

Redetermination of the trigonal prismatic complex tris(*cis*-1,2-diphenylethylene-1,2-dithiolato)rhenium \ddagger

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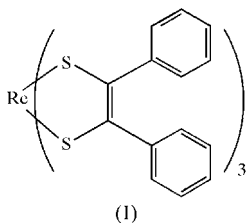
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The first trigonal prismatic molecular compound characterized by single-crystal X-ray diffraction, $[\text{Re}(\text{C}_{14}\text{H}_{10}\text{S}_2)_3]$, has been redetermined using modern laboratory equipment. The new experiment reaffirms the results of the original. Since then, numerous tris-dithiolene complexes have been structurally characterized, having geometries ranging from trigonal prismatic to nearly octahedral. An examination of the coordination geometries of these structures is included.

Comment

40 years ago, the first example of trigonal prismatic coordination in discrete metal complexes was reported (Eisenberg & Ibers, 1966). The particular example was the rhenium–tris-dithiolene complex (I) (Fig. 1), first reported by Schrauzer *et al.* (1964). A number of other tris-dithiolene complexes were subsequently studied structurally and found to possess coordination geometries ranging from trigonal prismatic (TP) to nearly octahedral (O), depending on the metal ion, overall complex charge and dithiolene substituent (Brown & Stiefel, 1973; Colmanet & Mackay, 1988; Yang *et al.*, 1991; Matsubayashi *et al.*, 1992, 1993; Goddard & Holm, 1999; Wang *et al.*, 1999; Lewis & Dance, 2000; Lim *et al.*, 2000; Fomitchev *et al.*, 2001).



The specific structure determination of (I), while widely cited as the first example of TP coordination, was based on intensity data collected by methods that would be viewed today as substandard (manually positioned crystal and

detector, and fixed stationary counting times) and led to a number of problems in the refinement of the structure. Specifically, because of reflection overlap in the counter window, a significant fraction of the intensity data were eliminated from the refinement, leading to a low ratio of observations to variables, the use of isotropic displacement parameters for all atoms and group refinement procedures for the six phenyl rings. While the final refinement of the structure converged to R values of 0.069 and 0.079, a wide range of C–S distances was noted and standard deviations in all metrical parameters were substantial.

In this paper, we report a redetermination of the structure of (I) using a crystal from the *originally prepared* sample and performed using state-of-the-art CCD instrumentation. Additionally, we tabulate a simple distortion parameter that allows one to assess the six-coordination geometry from TP to O more accurately for tris-dithiolene-chelated complexes.

The structure redetermination confirms the TP coordination geometry of (I) as originally reported. As expected, in the present determination the equivalent metrical parameters for the complex exhibit much better agreement and much smaller standard deviations than in the original report. For example, Re–S distances cover a range of 2.3274 (9)–2.3348 (10) Å and average 2.3322 (22) Å, while dithiolene S–C distances exhibit a range of 1.715 (4)–1.730 (4) Å and average 1.725 Å (10) Å. The latter numbers compare with 1.62 (4)–1.75 (3) and 1.69 (8) Å, respectively, in the initial report.

The crystal structure consists of the packing of neutral molecules with no notably short intermolecular contacts. A feature of the packing is that the molecules stack so that the stacking direction deviates by only 10.2° from the trigonal axis of the complex.

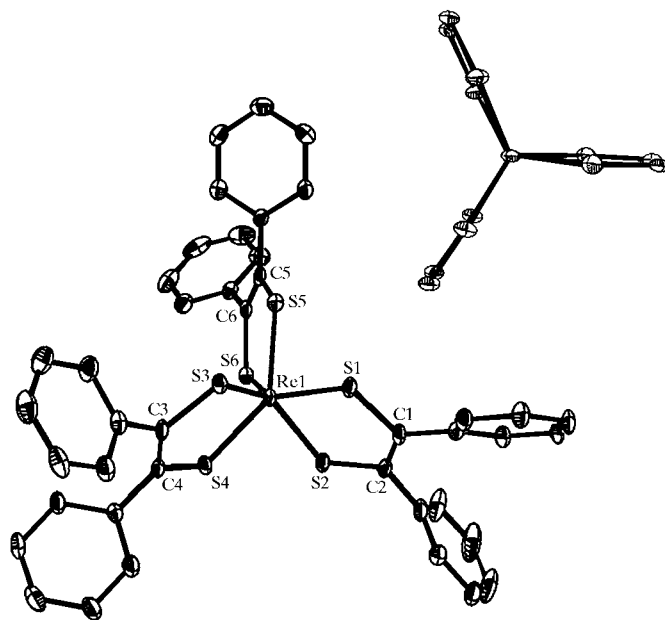


Figure 1

A displacement ellipsoid (50% probability) drawing of (I), with H atoms omitted. Inset: the view down the trigonal axis.

