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Structures of Dichloro[(*S*)-methionine-*N*,*S*]platinum(II) and Chloro[glycyl-(*S*)-methioninato-*N*,*N'*,*S*]platinum(II) Monohydrate

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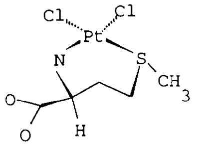
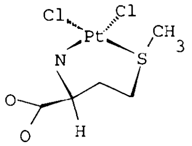
Abstract. (I) $[Pt\{CH_3SCH_2CH_2CH(NH_2)COOH\}Cl_2]$, $M_r = 415.20$, monoclinic, $P2_1$, $a = 7.578$ (2), $b = 10.213$ (2), $c = 13.563$ (4) Å, $\beta = 98.77$ (1)°, $V = 1037.4$ (4) Å^3, $D_x = 2.657$ g cm^{-3} for $Z = 4$, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 142.81$ cm^{-1}, $F(000) = 768$, $T = 294$ K, final $R = 0.029$ for 2980 reflections. (II) $[Pt\{H_2NCH_2CONCH(CO_2H)CH_2CH_2SCH_3\}Cl].H_2O$, $M_r = 453.81$, orthorhombic, $P2_12_12_1$, $a = 6.9971$ (4), $b = 10.6246$ (9), $c = 16.965$ (1) Å, $V = 1261.2$ (2) Å^3, $D_x = 2.389$ g cm^{-3} for $Z = 4$, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 115.69$ cm^{-1}, $F(000) = 856$, $T = 294$ K, final $R = 0.021$ for 1820 reflections. The structures of the title complexes have been redetermined using high-resolution data. In the asymmetric unit of (I) there are two independent diastereomeric molecules, the S atoms having opposite chiralities. The amino acid coordinates *via* the N(amino) and S(thioether) atoms, Pt—N(amino) 2.047 (8), 2.029 (8), Pt—S 2.246 (2), 2.247 (2) Å. In (II) the dipeptide coordinates *via* the N(amino), N(peptide) and S(thioether) atoms, Pt—N(amino) 2.046 (5), Pt—N(peptide) 2.004 (4), Pt—S 2.258 (2) Å.

Introduction. The use of Pt complexes in cancer chemotherapy (Rosenberg, Van Camp & Krigas, 1965; Rosenberg, Van Camp, Trosko & Mansour, 1969; Pinto & Lippard, 1985), and the role of Pt–protein and Pt–peptide interactions in processes which cause the wastage and toxic side effects of such drugs (Berners-Price & Kuchel, 1990; Lempers & Reedijk, 1990) have provided a new focus for interest in the structures of Pt–amino acid and Pt–peptide complexes. For example, the structures of the platinum(II) complexes of ethylcysteine (Theodorou, Photaki, Hadjiliadis, Gellert & Bau, 1982), ethionine (Khan, Venkatasubramanian, Najmuddin, Shamsuddin & Zakeeruddin, 1991) and thioglycine (Zahn, Polborn & Beck, 1989) have been reported recently. The structures of dichloro-(*S*)-methionineplatinum(II), (I), and of chloroglycl-(*S*)-methioninatoplatinum(II) monohydrate, (II), were reported in a preliminary publication by Freeman & Golomb (1970). We have redetermined these structures using high-resolution data.



(I) molecule 1: *R* chirality at sulfur.



(I) molecule 2: *S* chirality at sulfur.

Experimental. Heating equimolar H_2O solutions of K_2PtCl_4 and (*S*)-methionine for (I) and glycyl-(*S*)-methionine for (II) gave yellow solids, which when recrystallized from H_2O and dilute HCl yielded good yellow prismatic crystals.

Crystals were mounted on glass fibres with epoxy resin. Data were collected on an Enraf–Nonius CAD-4 automatic diffractometer using graphite-monochromated Mo $K\alpha$ radiation. 25 independent reflections with $20 \leq 2\theta \leq 30°$ were used for least-squares determination of cell constants. Intensities of three reflections were monitored, and indicated less than 2.5% decomposition for (I) and less than 1.0% for (II). Both structures were solved by heavy-atom methods and refined (on F) by full-matrix least squares with an empirical correction for extinction.

