

16.1. Oxytocin possesses  $[\alpha]^{22.5D} -23.1^\circ$  (*c* 0.51, 1 *N* acetic acid).<sup>13</sup>

A sample was hydrolyzed with 6 *N* HCl at 120° for 20 hr. and analyzed with a Beckman-Spinco amino acid analyzer according to the procedure of Spackman, Stein, and Moore.<sup>14</sup> The following molar ratios were obtained, glycine being taken as 1.0: aspartic acid 1.0, glutamic acid 1.0, proline 1.1, glycine 1.0, leucine 1.0, tyrosine 0.9, cystine 1.0, isoleucine 0.95, alloisoleucine 0.05, ammonia 3.0.

Paper electrophoresis, with pyridine acetate buffer pH 5.6 for 20 hr., showed D-oxytocin to have a mobility identical with that of oxytocin and to travel as a single spot. A similar finding was made when the compound was subjected to paper chromatography in two different solvent systems, 1-butanol-acetic acid-water (4:1:5) and pyridine-acetic acid-water (10:7:3).

No avian-vasodepressor<sup>9</sup> or oxytocic activity<sup>10</sup> was detected upon bioassay of D-oxytocin, whereas oxytocin possesses approximately 500 units/mg. of each of these activities. No indication of an inhibitory effect of D-oxytocin on these activities of oxytocin could be detected.

Recently Yajima and Kubo<sup>15</sup> synthesized D-histidyl-D-phenylalanyl-D-arginyl-D-tryptophylglycine, the enantiomer of which corresponds to positions 6 to 10 of  $\alpha$ -melanocyte-stimulating hormone. The L-pentapeptide was found to possess a slight degree of melanocyte-stimulating activity, whereas the D-pentapeptide was found to antagonize the action of its enantiomer as well as that of  $\alpha$ -MSH.<sup>15,16</sup> Schröder, *et al.*,<sup>17</sup> have synthesized the D-heptapeptide, glycyl-D-alanyl-D-phenylalanyl-D-valyl-glycyl-D-leucyl-D-methioninamide, the enantiomer of which corresponds to an analog of the heptapeptide sequence of positions 5 to 11 of eledoisin with glycine in place of aspartic acid and valine in place of isoleucine. The D-heptapeptide was reported to have  $1/2500$  of the activity of the L-isomer in lowering the blood pressure of the rabbit. More recently, Stewart and Woolley<sup>18</sup> have synthesized D-bradykinin and found that amounts of this D-nonapeptide up to 50,000 times the standard challenge of bradykinin showed neither any inhibition of the response to bradykinin nor any bradykinin-like effects on the isolated rat uterus, duodenum, and stomach.

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(13) C. Ressler and V. du Vigneaud, *J. Am. Chem. Soc.*, **79**, 4511 (1957).

(14) D. H. Spackman, W. H. Stein, and S. Moore, *Anal. Chem.*, **30**, 1190 (1958); S. Moore, D. H. Spackman, and W. H. Stein, *ibid.*, **30**, 1185 (1960).

(15) H. Yajima and K. Kubo, *J. Am. Chem. Soc.*, **87**, 2039 (1965).

(16) K. Hano, M. Koida, K. Kubo, and H. Yajima, *Biochim. Biophys. Acta*, **90**, 201 (1964).

(17) E. Schröder, K. Lübke, and R. Hempel, *Experientia*, **21**, 70 (1965).

(18) J. M. Stewart and D. W. Woolley, *Nature*, **206**, 619 (1965).

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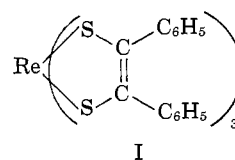
## Trigonal Prismatic Coordination.

### The Molecular Structure of

### Tris(*cis*-1,2-diphenylethene-1,2-dithiolato)rhenium<sup>1</sup>

Sir:

Since their initial preparation,<sup>2-4</sup> tris complexes of bidentate sulfur ligands have been under intensive study.<sup>4-7</sup> As with the square-planar bis compounds, these systems appear to 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.<sup>8,9</sup> 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 undertook the structure determination of what is probably a representative example of these compounds, the neutral complex tris(*cis*-1,2-diphenylethene-1,2-dithiolato)rhenium.<sup>9</sup> This communication reports the results of that investigation.