\ddagger Dedicated to Professor Edward Stiefel who first made the lead author of this article aware of the significance of trigonal prismatic coordination.

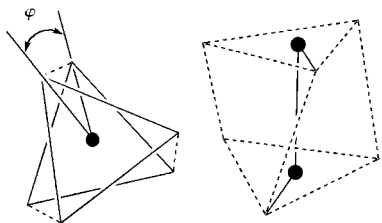


Figure 2
The dihedral (trigonal distortion) angle.

Studies on related dithiolene complexes following the initial report revealed that the tris-chelated complexes with MS_6 coordination environments exhibited a range of coordination geometries from purely TP to distorted O that have been analyzed by Stiefel & Brown (1972). If one calculates the position of the centroid (Cen) of the three S atoms in each trigonal face then it is possible to define a TP distortion as the dihedral angle formed by $S_{\text{upper}} - \text{Cen}_{\text{upper}} - \text{Cen}_{\text{lower}} - S_{\text{lower}}$, where upper and lower refer to the two trigonal faces, and S_{upper} and S_{lower} on the respective trigonal faces belong to the same ligand (Fig. 2). Each structure will therefore yield three distortion angles that can be averaged. For a pure trigonal prism the distortion angle would be 0° , and for an intermediate geometry half-way to O it would be 30° (ligand distance constraints preclude achieving a pure D_3 geometry with O angles). Table 1 contains a tabulation of the tris-dithiolene structures from the Cambridge Structural Database (Version 5.27; Allen, 2002) and their TP distortion angles as defined above. As can be seen, compound (I) has one of the smallest distortion angles for structures in which TP symmetry is not crystallographically imposed. Increasing negative charge on the tris-dithiolene complexes moves the coordination geometry towards O with an increasing distortion angle. A possible explanation for this effect is minimization of inter-ligand repulsions as the donor atoms acquire greater negative charge [see Brown & Stiefel (1973) for a detailed discussion].

Brown & Stiefel (1973) propose a second distortion parameter in analyzing TP coordination. The parameter involves the ratio s/h , where s is the nearest inter-ligand $S \cdots S$ contact and h is the distance between the two parallel trigonal faces. For TP, the s/h ratio is 1.0, meaning that the sides of the prism are squares, whereas for O, the ratio is $1.22 [= (3/2)^{1/2}]$; Stiefel & Brown, 1972]. In the case of (I), with $S \cdots S$ contacts averaging 3.054 (31) and 3.055 (23) Å, respectively, for intra-triangular and intra-ligand values, the s/h ratio is 1.0, the sides of the prism are square and the coordination geometry is truly undistorted TP.

Finally, it is reassuring how good the overall agreement is between the original structure determination and the more accurate and precise current determination given the quality of the earlier intensity measurements.

Experimental

The material used was the original sample kindly supplied by Professor G. N. Schrauzer in the mid-1960s.

Crystal data

$[\text{Re}(\text{C}_{14}\text{H}_{10}\text{S}_2)_3]$	$V = 1871.5 (3) \text{ \AA}^3$
$M_r = 913.22$	$Z = 2$
Triclinic, $P\bar{1}$	$D_x = 1.621 \text{ Mg m}^{-3}$
$a = 9.7949 (9) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 10.8765 (10) \text{ \AA}$	$\mu = 3.61 \text{ mm}^{-1}$
$c = 19.4517 (17) \text{ \AA}$	$T = 100.0 (1) \text{ K}$
$\alpha = 80.190 (1)^\circ$	Plate, red-black
$\beta = 76.770 (1)^\circ$	$0.28 \times 0.24 \times 0.06 \text{ mm}$
$\gamma = 68.758 (1)^\circ$	

Data collection

Bruker SMART APEX-II CCD	27614 measured reflections
Platform diffractometer	10391 independent reflections
φ and ω scans	8772 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Blessing, 1995)	$R_{\text{int}} = 0.039$
$T_{\text{min}} = 0.376$, $T_{\text{max}} = 0.806$	$\theta_{\text{max}} = 29.6^\circ$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0513P)^2 + 1.2114P]$
$R[F^2 > 2\sigma(F^2)] = 0.036$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.089$	$(\Delta/\sigma)_{\text{max}} = 0.004$
$S = 1.04$	$\Delta\rho_{\text{max}} = 3.47 \text{ e \AA}^{-3}$
10391 reflections	$\Delta\rho_{\text{min}} = -3.08 \text{ e \AA}^{-3}$
442 parameters	
H-atom parameters constrained	

Table 1

Average trigonal prismatic distortion angles ($^\circ$) for selected chromium and manganese group complexes; see *Comment* for definition of distortion angle.

