Fig. 1. A perspective view of the molecule along the approximate threefold axis, showing thermal ellipsoids at 50% probability. Hydrogen atoms are represented by spheres of 0·1 Å radius.

Discussion. Crystals of the title compound (I) consist of tris-chelate molecules of the complex [Co(S$_2$CNMe$_2$)$_3$]. Three dithiocarbamate ligands octahedrally coordinate to a Co atom through S atoms. The bond lengths and angles are listed in Table 2. A perspective view of the molecule is presented in Fig. 1. The molecule assumes 32 symmetry to a good approximation. The dimensions within the ligands are normal. The Co atom lies nearly in the plane of each ligand, the deviations being 0·18 (3), 0·02 (1) and 0·05 (1) Å for the three ligands respectively. The geometry of the CoS$_6$ part of the molecule is similar to those of [Co(S$_2$CNH$_2$)$_3$] (II) (Raston, White & Willis, 1975) and [Co(S$_2$CNEt$_2$)$_3$] (III) (Merlino, 1968), and is intermediate between (II) and (III). The mean Co—S

distances are 2·275, 2·264 and 2·258 Å for (II), (I) and (III) respectively. The molecules of (III) lie on crystallographic twofold axes, and hence the two Co—S lengths in each ligand are equal. In (II), one Co—S bond is significantly shorter than the other, the mean difference being 0·020 Å, and these three short bonds are related by the approximate threefold axis of the molecule. The corresponding difference in (I) is 0·013 Å. In this case, however, the shorter bonds are not related by the approximate threefold axis, and, therefore, the present molecule by no means has strict trigonal symmetry. As Raston *et al.* (1975) have suggested, the difference between the two Co—S distances within a ligand might result from the difference of the sulfur environment, but a close correlation between Co—S distances and intermolecular S—H interactions as reported for (II) could not be found in the present case. Relatively short intermolecular contacts of 2·8 (1)–3·0 (1) Å are observed for S(2)···H(71), S(3)···H(43), S(4)···H(93) and S(5)···H(42), though the H positions have been less accurately determined.

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The Structure of Tetraaqua(2,2,3,3-tetrafluorosuccinato)zinc(II)

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Abstract. [Zn(C$_4$F$_4$O$_4$)(H$_2$O)$_4$], C$_4$H$_8$F$_4$O$_8$Zn, monoclinic, P2$_1$/c, $a = 10\cdot799$ (2), $b = 9\cdot115$ (5), $c = 10\cdot995$ (3) Å, $\beta = 115\cdot53$ (2)°, $V = 976\cdot60$ Å^3, $Z = 4$, $d_c = 2\cdot20$, $d_m = 2\cdot2$ Mg m^{-3}, μ(Mo $K\alpha$) = 2·70 mm^{-1}, $R = 0\cdot034$ and $R_w = 0\cdot040$ for 1536 counter-collected reflections. The sixfold, approximately octahedral, coordination polyhedron around the Zn^{2+} ion consists of four water molecules and two carboxylate O atoms (*trans* configuration) from two different tetrafluorosuccinate ions.

Introduction. The title compound was prepared from the reaction of zinc(II) carbonate and aqueous tetrafluorosuccinic acid. The compound is hygroscopic, very soluble in water, and single-crystal growth is often difficult. A solution of the compound in deuterium oxide (D$_2$O), which was originally prepared for NMR studies, yielded suitable crystals after slow evaporation over a period of two months. A crystal with approximate dimensions 0·15 × 0·15 × 0·20 mm was placed in a thin-walled capillary tube and used in the X-ray

diffraction experiments. The percentage of D_2O in the crystal was not known. The systematic absences $h0l$, $l = 2n + 1$ and $0k0$, $k = 2n + 1$ indicated the space group $P2_1/c$. Unit-cell dimensions were determined by a least-squares refinement of the angular settings of 25 reflections obtained from an Enraf–Nonius CAD-4 diffractometer at the Molecular Structure Corp. Three-dimensional X-ray intensity data at 296 ± 1 K were collected on the aforementioned diffractometer equipped with a graphite monochromator and utilizing Mo $K\alpha$ ($\lambda = 0.71730$ Å) radiation. 1744 independent reflections out to 50° in 2θ and consistent with the space-group symmetry were measured using the θ–2θ scan technique.

