# Distorted Dodecahedral Co-ordination in the Crystal Structure of Isoquinolinium Tetrakis[4,4,4-trifluoro-1-(2-thienyl)butane-1,3-dionato]-cerium(III)

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The crystal structure of isoquinolinium tetrakis[4,4,4-trifluoro-1-(2-thienyl)butane-1,3-dionato]cerium(III) has been established by three-dimensional *X*-ray analysis and the molecular parameters refined by full-matrix least-squares calculations to *R* 0·128 over 5325 observed reflections from photographic data. The crystals are monoclinic, space group $P2_1/c$, $a = 22{\cdot}76(4)$, $b = 10{\cdot}85(2)$, $c = 20{\cdot}13(4)$ Å, $\beta = 112{\cdot}58(10)^\circ$, $Z = 4$. Eight oxygen atoms surround the cerium atom, mean Ce—O = 2·470 Å, in a dodecahedral arrangement distorted by an N–H · · · O hydrogen bond from the isoquinolinium ion.

EIGHT-CO-ORDINATE metal complexes of the type $MX_4$, where X = bidentate ligand, occur predominantly with either square antiprismatic ($\bar{8}2m$-$D_{4d}$) or dodecahedral ($\bar{4}2m$-$D_{2d}$) stereochemistry.[1-3] The small potential energy difference between these two favoured forms makes it difficult to predict which geometry will be preferred in a particular complex[4] and intermediate forms are sometimes found. Previous structural studies on anionic complexes of trivalent lanthanoids, M(β-diketone)$_4^-$, have involved either spherically symmetric $Cs^+$ cations or the $NH_4^+$ ion, neither of which would be expected to perturb significantly the co-ordination geometry around the lanthanoid ion. In contrast, the presence of a lower symmetry counterion which has the

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[1] J. L. Hoard and J. V. Silverton, *Inorg. Chem.*, 1963, **2**, 235.

[2] S. J. Lippard, *Progr. Inorg. Chem.*, 1967, **8**, 109.

[3] E. L. Muetterties and C. M. Wright, *Quart. Rev.*, 1967, **21**, 109.

[4] D. Blight and D. L. Kepert, *Inorg. Chem.*, 1972, **7**, 1556, and references therein.

potential to associate with the atoms in the co-ordination polyhedron might be expected further to complicate the situation. Accordingly, we have elucidated the crystal structure of the isoquinolinium salt of tetrakis[4,4,4-trifluoro-1-(2-thienyl)butane-1,3-dionato]cerium(III), $[Ce(ttb)_4]^-$, in order to define the geometry around the cerium(III) ion.

## EXPERIMENTAL

*Crystal Data.*—$C_{41}H_{24}CeF_{12}NO_8S_4$, $M = 1155$, Monoclinic, $a = 22{\cdot}76(4)$, $b = 10{\cdot}85(2)$, $c = 20{\cdot}13(4)$ Å, $\beta = 112{\cdot}58(10)^\circ$, $U = 4590$ Å$^3$; $D_m = 1{\cdot}66$, $Z = 4$, $D_c = 1{\cdot}676$, $F(000) = 2284$, $\mu(\text{Cu-}K_\alpha, \lambda = 1{\cdot}542$ Å$) = 99$ cm$^{-1}$. Space group $P2_1/c$ ($C^5_{2h}$) from absent spectra, $0k0$ when $k \neq 2n$, $h0l$ when $l \neq 2n$.

*Crystallographic Measurements.*—Unit cell dimensions were obtained from zero-level Weissenberg photographs taken with Cu-$K_\alpha$ radiation and precession photographs taken with Mo-$K_\alpha$ ($\lambda = 0{\cdot}7107$ Å) radiation. Three-dimensional intensity data were estimated visually from equi-inclination multiple-film Weissenberg photographs of the $h0$—$10l$ reciprocal lattice nets taken with Cu-$K_\alpha$ radiation. These data were corrected for spot shape, Lorentz, and polarization factors to yield 5325 independent structure amplitudes. No corrections were made for absorption or extinction. Initially the various layers of data were assumed to be on a common scale as each had been given similar exposure times. Absolute layer scales were established at the end of the isotropic refinement (*vide infra*) by correlation with the observed structure amplitudes.

*Structure Analysis.*—The initial position for the cerium atom was determined from the three-dimensional Patterson map, and approximate positions for the other non-hydrogen atoms were obtained from the cerium-phased ($R$ 0·36) three-dimensional $F_0$ map. The identity of the sulphur atoms in three of the ligands was established on the basis of peak heights, but in the remaining ligand two peaks of approximately equal height appeared in possible positions. Since the sulphur atom was consistently *cis*-planar with respect to the adjacent C=O group in three ligands, we decided to treat S(1) as a sulphur atom during the next series of calculations. The atomic positional and isotropic thermal parameters were then refined by full-matrix least-squares calculations from $R$ 0·275 to $R$ 0·155. During these iterations the large structure was refined in blocks, treating 37 atoms in any one cycle and rotating the atoms in alternate cycles. At the end of this refinement the temperature factor for C(4), $B = 1{\cdot}1$ Å$^2$, was significantly less than those of the atoms to which it was bonded, C(3), 7·4 Å$^2$; C(5), 4·0 Å$^2$; while that for S(1) was high (7·8 Å$^2$). These facts along with the earlier evidence from the electron density suggested that this thienyl group was disordered. A similar disordering of the thienyl moiety has been noted in 2-[(2)-dimethylaminoethyl-2-thienylamino]pyridine hydrochloride.[5] Since our least-squares program does not allow for the refinement of atom occupation factors, we assumed 50% population of each of two orientations resulting from rotation about the C(5)–C(6) bond, and employed the average atomic scattering factor $(f_S + f_C)/2$ for both S(1) and C(4). It was possible to identify atom (64) in the isoquinolinium ion as the nitrogen atom from its relatively low temperature factor. The