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Non-H atoms were refined with anisotropic thermal parameters. The positions of H atoms bonded to C atoms were calculated assuming tetrahedral geometry with a C—H distance of 0.97 Å. The methyl H atoms were placed so that the conformation about the S—C(methyl) bond was staggered. In (I), which has two molecules in the asymmetric unit, the H atoms of the carboxyl groups were not located. In (II) the H atoms of the carboxyl group and water molecule were located in electron density difference maps, and were refined with the O—H distances restrained to 0.87 Å and with the H···H distance in the water molecule restrained to 1.40 Å. At convergence, all shifts were $<0.05\sigma$ in (I) and $<0.03\sigma$ in (II). Maximum excursions in final difference maps were 1.8 and -2.2 e Å^{-3} for (I), and 1.7 and -1.4 e Å^{-3} for (II).

Data reduction and application of corrections for absorption and decomposition were carried out using the *Enraf–Nonius Structure Determination Package* (Frenz, 1985). All other calculations were performed using the program *SHELX76* (Sheldrick, 1976). Drawings were produced using the program *ORTEP* (Johnson, 1965). Scattering factors and anomalous-dispersion terms for Pt (treated as neutral Pt) were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The values supplied in *SHELX76* were used for all other atoms. Data collection and refinement parameters are presented in Table 1. Final positional parameters and bond lengths and angles are listed in Tables 2 to 5.*

Discussion. The crystals of (I) used in the present work belong to the monoclinic space group $P2_1$; those used in the original structure analysis belonged to the triclinic space group $P1$ (Freeman & Golomb, 1970). The volume of the monoclinic cell is twice the volume of the previously reported triclinic cell, but there are no other obvious relationships between the two cells. In both cells the asymmetric unit comprises two diasteromeric molecules, the respective S atoms having opposite chiralities.

Table 1. *Summary of data collection and processing parameters for* (I) *and* (II)

	Complex (I)	Complex (II)
Crystal dimensions (mm)	0.18 × 0.17 × 0.26	0.15 × 0.20 × 0.30
Crystal faces	$\{\bar{2}01\}$, $\{0\bar{1}\bar{1}\}$, $\{0\bar{1}1\}$	$\{0\bar{1}0\}$, $(1\bar{1}2)$, $(11\bar{2})$, $(\bar{1}11)$, $(\bar{1}\bar{1}\bar{1})$
Data collection range (°)	$2 \le 2\theta \le 55$	$2 \le 2\theta \le 60$
Scan width (°)	$(1.00 + 0.34\tan\theta)$	$(1.00 + 0.34\tan\theta)$
Horizontal counter aperture (mm)	$(2.70 + 1.05\tan\theta)$	$(2.70 + 1.05\tan\theta)$
Scan type	ω—$\frac{4}{3}\theta$	ω—$\frac{5}{3}\theta$
Absorption correction*		
Number of sampling points	14 × 10 × 12	14 × 10 × 14
Maximum correction	11.31	8.62
Minimum correction	5.78	3.90
Range of *hkl*	$\pm h \le 10 + k \le 14, + l \le 19$	$+ h \le 8, + k \le 14 + l \le 23$
$R_{\rm int}$	0.043	-
Total data collected	3294	2128
Unique data	3113	2003
Data with $I \ge 2.5\sigma(I)$	2980	1820
Total variables	218	147
R	0.029	0.022
wR	0.031	0.024
S	1.25	1.13
Weighting constants†	$k = 1.0$, $g = 0.0005$	$k = 0.76$ $g = 0.0005$

* Coppens, Leiserowitz & Rabinovich (1965).

† Weight $w = k/[\sigma^2(F_o) + gF_o^2]$, g and k refined.