The raw intensity data were assigned estimated standard deviations and reduced to values of F_o and $\sigma(F_o)$ in the manner previously described (Reed & Karipides, 1976). 1536 reflections had $F_o > \frac{1}{2}\sigma(F_o)$ and these were used in subsequent calculations. Refinement was by a full-matrix least-squares procedure, although the H atom parameters were not varied. The function minimized was $\sum w(|F_o| - |F_c|)^2$ where the weight, w, was taken to be $[\sigma(F_o)]^{-2}$. The structure converged to a conventional R index, $\sum ||F_o| - |F_c||/\sum |F_o|$, of 0.034 and a weighted R_w index, $[\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ of 0.040. In the last cycle of least-squares refinement the largest shift in any

positional or thermal parameter was 0.01 times its own standard deviation. The goodness-of-fit was 1.19. 154 parameters were refined yielding a data–parameter ratio of 10.0:1. An analysis of $\sum w(|F_o| - |F_c|)^2$ as a function of F_o or $\sin \theta/\lambda$ indicated no unusual trends. A final difference synthesis was essentially flat. The neutral scattering factors of all atoms were taken from *International Tables for X-ray Crystallography* (1974) and included corrections for the real and imaginary anomalous dispersion of Zn. In addition to local programs for the IBM 370/148 and HP-3000 computers, the following programs were used: *FORDAP* (Zalkin, 1980), *ORFLS* and *ORFFE* (Busing, Martin & Levy, 1962, 1964), and *ORTEP* (Johnson, 1965). The final positional parameters are given in Table 1.*

Discussion. Views of the structure and atom-numbering scheme are shown in Figs. 1 and 2. Bond distances and angles are given in Table 2. The irregular octahedral coordination polyhedron about the Zn^{II} ion consists of six O atoms, four from water molecules, O(5), O(6), O(7), O(8), and two carboxylate O atoms, O(1) and O(3^{ii}), from two different tetrafluorosuccinate ions. Thus, each tetrafluorosuccinate ligand binds two different Zn^{2+} ions in a unidentate fashion from each of its two carboxylate groups. The range in Zn—O bond lengths of 2.045 (2) to 2.157 (2) Å is similar to the ranges found in other zinc(II)–carboxylate structures (Reed & Karipides, 1976).

The four ligand C atoms are very nearly planar as indicated by the dihedral angle C(1)—C(2)—C(3)—C(4) of 179.5°. The two carboxylate-group planes, O(1)—C(1)—O(2) and O(3)—C(4)—O(4), are twisted to be approximately perpendicular to the C(1)—C(2)—C(3)—C(4) backbone plane with interplanar angles of 78.9 and 86.3°, respectively.

Table 1. *Positional parameters and their standard deviations ($\times 10^4$ for nonhydrogen atoms; $\times 10^3$ for hydrogen atoms)*

The isotropic temperature factors, B_{eq} (Å^2), were calculated from the deposited anisotropic coefficients following the definition given by Hamilton (1959).

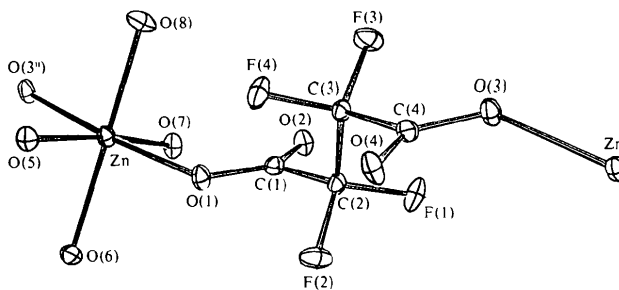|	x	y	z	B_{eq}
Zn	2382.5 (3)	1365.4 (4)	−61.2 (3)	1.64
O(1)	2640 (2)	−788 (2)	−424 (2)	2.21
O(2)	4495 (2)	−1458 (2)	1432 (2)	2.26
O(3)	2227 (2)	−6495 (2)	501 (2)	2.00
O(4)	599 (2)	−5628 (2)	−1427 (2)	2.40
O(5)	338 (2)	1322 (2)	−1519 (2)	2.04
O(6)	2884 (2)	2042 (2)	−1676 (2)	2.38
O(7)	4473 (2)	1562 (2)	1234 (2)	2.37
O(8)	1759 (3)	635 (3)	1378 (2)	3.19
C(1)	3465 (3)	−1683 (3)	368 (3)	1.70
C(2)	3120 (3)	−3307 (3)	−55 (3)	1.72
C(3)	1954 (3)	−3925 (3)	245 (3)	1.69
C(4)	1539 (3)	−5502 (3)	−282 (3)	1.71
F(1)	4230 (2)	−4159 (2)	574 (2)	3.03
F(2)	2724 (2)	−3450 (2)	−1395 (2)	2.90
F(3)	2384 (2)	−3872 (2)	1592 (2)	2.88
F(4)	857 (2)	−3028 (2)	−316 (2)	2.74
H1(O5)	5	80	−240	
H2(O5)	1	225	−180	
H1(O6)	260	170	−255	
H2(O6)	383	196	−133	
H1(O7)	485	222	195	
H2(O7)	480	73	172	
H1(O8)	192	110	221	
H2(O8)	110	−10	130	