Green crystals of I, kindly supplied by G. N. Schrauzer, were examined by precession techniques and found to be triclinic. A Delaunay reduction failed to suggest a higher crystal system. The compound crystallizes in a cell with dimensions  $a = 19.73 \pm 0.04$ ,  $b = 11.94 \pm 0.03$ ,  $c = 9.87 \pm 0.03$  Å.,  $\alpha = 120.1 \pm 0.1$ ,  $\beta = 73.6 \pm 0.1$ ,  $\gamma = 102.5 \pm 0.1^\circ$ . 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  $1.53 \pm 0.05$  g./cm.<sup>3</sup>, determined by flotation in zinc chloride solutions, agrees well with a calculated value of  $1.572$  g./cm.<sup>3</sup> for two molecules in the unit cell. Thus, all atoms are in general positions and no crystallographic symmetry conditions need be imposed on the molecule.

Intensity data were collected at room temperature from a single crystal with the G.E. XRD-5 goniostat.

(1) Research performed under the auspices of the U. S. Atomic Energy Commission and the National Science Foundation.

(2) R. B. King, *Inorg. Chem.*, **2**, 641 (1963).

(3) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *J. Am. Chem. Soc.*, **86**, 2799 (1964).

(4) (a) G. N. Schrauzer, H. W. Finck, and V. 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**, 4198 (1964).

(5) C. H. Langford, E. Billig, S. I. Shupack, and H. B. Gray, *ibid.*, **86**, 2958 (1964).

(6) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, **4**, 55 (1965).

(7) E. Stiefel and H. B. Gray, *J. Am. Chem. Soc.*, in press.

(8) However, Langford, *et al.*,<sup>5</sup> speculated that an "interesting possibility" for the structure might be a "trigonal prismatic, or at least a strongly trigonally distorted, six-coordinate structure."

(9) Previous names for these compounds have included<sup>4</sup> tris(dithiobenzil)metal(0) and tris(*cis*-1,2-stilbenedithiolato)metal(VI). We suggest the present name because it is more descriptive of the ligand; we do not wish to imply that we know the formal charge on the metal atom.

The stationary crystal-stationary counter technique was used; a niobium  $\beta$  filter was employed in conjunction with Mo  $K\alpha$  radiation. The structure was solved by the usual combination of three-dimensional Patterson, Fourier, and least-squares calculations. In the least-squares procedures, the phenyl rings were treated as rigid groups.<sup>10,11</sup> Each ring was described by six variable positional parameters and a single variable isotropic thermal parameter. The conventional  $R$  factor for 1260 independent reflections has converged to a value of 6.4% for isotropic refinement. The isotropic temperature factors are reasonable. An overlap problem in the  $a^*$  direction resulted in the rejection of several hundred data, including many higher angle reflections along that direction. The elimination of these data does not permit an unbiased anisotropic thermal refinement of the molecule. The nature and treatment of the overlap problem will be discussed more fully in the final report of the structure determination.

In the molecule, rhenium is surrounded by the six equidistant sulfur atoms in a trigonal prismatic coordination. A perspective drawing of the coordination geometry is shown in Figure 1. The average Re-S distance is  $2.325 \pm 0.004$  Å.; the average S-Re-S bond angle is  $81.4^\circ$ . The sides of the prism are near perfect squares with an average edge of 3.043 Å. Intra- and interligand S-S distances lie within experimental limits of each other, the average intraligand value being 3.032 and the nearest neighbors interligand value being 3.050 Å. The estimated errors for these distances are 0.01 and 0.008 Å., respectively. Although  $D_{3h}$  symmetry allows elongation or compression along the threefold axis, the trigonal prism found here is essentially perfect. The metal-ligand planes, defined by the five-membered chelate rings, radiate out from the threefold symmetry axis in a "paddle-wheel" fashion. Only one atom, C<sub>4</sub>, shows a possibly significant deviation from the best least-squares planes through the three chelate rings. The carbon-carbon double bond appears to be a true one with an average distance of 1.34 Å. Surprisingly, the S-C bond lengths exhibit the greatest variation, ranging from a minimum value of 1.62 to a maximum of 1.75 Å. The differences do not appear regular or systematic. The estimated standard deviations of these bond distances are about 0.03 Å. The phenyl rings, not shown in Figure 1, are twisted out of the ligand planes. Calculated values for the dihedral angles between the chelate and phenyl rings 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 ligands has an average length of 1.53 Å., 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.

All intermolecular contacts appear normal. The rheniums are well separated, nearest neighbors being over 9 Å. apart. The closest intermolecular approaches to the rhenium are made by phenyl hydrogens at about 3.2 Å. No contacts appear closer than those predicted from van der Waals radii.

