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The Crystal Structure of Tetrakis(dithioacetato)vanadium(IV)

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Tetrakis(dithioacetato)vanadium(IV), V(CH$_3$CS$_2$)$_4$, crystallizes in the monoclinic space group $P2/c$, with $a=13{\cdot}36$, $b=8{\cdot}09$, $c=16{\cdot}41$ Å, and $\beta=114{\cdot}0°$. The crystal structure was solved by the Patterson method and refined by least-squares calculations to an R index of 0·12. The structure confirms the existence of VS$_8$ chromophores, with vanadium–sulphur distances of two types: V–S$_A$ and V–S$_B$, having mean values 2·50 and 2·46 Å respectively. There are two non-equivalent complexes, lying on twofold axes, in the structure. These complexes are different stereoisomers, belonging to dodecahedral subclasses *Id* (symmetry D_{2d}–$\bar{4}2m$) and *Vd* (symmetry C_2–2), according to the notation of Hoard & Silverton.

Introduction

Recent spectroscopic and magnetic studies of complexes involving sulphur and ions of the first-period transition metals (such as Ti^{4+} and V^{4+}) suggest the possibility of the existence of MS$_8$ chromophores (Bradley & Gitlitz, 1969; Alyea & Bradley, 1969; Bradley, Moss & Sales, 1969; Piovesana & Furlani, 1971; Piovesana & Cappuccilli, 1971). Crystallographic evidence of titanium coordinated by eight sulphur atoms is given by Colapietro, Vaciago, Bradley, Hursthouse & Rendall (1970) in tetrakis-(N,N-diethyldithiocarbamato)titanium(IV), Ti(S$_2$CNEt$_2$)$_4$; the analogous vanadium(IV) compound is isomorphous with this complex. The existence of VS$_8$ chromophores is proved by the X-ray work of Bonamico, Dessy, Fares, Porta and Scaramuzza (1971) on tetrakis(dithiophenylacetato)vanadium(IV), V(dtpa)$_4$.

The present study on tetrakis(dithioacetato)vanadium(IV), V(dta)$_4$, confirms the eight coordination around V^{4+} and the dodecahedral geometry of the VS$_8$ group.

Experimental

Crystals of V(dta)$_4$ were kindly supplied by Dr Piovesana of the Institute of Inorganic Chemistry of Perugia University. They have a short prismatic habit and are black in colour, while the powder is red-brown in transparence. A well formed crystal of dimensions 0·4 × 0·4 × 0·3 mm, with the symmetry $2/m$, was chosen and used for intensity data collection. Cell parameters were determined by basal Weissenberg photographs and refined by least-squares analysis to obtain the best agreement between calculated and observed θ angles. The results are: $a=13{\cdot}36\pm0{\cdot}02$, $b=8{\cdot}09\pm0{\cdot}02$, $c=16{\cdot}41\pm0{\cdot}02$ Å, $\beta=114{\cdot}0\pm0{\cdot}5°$. Assuming four formula units per unit cell, the calculated density is 1·704 g.cm^{-3}, which compares quite well with the observed value of 1·66 g.cm^{-3} as measured by the flotation method in an aqueous solution of potassium iodomercurate.

The space group was first assigned as $P2_1/c$ on the basis of the absence of reflexions $h0l$ with $l=2n+1$ and $0k0$ with $k=2n+1$. During the structure determination it appeared that the last condition is only simulated and the correct space group was found to be $P2/c$.

The reflexions from the $h0l$ to $h6l$, and $hk0$ reciprocal lattice layers were recorded with Cu $K\alpha$ radiation on equiinclination Weissenberg photographs taken employing the multiple-film technique. Intensity data were estimated by using a microdensitometer. In spite of long exposure times only 850 out of a total of 2540 independent reflexions collected were in the observable range, a high percentage of high-angle reflexions being too weak to be measured.

Intensity data were corrected for the usual geometrical factors; an absorption correction ($\mu=144{\cdot}19$ cm^{-1}) was applied with the program of De Meulenaer & Tompa (1965).

