between the ligands coordinated to two centrosymmetrically related Mo atoms. A similar but consequently greater deviation (mean value 12°) was found in the structure of the analogous *i*-propoxo complex (Chisholm *et al.*, 1981).

The Mo_2O_2 bridging system is almost square planar, the internal angles O(1)—Mo—O(1′) and Mo—O(1)—Mo′ being 95·3 (3) and 84·7 (3)°, respectively. The lateral distances Mo—O(1) and Mo—O(1′) are equal within experimental error [2·027 (5) and 2·029 (5) Å]. The bond lengths Mo—Cl(1) of 2·391 (2) and Mo—Cl(2) of 2·393 (2) Å agree with the values of 2·317 (3) and 2·360 (4) Å found in $Mo_2Cl_4(OPh)_6$ (Kamenar & Penavić, 1977) and agree even better with those of 2·421 (2) and 2·416 (1) Å in the above mentioned $Mo_2Cl_4(O\text{-}i\text{-}Pr)_6$. However, all these Mo—Cl bond lengths are considerably longer than molybdenum—terminal-chlorine bond lengths of 2·26 (2) Å in $MoCl_3O$ (Drew & Tomkins, 1970), and of 2·24 (3) Å in Mo_2Cl_{10} (Sands & Zalkin, 1959). This bond lengthening may indicate the *trans* influence of the alkoxo ligands. The bond lengths between Mo and terminal methoxo O atoms [Mo—O(2) of 1·811 (5) and Mo—O(3) of 1·801 (5) Å] are short and suggest Mo=O double bonds (Schröder, 1975; Manojlović-Muir & Muir, 1972), indicating the existence of additional π bonding between the metal and alkoxo ligands (Huffman, Molloy, Marsella & Caulton, 1980). The same shortening of the Mo—O*R* bonds was found in the Mo—phenoxo (Kamenar & Penavić, 1977) and Mo—propoxo complexes (Chisholm *et al.*, 1981); in both structures such Mo—O bond lengths have a mean value of 1·81 Å. The Mo—Mo bond is also of interest because in the Mo complexes it varies with the metal oxidation state, the nature of the bridging ligands, as well as with the steric and electronic properties of the terminal ligands. In this structure the Mo—Mo bond length of 2·733 (1) Å is of the d^1—d^1 type and corresponds to a single bond (Cotton, 1977). It is the same as already found in the above mentioned analogous Mo(chloro)(propoxo) [2·731 (1) Å] and Mo(bromo)(propoxo) [2·739 (1) Å] complexes.

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Structure of Tris(thioacetyltrifluoroacetonato)rhodium(III)

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Abstract. $[Rh(C_5H_4F_3OS)_3]$, $M_r = 610{\cdot}340$, monoclinic, $P2_1/n$, $a = 9{\cdot}065\,(2)$, $b = 13{\cdot}302\,(2)$, $c = 18{\cdot}360\,(2)$ Å, $\beta = 93{\cdot}08\,(2)°$, $V = 2210{\cdot}7$ Å^3, $Z = 4$, $D_x = 1{\cdot}833$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 22{\cdot}2$ cm^{-1}, $F(000) = 1200$, $T = 294$ K, $R = 0{\cdot}043$ for 2206 unique observed reflections. The octahedral

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RhL_3 complex exhibits approximate C_3 symmetry with a *facial* arrangement of the S atoms. An intraligand F···H bond of 2·26 Å is inferred from the structure analysis. A comparison with other metal monothio-β-ketoenolates suggests that metal→ligand π bonding is manifested in the present Rh complex to a significant extent in the metal—sulfur bonds and only negligibly in the metal—oxygen bonds.