TABLE 1

Fractional atomic co-ordinates (×10$^4$) and temperature factor parameters, with estimated standard deviations in parentheses

| | $x/a$ | $y/b$ | $z/c$ | $B$ (Å$^2$) |
|---|---|---|---|---|
| Ce | 2410·3(4) | 709·3(9) | 319·6(4) | † |
| CS(1) | 3784(6) | −327(13) | −1181(7) | 7·0(3) |
| C(2) | 4257(13) | −306(29) | −1564(15) | 6·9(7) |
| C(3) | 4715(14) | 567(30) | −1256(16) | 7·4(7) |
| CS(4) | 4666(5) | 1469(11) | −666(6) | 6·0(2) |
| C(5) | 4030(9) | 749(21) | −627(10) | 4·1(4) |
| C(6) | 3709(8) | 1129(18) | −145(9) | 3·4(3) |
| O(7) | 3152(7) | 812(15) | −323(8) | 4·5(3) |
| C(8) | 4101(10) | 1769(22) | 515(11) | 4·3(4) |
| C(9) | 3833(10) | 2204(23) | 988(12) | 4·6(4) |
| O(10) | 3272(6) | 2127(14) | 935(7) | 4·2(3) |
| C(11) | 4288(12) | 2751(27) | 1718(14) | 5·8(6) |
| F(12) | 4857(10) | 3030(23) | 1715(12) | 9·8(6) |
| F(13) | 4352(12) | 2044(26) | 2247(13) | 11·7(7) |
| F(14) | 4098(10) | 3783(22) | 1823(11) | 9·0(5) |
| S(15) | 972(3) | −679(7) | 1596(4) | 6·0(1) |
| C(16) | 324(12) | −1109(25) | 1710(14) | 5·6(5) |
| C(17) | −150(11) | −1543(24) | 1115(13) | 5·1(5) |
| C(18) | 29(8) | −1674(17) | 475(9) | 2·8(3) |
| C(19) | 667(9) | −1141(20) | 736(10) | 3·8(4) |
| C(20) | 1102(8) | −920(18) | 308(9) | 3·1(3) |
| O(21) | 1579(6) | −349(13) | 621(7) | 3·8(3) |
| C(22) | 872(9) | −1404(21) | −402(10) | 3·9(4) |
| C(23) | 1190(9) | −1108(20) | −841(10) | 3·9(4) |
| O(24) | 1671(6) | −405(13) | −729(7) | 3·5(2) |
| C(25) | 940(11) | −1613(24) | −1584(13) | 5·1(5) |
| F(26) | 458(11) | −2451(23) | −1732(12) | 10·7(6) |
| F(27) | 771(11) | −808(22) | −2086(12) | 9·9(6) |
| F(28) | 1368(11) | −2300(23) | −1720(12) | 10·2(6) |
| S(29) | 1035(3) | 2938(8) | 1437(4) | 6·2(1) |
| C(30) | 621(11) | 3988(24) | 1629(13) | 5·1(5) |
| C(31) | 496(13) | 5068(29) | 1234(14) | 6·3(6) |
| C(32) | 798(7) | 5078(17) | 645(8) | 2·5(3) |
| C(33) | 1132(9) | 3796(20) | 759(10) | 3·5(3) |
| C(34) | 1477(8) | 3251(18) | 365(9) | 3·0(3) |
| O(35) | 1764(6) | 2285(13) | 602(7) | 3·7(2) |
| C(36) | 1452(10) | 3833(21) | −274(11) | 4·2(4) |
| C(37) | 1703(9) | 3288(20) | −712(10) | 4·2(4) |
| O(38) | 2011(5) | 2325(11) | −684(6) | 3·0(2) |
| C(39) | 1574(15) | 4010(32) | −1446(18) | 8·0(8) |
| F(40) | 1224(11) | 5004(25) | −1507(13) | 11·4(7) |
| F(41) | 1276(11) | 3317(24) | −1977(13) | 11·8(7) |
| F(42) | 2074(12) | 4372(23) | −1483(14) | 11·7(7) |
| S(43) | 3466(4) | −3111(8) | −171(4) | 7·2(2) |
| C(44) | 4033(15) | −4252(31) | −33(17) | 7·8(8) |
| C(45) | 4403(16) | −4330(35) | 641(19) | 8·7(9) |
| C(46) | 4321(11) | −3491(24) | 1159(13) | 5·5(5) |
| C(47) | 3771(9) | −2719(20) | 722(10) | 4·0(4) |
| C(48) | 3448(7) | −1731(17) | 961(8) | 2·9(3) |
| O(49) | 2986(7) | −1224(15) | 490(8) | 4·6(3) |
| C(50) | 3677(9) | −1480(19) | 1688(10) | 3·6(4) |
| C(51) | 3333(9) | −660(20) | 1935(10) | 4·0(4) |
| O(52) | 2897(6) | 124(14) | 1597(7) | 4·2(3) |
| C(53) | 3523(12) | −521(25) | 2749(13) | 5·7(6) |
| F(54) | 3850(11) | −1420(24) | 3133(13) | 11·2(7) |
| F(55) | 3774(12) | 538(23) | 3028(13) | 11·4(7) |
| F(56) | 3037(10) | −601(20) | 2952(12) | 9·4(6) |
| C(57) | 2255(13) | −1844(28) | −3418(14) | 6·5(6) |
| C(58) | 2461(11) | −1139(23) | −3835(12) | 4·9(5) |
| C(59) | 2687(10) | 97(22) | −3590(11) | 4·6(4) |
| C(60) | 2573(8) | 507(18) | −2999(9) | 3·6(3) |
| C(61) | 2303(8) | −251(18) | −2606(9) | 3·4(3) |
| C(62) | 2144(11) | −1474(23) | −2822(12) | 5·1(5) |
| C(63) | 2192(9) | 339(20) | −2030(10) | 4·1(4) |
| N(64) | 2370(7) | 1445(15) | −1820(8) | 4·0(8) |
| C(65) | 2653(10) | 2212(22) | −2180(11) | 4·5(4) |
| C(66) | 2751(10) | 1782(22) | −2734(11) | 4·7(4) |