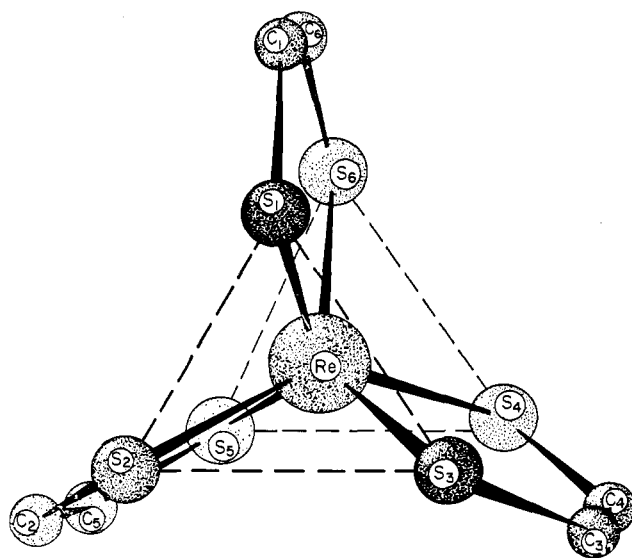


Figure 1. A perspective drawing of the coordination geometry of the molecule. The phenyl rings are not shown.

Although the over-all molecular symmetry is approximately  $C_3$ , the coordination geometry is clearly trigonal prismatic. A complete molecular orbital calculation is in progress to describe the bonding in such  $D_{3h}$  systems.<sup>12</sup>

Previous reports from diffraction studies of trigonal prisms in transition metal compounds have been of the infinitely extended ionic systems, such as  $MoS_2$  and  $WS_2$  in hexagonal lattices.<sup>13</sup> There have been no structures reported of monomeric trigonal prisms. Thus tris(*cis*-1,2-diphenylethene-1,2-dithiolato)rhenium is the first example of a trigonal prismatic complex in transition metal chemistry. The  $ReH_9^{-2}$  ion in  $K_2ReH_9$ <sup>14</sup> may 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. The question thus arises: Is the trigonal prismatic configuration found here peculiar to Re or is this the first example of a class of trigonal prismatic complexes in transition metal chemistry? In an attempt to answer this question we have examined the X-ray powder photographs of the Re complex, and also of the W, Mo, V, and Cr analogs. The Re and W complexes appear to be isomorphous, as do the Mo, V, and Cr complexes. Owing to the changes in scattering power of the transition metal on 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 have unit cells which differ from those of Mo, V, and Cr. Since generally substances which are isomorphous are isostructural, these data lead us to the conclusion that the W analog, and possibly also the Mo, V, and Cr analogs, will be found to have the trigonal prismatic configuration. Thus we believe that tris(*cis*-1,2-diphenylethene-1,2-dithiolato)rhenium is the first example of what will become a class of trigonal prismatic complexes in transition metal chemistry.

(10) S. J. La Placa and J. A. Ibers, *J. Am. Chem. Soc.*, **85**, 3501 (1963); *Acta Cryst.*, **18**, 511 (1965).

(11) R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **4**, 773 (1965).

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

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

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

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## Energy Level of the First Excited Singlet State of 1,3-Butadiene

Sir:

It is well known that the intense absorption in the ultraviolet spectrum of 1,3-butadiene, which has a maximum at 2100 Å., corresponds to a  $\pi \rightarrow \pi^*$  transition from the ground singlet to an upper singlet state. Although this absorption has been studied extensively from both an experimental and a theoretical point of view,<sup>1,2</sup> it has not been possible to identify the  $0 \rightarrow 0$  band as the absorption shows very little detailed structure, and fluorescent emission has never been observed from this state. It has been assumed that the  $0 \rightarrow 0$  band lies not far from the point where the absorption falls off in intensity, which is approximately 2300 Å.<sup>3</sup> The exact position of the singlet excited state is a matter of importance for photochemical purposes. Thus, it is believed that a considerable energy gap separates the first excited singlet from the lowest triplet state.<sup>4</sup> Obviously, the magnitude of the gap can be known only if the limits of the gap are defined. Again it is very useful to bring about the photolysis of 1,3-butadiene at 2537 Å. It is necessary to know the reactive state that is produced at this wave length. Since data on the energy levels of the excited singlet states of none of the simple 1,3-dienes are available, the discussion here is of a fairly general nature.