Introduction. Monothio-β-ketoenols (HL) form stable complexes with class b metals (M). Structural studies by X-ray crystallography have shown that ML_3 complexes adopt a six-coordinate *facial* pseudo-octahedral geometry (Bandoli, Mazzi, Spies, Münze, Ludwig, Ulhemann & Scheller, 1987; Hoskins & Pannan, 1975; Ollis, Das, James, Livingston & Nimgirawath, 1976; Sreelatha, Gupta, Narula & Nöth, 1985) while a *cis* geometry has been observed for a square-planar Ni^{II} complex (Siiman, Titus, Cowman, Fresco & Gray, 1974). To complement our other studies (mass, IR and NMR spectroscopies) of transition-metal complexes formed from these ligands we have determined the structure of tris(thioacetyltrifluoroacetonato)rhodium(III), which is shown by our ^{19}F NMR studies to exist as the *facial* isomer in organic solvents. This observation is confirmed by the present study which also provides insights into the bonding in the chelate ring, and between rhodium and the ligand.

Experimental. Crystals of the title compound were grown by sublimation in a vacuum. The one chosen for data collection measured 0·8 × 0·6 × 0·5 mm and could not be cut to smaller dimensions because of the extremely fragile nature of the crystals. Reflection data were measured on a Nicolet *R*3*m* automated diffractometer; orientation and unit-cell constants from 20 centered reflections; data collected in the range $3 \leq 2\theta \leq 58°$ using an ω–2θ scan mode; scan speeds in the range 0·49–29·30° min^{-1}; 3298 reflections measured in the region of reciprocal space bounded by $\pm h, k, l$; space group determined uniquely from absences; 2915 considered unique after symmetry equivalents were averaged ($R_{\rm sym}$ = 0·011); 2206 reflections considered observed with $I \geq 3\sigma(I)$, where $\sigma(I) = {\rm SR(SC + BL + BR)}^{1/2}$, SR = scan rate, SC = total scan count, BL, BR are left and right backgrounds; no scaling required for the negligible intensity variation; corrections for Lorentz, polarization and absorption effects applied to the data.

A Patterson map revealed the position of the Rh atom. Refinement of Rh, followed by difference Fourier syntheses, yielded the remaining non-H atoms. Chemically reasonable positions for most H atoms were observed in difference maps. However, refinement of these positions as H atoms would not converge. Therefore, H atoms were placed at calculated positions (near observed electron density peaks) with fixed isotropic temperature factors and included in the structure-factor calculations, but not refined. The anisotropic thermal parameters and positions of all non-H atoms were refined by full-matrix least-squares procedures. Convergence was reached at R = 0·043 and wR = 0·037. Analysis of the error distribution over ranges of F_o, $(\sin\theta)/\lambda$ and the indices confirmed the suitability of the chosen weights, $w = \sigma(F_o)^{-2}$ in the function minimized during refinement, $\sum w(|F_o| - k|F_c|)^2$. For all 2915 data, R = 0·080 and wR = 0·039; mean and max. Δ/σ on last cycle were 0·004 and 0·048, respectively, and the goodness of fit, S = 1·876. A final difference map showed max. and min. residuals of 0·628 and −0·544 e Å^{-3}. Anomalous scattering was assumed for Rh and S; scattering factors for all non-H atoms were from Cromer & Mann (1968), and from Stewart, Davidson & Simpson (1965) for H atoms.* Final atomic positional parameters and equivalent isotropic thermal parameters are given in Table 1.†

Discussion. Because monothio-β-diketones act as bidentate ligands, this complex is expected to adopt a pseudo-octahedral geometry about the Rh atom. The results of the structure determination confirm this, showing that it possesses a *facial* octahedral geometry about rhodium (Fig. 1).

All Rh—S bond lengths are equal within experimental error and the S—Rh—S angles show a range of only 1·3° (Table 2). Consequently, the S atoms lie at the vertices of an almost perfect equilateral triangle. Although there are no significant differences among the Rh—O bonds, the O—Rh—O angles differ from each other by as much as 4·1°, with the result that only two edges of the triangle defined by the O atoms are of equal length [O(1)···O(2), 2·890 (6); O(1)···(3), 2·868 (6); O(2)···O(3), 2·773 (3) Å]. The most prominent distortion from ideal octahedral angles is found in the O(2)—Rh—O(3) angle (83·8°). Based on the sum of the bond angles about the ring C atoms and the

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* Computation was carried out on the University of Manitoba Computer Services Department's Amdahl 580/5850 mainframe computer using locally written programs for processing and modified versions of the following programs for structure solution, refinement and calculations: *FORDAP* (A. Zalkin, unpublished); *ORFLS* (Busing, Martin & Levy, 1962); *ORFFE* (Busing, Martin & Levy, 1964); *ORTEP*II (Johnson, 1976).