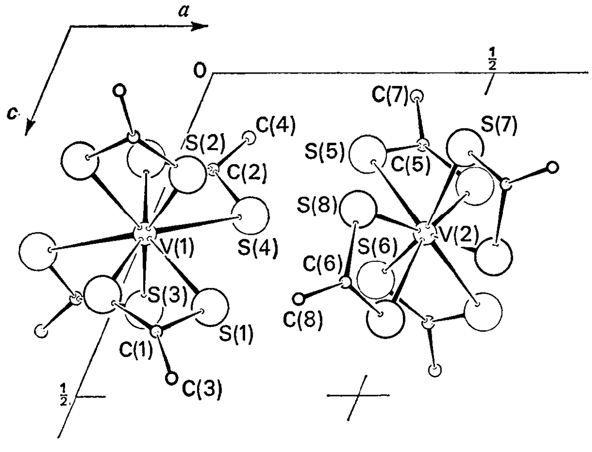

Fig. 1. The crystal structure of V(dta)$_4$ projected along [010].

The F^2's were put on approximately the same relative scale using the common reflexions from different zones.

A three-dimensional Patterson function was then computed, and vanadium ions and two non-equivalent sulphur atoms were located in positions consistent with the symmetry of space group $P2_1/c$. A Fourier synthesis computed with the contribution of these atoms showed curious splitting of maxima in positions presumably corresponding to those of the sulphur atoms of the complex. This fact led us to think that the symmetry of space group $P2_1/c$ was only simulated. In particular, the presence of the screw axis, inferred from a few $0k0$ reflexions, became doubtful. Indeed a careful inspection of the photographs revealed the presence of a very weak 090 reflexion, first considered as a spurious spot. The Patterson function was then reinterpreted according to $P2/c$ space group symmetry, locating two non-equivalent vanadium ions in the special position on twofold axes instead of one vanadium ion and its equivalent for the screw axis symmetry operation.

A Fourier synthesis revealed the locations of the remaining sulphur and carbon atoms. The structure was first refined by successive electron density maps, then by the least-squares method, using the block-diagonal approximation.

After four isotropic and three anisotropic cycles, the R index dropped to 0·12 for all observed reflexions. The weighting scheme was: $\sqrt{w}=1$, for reflexions having $|F_o|\le 4|F_{\min}|$; $\sqrt{w}=4|F_{\min}|/|F_o|$, for those having $|F_o|>4|F_{\min}|$. Unobserved reflexions were given $\sqrt{w}=0$. Final atomic coordinates and thermal parameters are listed in Table 1; observed and calculated structure factors are given in Table 2. Atomic scattering factors from *International Tables for X-ray Crystallography* (1962) were used.

Table 1. *Atomic coordinates and thermal parameters* (*with e.s.d.'s*)

Thermal parameters are given in the form: $\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})]$.
All values are × 10^4.

