Acta Cryst. (1979). B**35**, 2317–2321

A Neutron Diffraction Study of Yttrium Tris(ethyl sulfate) Nonahydrate, $Y(C_2H_5SO_4)_3.9H_2O$*

By Robert W. Broach and Jack M. Williams†

Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439, *USA*

and Gian P. Felcher and David G. Hinks

Solid State Science Division, Argonne National Laboratory, Argonne, Illinois 60439, *USA*

(*Received* 12 *December* 1978; *accepted* 1 *June* 1979)

Abstract

The low-temperature (110 K) crystal and molecular structure of $Y(C_2H_5SO_4)_3.9H_2O$, $3C_2H_5O_4S^-.Y^{3+}.9H_2O$, has been determined by single-crystal neutron diffraction techniques. Lattice parameters at 110 K for the hexagonal space group $P6_3/m$ are a = 13·871 (5), c = 7·007 (3) Å, and V = 1167·5 Å^3. The structure was refined using the 847 unique data with a maximum $\sin\theta/\lambda$ = 0·619 Å^{-1} [λ = 1·142 (1) Å] to $R(F_o)$ = 0·073, $R(F_o^2)$ = 0·059, and $Rw(F_o^2)$ = 0·085. The basic coordination sphere around the Y ion involves nine water molecules in a tricapped trigonal-prismatic array. Successful refinement of the H positions in the space group $P6_3/m$ indicates the point symmetry of the Y ion is $\bar{6}$. Two hydrogen bonds link each of the two independent water molecules to two ethyl sulfate oxygen (O_S) atoms. Bond lengths and angles involving the axial (ax) and trigonal-prismatic (tp) waters are $Y-O_{ax}$ = 2·518 (2), $Y-O_{tp}$ = 2·368 (2), $O-H_{ax}$ = 0·963 (3), $O-H_{tp}$ = 0·957 (4), 0·963 (4), $H_{ax}\cdots O_S$ = 1·887 (3), and $H_{tp}\cdots O_S$ = 1·790 (3), 1·885 (3) Å; $H_{ax}-O-H_{ax}$ = 106·8 (4) and $H_{tp}-O-H_{tp}$ = 106·6 (3)°.

Introduction

Yttrium tri(ethyl sulfate) (YES), because of its particular composition and crystalline structure, has been found to have important scientific applications. The compound has a high abundance of H, whose tiny nuclear moments are only slightly polarized by an external magnetic field (0·07% at 1 K for ~8 × 10^5 A m^{-1}); yet, if yttrium is partially substituted by a minute amount of ytterbium, whose electronic magnetic moment can be easily polarized, a polarization of the hydrogen nuclei can be obtained of the same order of magnitude as that of the paramagnetic impurity or a thousandfold that obtained for the undoped material. The principles under which a refrigeration of the proton spins can be achieved were described by Jeffries (1963) and Abragam (1963). Early experimental attempts on ytterbium-doped YES (Yb:YES) showed a sizeable proton polarization (Langley & Jeffries, 1966; McColl & Jeffries, 1970; Potter & Stapleton, 1972); but it was only recently (Button-Shafer, Lichti & Potter, 1977) that a large enough proton polarization was achieved (65% at a temperature of 1·25 K for ~8 × 10^5 A m^{-1} using a sample containing 0·02 at.% Yb in YES) to make this material suitable as a polarized proton target, which finds applications in nuclear and high-energy experiments, as well as in neutron-scattering research.

In a sample of Yb:YES, the Yb^{3+} cations are easily magnetized by a magnetic field applied parallel to the c axis of the hexagonal crystal. However, when the field is applied in a direction approximately normal to the c axis, the induced magnetization is quite small.

The anisotropy in the magnetic response of Yb^{3+} is due to the splitting of the energy levels of its electronic configuration ($4f^{13}$) in the presence of the crystal field. On the basis of the X-ray determination of the crystal structure (Fitzwater & Rundle, 1959) the symmetry of the Y site should be C_{3h} ($\bar{6}$). In a crystal field of such symmetry, the magnetic behavior of Yb^{3+} at low temperature is that of an effective spin $\frac{1}{2}$ system which can be aligned only parallel or antiparallel to the c axis of the hexagonal crystal. An external magnetic field applied along the c axis causes a large Zeeman splitting of the electronic levels of Yb (with a large polarization of the magnetic moments); if the field is approximately normal to the c axis, the Zeeman splitting of the Yb electronic levels is quite small, down to the order of magnitude of the Zeeman splitting of the protons. In this peculiar condition, the two magnetic systems couple and, with a double spin flip, polarization can be

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* Work performed under the auspices of the Office of Basic Energy Sciences of the US Department of Energy.