Fig. 1. A view of the structure showing the ligand conformation, mode of ligand—Zn^{2+} binding and the ZnO$_6$ coordination polyhedron. H atoms have been omitted for clarity. Superscripts (i) and (ii) are defined in Table 2.

The range in C—F bond lengths as well as the average ($1\cdot348 \pm 0\cdot002$ Å) are consistent with the C—F bond distances found in compounds containing C atoms with two F substituents (Wei & Ward, 1976; Yokozeki & Baur, 1975). An effect of the F atoms is manifested in the opening of the two O—C—O bond angles to $129\cdot4$ (3) and $128\cdot2$ (3)°. These angles are significantly greater than the O—C—O angles observed in metal complexes of the corresponding H-substituted ligand, succinate, where the range is 117 (3) to $124\cdot7$ (9)° (Karipides & Reed, 1980). A similar opening of the O—C—O angle occurs in going from acetates to various fluoroacetates (Wei & Ward, 1976; Macdonald, Speakman & Hadzi, 1972; Curie, 1972; Nahringbauer, 1967; Cruickshank, Jones & Walker, 1964).

The crystal structure consists of chains of ... $(H_2O)_4ZnO_2CCF_2CF_2CO_2Zn(H_2O)_4$ ... units linked together along [010]. Besides Coulombic interactions, these chains are held together by a network of hydrogen bonds involving all eight H atoms from the four water molecules. Included in the hydrogen-bonding scheme are intra-chain hydrogen bonds, O(7)—H2(O7)$\cdots$O(2) and O(5)—H2(O5)$\cdots$O(4^{ii}) which serve to link the carboxylate O atoms, O(2) and O(4^{ii}) respectively, to the Zn^{2+} ion (Table 3).

There is no significant hydrogen bonding involving the F atoms. The shortest H$\cdots$F non-bonded contact is $2\cdot51$ Å which is not much shorter than the van der Waals distance of $2\cdot67$ Å (Bondi, 1964). However, the O(5)—H2(O5)$\cdots$F(4^{iii}) angle is 129° which compares with the angle O(5)—H2(O5)—O(4^{ii}) of 141°. This suggests that H2(O5) may be in a position to participate in a very weak bifurcated hydrogen bond.
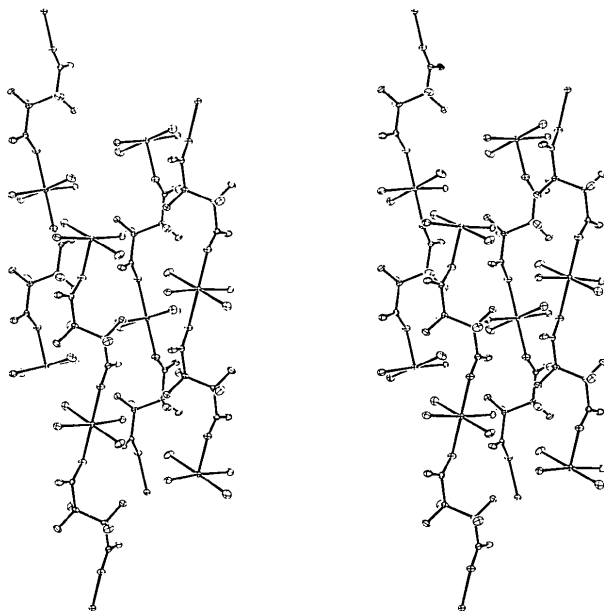

Fig. 2. A stereoscopic view of the unit-cell contents.