Table 2. *Final atomic coordinates for* (I) *with e.s.d.'s in parentheses, and equivalent isotropic thermal parameters* (Å^2)

$$B_{\rm eq} = (8\pi^2/3)\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
Pt(1)	0.4534 (1)	0.2500†	0.1101 (1)	1.86
S(1)	0.1735 (3)	0.3174 (3)	0.1172 (2)	2.49
Cl(1)	0.3274 (4)	0.0445 (3)	0.0850 (2)	3.31
Cl(2)	0.7375 (3)	0.1674 (3)	0.1047 (2)	3.15
N(1)	0.5822 (10)	0.4262 (8)	0.1320 (6)	2.53
C(1)	0.4878 (11)	0.5505 (9)	0.1437 (6)	1.97
C(2)	0.6179 (13)	0.6568 (10)	0.1778 (7)	2.74
C(3)	0.3468 (11)	0.5383 (11)	0.2104 (7)	2.79
C(4)	0.1684 (13)	0.4843 (10)	0.1557 (8)	3.15
C(5)	0.0703 (13)	0.3282 (15)	−0.0121 (7)	3.87
O(1)	0.5467 (11)	0.7686 (9)	0.1903 (8)	4.64
O(2)	0.7765 (10)	0.6373 (8)	0.1894 (6)	3.56
Pt(2)	1.0680 (1)	0.3197 (1)	0.3920 (1)	2.06
Cl(3)	0.7701 (3)	0.3823 (3)	0.3661 (2)	3.47
Cl(4)	1.1594 (4)	0.5286 (3)	0.4411 (2)	3.55
S(2)	1.3574 (3)	0.2624 (3)	0.4235 (2)	3.15
N(2)	0.9684 (11)	0.1408 (8)	0.3486 (7)	2.84
C(6)	1.0706 (11)	0.0380 (10)	0.3068 (6)	2.43
C(7)	0.9515 (14)	−0.0804 (10)	0.2835 (7)	2.93
C(8)	1.2486 (13)	0.0041 (10)	0.3703 (8)	3.21
C(9)	1.3951 (13)	0.1053 (14)	0.3679 (8)	3.56
C(10)	1.3944 (18)	0.2194 (14)	0.5551 (8)	4.77
O(3)	1.0299 (11)	−0.1839 (9)	0.2530 (7)	4.26
O(4)	0.7900 (10)	−0.0741 (8)	0.2834 (7)	3.91

† Fixed to define origin in space group $P2_1$.

The Pt atom in (I) is coordinated by the methionine N(amino) and S(thioether) atoms and by two Cl atoms (Fig. 1). The square-planar coordination geometry is only slightly distorted [deviations from the plane defined by N, S and Cl atoms: Pt(1) 0.012, N(1) 0.011, S(1) −0.011, Cl(1) 0.010, Cl(2) −0.011 Å; Pt(2) 0.020, N(2) 0.009, S(2) −0.019, Cl(3) −0.019, Cl(4) 0.009 Å]. The Pt–methionine chelate ring has a chair-like conformation with the carboxyl group equatorial to the ring. Both diastereomers have the thioether methyl group [C(5),C(10)] in an axial orientation, but the respective S—C bonds lie on opposite sides of the ring (see scheme). The Pt—S bond lengths, 2.246 (2) and 2.247 (2) Å, are not significantly different from the values of 2.244 (2) Å in dichloro-(*R*,*S*)-ethionineplatinum(II) (Khan *et al.*, 1991) and 2.218 (8), 2.260 (7) Å in dichloro-(*S*)-ethylcysteineplatinum(II) (Theodorou *et al.*, 1982). In both molecules of (I) the Pt—Cl bond distance *trans* to S [2.323 (2), 2.320 (2) Å] is marginally longer than that *trans* to N [2.309 (2),

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* Lists of structure amplitudes, anisotropic thermal parameters of non-H atoms, positional and thermal parameters of H atoms, torsion angles, least-squares planes and close contacts have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54841 (41 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Final atomic coordinates for* (II) *with e.s.d.'s in parentheses, and equivalent isotropic thermal parameters* (Å^2)

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Pt(1)	0.5286 (1)	0.0208 (1)	0.5020 (1)	1.80
Cl(1)	0.7080 (3)	−0.0316 (2)	0.6112 (1)	4.14
S(1)	0.7413 (2)	−0.0890 (2)	0.4293 (1)	2.81
N(1)	0.3375 (7)	0.1215 (5)	0.5680 (3)	2.06
C(1)	0.1519 (9)	0.1299 (6)	0.5254 (3)	2.24
C(2)	0.1848 (8)	0.1219 (5)	0.4377 (3)	1.71
O(1)	0.0546 (6)	0.1561 (4)	0.3924 (2)	2.32
N(2)	0.3536 (7)	0.0796 (4)	0.4160 (2)	1.67
C(3)	0.3903 (8)	0.0799 (6)	0.3310 (3)	2.04
C(4)	0.2812 (9)	−0.0217 (7)	0.2880 (3)	2.52
O(2)	0.2232 (8)	−0.1186 (5)	0.3319 (3)	3.96
O(3)	0.2568 (11)	−0.0140 (6)	0.2186 (3)	5.23
C(5)	0.6018 (9)	0.0712 (7)	0.3121 (3)	2.80
C(6)	0.6934 (10)	−0.0568 (8)	0.3249 (3)	3.52
C(7)	0.6685 (15)	−0.2529 (6)	0.4387 (7)	5.49
O(4)	−0.0051 (7)	0.2200 (5)	0.2353 (2)	3.23