	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
V(1)	0	1828 (8)	¼	45 (5)	102 (12)	34 (3)	–	15 (3)	–
V(2)	½	3024 (8)	¼	54 (5)	99 (12)	33 (3)	–	15 (3)	–
S(1)	1735 (7)	3059 (11)	3621 (5)	82 (7)	178 (17)	55 (4)	−9 (10)	11 (5)	−12 (7)
S(2)	333 (7)	3907 (11)	1563 (5)	84 (7)	214 (18)	55 (4)	−9 (9)	22 (5)	42 (7)
S(3)	572 (7)	−273 (11)	3695 (6)	97 (7)	178 (17)	68 (5)	4 (10)	28 (5)	44 (8)
S(4)	1590 (7)	583 (12)	2311 (6)	79 (7)	258 (21)	77 (5)	15 (11)	42 (5)	−5 (9)
S(5)	3398 (6)	1786 (11)	1237 (4)	75 (6)	196 (17)	36 (3)	−10 (9)	10 (4)	−10 (7)
S(6)	4477 (6)	728 (12)	3216 (5)	73 (6)	182 (17)	57 (4)	−12 (9)	22 (4)	−37 (7)
S(7)	5043 (9)	4404 (14)	1156 (6)	162 (10)	338 (25)	39 (4)	−73 (14)	31 (6)	23 (9)
S(8)	3590 (9)	5188 (13)	2152 (7)	140 (10)	286 (27)	66 (5)	70 (14)	20 (6)	−24 (9)
C(1)	974 (24)	4266 (33)	4004 (18)	94 (27)	278 (80)	38 (14)	50 (40)	28 (17)	64 (29)
C(2)	751 (21)	−504 (35)	1505 (16)	79 (24)	172 (58)	34 (13)	41 (31)	37 (15)	0 (23)
C(3)	1581 (24)	5461 (41)	4725 (20)	85 (26)	252 (72)	58 (18)	43 (39)	26 (19)	−25 (30)
C(4)	1132 (31)	−1787 (44)	972 (21)	187 (44)	232 (77)	64 (20)	23 (48)	69 (26)	−56 (34)
C(5)	4321 (20)	478 (30)	1119 (14)	90 (23)	97 (49)	19 (10)	8 (28)	31 (13)	−4 (28)
C(6)	3939 (22)	5491 (33)	3250 (17)	93 (24)	103 (53)	48 (14)	8 (30)	55 (16)	9 (22)
C(7)	3798 (28)	−905 (42)	368 (18)	143 (34)	259 (75)	29 (15)	−76 (43)	17 (19)	−53 (27)
C(8)	3304 (28)	6701 (42)	3552 (23)	133 (35)	157 (74)	99 (24)	11 (40)	71 (25)	−18 (35)

Discussion of the structure

The crystal structure of V(dta)$_4$ projected along [010] is shown in Fig. 1. Bond distances and angles are listed in Tables 3 and 4.

Coordination around both non-equivalent vanadium ions is eightfold. The V(1) complex exhibits a nearly regular dodecahedral configuration with the sulphur atoms lying at the vertices of two interlocking trapezoids. The angle between these trapezoids (90° 33′) is very close to the theoretical value; the maximum deviations of atoms from planarity in each trapezoid is 0·02 Å.

The V(2) complex is more distorted: atoms are out of the planes of the trapezoids by up to 0·16 Å, and the angle between the two planes is 82°6′.

Table 2. *Observed and calculated structure factors of reflexions included in the refinement* (×10)