† For the cerium atom an anisotropic temperature factor of the form $B \sin^2\theta/\lambda^2 = 10^5[b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl]$ was employed with parameters

| $b_{11}$ | $b_{22}$ | $b_{33}$ | $b_{12}$ | $b_{13}$ | $b_{23}$ |
|---|---|---|---|---|---|
| 131(1) | 523(7) | 170(1) | −41(8) | 70(2) | 15(9) |

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[5] G. R. Clark and G. J. Palenik, *J. Amer. Chem. Soc.*, 1972, **94**, 4005.

### TABLE 2

### (a) Interatomic distances (Å)

In the ligands

| Bond ($n_1$—$n_2$) | Atoms ($n$) | Atoms ($n + 14$) | Atoms ($n + 28$) | Atoms ($n + 42$) | Mean |
|---|---|---|---|---|---|
| S(1)–C(2) | 1·54(3) | 1·65(3) | 1·62(3) | 1·73(3) | 1·67 * |
| S(1)–C(5) | 1·56(3) | 1·68(2) | 1·73(2) | 1·71(2) | 1·71 * |
| C(2)–C(3) | 1·37(4) | 1·35(4) | 1·38(4) | 1·30(5) | 1·34 * |
| C(3)–C(4) | 1·58(3) | 1·50(3) | 1·58(3) | 1·45(5) | 1·51 * |
| C(4)–C(5) | 1·67(2) | 1·46(3) | 1·56(3) | 1·48(3) | 1·50 * |
| C(5)–C(6) | 1·48(3) | 1·56(3) | 1·44(3) | 1·48(3) | 1·49 |
| C(6)–O(7) | 1·23(2) | 1·20(2) | 1·23(2) | 1·24(2) | 1·23 |
| C(6)–C(8) | 1·46(3) | 1·42(3) | 1·41(3) | 1·38(3) | 1·42 |
| C(8)–C(9) | 1·40(3) | 1·38(3) | 1·36(3) | 1·40(3) | 1·39 |
| C(9)–O(10) | 1·24(3) | 1·28(3) | 1·25(2) | 1·28(3) | 1·26 |
| C(9)–C(11) | 1·55(4) | 1·49(3) | 1·60(4) | 1·53(3) | 1·54 |
| C(11)–F(12) | 1·33(4) | 1·37(4) | 1·32(4) | 1·29(4) | 1·30 |
| C(11)–F(13) | 1·27(4) | 1·28(4) | 1·27(4) | 1·31(4) | |
| C(11)–F(14) | 1·25(4) | 1·33(4) | 1·24(4) | 1·32(4) | |
| S(1) · · · O(7) | 2·92(2) | 2·82(2) | 2·87(2) | 2·88(2) | 2·87 |
| O(10) · · · F(13) | 2·84(3) | 2·75(2) | 2·72(3) | 2·84(3) | 2·77 |
| O(10) · · · F(14) | 2·72(3) | 2·76(2) | 2·78(3) | 2·74(3) | |

In the isoquinolinium ion

| | | | | | |
|---|---|---|---|---|---|
| C(57)–C(58) | 1·35(4) | C(60)–C(61) | 1·43(3) | C(63)–N(64) | 1·28(3) |
| C(57)–C(62) | 1·38(4) | C(60)–C(66) | 1·48(3) | N(64)–C(65) | 1·41(3) |
| C(58)–C(59) | 1·45(3) | C(61)–C(62) | 1·40(3) | C(65)–C(66) | 1·31(3) |
| C(59)–C(60) | 1·39(3) | C(61)–C(63) | 1·43(3) | | |

Mean C–C = 1·40
C–N = 1·35

Dodecahedron parameters

| | | | | |
|---|---|---|---|---|
| Ce–O(7) | 2·492(15) | Ce–O(35) | 2·460(14) | Mean Ce–O = 2·470 |
| Ce–O(10) | 2·425(15) | Ce–O(38) | 2·563(12) | |
| Ce–O(21) | 2·480(14) | Ce–O(49) | 2·426(16) | |
| Ce–O(24) | 2·454(13) | Ce–O(52) | 2·461(14) | |