† Tables of H-atom positional and isotropic thermal parameters, anisotropic thermal parameters, bond distances and angles involving H atoms, torsion angles and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52216 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final positional parameters (fractional* × 10^5 *for* Rh *and* S, × 10^4 *for* C, O *and* F) *and equivalent isotropic thermal parameters* (Å^2 × 10^3) *with e.s.d.'s in parentheses*

	x	y	z	U_{eq}*
Rh(1)	1551 (6)	−1493 (4)	21890 (3)	52
S(1)	12461 (23)	−8850 (16)	12505 (11)	69
S(2)	24033 (21)	3713 (15)	26176 (11)	66
S(3)	5593 (22)	−15717 (15)	28419 (11)	70
C(1)	1675 (8)	−6 (7)	655 (4)	69
C(3)	1371 (9)	1007 (7)	667 (4)	69
C(2)	2531 (8)	−410 (6)	28 (4)	91
O(1)	−162 (5)	1236 (3)	1665 (2)	54
C(6)	2274 (8)	784 (5)	3475 (4)	63
C(9)	−410 (9)	664 (5)	3651 (4)	56
C(10)	−1611 (11)	798 (8)	4207 (5)	83
F(10*a*)	−2228 (6)	−72 (4)	4332 (3)	131
F(10*b*)	−1091 (6)	1132 (5)	4843 (3)	127
F(10*c*)	−2648 (5)	1419 (4)	3978 (3)	112
O(2)	−998 (5)	419 (3)	3042 (3)	58
C(11)	−999 (9)	−2252 (5)	2807 (4)	67
C(13)	−2315 (8)	−2067 (5)	2411 (5)	65
C(14)	−2670 (8)	−1287 (6)	1932 (4)	55
C(15)	−4196 (10)	−1300 (7)	1534 (6)	79
F(15*a*)	−4067 (6)	−1636 (5)	865 (3)	133
F(15*b*)	−5114 (5)	−1942 (4)	1807 (3)	124
F(15*c*)	−4798 (5)	−449 (4)	1474 (3)	121
O(3)	−1938 (5)	−539 (4)	1758 (2)	59
F(5*a*)	−1161 (7)	2796 (4)	762 (4)	150
F(5*b*)	411 (8)	3193 (4)	1519 (4)	152
F(5*c*)	961 (8)	3024 (4)	468 (4)	183
C(4)	490 (8)	1526 (6)	1125 (4)	60
C(8)	1035 (9)	836 (6)	3881 (4)	64
C(12)	−879 (9)	−3201 (6)	3262 (5)	97
C(7)	3727 (9)	1101 (7)	3837 (4)	91
C(5)	200 (12)	2631 (8)	958 (6)	87

* $U_{eq} = \frac{1}{3}$(trace of the diagonalized anisotropic-temperature-factor matrix).

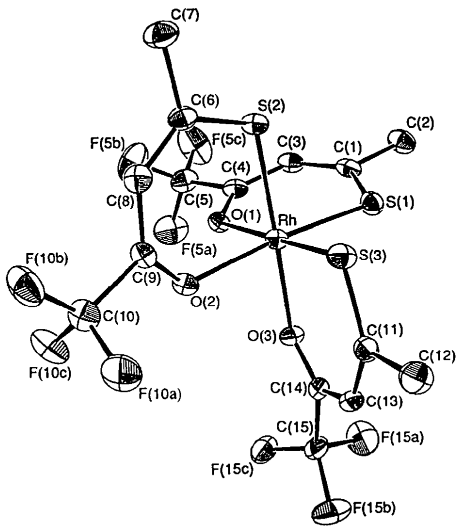


Fig. 1. *ORTEP* plot (Johnson, 1976) of the tris(thioacetyltrifluoroacetonato)rhodium(III) complex with ellipsoids at 50% probability level.