Table 4. *Bond lengths* (Å) *and angles* (°) *in* (I) *with e.s.d.'s in parentheses*

Pt(1)—Cl(1)	2.309 (3)	Pt(2)—Cl(3)	2.320 (2)
Pt(1)—Cl(2)	2.323 (2)	Pt(2)—Cl(4)	2.310 (3)
Pt(1)—S(1)	2.246 (2)	Pt(2)—S(2)	2.247 (2)
Pt(1)—N(1)	2.047 (8)	Pt(2)—N(2)	2.029 (8)
N(1)—C(1)	1.478 (12)	N(2)—C(6)	1.469 (12)
C(1)—C(2)	1.491 (12)	C(6)—C(7)	1.514 (13)
C(2)—O(1)	1.285 (13)	C(7)—O(3)	1.310 (13)
C(2)—O(2)	1.205 (12)	C(7)—O(4)	1.225 (12)
C(1)—C(3)	1.507 (11)	C(6)—C(8)	1.526 (12)
C(3)—C(4)	1.542 (13)	C(8)—C(9)	1.521 (16)
C(4)—S(1)	1.785 (11)	C(9)—S(2)	1.814 (13)
S(1)—C(5)	1.811 (9)	S(2)—C(10)	1.819 (12)
Cl(1)—Pt(1)—Cl(2)	91.7 (1)	Cl(3)—Pt(2)—Cl(4)	91.8 (1)
Cl(1)—Pt(1)—S(1)	85.0 (1)	Cl(3)—Pt(2)—S(2)	177.6 (1)
Cl(1)—Pt(1)—N(1)	176.0 (2)	Cl(3)—Pt(2)—N(2)	83.9 (2)
S(1)—Pt(1)—Cl(2)	176.5 (1)	S(2)—Pt(2)—Cl(4)	86.8 (1)
N(1)—Pt(1)—Cl(2)	84.3 (2)	N(2)—Pt(2)—Cl(4)	175.7 (2)
N(1)—Pt(1)—S(1)	99.0 (2)	N(2)—Pt(2)—S(2)	97.5 (2)
Pt(1)—S(1)—C(4)	111.6 (3)	Pt(2)—S(2)—C(9)	111.3 (3)
Pt(1)—S(1)—C(5)	104.4 (4)	Pt(2)—S(2)—C(10)	104.5 (4)
C(4)—S(1)—C(5)	101.6 (6)	C(9)—S(2)—C(10)	100.6 (6)
Pt(1)—N(1)—C(1)	122.9 (5)	Pt(2)—N(2)—C(6)	124.1 (6)
N(1)—C(1)—C(2)	110.5 (7)	N(2)—C(6)—C(7)	108.6 (7)
N(1)—C(1)—C(3)	113.1 (7)	N(2)—C(6)—C(8)	114.7 (8)
C(2)—C(1)—C(3)	111.7 (8)	C(7)—C(6)—C(8)	112.6 (9)
C(1)—C(2)—O(1)	114.6 (9)	C(6)—C(7)—O(3)	115.2 (8)
C(1)—C(2)—O(2)	121.3 (9)	O(4)—C(7)—C(6)	121.5 (9)
O(1)—C(2)—O(2)	124.1 (9)	O(3)—C(7)—O(4)	122.9 (9)
C(1)—C(3)—C(4)	113.0 (8)	C(6)—C(8)—C(9)	114.8 (9)
C(3)—C(4)—S(1)	115.2 (7)	C(8)—C(9)—S(2)	115.5 (7)