Type *g*

| | | |
|---|---|---|
| O(7)–O(38) | 2·92(2) | Mean O–O = 2·99 |
| O(7)–O(49) | 2·86(2) | |
| O(10)–O(35) | 3·24(2) | |
| O(10)–O(52) | 2·85(2) | |
| O(21)–O(35) | 2·89(2) | |
| O(21)–O(52) | 2·93(2) | |
| O(24)–O(38) | 3·05(2) | |
| O(24)–O(49) | 3·18(2) | |

Type *m*

| | | |
|---|---|---|
| O(7)–O(10) | 2·83(2) | Mean O–O = 2·81 |
| O(21)–O(24) | 2·81(2) | |
| O(35)–O(38) | 2·85(2) | |
| O(49)–O(52) | 2·74(2) | |

Type *b*

| | | |
|---|---|---|
| O(10)–O(38) | 3·42(2) | Mean O–O = 3·72 |
| O(10)–O(49) | 3·74(2) | |
| O(21)–O(38) | 4·27(2) | |
| O(21)–O(49) | 3·45(2) | |

Type *a*

| | | |
|---|---|---|
| O(7)–O(24) | 3·41(2) | Mean O–O = 3·45 |
| O(35)–O(52) | 3·49(2) | |

### (b) Interatomic angles (°)

In the ligands

| | Atoms ($n$) | Atom ($n + 14$) | (Atoms ($n + 28$) | (Atoms ($n + 42$) | **Mean** |
|---|---|---|---|---|---|
| C(2)–S(1)–C(5) | 102·6(16) | 91·2(12) | 94·1(12) | 91·9(14) | 92·4 * |
| S(1)–C(2)–C(3) | 109·9(25) | 115·3(21) | 118·0(21) | 111·0(28) | 114·8 * |
| C(2)–C(3)–C(4) | 120·6(25) | 114·0(22) | 112·6(23) | 120·1(33) | 115·6 * |
| C(3)–C(4)–C(5) | 93·4(15) | 102·4(17) | 102·2(17) | 103·9(23) | 102·8 * |
| S(1)–C(5)–C(4) | 113·2(13) | 116·8(15) | 113·1(13) | 113·0(16) | 114·3 * |
| S(1)–C(5)–C(6) | 123·1(16) | 115·1(14) | 118·4(15) | 118·0(14) | 117·2 * |
| C(4)–C(5)–C(6) | 123·7(16) | 128·0(17) | 128·5(18) | 128·9(18) | 128·5 * |
| C(5)–C(6)–O(7) | 116·5(17) | 115·3(16) | 117·1(17) | 117·0(16) | 116·5 |
| C(5)–C(6)–C(8) | 116·4(17) | 115·6(17) | 118·6(18) | 117·1(16) | 116·9 |
| O(7)–C(6)–C(8) | 127·0(18) | 129·1(18) | 124·2(18) | 125·9(17) | 126·6 |
| C(6)–O(7)–Ce | 133·7(13) | 137·1(13) | 141·1(12) | 138·1(13) | 137·5 |
| C(6)–C(8)–C(9) | 120·4(20) | 118·5(19) | 121·1(20) | 117·9(18) | 119·5 |
| C(8)–C(9)–O(10) | 128·5(22) | 130·6(20) | 134·9(20) | 131·2(18) | 131·4 |
| C(8)–C(9)–C(11) | 117·8(21) | 117·9(20) | 114·5(21) | 118·4(19) | 117·2 |
| O(10)–C(9)–C(11) | 113·4(20) | 111·5(19) | 110·7(20) | 110·1(18) | 111·4 |
| C(9)–O(10)–Ce | 133·6(15) | 134·6(13) | 129·1(12) | 132·0(12) | 132·4 |
| C(9)–C(11)–F(12) | 112·3(23) | 115·3(22) | 112·1(27) | 115·3(23) | 113·1 |
| C(9)–C(11)–F(13) | 112·4(25) | 115·3(23) | 109·7(27) | 116·2(24) | |
| C(9)–C(11)–F(14) | 110·8(24) | 112·6(22) | 111·5(28) | 113·4(22) | |
| F(12)–C(11)–F(13) | 109·9(26) | 108·1(23) | 107·3(30) | 110·5(25) | 106·3 |
| F(12)–C(11)–F(14) | 101·3(25) | 99·9(22) | 105·8(30) | 97·1(23) | |
| F(13)–C(11)–F(14) | 109·6(26) | 104·0(23) | 110·2(31) | 101·9(24) | |
| O(7)–Ce–O(10) | 70·1(5) | 69·3(4) | 69·1(4) | 68·1(5) | 69·2 |

TABLE 2 (*Continued*)

(b) Interatomic angles (*continued*)

In the isoquinolium ion

| | | | |
|---|---|---|---|
| C(58)–C(57)–C(62) | 127·0(27) | C(60)–C(61)–C(63) | 115·9(18) |
| C(57)–C(58)–C(59) | 118·4(23) | C(57)–C(62)–C(61) | 115·9(23) |
| C(58)–C(59)–C(60) | 115·4(20) | C(61)–C(63)–N(64) | 123·6(19) |
| C(59)–C(60)–C(61) | 123·5(19) | C(63)–N(64)–C(65) | 122·1(18) |
| C(61)–C(60)–C(66) | 117·0(17) | N(64)–C(65)–C(66) | 119·3(21) |
| C(60)–C(61)–C(62) | 119·1(18) | C(60)–C(66)–C(65) | 121·8(21) |

* Omitting the distances and angles in the disordered thienyl ring.