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Rh(1)—S(1)	2·256 (2)	C(9)—C(8)	1·373 (9)
Rh(1)—S(2)	2·254 (2)	C(10)—F(10*a*)	1·311 (9)
Rh(1)—S(3)	2·259 (2)	C(10)—F(10*b*)	1·313 (9)
Rh(1)—O(1)	2·091 (4)	C(10)—F(10*c*)	1·304 (9)
Rh(1)—O(2)	2·073 (5)	C(11)—C(13)	1·385 (10)
Rh(1)—O(3)	2·081 (4)	C(11)—C(12)	1·514 (10)
S(1)—C(1)	1·661 (8)	C(13)—C(14)	1·388 (9)
S(2)—C(6)	1·678 (8)	C(14)—C(15)	1·530 (10)
S(3)—C(11)	1·676 (7)	C(14)—O(3)	1·246 (7)
C(1)—C(3)	1·377 (10)	C(15)—F(15*a*)	1·317 (10)
C(1)—C(2)	1·519 (10)	C(15)—F(15*b*)	1·311 (9)
C(3)—C(4)	1·375 (10)	C(15)—F(15*c*)	1·259 (9)
O(1)—C(4)	1·244 (8)	F(5a)—C(5)	1·286 (10)
C(6)—C(8)	1·383 (9)	F(5b)—C(5)	1·279 (10)
C(6)—C(7)	1·503 (9)	F(5c)—C(5)	1·275 (10)
C(9)—C(10)	1·543 (11)	C(4)—C(5)	1·522 (11)
C(9)—O(2)	1·255 (8)		
S(1)—Rh(1)—S(2)	88·55 (8)	C(9)—C(10)—F(10*b*)	113·3 (8)
S(1)—Rh(1)—S(3)	88·66 (8)	C(9)—C(10)—F(10*c*)	112·4 (7)
S(1)—Rh(1)—O(1)	94·95 (14)	F(10*a*)—C(10)—F(10*b*)	106·2 (8)
S(1)—Rh(1)—O(2)	174·53 (14)	F(10*a*)—C(10)—F(10*c*)	108·0 (9)
S(1)—Rh(1)—O(3)	91·71 (14)	F(10*b*)—C(10)—F(10*c*)	106·9 (9)
S(2)—Rh(1)—S(3)	87·38 (7)	Rh(1)—O(2)—C(9)	124·1 (5)
S(2)—Rh(1)—O(1)	89·38 (13)	S(3)—C(11)—C(13)	128·6 (6)
S(2)—Rh(1)—O(2)	96·17 (14)	S(3)—C(11)—C(12)	113·2 (6)
S(2)—Rh(1)—O(3)	176·22 (14)	C(13)—C(11)—C(12)	118·2 (7)
S(3)—Rh(1)—O(1)	175·08 (14)	C(11)—C(13)—C(14)	129·0 (7)
S(3)—Rh(1)—O(2)	88·78 (13)	C(13)—C(14)—C(15)	117·9 (7)
S(3)—Rh(1)—O(3)	96·40 (14)	C(13)—C(14)—O(3)	130·6 (7)
O(1)—Rh(1)—O(2)	87·9 (2)	C(15)—C(14)—O(3)	111·5 (7)
O(1)—Rh(1)—O(3)	86·8 (2)	C(14)—C(15)—F(15*a*)	109·0 (8)
O(2)—Rh(1)—O(3)	83·8 (2)	C(14)—C(15)—F(15*b*)	113·6 (8)
Rh(1)—S(1)—C(1)	109·0 (3)	C(14)—C(15)—F(15*c*)	114·0 (7)
Rh(1)—S(2)—C(6)	108·7 (3)	F(15*a*)—C(15)—F(15*b*)	103·1 (7)
Rh(1)—S(3)—C(11)	108·6 (3)	F(15*a*)—C(15)—F(15*c*)	106·5 (9)
S(1)—C(1)—C(3)	128·6 (6)	F(15*b*)—C(15)—F(15*c*)	109·7 (8)
S(1)—C(1)—C(2)	113·4 (7)	Rh(1)—O(3)—C(14)	126·1 (5)
C(3)—C(1)—C(2)	118·0 (8)	C(3)—C(4)—O(1)	130·5 (8)
C(1)—C(3)—C(4)	128·6 (8)	C(3)—C(4)—C(5)	117·5 (8)
Rh(1)—O(1)—C(4)	125·5 (5)	O(1)—C(4)—C(5)	112·0 (8)
S(2)—C(6)—C(8)	128·4 (6)	C(6)—C(8)—C(9)	127·9 (7)
S(2)—C(6)—C(7)	113·7 (6)	F(5*a*)—C(5)—F(5*b*)	103·0 (10)
C(8)—C(6)—C(7)	117·8 (7)	F(5*a*)—C(5)—F(5*c*)	106·2 (9)
C(10)—C(9)—O(2)	109·8 (7)	F(5*a*)—C(5)—C(4)	112·0 (8)
C(10)—C(9)—C(8)	118·2 (8)	F(5*b*)—C(5)—F(5*c*)	105·4 (9)
O(2)—C(9)—C(8)	132·0 (7)	F(5*b*)—C(5)—C(4)	112·7 (8)
C(9)—C(10)—F(10*a*)	109·7 (8)	F(5*c*)—C(5)—C(4)	116·3 (9)