Table 2. *Bond distances* (Å) *and angles* (°)

The superscripts (i) and (ii) refer to the operations $x, y - 1, z$ and $x, y + 1, z$, respectively.

Zn—O(1)	2·045 (2)	C(2)—F(1)	1·343 (4)
Zn—O(3^{ii})	2·075 (2)	C(2)—F(2)	1·353 (4)
Zn—O(8)	2·079 (2)	C(2)—C(3)	1·539 (5)
Zn—O(7)	2·093 (2)	C(3)—C(4)	1·543 (4)
Zn—O(5)	2·097 (2)	C(3)—F(3)	1·348 (3)
Zn—O(6)	2·157 (2)	C(3)—F(4)	1·350 (4)
C(1)—O(1)	1·244 (4)	C(4)—O(3)	1·249 (3)
C(1)—O(2)	1·236 (4)	C(4)—O(4)	1·235 (4)
C(1)—C(2)	1·548 (4)		

O(1)—Zn—O(3^{ii})	174·52 (19)	O(1)—C(1)—O(2)	129·4 (3)
O(1)—Zn—O(8)	87·54 (10)	O(2)—C(1)—C(2)	116·4 (3)
O(1)—Zn—O(7)	91·02 (8)	O(1)—C(1)—C(2)	114·2 (3)
O(1)—Zn—O(5)	91·13 (8)	O(3)—C(4)—O(4)	128·2 (3)
O(1)—Zn—O(6)	90·61 (9)	O(3)—C(4)—C(3)	115·2 (2)
O(3^{ii})—Zn—O(8)	88·79 (9)	O(4)—C(4)—C(3)	116·6 (3)
O(3^{ii})—Zn—O(7)	85·37 (8)	C(1)—C(2)—C(3)	113·5 (2)
O(3^{ii})—Zn—O(5)	92·92 (8)	C(2)—C(3)—C(4)	113·1 (2)
O(3^{ii})—Zn—O(6)	93·34 (9)	F(1)—C(2)—F(2)	107·4 (2)
O(8)—Zn—O(7)	96·77 (10)	F(1)—C(2)—C(3)	108·0 (2)
O(8)—Zn—O(5)	89·73 (9)	F(2)—C(2)—C(3)	107·2 (2)
O(8)—Zn—O(6)	175·37 (7)	F(1)—C(2)—C(1)	110·6 (2)
O(7)—Zn—O(5)	173·24 (9)	F(2)—C(2)—C(1)	109·9 (2)
O(7)—Zn—O(6)	87·50 (9)	F(3)—C(3)—F(4)	107·4 (2)
O(5)—Zn—O(6)	86·06 (8)	F(3)—C(3)—C(2)	107·2 (2)
C(1)—O(1)—Zn	127·6 (2)	F(4)—C(3)—C(2)	108·6 (2)
C(1)—O(3)—Zn^i	125·2 (2)	F(3)—C(3)—C(4)	110·6 (2)
		F(4)—C(3)—C(4)	109·7 (2)

Table 3. *Hydrogen-bond distances* (Å) *and angles* (°)

Donor (D) and H atoms have the coordinates listed in Table 2. Superscripts specify the symmetry-related positions of the acceptor (A) atoms.

