	52	55
7	-2	76	85
7	-3	69	75
7	-4	13	8
7	-5	10	18
7	-6	15	15
7	-7	16	22
8	0	47	46
8	-1	37	37
8	-2	46	45
8	-3	67	78
8	-5	37	40
8	-6	41	46
9	-2	21	17
9	-3	41	43
9	-4	27	27
9	-5	26	29
-1	-3	119	121
-1	-4	113	119
-1	-5	73	77
-1	-6	35	31
-2	-3	104	106
-4	-4	77	76
*****H=-2*****			
0	-5	72	69
0	-6	74	69
1	-4	79	78
1	-5	88	85
1	-6	88	90
1	-7	75	82
2	-4	53	56
2	-5	95	93
2	-6	62	64
2	-7	72	76
3	-5	86	83
3	-6	80	79
3	-7	53	58
4	-3	64	69
4	-4	70	72
4	-5	91	94
4	-6	132	131
4	-7	87	86
5	-3	115	119
5	-4	78	85
5	-5	113	118
5	-6	147	152
5	-7	95	96
6	-3	123	137
6	-4	95	99
6	-5	100	112
6	-6	91	97
6	-7	98	96
7	-2	70	72
7	-3	117	124
7	-4	85	91
7	-5	49	57
7	-6	71	85
7	-7	79	85
8	-2	91	95
8	-3	57	58
8	-4	81	94
8	-5	66	66
8	-6	34	45
9	-2	81	88
9	-3	79	92
9	-4	54	57
9	-5	61	67
-1	-5	42	40
-1	-6	41	39
*****H=-3*****			
1	-7	15	16
2	-6	17	22
2	-7	11	11
3	-6	60	60
3	-7	15	22
4	-6	51	52
4	-7	43	50
5	-5	30	31
5	-6	56	56
5	-7	58	64
6	-5	10	1
6	-6	29	31
6	-7	45	45
7	-4	37	41
7	-5	24	32
7	-6	24	25
7	-7	32	30
8	-4	32	37
8	-5	27	29
8	-6	33	42
9	-4	33	36
*****H=-4*****			
5	-7	91	99
6	-7	97	103
7	-7	70	83
8	-6	25	32
8	-7	63	70

spin resonance work on these complexes by Stiefel and Gray.[31] From the energy level scheme no unambiguous ordering of the metal levels can be established because of the existence of two e′ levels, one completely occupied and the other empty, which are each found to have more ligand than metal d character (d_{xy}, $d_{x^2-y^2}$). The highest energy d orbitals are the d_{xz} and d_{yz} which transform as the doubly degenerate e″ representation. This agrees with the results obtained by Abrahams, *et al.*,[32] for the ReH_9^{2-} anion which can be thought of as having been derived from a trigonal prismatic ReH_6 group by the addition of a hydrogen along the normal to each of the centers of the square faces.

Prior to the present structure determination of $Re(S_2C_2(C_6H_5)_2)_3$, reports of trigonal prismatic coordination for transition metals in inorganic chemistry were of infinitely extended ionic systems such as MoS_2 and WS_2 in hexagonal lattices.[33] Since then, the structure of the analogous complex $Mo(S_2C_2H_2)_3$ has been determined by X-ray methods and it too shows the extraordinary trigonal prismatic coordination.[34] As we

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(31) E. Stiefel and H. B. Gray, *J. Am. Chem. Soc.*, **87**, 4012 (1965).

(32) S. C. Abrahams, A. P. Ginsberg, and K. Knox, *Inorg. Chem.*, **3**, 558 (1964).

(33) R. Dickinson and L. Pauling, *J. Am. Chem. Soc.*, **45**, 1466 (1923).

(34) A. E. Smith, G. N. Schrauzer, V. P. Mayweg, and W. Heinrich, *ibid.*, **87**, 5798 (1965).