Table 3. *Least-squares planes by Hamilton's* (1961) *method*

Plane	Equation/deviations from plane (Å)	Defining atoms/average deviation (Å)
1	$7{\cdot}5091x + 3{\cdot}1206y + 8{\cdot}5090z - 1{\cdot}8276 = 0$ Rh, 0·105; S(1), −0·104; O(1), −0·146	C(1), C(2), C(3), C(4), C(5) 0·039
2	$1{\cdot}0496x + 12{\cdot}550y + 5{\cdot}5801z - 1{\cdot}1848 = 0$ Rh, 0·240; S(2), 0·062; O(2), −0·118	C(6), C(7), C(8), C(9), C(10) 0·022
3	$3{\cdot}7511x - 6{\cdot}5660y - 14{\cdot}422z + 2{\cdot}9542 = 0$ Rh, −0·049; S(3), 0·095; O(3), 0·044	C(11), C(12), C(13), C(14), C(15) 0·018

approximate planarity of the ligand, all of the C atoms that are part of the chelate rings appear to be sp^2-hybridized. It is interesting to note, however, that the C—C—C angles of the central methine unit have widened to *ca* 129°.

Overall, the complex exhibits approximate C_3 symmetry with the rotation axis passing through the Rh atom and the center of the triangle defined by the S atoms. Slight differences in the conformations of the CF_3 groups prevent the ligands from possessing C_s symmetry. Furthermore, least-squares planes calculated with various combinatons of the atoms belonging to the chelate rings and their substituents showed that no moiety of four atoms or greater was truly planar. The lack of planarity suggests that the ring C atoms are not perfectly sp^2-hybridized. The carbon skeletons of the ligands were found to constitute the closest approximations to planes, with the Rh, S and O atoms of the respective ligands deviating from the planes in an irregular manner (Table 3).

Table 4. *Mean bond lengths and related lengths* (Å) *in chelate rings of monothio-β-ketoenolates,* $M(R_s\text{CSCHCOR}_o)_n$

The subscripts S and O identify atoms and groups on the S and O sides of the chelate ring respectively.