† Author to whom correspondence should be addressed.

transferred from one Yb ion to one H nucleus. In the spin refrigerator device, a Yb-doped crystal is set in a magnetic field rapidly rotating in the *ac* plane. Whenever the field is parallel to the *c* axis the Yb moments become highly polarized. If the rotation is fast enough to prevent relaxation, then whenever the field is normal to the *c* axis the polarization will be transmitted to adjacent protons, and by diffusion to protons further away. After an adequate number of cycles, the polarization of the proton bath becomes comparable to that of the polarization of the Yb impurities as averaged over one cycle.

The transfer of magnetic polarization from the rare-earth site has been the subject of extended studies (McColl & Jeffries, 1970; Wolfe & Jeffries, 1971; Potter & Stapleton, 1972). Yet it was not clear if the site symmetry of the rare-earth ion was exactly C_{3h}, or if a minute amount of distortion would prevent good coupling of the Yb and proton spins, thus inherently limiting the performance of this system as a spin refrigerator. Furthermore, a detailed evaluation of the transfer of magnetic polarization demands a knowledge of the positions of all the atoms. While the nonhydrogen atom positions are known from the X-ray structure refinement by Fitzwater & Rundle (1959), until this time the H positions have only been estimated, with the assumption that they conform to the $P6_3/m$ space group found for the heavier atoms. In the present experiment, we determined the H positions in yttrium tris(ethyl sulfate) nonahydrate by neutron diffraction; while the data were taken for a limited set of reflections (*h*, *k*, *l* positive), the refinement of the atomic positions, and the values obtained for the thermal coefficients, allowed us to infer some conclusions about the symmetry.

Experimental

Crystal preparation

The title compound was formed by reacting stoichiometric amounts of yttrium sulfate and barium ethyl sulfate in water. The solution was filtered to remove insoluble barium sulfate and evaporated under nitrogen. Large single crystals were grown in a rotary crystallizer containing about 2 litre of a saturated aqueous solution of YES. The temperature of the crystallizer was lowered by 0·15 K per day starting at 286·5 K. The growth rate was ~1·3 g per day and the final crystal weighed about 35 g. A box-shaped sample suitable for collection of neutron diffraction data with approximate dimensions 3·0 × 3·5 × 6·0 mm and weighing approximately 110 mg was cut from the larger single crystal.

Data collection

The specimen was sealed in a lead-glass capillary and mounted in an arbitrary orientation on the fully automated (Day & Hines, 1973) Electronics and Alloys four-circle diffractometer at the Argonne CP-5 reactor. The sample was cooled and maintained at 110 K using a cold N_2 stream device (Strouse, 1976) throughout the alignment and data collection. Alignment and data-collection procedures followed those outlined previously (Petersen, Dahl & Williams, 1974). Reflections were measured, using coupled θ–2θ scans, in one independent unit (one-twelfth sphere; $+h$, $+k$, $+l$) up to a maximum 2θ value of 90°. Step intervals were set at 0·1°, scan ranges at 50 steps when $2\theta \leq 70°$, 54 steps when $70° < 2\theta \leq 85°$, and 56 steps when $2\theta > 85°$. The diffracted-reflection intensities, I, and estimated errors, $\sigma(I)$, were obtained (Broach, 1977) from the step-scan data by optimizing the positions of the peak boundary points using a modification of the Lehmann & Larsen (1974) algorithm. Intensities were corrected for absorption and the minimum and maximum transmission coefficients were 0·400 and 0·541, respectively ($\mu_{\text{calc}} = 0{\cdot}2364\ \text{mm}^{-1}$).