The intensity of the absorption spectrum of 1,3-butadiene decreases from its maximum value of 24,000 cm.<sup>2</sup> mole<sup>-1</sup> at 2100 Å. to 280 at 2300 Å., but at 2500 Å. it is still 4.4.<sup>5</sup> It is the purpose of this communication to point out that the excited state that is generated on the absorption of 2537-Å. radiation is probably an upper singlet and that the  $0 \rightarrow 0$  band for this state must lie at a wave length considerably larger than this.

We have now observed that photolysis of 1,3-butadiene in hydrocarbon solution at 2537 Å. gives rise *exclusively* to cyclobutene and bicyclo[1.1.0]butane in dilute solution. The ratio of cyclobutene to bicyclobutane is independent of temperature from 0 to 50° and changes with the nature of the solvent (ether, 7; isooctane, 14).<sup>6</sup> These valence tautomerization

(1) A. Smakula, *Angew. Chem.*, **47**, 657 (1934); G. Scheibe and H. Grieneisen, *Z. physik. Chem.*, **B25**, 54 (1934).

(2) N. L. Allinger and J. C. Tai, *J. Am. Chem. Soc.*, **87**, 2081 (1965), and references therein.

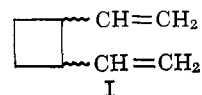
(3) The specific instance of 1,3-pentadiene is discussed by G. S. Hammond, N. J. Turro, and P. A. Leermakers, *J. Phys. Chem.*, **66**, 1144 (1962).

(4) I. Haller and R. Srinivasan, *J. Chem. Phys.*, **40**, 1992 (1964).

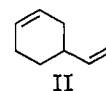
(5) American Petroleum Institute Research Project 44, Ultraviolet Spectral Data, Serial No. 65.

reactions cannot be ground-state reactions since in the ground state the thermodynamic equilibria are in favor of 1,3-butadiene. The choice is then between the excited singlet and the lowest triplet states. Since photosensitization of 1,3-butadiene by a variety of sensitizers in their triplet states does not give either of these valence tautomers,<sup>7</sup> it seems unlikely that the triplet state is the reactant during photolysis at 2537 Å. This reduces the choice to the upper singlet state alone.

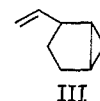
We have also observed that the dimerization of 1,3-butadiene at 2537 Å. in the absence of any sensitizer differs markedly from the dimerization initiated by a triplet sensitizer<sup>7</sup> and from the thermal process. In the first place, even at an optimum concentration, photodimerization accounts for less than 10% of the butadiene that is consumed, whereas in the triplet-sensitized reaction, the yield of dimers is nearly 75%. [At high concentrations, polymeric materials are formed predominantly, but these do not seem to be related to polymers formed by free radical (thermal) polymerization.] In the second place, the most important dimer (50%) that is observed is neither 1,2-divinylcyclobutane (I) (although this accounts for 30% of the yield) nor 4-vinylcyclohexene (II) (which is



negligible, if at all present), but a compound which



on analysis fit the formula C<sub>8</sub>H<sub>12</sub> (*Anal.* Calcd. for C<sub>8</sub>H<sub>12</sub>: C, 88.82; H, 11.17. Found: C, 89.02; H, 11.17) and showed the presence of a vinyl group (1640, 994, and 915 cm.<sup>-1</sup>) and a cyclopropyl group (1026 cm.<sup>-1</sup>) in its infrared spectrum. The n.m.r. spectrum showed the presence of three vinyl protons, four cyclopropyl protons, one allylic proton, and four other protons centered at  $\tau$  8.5. This would correspond to the structure 2-vinylbicyclo[3.1.0]hexane (III).<sup>8</sup>



About 8% of the products was 1,5-cyclooctadiene, which has been reported in the triplet-sensitized reaction as well as in the thermal dimerization. A fourth dimer, which amounted to about 10% of the total, was not identified.

It is possible that on absorption of a photon at 2537 Å. butadiene undergoes a transition from a ground singlet to a high vibrational level of the second triplet observed by Evans.<sup>9</sup> However, in this state bimolecular processes, such as those necessary to lead to dimerization, would compete unfavorably with vibrational deactivation and electronic quenching to the

(6) Details of these studies will be published elsewhere.

(7) G. S. Hammond, N. J. Turro, and A. Fisher, *J. Am. Chem. Soc.*, **83**, 4674 (1961).

(8) The alternative structure of 3-vinylbicyclo[3.1.0]hexane is not rigorously excluded.

(9) D. F. Evans, *J. Chem. Soc.*, 1735 (1960).