Intermolecular distances $\leqslant 3{\cdot}4$ Å

| | | | |
|---|---|---|---|
| O(38) · · · N(64) | 2·87 | C(34) · · · C(59$^{I}$) | 3·28 |
| F(54) · · · F(12$^{V}$) | 2·90 | C(31) · · · F(27$^{I}$) | 3·29 |
| O(7) · · · N(64) | 2·93 | S(29) · · · F(41$^{I}$) | 3·32 |
| F(40) · · · F(28$^{II}$) | 2·99 | O(7) · · · C(63) | 3·33 |
| F(26) · · · C(30$^{III}$) | 3·04 | F(14) · · · F(46$^{II}$) | 3·36 |
| F(41) · · · N(64) | 3·13 | O(24) · · · C(63) | 3·36 |
| F(56) · · · F(42$^{I}$) | 3·13 | C(33) · · · C(60$^{I}$) | 3·36 |
| C(30) · · · F(27$^{I}$) | 3·17 | C(48) · · · C(58$^{IV}$) | 3·36 |
| F(40) · · · F(26$^{II}$) | 3·20 | F(42) · · · N(64) | 3·37 |
| F(14) · · · C(59$^{I}$) | 3·23 | O(35) · · · C(66$^{I}$) | 3·39 |
| F(42) · · · C(65) | 3·26 | | |

Roman numeral superscripts refer to the following transformations of the co-ordinates of Table 1

I $x, \frac{1}{2} - y, \frac{1}{2} + z$
II $x, 1 + y, z$
III $-x, -y, -z$
IV $x, -\frac{1}{2} - y, \frac{1}{2} + z$
V $1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$

refinement process was brought to convergence at *R* 0·128 by two more least-squares cycles during which the cerium atom was allowed to assume anisotropic vibration parameters. Final atomic positional and thermal parameters are given in Table 1.

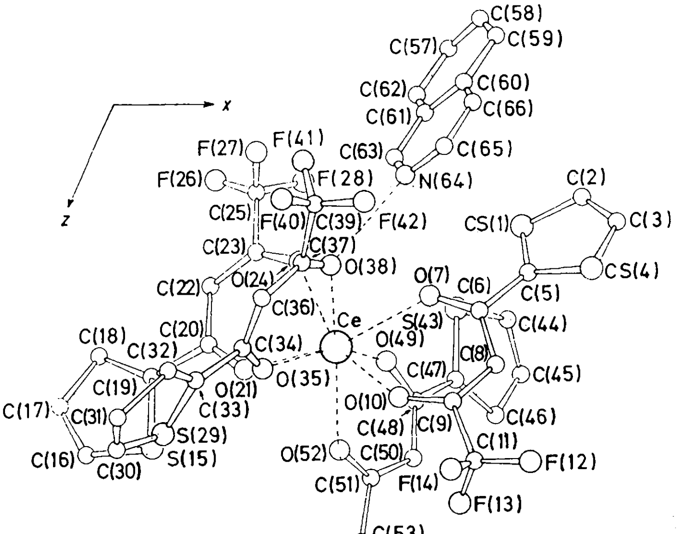

FIGURE 1 Atom numbering scheme and solid state configuration of $C_9H_8N[(C_8H_4F_3O_2S)_4Ce]$

For all the structure factor calculations, scattering factors for cerium from ref. 6, and carbon, oxygen, and fluorine from ref. 7 were used. In the least-squares calculations $\Sigma w(F_o - F_c)^2$ was minimized with weights $w$ assigned according to the scheme $\sqrt{w} = 1$ for $|F_o| \leqslant 50$ and $\sqrt{w} = 50/|F_o|$ for $|F_o| > 50$, and this appeared to be adequate when $\langle w\Delta^2\rangle$ was analysed in ranges of $|F_o|$.

A Table of observed structure amplitudes and calculated structure factors has been deposited in Supplementary Publication No. SUP 20985 (25 pp., 1 microfiche).*

## RESULTS AND DISCUSSION

Figure 1 shows the molecular configuration in the asymmetric crystal unit and the atom numbering scheme employed. Interatomic distances and angles are reported in Table 2, and the results of mean plane calculations through groups of atoms are presented in Table 3.

The cerium atom is co-ordinated by eight oxygen atoms with Ce–O distances ranging from 2·425 to 2·563 Å, and there are significant deviations from the mean of 2·470 Å which is close to the corresponding M–O distance of 2·46 Å in $NH_4[Pr(ttb)_4]H_2O$ [8] and it is slightly longer than those of 2·40 and 2·32 Å in α- [9] and β- [10] Ce(acac)$_4$ (acac = acetylacetonate) and 2·323 Å in Cs[Y(hfac)$_4$] [11] (hfac = hexafluoroacetylacetonate). In spite of the significant distortions from ideal geometry it is still possible to recognize that the oxygen atoms surround the cerium atom in a distorted $D_{2d}$ dodecahedral arrangement with the bidentate ligands spanning the *m* edges (Hoard and Silverton [1] notation, see Figure 2) of the trapezoids O(7)O(10)O(21)O(24) and O(35)-O(38)O(49)O(52) between which the 89·8° angle is not significantly different from the ideal $D_{2d}$ value of 90°.[1,12] Moreover, the angular shape parameters $\theta_A$ = 38·7–48·6°, mean 44·4°, and $\theta_B$ = 64·9–71·0°, mean 67·9°, compare favourably with $\theta_A$ = 36·9°, $\theta_B$ = 69·5°

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue.