The observed squared structure factors, F_o^2, were obtained from the intensities by application of the following equation (Peterson & Levy, 1952); $F_o^2 = (\omega I \times \sin 2\theta)/(I_o\lambda^3N^2V)$ where ω is the angular velocity of rotation of the crystal, θ the Bragg angle, I_o the incident intensity, λ the wavelength, N the number of unit cells per unit volume, and V the specimen volume. A well characterized NaCl crystal, for which precise absorption and secondary-extinction corrections had been made for all sampled reflections, was used to obtain I_o in order to place the F_o^2 on an approximate absolute scale. The variances of F_o^2 were calculated from $\sigma^2(F_o^2) = \sigma_c^2(F_o^2) + (0{\cdot}03\ F_o^2)^2$, where $\sigma_c^2(F_o^2)$ is determined from the counting statistics. The estimate of standard error of 0·03 was based on the maximum 3% variation in the intensities of two check reflections which were measured after every 90 data reflections. The total 971 data were then sorted and merged under $6/m$ symmetry to give 847 unique data, all of which were used in subsequent calculations. The agreement factor for averaged reflections, defined as $[\sum (F_o^2 - F_{o\text{av}}^2)/\sum (F_o^2)] \times 100\%$, was 4·1%. For reflections with negative intensities, F_o^2 was set to zero.

Hydrogen atom location and refinement

Four of the total of six independent H atoms were located from a difference Fourier map phased using the nonhydrogen positional parameters of Fitzwater & Rundle (1959). The two remaining H atoms were located from successive Fourier and least-squares analyses. Full-matrix least-squares refinement of the positional and anisotropic temperature factors for all atoms converged, with final discrepancy indices of $R(F_o) = 0{\cdot}073$, $R(F_o^2) = 0{\cdot}059$, and $R_w(F_o^2) = 0{\cdot}085$. The final data-to-parameter ratio was 7·8 and the standard deviation in an observation of unit weight was 1·05. The scale factor was 0·666 (3). In the later stages of refinement the data were corrected for secondary extinction (Zachariasen, 1967; Coppens & Hamilton, 1970), with a final isotropic extinction parameter $g = 0{\cdot}34\ (3) \times 10^{-4}$. At the conclusion of refinement, a difference Fourier synthesis of nuclear scattering density revealed no unusual features.

All least-squares refinements, using a modified version of *ORFLS* (Busing, Martin & Levy, 1962), were based on the minimization of $\sum w_i(F_o^2 - F_c^2)^2$, with the weights w_i set equal to $1/\sigma^2(F_o^2)$. The coherent neutron scattering lengths used (Bacon, 1972) were Y = 0·79, S = 0·28, O = 0·580, C = 0·665, and H = –0·374 (all in units of 10^{-14} m).

Crystal parameters at 100 K are given in Table 1. Positional parameters are given in Table 2.* Selected interatomic distances and bond angles are shown in Tables 3 and 4. Estimated standard deviations given in the tables were calculated (Busing, Martin & Levy, 1964) from the full variance–covariance matrix obtained from the last least-squares cycle. Molecular figures were drawn using the thermal ellipsoid plotting program *ORTEP* II (Johnson, 1976).

Table 1. *Crystal parameters at* 110 K *for* $\mathrm{Y(C_2H_5SO_4)_3.9H_2O}$

Lattice constants were determined from a least-squares fit of the setting angles for 23 carefully centered reflections with $40° < 2\theta < 60°$ at $\lambda = 1{\cdot}142\ (1)$ Å.

a = 13·871 (5) Å
c = 7·007 (3)
V = 1167·5 Å^3
Space group: $P6_3/m$ (C_{6h}^2, No. 176)
$Z = 2$
$M_r = 626{\cdot}5$
ρ(calc.) = 1·78 Mg m^{-3}

Table 2. *Final positional parameters for* $\mathrm{Y(C_2H_5SO_4)_3.9H_2O}$

	x	y	z
Y	0·3333	0·6667	0·2550
S	0·3163 (3)	0·3682 (3)	0·7500
O(1)	0·2464 (2)	0·4185 (2)	0·7500
O(2)	0·2293 (2)	0·2407 (2)	0·7500
O(3)	0·3827 (1)	0·3918 (1)	0·5777 (2)
O(4)	0·3525 (2)	0·4955 (2)	0·2500
O(5)	0·2130 (1)	0·5457 (1)	0·4891 (2)
C(1)	0·1807 (2)	0·0489 (2)	0·7500
C(2)	0·2738 (2)	0·1656 (2)	0·7500
H(1*A*)	0·0088 (4)	0·2208 (4)	0·7500
H(1*B*)	0·1303 (4)	0·0324 (3)	0·6299 (9)
H(2)	0·3232 (4)	0·1821 (3)	0·6251 (11)
H(4)	0·3638 (2)	0·4610 (2)	0·1397 (4)
H(5*A*)	0·1354 (2)	0·4965 (2)	0·4662 (4)
H(5*B*)	0·2367 (2)	0·5079 (2)	0·5763 (4)