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

Hydrogen bond	$D\cdots A$	$H\cdots A$	$\angle D$—H$\cdots A$
O(5)—H2(O5)$\cdots$O(4^{ii})	2·792 (3)	2·02	141
O(5)—H1(O5)$\cdots$O(4^{iii})	2·705 (3)	1·75	158
O(6)—H1(O6)$\cdots$O(3^{iv})	2·913 (3)	2·01	164
O(6)—H2(O6)$\cdots$O(2^{v})	2·777 (3)	1·92	154
O(7)—H1(O7)$\cdots$O(2^{vi})	2·936 (3)	2·01	173
O(7)—H2(O7)$\cdots$O(2^{ix})	3·153 (3)	2·02	137
O(8)—H1(O8)$\cdots$O(6^{vii})	2·880 (3)	2·09	140
O(8)—H2(O8)$\cdots$O(5^{viii})	2·939 (3)	2·01	165

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trans-Dichlorobis[*o*-phenylenebis(dimethylarsine)]technetium(III), Perchlorate and Chloride Salts

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Abstract. *trans*-[TcCl$_2$(diars)$_2$]Cl, diars = *o*-C$_6$H$_4$[As(CH$_3$)$_2$]$_2$, $P2_1/c$, $a = 9.354$ (5), $b = 9.662$ (2), $c = 15.341$ (4) Å, $\beta = 98.75$ (6)°, $U = 1370.3$ Å^3, $Z = 2$, $d_{meas} = 1.86$, $d_{calc} = 1.88$ Mg m^{-3}, $R_1 = 0.041$, $R_2 = 0.049$. *trans*-[TcCl$_2$(diars)$_2$]ClO$_4$, $C2$, $a = 13.001$ (10), $b = 10.409$ (3), $c = 11.796$ (8) Å, $\beta = 114.50$ (15)°, $U = 1452.6$ Å^3, $Z = 2$, $d_{meas} = 1.92$, $d_{calc} = 1.93$ Mg m^{-3}, $R_1 = 0.027$, $R_2 = 0.028$. The six-coordinate Tc complex has *trans* chloride ligands and four As atoms from two nearly coplanar *o*-phenylenebis(dimethylarsine) ligands, giving ideal D_{2h} symmetry in each case (Cl$^-$ salt, site symmetry $\bar{1}$; ClO$_4^-$ salt, site symmetry 2). The mean Tc–As distance is 2.512 (2) Å (four independent distances, range 0.011 Å), whereas those for Tc–Cl are 2.348 (8), 2.288 (7), and 2.329 (1) Å. The ClO$_4^-$ salt is yellow-orange, whereas the Cl$^-$ salt is dark red.

Introduction. As part of a program studying Tc complexes as radiopharmaceuticals (Deutsch, 1979) we synthesized the title complexes, and, owing to the large difference in color between the two salts, determined the single-crystal structure of each. The syntheses, characterizations and recrystallization procedures will be given elsewhere (Glavan, Whittle, Johnson, Elder & Deutsch, 1980). A dark-red crystal of the Cl$^-$ salt, *trans*-[TcCl$_2$(diars)$_2$]Cl, (0.17 × 0.26 × 0.51 mm) examined *via* precession photographs (*hk*0, *hk*1, *h*0*l*, *h*1*l*) exhibited Laue symmetry and absences

consistent with the monoclinic space group $P2_1/c$. Least-squares refinement of 15 pairs of reflections (±2θ) was used to determine cell constants. Intensity data were measured for 4037 reflections (2.5 < 2θ < 55.3°) using Mo $K\alpha$ radiation on a Syntex P$\bar{1}$ diffractometer equipped with a graphite single-crystal monochromator. From these, 3417 unique reflections were obtained by averaging (mean discrepancy for multiply measured reflections, 0.009). Of the unique reflections, 2972 had $I > 2\sigma(I)$. Other conditions of data collection were: scan range 2.0° in 2θ; scan rate 1.0 to 4.0° min^{-1}; four standard reflections measured after every 36 reflections; drift correction (from standards) 1.006 to 0.980. No absorption corrections were applied ($\mu = 0.562$ mm^{-1}) since the crystal had a large cavity of ~30% the volume of the crystal. The estimated maximum error in $|F_o|$ owing to uncorrected absorption is 8%.

All atoms including H were located from Patterson and electron density syntheses. In the final cycles of least-squares refinement, 178 parameters were refined including positional parameters for all atoms and anisotropic thermal parameters for all non-hydrogen atoms. In the last cycle of refinement one parameter [H(23), z coordinate] shifted by 1.1σ and another [H(12), x coordinate] by 0.6σ; the average shift was 0.1σ. The highest peak on a final difference electron density map, 0.70 e Å^{-3}, was within 0.9 Å of Tc. Complex scattering factors corrected for anomalous