Table 5. *Bond lengths* (Å) *and angles* (°) *in* (II) *with e.s.d.'s in parentheses*

Pt(1)—Cl(1)	2.307 (2)	N(2)—C(3)	1.465 (6)
Pt(1)—N(1)	2.046 (5)	C(3)—C(4)	1.509 (8)
Pt(1)—N(2)	2.004 (4)	C(4)—O(2)	1.335 (8)
Pt(1)—S(1)	2.258 (2)	C(4)—O(3)	1.192 (8)
N(1)—C(1)	1.489 (7)	C(3)—C(5)	1.517 (8)
C(1)—C(2)	1.509 (7)	C(5)—C(6)	1.520 (10)
C(2)—O(1)	1.246 (7)	C(6)—S(1)	1.834 (6)
C(2)—N(2)	1.317 (7)	S(1)—C(7)	1.821 (7)
Cl(1)—Pt(1)—N(1)	92.4 (1)	N(1)—C(1)—C(2)	110.0 (5)
Cl(1)—Pt(1)—N(2)	173.0 (1)	C(1)—C(2)—O(1)	118.7 (5)
Cl(1)—Pt(1)—S(1)	87.4 (1)	C(1)—C(2)—N(2)	115.6 (5)
N(1)—Pt(1)—N(2)	80.6 (2)	O(1)—C(2)—N(2)	125.7 (5)
N(1)—Pt(1)—S(1)	179.5 (1)	C(2)—N(2)—C(3)	115.6 (4)
N(2)—Pt(1)—S(1)	99.6 (1)	N(2)—C(3)—C(4)	112.7 (5)
Pt(1)—N(1)—C(1)	109.6 (3)	N(2)—C(3)—C(5)	112.2 (4)
Pt(1)—N(2)—C(2)	116.8 (3)	C(4)—C(3)—C(5)	110.4 (5)
Pt(1)—N(2)—C(3)	127.6 (4)	C(3)—C(4)—O(2)	115.8 (5)
Pt(1)—S(1)—C(6)	108.1 (2)	C(3)—C(4)—O(3)	120.1 (6)
Pt(1)—S(1)—C(7)	105.2 (3)	O(2)—C(4)—O(3)	124.1 (7)
C(6)—S(1)—C(7)	102.2 (5)	C(3)—C(5)—C(6)	115.8 (6)
S(1)—C(6)—C(5)	112.4 (4)		

2.310 (3) Å]. A similar *trans* effect is seen in the structure of dichloro-(*R*,*S*)-ethionineplatinum(II) where the corresponding Pt—Cl bond lengths are 2.325 (2) and 2.302 (2) Å (Khan *et al.*, 1991).

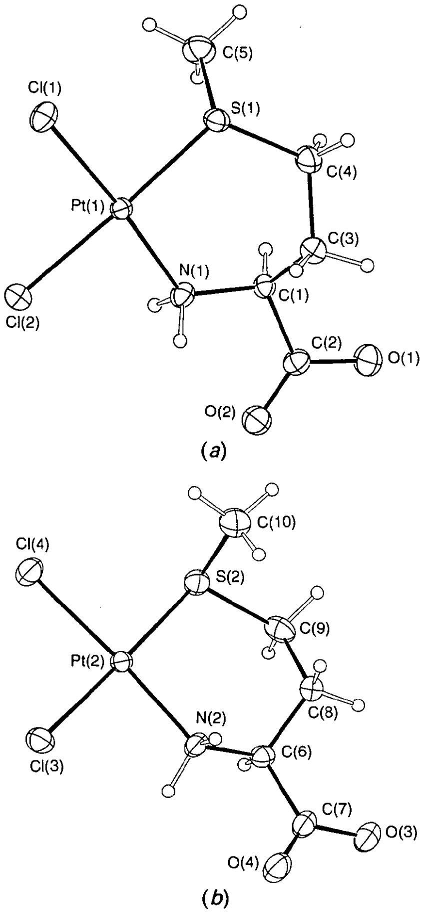

Fig. 1. *ORTEP* plots (Johnson, 1965) of the diastereomeric molecules of (I), showing atomic labels (30% thermal ellipsoids). (*a*) [Pt{(1*S*,*SR*)-Met}Cl_2]. (*b*) [Pt{(1*S*,*SS*)-Met}Cl_2].