Results and discussion

The structures of the hydrated rare-earth and yttrium tris(ethyl sulfates) were studied by Ketelaar (1937). With only limited X-ray data, reasonable rare-earth and S atomic positions were determined, and a prediction of the water polyhedron around the cation was suggested. By using more complete X-ray film data, Fitzwater & Rundle (1959) refined positions for all the non-hydrogen atoms in the erbium, yttrium, and praseodymium compounds. Their atomic parameters, and derived bond distances and angles involving the non-hydrogen atoms in the yttrium analogue compare favorably with the values determined in this study. However, corresponding errors are considerably smaller in the neutron diffraction refinement, particularly for parameters involving the lighter atoms.

As is shown in Fig. 1, the Y ion is surrounded by nine water molecules in a distorted tricapped trigonal-prismatic array. This geometry is common for Y,

Table 3. *Interatomic distances* (Å) *for* $\mathrm{Y(C_2H_5SO_4)_3.9H_2O}$

The superscript (i) refers to the symmetry position $y, y-x, 1-z$.

Y–O(4)	2·518 (2)	O(4)–H(4)	0·963 (3)
Y–O(5)	2·368 (2)	O(5)–H(5*A*)	0·957 (4)
Y···H(4)	3·182 (3)	O(5)–H(5*B*)	0·963 (4)
Y···H(5*A*)	2·988 (3)	O(1)···H(5*B*)	1·790 (3)
Y···H(5*B*)	2·987 (3)	O(3)···H(4)	1·887 (3)
S–O(1)	1·450 (4)	O(3)···H(5A^{i})	1·885 (3)
S–O(2)	1·566 (4)	C(1)–H(1*A*)	1·085 (5)
S–O(3)	1·453 (3)	C(1)–H(1*B*)	1·044 (6)
O(2)–C(2)	1·452 (3)	C(2)–H(2)	1·064 (6)
C(1)–C(2)	1·482 (3)		

Table 4. *Interatomic angles* (°) *for* $\mathrm{Y(C_2H_5SO_4)_3.9H_2O}$

Superscripts refer to symmetry positions listed below. If no superscript appears x,y,z is implied.

(i)	$1-y, 1+x-y, z$	(v)	$x-y, x, 1-z$
(ii)	$y-x, 1-x, z$	(vi)	$x, y, \frac{3}{2}-z$
(iii)	$x, y, \frac{1}{2}-z$	(vii)	$y, y-x, 1-z$
(iv)	$1-y, 1+x-y, \frac{1}{2}-z$	(viii)	$y-x, -x, z$

O(4)–Y–O(5)	72·59 (5)	O(1)–S–O(2)	102·7 (3)
O(4^{i})–Y–O(5)	134·76 (4)	O(1)–S–O(3)	113·1 (2)
O(4^{ii})–Y–O(5)	66·12 (5)	O(2)–S–O(3)	107·4 (2)
O(5)–Y–O(5^{i})	75·48 (6)	O(3)–S–O(3^{vi})	112·4 (3)
O(5)–Y–O(5^{iii})	90·05 (8)	S–O(2)–C(2)	116·5 (2)
O(5)–Y–O(5^{iv})	138·61 (3)	C(1)–C(2)–O(2)	109·5 (2)
Y–O(4)–H(4)	126·1 (2)	C(1)–C(2)–H(2)	110·6 (3)
Y–O(5)–H(5*A*)	122·0 (2)	O(2)–C(2)–H(2)	107·7 (3)
Y–O(5)–H(5*B*)	121·6 (2)	H(2)–C(2)–H(2^{vi})	110·7 (9)
H(4)–O(4)–H(4^{iii})	106·8 (4)	C(2)–C(1)–H(1A^{viii})	110·7 (3)
H(5*A*)–O(5)–H(5*B*)	106·6 (3)	C(2)–C(1)–H(1*B*)	111·2 (3)
O(4)–H(4)···O(3^{iii})	178·7 (3)	H(1A^{viii})–C(1)–H(1*B*)	108·1 (3)
O(5)–H(5*A*)···O(3^{v})	170·5 (3)	H(1*B*)–C(1)–H(1B^{vi})	107·5 (7)
O(5)–H(5*B*)···O(1)	166·5 (3)	S–O(1)···H(5*B*)	129·3 (1)
H(5*B*)···O(1)···H(B^{vi})	85·7 (2)	S–O(3)···H(4^{iii})	123·5 (2)
H(4^{iii})···O(3)···H(5A^{vii})	109·5 (1)	S–O(3)···H(5A^{vii})	127·0 (2)