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TABLE 3

Equations of mean planes in the form * $AX + BY + CZ - D = 0$, and displacements (Å) of some atoms from the planes. Atoms not included in the derivation of the plane are italicized

Plane $A$: $-0{\cdot}4195X + 0{\cdot}8045Y - 0{\cdot}4205Z + 1{\cdot}878 = 0$

O(7) −0·28, O(10) 0·18, O(21) −0·22, O(24) 0·26, Ce 0·05

Plane $B$: $-0{\cdot}7836X - 0{\cdot}5527Y - 0{\cdot}2837Z + 4{\cdot}774 = 0$

O(35) 0·31, O(38) −0·26, O(49) 0·22, O(52) −0·34, Ce 0·08

Plane $C$: $-0{\cdot}3437X + 0{\cdot}6389Y - 0{\cdot}6882Z + 1{\cdot}985 = 0$

CS (1) 0·00, C(2) 0·03, C(3) −0·04, CS(4) 0·03, C(5) −0·01, C(6) 0·01

Plane $D$: $-0{\cdot}2890X + 0{\cdot}9150Y - 0{\cdot}2815Z + 1{\cdot}800 = 0$

S(15) 0·01, C(16) −0·03, C(17) 0·03, C(18) −0·02, C(19) 0·01, *C(20) 0·07*

Plane $E$: $-0{\cdot}6309X - 0{\cdot}4020Y - 0{\cdot}6636Z + 3{\cdot}843 = 0$

S(29) 0·00, C(30) 0·00, C(31) 0·00, C(32) 0·00, C(33) 0·00, *C(34) 0·03*

Plane $F$: $0{\cdot}7377X + 0{\cdot}6557Y - 0{\cdot}1607Z - 3{\cdot}764 = 0$

S(43) −0·01, C(44) 0·01, C(45) −0·01, C(46) 0·00, C(47) 0·01, *C(48) −0·04*

Plane $G$: $-0{\cdot}0473X + 0{\cdot}8560Y - 0{\cdot}5147Z - 0{\cdot}742 = 0$

C(6) 0·04, O(7) −0·03, C(8) −0·01, C(9) −0·02, O(10) 0·02, *Ce −0·64, C(5) 0·10, C(11) −0·23*

Plane $H$: $-0{\cdot}4957X + 0{\cdot}8171Y - 0{\cdot}2944Z + 2{\cdot}155 = 0$

C(20) 0·05, O(21) −0·04, C(22) −0·01, C(23) −0·03, O(24) 0·03, *Ce 0·01, C(19) 0·27, C(25) −0·08*

Plane $I$: $-0{\cdot}7228X - 0{\cdot}4903Y - 0{\cdot}4871Z + 4{\cdot}311 = 0$

C(34) 0·03, O(35) −0·01, C(36) −0·02, C(37) 0·01, O(38) 0·00, *Ce −0·14, C(33) 0·17, C(39) 0·09*

Plane $J$: $0{\cdot}7146X + 0{\cdot}6936Y - 0{\cdot}0909Z - 3{\cdot}604 = 0$

C(48) 0·01, O(49) −0·02, C(50) 0·04, C(51) −0·08, O(52) 0·05, *Ce 0·62, C(47) −0·04, C(53) −0·25*

Plane $K$: $-0{\cdot}7399X + 0{\cdot}3088Y - 0{\cdot}5977Z + 2{\cdot}540 = 0$

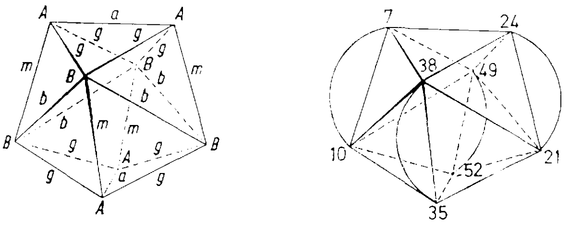
C(57) −0·03, C(58) 0·08, C(59) −0·02, C(60) −0·01, C(61) −0·02, C(62) −0·04, C(63) 0·06, N(64) 0·01, C(65) −0·01, C(66) −0·02

* Cartesian co-ordinates ($X$, $Y$, $Z$) are related to the fractional atomic co-ordinates ($x$, $y$, $z$) by the transformation $[X, Y, Z] = [xa + zc \cos \beta, yb, zc \sin \beta]$