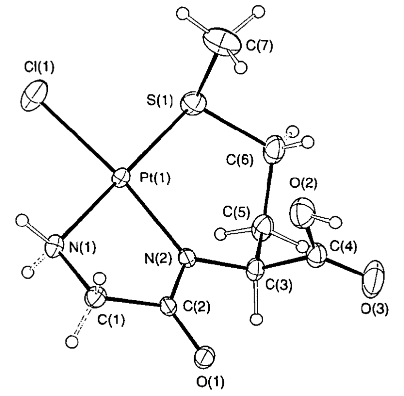

Fig. 2. *ORTEP* plot (Johnson, 1965) of (II), showing atomic labels (30% thermal ellipsoids).

Intermolecular distances show all acidic H atoms in (I) to be involved in hydrogen bonding. The molecules form dimers by means of strong hydrogen bonds between their carboxyl groups, $O(2^{i})\cdots H—O(3)$ 2.695 Å and $O(1)—H\cdots O(4^{i})$ 2.620 Å.* Although carboxyl H atoms were not located in difference maps, O(1) and O(3) are assumed to be protonated on the basis of the C—O bond lengths. The two carboxyl groups are not coplanar, the interplanar angle being 12.3°. Similar hydrogen bonds, 2.69 Å, occur in the crystals of dichloro-(*R*,*S*)-ethionineplatinum(II) (Khan *et al.*, 1991).

In (II), the peptide glycyl-(*S*)-methionine acts as a tridentate ligand *via* the N(amino), N(peptide) and S(thioether) atoms (Fig. 2). The six-membered chelate ring has a boat-like conformation with the S—C(methyl) and C—C(carboxyl) bonds in axial positions on the same side of the ring. The Pt—N(peptide) bond [2.004 (2) Å] is, as expected, shorter than the Pt—N(amino) bond [2.046 (2) Å]. The Pt—S bond length, 2.258 (2) Å, is at the upper end of the range in the amino acid complexes noted above. As in (I), the square-planar geometry of the Pt atom is slightly distorted but the deviations from the plane of best fit are smaller [Pt(1) −0.009, N(1) 0.0001, S(1) 0.0005, N(2) 0.004, Cl(1) 0.004 Å]. There are significant deviations from 90° among the bond angles at the Pt atom.

The N(amino) atom in (II) is hydrogen bonded to an O(peptide) atom O(1) and to an unprotonated O(carboxyl) atom O(3) in adjacent complexes. The protonated O(carboxyl) atom O(2) forms a strong hydrogen bond to the water O atom O(4): $O(2)\cdots O(4^{ii})$ 2.562, $H(2)\cdots O(4^{ii})$ 1.753 Å. Both H atoms of the water molecule are involved in hydrogen bonds to adjacent complexes: $O(4)\cdots O(1)$ 2.782, $H(4a)\cdots O(1)$ 1.92 Å and $O(4)\cdots Cl(1^{iii})$ 3.233, $H(4b)\cdots Cl(1^{iii})$ 2.39 Å.*

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* Symmetry operation: (i) $x, y-1, z$.

* Symmetry operations: (ii) $-x, \frac{1}{2}-y, \frac{1}{2}-z$; (iii) $\frac{1}{2}-x, -y, \frac{1}{2}-z$.

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Structure of Calcium 2,6-Difluorobenzoate Dihydrate

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Abstract. $Ca^{2+}.2C_7H_3O_2F_2^-.2H_2O$, $M_r = 390.3$, monoclinic, $C2/c$, $a = 17.584$ (4), $b = 10.771$ (3), $c = 7.887$ (2) Å, $\beta = 91.28$ (2)°, $V = 1493$ Å^3, $Z = 4$, $D_m = 1.75$, $D_x = 1.74$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 4.92$ cm^{-1}, $F(000) = 792$, $T = 293$ K, final $R = 0.037$ for 2415 unique observed reflections. The eight-coordinate Ca^{2+} ion is linked to six carboxylate O atoms from four different 2,6-difluorobenzoate ions and two water molecules. Each 2,6-difluorobenzoate ion chelates one Ca^{2+} ion and forms unidentate bridging linkages to two other Ca^{2+} ions leading to a polymeric structure. Unlike

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