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* Lists of structure factors and anisotropic thermal parameters and details of the mean planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34524 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

lanthanide, and actinide complexes (Sinha, 1976), including complexes of the type $M(H_2O)_9^{3+}$, and MX_3 (X = OH, Cl, F). Since the metal–ligand bonding is primarily electrostatic in nature, the nine ligands arrange themselves in a fashion which best preserves spherical symmetry and minimizes interligand repulsion. Utilizing simple geometrical arguments, Mackay, Finney & Gotoh (1977) have shown that the best manner in which to arrange nine equivalent ligands on a spherical surface, such that interligand repulsion is minimized, is that of a tricapped trigonal prism.

With regard to the water-molecule coordination about Y, the water dipoles do not point exactly toward the cation. Angles between the normals to the H—O—H planes and the Y—O vector are 98·5 and 61·9° for the water ligands containing O(4) and O(5) respectively. Deviations from 90° are presumably due to hydrogen bonding and packing forces. The point symmetry of the $Y(OH_2)_9^{3+}$ cation is C_{3h}. Ideally the symmetry could be D_{3h}, but there is a slight distortion involving rotation of the three axial O atoms along the threefold axis. The Y—O bond lengths to the two different water ligands are distinctly non-equivalent. The distance from the rare-earth ion to the trigonal-prism O atoms is 2·368 (2) Å, while it is 2·518 (2) Å to the axial O atoms. The same bond-length variation is observed for the isomorphous and isostructural compounds $M(C_2H_5SO_4)_3.9H_2O$ (M = Pr, Er) (Fitzwater & Rundle, 1959). However, in the compound $Nd(BrO_3)_3.9H_2O$ (Helmholz, 1939), in which the nine water molecules also form a tricapped trigonal prism around the lanthanide ion, the nine M—O distances are more nearly equal. Apparently in the ethyl sulfate complexes the bond lengthening of the axial ligands relative to the trigonal-prism ligands must be influenced by hydrogen-bonding effects. The hydrogen-bonding interactions with the ethyl sulfate anions are shown in Fig. 1. Further details are shown in a stereoview of the unit-cell contents given in Fig. 2. Each water molecule H atom is hydrogen bonded to one ethyl sulfate O atom. Significantly, the ethyl sulfate O to water H distance for the axial water ligands [O(3)···H(4) = 1·887 (3) Å] is longer than the mean of the two distances to the trigonal-prism water ligands [1·838 (av.); O(1)···H(5B) = 1·790 (3) and O(3)···H(5A) = 1·885 (3) Å], which is an indication that the axial Y—O bonds are stretched to accommodate reasonable O···H hydrogen-bonding interactions. This stretching is also accompanied by the above-mentioned twist which distorts the coordination sphere from D_{3h} to C_{3h} symmetry. These conclusions are in agreement with those reached by Fitzwater & Rundle (1959), which were based on reasonable assumptions for the type of hydrogen bonding involved. As shown in Fig. 3, the two O atoms, O(1) and O(3), of the ethyl sulfate anions are hydrogen bonded to water molecules. The O—H···O angles are nearly linear [O(4)–H(4)···O(3) = 178·7 (3), O(5)–H(5)···O(3) = 170·5 (3), and O(5)–H(5B)···O(1) = 166·5 (3)°]. The group S, O(3), H(4), H(5A) is strictly planar, but the group S, O(1), H(5B), H(5B') is slightly distorted from planarity. Distances and angles among the non-hydrogen atoms in the ethyl sulfate anion compare favorably with those observed in potassium ethyl sulfate (Truter, 1958; Jarvis, 1953).