Dihedral angles (°) between the planes are

| | | | |
|---|---|---|---|
| $A/B$ | 89·8 | $E/I$ | 12·5 |
| $C/G$ | 23·4 | $F/J$ | 4·7 |
| $D/H$ | 13·2 | | |

calculated by Hoard and Silverton [1] for the hard-sphere model. Normally, complexes of $D_{2d}$ dodecahedral co-ordination have the order of magnitudes of the sides $g > a = m$ and bidentate ligands span the $m$ edges.[13] However, noteworthy exceptions to this general rule have been reported for $NH_4[Pr(ttb)_4]H_2O$,[8] $Cs[Y(hfac)_4]$,[11] and isomorphous $Cs[Eu(hfac)_4]$ [14] and $Cs[Am(hfac)_4]$,[14] where it has been found that $g = m < a$ and the bidentate ligands span the $g$ edges. We also find from the present study that $g = m < a$ but here the ligands span the $m$ edges. Inspection of the dodecahedral $b$ parameters (Table 2) reveals significant differences among them, especially noteworthy is the long O(21)–O(38) distance of 4·27 Å which is a consequence of N–H ··· O hydrogen bonding, N ··· O = 2·87 Å, between the isoquinolinium ion and O(38) in the cerium co-ordination sphere. The presence of this hydrogen bonded association weakens the Ce–O(38) interaction and increases the separation between these atoms to 2·563 Å which is significantly longer than the 2·470 Å Ce–O mean; a concomitant reduction in the Ce–O(10) = 2·425 and Ce–O(49) = 2·426 Å distances takes place. The net result is that the hydrogen bond causes significant distortion from a regular $D_{2d}$ dodecahedral arrangement around the cerium atom, and molecular models show clearly that in the absence of this interaction a regular configuration can be attained when the O(21) ··· O(38) distance is restored to a more normal value. It is of note that the hydrogen bond involves an oxygen atom in the cerium(III) co-ordination sphere rather than one of the electronegative peripheral fluorine atoms which could act as proton acceptors. However, in addition to the hydrogen bond, the observed arrangement positions the positively charged nitrogen atom close to two fluorine atoms and another oxygen atom as shown in Figure 1. If we distinguish between the terminal groups of the ligands, then the $Ce(ttb)_4^-$ anion has $C_1$ symmetry, for occupation of dodecahedral A and B sites by different ends of the ligands is not conserved in this complex. A like result was noted in the crystal structure of $NH_4[Pr(ttb)_4]H_2O$ [8] where one of the ligands has its terminal groupings reversed.



(a) (b)

FIGURE 2 The $D_{2d}$ dodecahedron (a) from ref. 8, and (b) in $(C_8H_4F_3O_2S)_4Ce^-$ with oxygen sites labelled

The distances of the cerium atom from the β-diketone OCCCO least-squares planes are in Table 3. From these we find that the cerium atom is approximately coplanar with the other five atoms in two chelate rings, C(20)–O(24) and C(34)–O(38), whereas it is significantly displaced from the corresponding planes, C(6)–O(10) and C(48)–O(52), in the other two ligands, the displacements corresponding to folding of 18° about the O–O line. It has been pointed out elsewhere that while such folding is common it is not an essential feature [15] of β-diketone complexes. The differences noted here may be ascribed to differences in the intra- and inter-molecular forces exerted on each of the ligands. In the β-diketone chelate rings the mean C–C and C–O distances, 1·41 and 1·25 Å, and the mean C–C–C angle 119·5°, are compatible with the values expected for a delocalized system, and they are in satisfactory agreement with, for example, the

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[13] See *e.g.* W. D. Bonds, jun., R. D. Archer, and W. C. Hamilton, *Inorg. Chem.*, 1971, **8**, 1764.

[14] J. H. Burns and M. D. Danford, *Inorg. Chem.*, 1969, **8**, 1780.

[15] F. A. Cotton and J. S. Wood, *Inorg. Chem.*, 1964, **2**, 245.

corresponding mean dimensions 1·390(3), 1·274(3) Å, and 124·0(3)° in a number of acetylacetonate complexes.[16]

Significant differences occur in the angles subtended at the carbonyl carbon atoms. Adjacent to the trifluoromethyl group the mean C–C–O ring angle is 131·4° whereas at the other end of the ligand the mean of the C–C–O angles is 126·6°. The latter is close to that of 124·0° in $NH_4[Pr(ttb)_4]H_2O$ [8] and to the average of 125·3(3)° in acetylacetonate complexes.[16] The angle at the trifluoromethyl group is in good agreement with the values found in other trifluoroacetate ligands, *e.g.*, 129·7° in $Cu(hfac)_2H_2O(dmed)_2$ [17] (dmed = *NN*-dimethylethylenediamine), 132·3° in $Cs[Eu(hfac)_4]$ [14] and $Cs[Am(hfac)_4]$,[14] and 130·4° in $NH_4[Pr(htta)_4]H_2O$. Thus substitution of the methyl group by the more electronegative trifluoromethyl group results in an increase in β-diketone chelate ring angle at the carbon atoms bearing these groups.

The dimensions of chemically equivalent bonds and valency angles in the thienyl rings are in rather poor agreement and a detailed discussion is not justified. For one of these groups we assumed a 50% occupation of each of two orientations obtained by rotation about the C(5)–C(6) bond. It is possible that the individual variations in the other three rings reflect some further disordering and that the isotropic model employed is an entirely inadequate description. In each ligand the thienyl rings are planar within the accuracy of the analysis, and their substituent carbon atoms lie close to the ring plane (Table 3). Dihedral angles between the intraligand thienyl and the OCCCO β-diketone planes range from 5 to 23° and the variation is probably due to differences in crystal packing forces.