Complex	Average distortion angle	CSD Refcode
$[\text{Re}(\text{S}_2\text{C}_2\text{Ph}_2)_3]$	3.4	REPETD10 ^a
$[\text{Re}(\text{S}_2\text{C}_2\text{Ph}_2)_3]^b$	3.8	
$[\text{Cr}(\text{S}_2\text{C}_2(\text{CN})_2)_3]^{2-}$	45.4	DUJDAN ^c
$[\text{Cr}(\text{S}_2\text{C}_2(\text{CN})_2)_3]^{3-}$	51.5	DUJCIU ^c
$[\text{Mo}(\text{S}_2\text{C}_2\text{Me}_2)_3]$	2.4	DIZQOS ^d
$[\text{Mo}(\text{S}_2\text{C}_2\text{Me}_2)_3]^-$	1.6	DIZQUY ^d
$[\text{Mo}(\text{S}_2\text{C}_2\text{Me}_2)_3]^{2-}$	2.6	QEPDOE ^e
$[\text{Mo}(\text{S}_2\text{C}_2\text{S}_2\text{CS})_3]^{2-}$	16.6	KUWWII, ^f KUWWII10 ^g
$[\text{Mo}(\text{S}_2\text{C}_2(\text{CF}_3)_2)_3]$	0.0 ^h	QUQBOT ⁱ
$[\text{Mo}(\text{S}_2\text{C}_2(\text{CF}_3)_2)_3]^{2-}$	16.1	QUPZUW ⁱ
$[\text{Mo}(\text{S}_2\text{C}_2(\text{CN})_2)_3]^{2-}$	28.2	PASMOD10 ^j
$[\text{W}(\text{S}_2\text{C}_2\text{Me}_2)_3]^{2-}$	2.8, 2.4	QEPDUK, QEPFAS ^e
$[\text{W}(\text{S}_2\text{C}_2\text{Ph}_2)_3]$	3.2	CUNMIH ^k
$[\text{W}(\text{S}_2\text{C}_2\text{Ph}_2)_3]^-$	2.2, 14.3 ^l	CUNBIW ^k
$[\text{W}(\text{S}_2\text{C}_2\text{S}_2\text{CS})_3]$	0.8	LEFHOT ^g
$[\text{W}(\text{S}_2\text{C}_2\text{S}_2\text{CS})_3]^{2-}$	15.5	LEFHEJ ^g
$[\text{W}(\text{S}_2\text{C}_2\text{S}_2\text{CO})_3]^{2-}$	24.9	SOLKEJ ^m
$[\text{W}(\text{S}_2\text{C}_2(\text{CF}_3)_2)_3]^{2-}$	15.8	QUQBFA ⁱ
$[\text{W}(\text{S}_2\text{C}_2(\text{CN})_2)_3]^-$	27.8	ASCETU ^j
$[\text{Tc}(\text{S}_2\text{C}_2(\text{CN})_2)_3]^{2-}$	38.9	GOKCUE ⁿ

Notes: (a) Eisenberg & Ibers (1966); (b) this work; (c) Lewis & Dance (2000); (d) Lim *et al.* (2000); (e) Fomitchev *et al.* (2001); (f) Matsubayashi *et al.* (1992); (g) Matsubayashi *et al.* (1993); (h) Mo atom on $\bar{6}$ position; (i) Wang *et al.* (1999); (j) Brown & Stiefel (1973); (k) Goddard & Holm (1999); (l) two unique molecules; (m) Yang *et al.* (1991); (n) Colmanet & Mackay (1988).

The current standard setting differs from the original cell setting, which was chosen arbitrarily based on preliminary precession photographs (Eisenberg & Ibers, 1966), by the transformation $[001/011/\bar{1}01]$. H atoms were placed geometrically and refined with relative isotropic displacement parameters. The maximum residual peak and hole in the final difference map, located 0.86 and 0.82 Å from the Re atom, respectively, are probably a result of residual absorption or Fourier termination errors.

Data collection: APEX2 (Bruker, 2004); cell refinement: SAINT (Bruker, 2003); data reduction: SAINT; program(s) used to solve

structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2000); software used to prepare material for publication: *SHELXTL*.

We once again thank Professor G. N. Schrauzer for the very robust crystals he supplied 40 years ago.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3033). Services for accessing these data are described at the back of the journal.

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