The only evidence from the refinements that the space-group symmetry could be lower than $P6_3/m$ comes from the fact that the thermal motion for H atoms on the ethyl sulfate anion [in particular atom H(2)] is

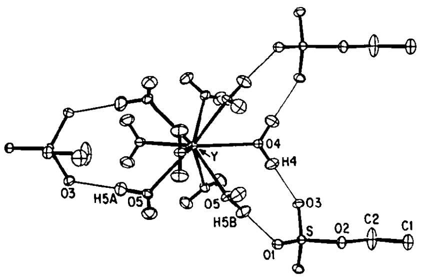

Fig. 1. Molecular configuration of the $Y(OH_2)_9^{3+}$ cation in $Y(C_2H_5SO_4)_3.9H_2O$ determined by neutron diffraction at 110 K. Three of the nine symmetry-related ethyl sulfate anions which are hydrogen bonded to the water ligands are shown. The ellipsoids of thermal motion for all atoms in this figure and in Fig. 3 are scaled to enclose 50% probability.

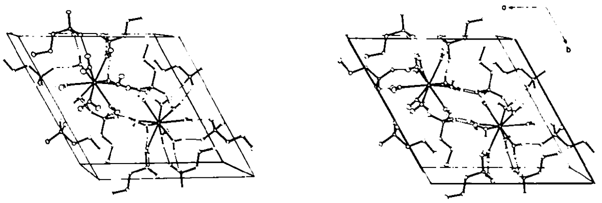

Fig. 2. Stereoview of the unit cell of $Y(C_2H_5SO_4)_3.9H_2O$. Lighter bonds indicate hydrogen-bonding interactions.

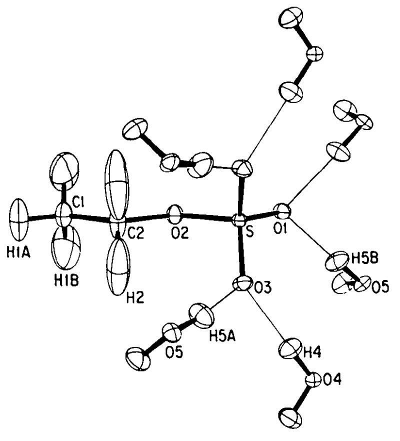

Fig. 3. The ethyl sulfate anion with associated hydrogen-bonded water atoms in $Y(C_2H_5SO_4)_3.9H_2O$.

rather large (see Fig. 3). For this reason an attempt was made to refine the structure in the noncentrosymmetric space group $P6_3$. Isotropic least-squares refinement converged with positional and isotropic thermal parameters equivalent within error to those obtained in the similar refinement in the centrosymmetric space group, except for atoms H(1*A*), H(1*B*), and H(2) on the ethyl sulfate group. However, attempts to continue refinement with anisotropic thermal parameters were unsuccessful, in that the temperature factors for the S atom and atom H(1*A*) became non-positive definite. It is our feeling that the true space group is $P6_3/m$, and that the large ellipsoids for the ethyl sulfate hydrogens are due to extreme thermal motion. It is possible that the H atoms are disordered, in which case a lowering of the local symmetry of the Y site is not completely ruled out. However, since the $Y(OH_2)_9^{3+}$ moiety still conformed, within error, to C_{3h} site symmetry when refinement was attempted in the $P6_3$ space group, it is likely that the possible perturbation of the crystal-field levels of Yb^{3+} (which partially substitutes Y in the crystals used in a spin refrigerator) would be extremely small.

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Acta Cryst. (1979). B**35**, 2321–2325

The Crystal and Molecular Structure of *μ*-Carbonyl-bis(*η*-cyclopentadienyl)-*μ*-*η*-(hexafluoro-2-butyne)-dirhodium(*Rh*–*Rh*)

By Ron S. Dickson and Geoff N. Pain

Department of Chemistry, Monash University, Wellington Road, Clayton, Victoria, Australia 3168

and Maureen F. Mackay

Department of Physical Chemistry, La Trobe University, Bundoora, Victoria, Australia 3083

(*Received* 8 *May* 1979; *accepted* 20 *June* 1979)

Abstract

The structure of $Rh_2(C_4F_6)(C_5H_5)_2(CO)$, $C_{15}H_{10}F_6ORh_2$, has been determined from 4084 diffractometer data and refined to $R = 0.043$. The compound is triclinic, space group $P\bar{1}$, with $a = 8.907\,(4)$, $b = 9.534\,(2)$, $c = 10.269\,(5)$ Å, $\alpha = 90.57\,(4)$, $\beta = 106.35\,(4)$, $\gamma = 92.56\,(3)$°, $Z = 2$. The hexafluoro-2-butyne ligand is *cis* bent and lies perpendicular to and 1.41 Å above the Rh–Rh bond. The coordinated C≡C

0567-7408/79/102321-05$01.00