TABLE IV

SELECTED INTRAMOLECULAR DISTANCES AND ANGLES

Distances, A		Angles, deg	
Re–S_1	2.32 (1)	S_1–Re–S_6	81.9 (3)
Re–S_2	2.30 (1)	S_2–Re–S_5	81.5 (4)
Re–S_3	2.33 (1)	S_3–Re–S_4	80.9 (4)
Re–S_4	2.32 (1)	Re–S_1–C_1	109 (1)
Re–S_5	2.33 (1)	Re–S_2–C_2	108 (1)
Re–S_6	2.33 (1)	Re–S_3–C_3	111 (1)
S_1–C_1	1.75 (3)	Re–S_4–C_4	107 (1)
S_2–C_2	1.72 (4)	Re–S_5–C_5	109 (1)
S_3–C_3	1.63 (3)	Re–S_6–C_6	110 (1)
S_4–C_4	1.70 (3)	S_1–C_1–C_6	119 (2)
S_5–C_5	1.62 (4)	S_6–C_6–C_1	120 (2)
S_6–C_6	1.70 (2)	S_2–C_2–C_5	119 (3)
		S_5–C_5–C_2	122 (3)
C_1–C_6	1.34 (3)	S_3–C_3–C_4	119 (2)
C_2–C_5	1.33 (3)	S_4–C_4–C_3	122 (2)
C_3–C_4	1.34 (3)	S_1–C_1–R_1C_1	112
C_1–R_1C_1	1.51	S_2–C_2–R_2C_1	112
C_2–R_2C_1	1.52	S_3–C_3–R_3C_1	119
C_3–R_3C_1	1.53	S_4–C_4–R_4C_1	112
C_4–R_4C_1	1.54	S_5–C_5–R_5C_1	118
C_5–R_5C_1	1.53	S_6–C_6–R_6C_1	118
C_6–R_6C_1	1.52		

mentioned above, the W analog and possibly the Mo, Cr, and V analogs of the Re complex probably have the trigonal prismatic configuration. Thus tris(*cis*-1,2-diphenylethene-1,2-dithiolato)rhenium is the first example of what will undoubtedly become a class of trigonal prismatic complexes in transition metal chemistry.

Acknowledgments.—We are indebted to G. N. Schrauzer for the crystals and to H. B. Gray for his helpful and enlightening comments.

TABLE V

THE EQUATIONS OF THE BEST LEAST-SQUARES PLANES THROUGH THE CHELATE RINGS AND THE DISTANCES OF THE ATOMS FROM THEIR RESPECTIVE PLANES (A)

(1) The Plane through the Chelate Ring Defined by Re, S_1, S_6, C_1, and C_6

$$19.121x - 0.867y + 0.509z = 4.751 \text{ (triclinic coordinates)}$$

Atom	Distance	Atom	Distance
Re	0.000 (2)	C_1	0.03 (4)
S_1	0.003 (11)	C_6	−0.04 (4)
S_6	0.003 (10)		

(2) The Plane through the Chelate Ring Defined by Re, S_2, S_5, C_2, and C_5

$$9.457x - 9.213y - 0.213z = 2.190 \text{ (triclinic coordinates)}$$

Atom	Distance	Atom	Distance
Re	0.000 (1)	C_2	−0.08 (3)
S_2	0.007 (8)	C_5	0.04 (2)
S_5	−0.002 (8)		

(3) The Plane through the Chelate Ring Defined by Re, S_3, S_4, C_3, and C_4

$$9.730x + 7.465y + 1.718z = 2.586 \text{ (triclinic coordinates)}$$

Atom	Distance	Atom	Distance
Re	0.000 (1)	C_3	−0.05 (3)
S_3	0.016 (9)	C_4	−0.11 (3)
S_4	0.016 (8)		

TABLE VI

CALCULATED VALUES FOR THE DIHEDRAL ANGLES BETWEEN THE CHELATE AND PHENYL RINGS

Chelate ring[a]	Phenyl ring	Dihedral angle, deg
1	1	50.4
1	6	55.0
2	2	62.3
2	5	46.4
3	3	38.2
3	4	65.2

[a] The chelate rings are numbered according to the order given in Table V.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASSACHUSETTS

Chemical and Structural Studies of Rhenium(V) Oxyhalide Complexes. III. The Crystal and Molecular Structure of Tetraphenylarsonium Oxotetrabromoacetonitrilerhenate(V)[1]

BY F. A. COTTON AND STEPHEN J. LIPPARD[2]

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The crystal and molecular structure of $[(C_6H_5)_4As][ReBr_4O(CH_3CN)]$ has been investigated by X-ray diffraction. The anion is shown to consist of a square-pyramidal (C_{4v}) $ReBr_4O$ group, with a molecule of acetonitrile weakly bonded to the rhenium atom at a distance Re–N of 2.31 A. The Re–O distance of 1.73 A is indicative of considerable multiple bond character. The structure of the cation is discussed in terms of idealized S_4 symmetry. Various features of the molecular geometry of the $[ReBr_4O(CH_3CN)]^-$ ion are compared with the structural results of other related complexes reported in the literature.

Introduction

Recently, we have reported the preparation and characterization of several new rhenium(V) oxyhalide complexes.[3-5] From rhenium(III) bromide in concentrated aqueous HBr, compounds containing either the $[ReBr_4O]^-$ or $[ReBr_4O(H_2O)]^-$ anions are obtained.[4] A complete X-ray structure investigation of

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[2] National Science Foundation Predoctoral Fellow, 1962–1965.

[3] F. A. Cotton and S. J. Lippard, *Chem. Commun.* (London), 245 (1965).

[4] F. A. Cotton and S. J. Lippard, *Inorg. Chem.*, **4**, 1621 (1965).

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