	$\text{Fe}^{\text{III}}L_3$	$\text{In}^{\text{III}}L_3$	$\text{Fe}^{\text{III}}L_3$	$\text{Tc}^{\text{III}}L_3$†	$\text{Co}^{\text{III}}L_3$	$\text{Rh}^{\text{III}}L_3$
R_s, R_o	C_6H_5, CH_3	C_6H_5, CH_3	C_6H_5, CF_3	C_6H_5, C_6H_5	CH_3, CF_3	CH_3, CF_3
Configuration	$(t_{2g})^3(e_g)^2$	d^{10}	$(t_{2g})^5$	$(t_{2g})^4$	$(t_{2g})^6$	$(t_{2g})^6$
Reference	1	2	1	3	4	5
M—S (a)	2·368 (2)	2·527 (3)	2·239 (2)	2·330 (4)	2·195 (1)	2·256 (2)
M—O (b)	1·988 (4)	2·205 (3)	1·942 (4)	2·053 (4)	1·944 (2)	2·082 (4)
C_S—S	1·705 (4)	1·728 (4)	1·693 (6)	1·707 (10)	1·703 (3)	1·672 (8)
C_O—O	1·259 (6)	1·257 (4)	1·260 (7)	1·267 (20)	1·253 (3)	1·248 (8)
C_S—C	1·378 (7)	1·369 (5)	1·380 (8)	1·360 (20)	1·372 (4)	1·382 (10)
C_O—C	1·403 (7)	1·432 (5)	1·382 (8)	1·427 (20)	1·393 (4)	1·379 (10)
$a-b$	0·380 (5)	0·322 (5)	0·297 (5)	0·277 (6)	0·251 (3)	0·174 (5)
r*	0·79	0·94	0·69	(0·79)	0·69	0·81
$a-r$	1·58	1·59	1·55	(1·54)	1·51	1·45
$b-r$	1·20	1·27	1·25	(1·26)	1·25	1·27

References: (1) Hoskins & Pannan (1975); (2) Sreelátha *et al.* (1985); (3) Bandoli *et al.* (1987); (4) Ollis *et al.* (1976); (5) present study.

*Ionic radii (r) are from Cotton & Wilkinson (1988).

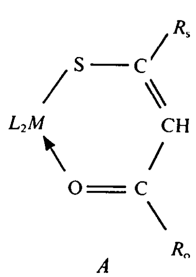
†Values in parentheses for Tc^{III} are derived by assuming that $b-r = 1{\cdot}26$ Å, for consistency with values for the other complexes.

Intramolecular hydrogen bonding between an F atom of each CF_3 group and the H atom of the central methine moiety can be inferred from the structure. In ring 1 [S(1),C(1),...], the deviations of F(5*c*) and H(3) from the plane defined by C(3), C(4) and C(5) are −0·187 and −0·126 Å, respectively; the F···H distance of 2·26 Å is 0·44 Å less than the sum of the van der Waals radii of the two atoms (Bondi, 1964) and the C—F···H angle is 85·6°. This geometry suggests an intramolecular F···H interaction. The F···H distances in the other two ligands are 2·24 and 2·28 Å, with the H and F atoms in each of these ligands lying similarly close to their respective C—C—C planes.

Mean bond lengths in the chelate rings of the present rhodium complex and monothio-β-ketoenolates of other metal ions are given in Table 4. Each of the ML_3 complexes is pseudo-octahedral, with a *facial* arrangement of S atoms. The data have been arranged so that, on proceeding from left to right across this table, the difference between metal—sulfur and metal—oxygen bond lengths decreases.