Evaluation of the torsion angles about the C–C bonds at the trifluoromethyl groups indicates that a conformational preference exists, for in all four cases one fluorine atom lies close to *trans*-planar with respect to the adjacent β-diketone oxygen atom while the other two fluorine atoms are approximately equidistant from this atom. A similar result was noted in crystalline $NH_4[Pr(ttb)_4]H_2O$. In the trifluoromethyl groups the mean dimensions are C–F = 1·30 Å, C–C–F = 113·1°, and F–C–F = 106·3°. Although the mean C–F bond length is notably shorter than the sum of the single bond covalent radii,[18] 1·41 Å, it is not atypical for such bonds

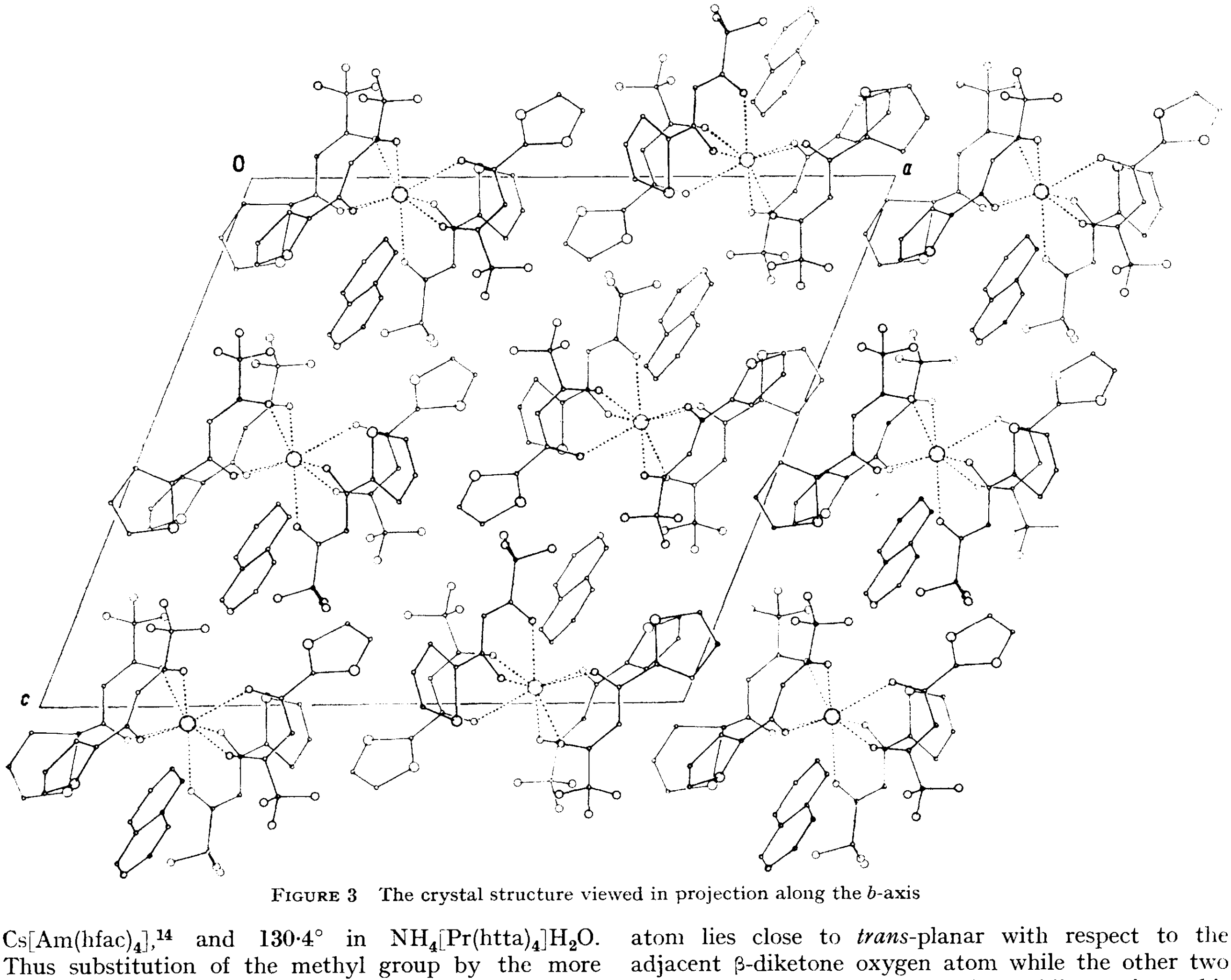

FIGURE 3 The crystal structure viewed in projection along the *b*-axis

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[16] E. C. Lingafelter and R. L. Braun, *J. Amer. Chem. Soc.*, 1966, **88**, 2951.

[17] M. A. Bush and D. E. Fenton, *J. Chem. Soc.* (*A*), 1971, 2446.

[18] L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, New York, 1960.

in fluoroalkyl groups which are subject to substantial librational motion as in the present complex.[17,19,20] The differences in C–C–F and F–C–F angles represent a consistent feature of trifluoromethyl groups. Corresponding values in some other complexes are 114 and 104° in $Cs[Y(hfac)_4]$,[11] 112·9 and 105·9° in $Cu(hfac)_2H_2O(dmed)_2$,[17] 112 and 104° in $Cu(hfac)_3^-$.[19] In hfacH and hexafluoroacetic anhydride[21] the respective values are 110·6 and 108·3° and 110·2 and 108·7°.

The atoms of the isoquinolinium cation are approximately coplanar as would be expected and the mean bond lengths and angles compare favourably with normal values.[22]

A view of the molecular packing in the crystal is shown in Figure 3 and the shorter intermolecular separations are in Table 2. Apart from the short NH · · · O hydrogen bonded separation (*vide supra*) the distances correspond to normal van der Waals separations.

The extensive crystallographic calculations were carried out on the IBM 370/165 computer located at the Triangle Universities Computation Centre, Research Triangle Park, North Carolina. We thank Dr. F. E. Mabbs for supplying the crystals used for this analysis.

[3/2204 *Received, 26th October*, 1973]

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