In the following discussion we consider that variation of the metal ion plays the major role in effecting changes in the chelate ring because any *d* electrons that the metal possesses are *directly* involved in metal—ring bonding. Substituents attached to the chelate ring could also have some influence, but their effects (inductive and mesomeric) are probably less important. The metal—sulfur and metal—oxygen bond lengths in these complexes can be compared by attempting to remove the effects of differing sizes of the metal ions by assuming that their sizes are proportional to tabulated ionic radii. The values given in Table 4 are ionic radii of metal ions in a similar coordination environment and high/low-spin state to those in the corresponding complexes. When these radii are subtracted from the metal—oxygen bond lengths a nearly constant value (1·26 ± 0·01 Å) for the difference is obtained (with the exception of high-spin Fe^{III}, for which a significantly lower value is given). The value of 1·26 Å is somewhat larger than the 1·19 ± 0·01 Å value that results from a similar treatment of β-ketoenolate complexes (De Villiers & Boeyens, 1972; Hon, Pfluger & Belford, 1966, 1967; Iball & Morgan, 1967; Mehrotra, Bohra & Gaur, 1978; Morosin & Brathovde, 1964; Okeya, Ooi, Matsumoto, Nakamura & Kawaguchi, 1981; Palenik & Dymock, 1980; Rodriguez, Cano & García-Blanco, 1979; Wenclawiak, Pinkerton & Terrill, 1988) and implies that, in the monothio complexes, there is little shortening of the metal—oxygen bond due to covalency and that metal—ligand π bonding makes a minor contribution to the metal—oxygen bonding. On the other hand, when the ionic radii are subtracted from the metal—sulfur bond lengths there is a significant decrease in the resulting differences for ML_3 complexes on proceeding from left to right of Table 4. The shortening of the metal—sulfur bond implied by this decrease can be assigned to increasing metal→sulfur $d\pi$ bonding in this sequence. Such bonding requires the presence of electrons in metal t_{2g} orbitals (in O_h symmetry) but their bonding effects are reduced by the presence of electrons in metal e_g orbitals. Furthermore, metal→ligand π bonding is stronger for second- than for first-series transition elements. Thus, it is possible to predict that metal→ligand π bonding should increase according to: high-spin Fe^{III} < [low-spin Fe^{III}, Tc^{III}] < Co^{III} < Rh^{III}, an order consistent with the trends in Table 4 and with known trends in the properties of this set of transition metals. It is also possible to predict that metal→sulfur π bonding should make a minor contribution in the case of In^{III} complexes, again in agreement with the trends observed in Table 4.

The carbon—oxygen bond lengths in the monothio complexes (Table 4) fall in the narrow range 1·26 ± 0·01 Å and are only slightly longer than that typical for a double bond (1·24 Å). In contrast, the carbon—sulfur bond length in the Rh^{III} complex is significantly shorter than in the other ML_3 complexes, reflecting an increase in metal→sulfur π bonding. Furthermore, in the RhL_3 complex the carbon—carbon bond lengths are equal. These observations are all consistent with the following qualitative description of the bonding in the metal–chelate ring, which again assumes a major role for the metal. The inequality of the two carbon—carbon bond lengths for some ML_3 complexes is usually explained by predominance of the canonical form, *A*. With increasing π electron density in the ring, caused by enhanced metal→ligand π bonding, the increased carbon—sulfur bond order results in bond shortening. On the other hand, there is little scope for shortening the carbon—oxygen bond, which has an order of two in the predominating canonical form. Also to be expected, the chelate ring becomes more aromatic, *i.e.* both carbon—carbon bond lengths approach 1·39 Å, the value in benzene, as the ring π-electron density increases.



A

In the crystal structure (Fig. 2), centrosymmetrically related molecules pack such that ring 1, characterized by S(1),C(1),... of one molecule is parallel to ring 1 of the other molecule and each has its methyl group lying almost directly above C(4) of the symmetry-related ring. While the major packing consideration appears to be accommodation of the bulky CF_3 groups, which are perfectly staggered with respect to each other in a centrosymmetrically related pair of molecules, a stabilizing π–π orbital interaction between the rings is not impossible, given the parallel orientation of these rings and their interplanar spacing of 3·40 Å; C(1) is above, but offset slightly from C(3) of the symmetry-related molecule and at a distance of 3·81 Å.

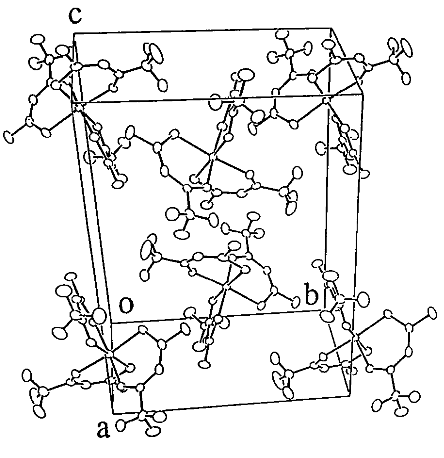


Fig. 2. Packing diagram of the tris(thioacetyltrifluoroacetonato)-rhodium(III) complex.

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