H, 0, 0		
2	1282	2095
4	340	-269
6	1319	1399
7	213	-280
9	234	-239
10	340	-276
12	261	322
H, 0, 2		
0	2228	-2287
-2	1587	-1688
-3	250	-142
4	1111	-1136
-4	384	527
-5	667	-802
6	1035	-1004
-6	539	-568
-7	281	-265
-8	345	-336
9	239	-211
-9	330	364
10	340	-312
-10	395	371
12	245	-224
-16	122	-53
H, 0, 4		
0	1515	-1450
-1	281	-236
2	250	191
-2	1763	-1262
3	245	-295
4	710	686
-4	517	-623
-5	1004	970
6	475	571
7	352	360
-7	618	543
8	747	719
-8	567	698
9	201	137
-9	287	-268
10	357	297
-10	287	375
13	138	180
H, 0, 6		
1	239	-266
-1	662	556
2	555	-605
-2	555	430
-3	683	572
-4	309	-307
5	463	430
6	688	-637
-6	324	-308
8	698	-618
-8	416	-540
-10	827	-901
12	207	-129
-12	530	-567
H, 0, 8		
0	1549	1455
1	747	761
-1	368	-329
-2	557	660
-3	281	-245
-4	1057	1093
5	565	-512
-5	309	396
6	608	522
-6	1389	1405
-7	530	-609
9	158	-123
11	213	-151
H, 0, 10		
0	523	-511
1	753	-809
2	420	375
-2	1105	-1149
3	266	-222
4	218	-201
-4	726	-724
-5	624	-739
6	234	-169
-6	683	-753
8	207	118
10	164	-140
-12	287	-143
H, 0, 12		
1	373	295
2	281	338
-2	378	369
-3	330	-329
4	362	370
-4	479	496
7	293	180
H, 0, 14		
0	298	-302
1	261	311
-1	266	365
2	581	-604
-3	357	344
4	207	-166
-4	362	-338
-5	340	299
H, 0, 16		
0	223	212
-1	266	-309
2	272	201
-4	362	347
H, 0, 18		
1	90	-127
-5	281	-260
H, 1, 0		
4	231	-235
5	202	175
6	462	-501
7	462	453
8	567	-558
9	252	245
H, 1, 1		
2	350	252
-2	1150	-1429
3	385	-447
-3	293	337
4	898	1216
6	996	1103
-6	694	-821
-12	301	-276
H, 1, 2		
1	1143	-1208
3	933	1152
-3	799	838
-4	469	-641
5	757	759
-5	821	-955
-6	595	-494
7	301	-236
-7	911	-969
-8	399	430
-9	356	-284
13	343	-266
H, 1, 3		
0	427	-289
-1	356	269
1	371	-338
-2	1354	1309
4	1024	-1207
-4	476	-409
6	391	-410
-6	223	-136
8	314	-298
10	511	-421
-14	258	252
H, 1, 4		
-1	588	567
2	420	482
-2	427	-441
3	1017	-1086
4	350	295
-4	497	498
-5	665	654
6	371	358
-6	630	656
-7	743	730
8	371	314
9	258	-225
-10	329	365
13	181	118
H, 1, 5		
0	350	-242
-2	525	328
-3	231	-71
4	321	281
-4	799	-762
-5	321	240
-6	314	-196
8	539	500
-8	266	-260
-10	484	-530
13	168	89
H, 1, 6		
1	504	-510
-1	1038	-1016
2	454	-455
-2	1185	1223
-3	252	-316
-4	293	314
5	582	-583
-5	434	-476
6	279	-356
-6	223	-163
-7	432	-440
8	378	-330
-8	427	459
-12	336	-341
H, 1, 7		
0	898	-857
-1	266	-250
2	588	-610
-3	321	252
4	286	294
-4	1115	940
6	279	-362
-6	1109	971
-7	252	-205
8	399	-319
-10	560	575
12	202	-167
-12	399	427
-14	286	75
H, 1, 8		
1	539	534
-1	834	816
-2	694	-710
3	645	677
-3	672	616
4	350	-277
-4	420	-350
5	504	484
-7	321	-248
-8	343	-367
-10	308	-317
H, 1, 9		
0	694	739
-2	525	-530
-4	504	-410
-5	314	-313
6	413	387
-6	883	-843
-8	449	-437
-10	308	-217
-12	356	-251
H, 1, 10		
1	252	-210
4	336	365
-4	364	-385
-6	434	-433
-7	659	604
-11	314	-315
H, 1, 11		
0	252	-218
-2	519	511
4	413	-419
-6	343	338
-8	469	437
H, 1, 12		
3	314	-239
-4	314	325
-6	391	441
-11	301	395
H, 1, 13		
2	434	421
-2	301	-320
-4	476	-424
H, 1, 14		
-2	244	272
5	195	-155
-5	484	-332
H, 1, 15		
2	252	-262
H, 1, 16		
3	202	181
H, 2, 0		
1	203	-197
2	677	723
4	457	-497
6	620	-569
8	240	-247
9	228	-205
10	395	-391
12	215	-225
H, 2, 1		
1	633	501
-1	939	753
2	375	434
-2	587	544
3	203	-239
-3	681	-679
4	489	486
-4	501	506
-5	800	-782
7	403	-511
-7	432	-456
9	428	-383
-9	616	-559
10	231	215
11	301	-131
-11	428	-381
H, 2, 2		
0	305	-269
-1	231	208
2	256	286
-2	514	548
3	138	237
-3	661	-629
4	1049	1115
-4	194	260
5	154	211
-5	580	-581
6	162	164
-6	252	283
-8	527	489
-10	277	283
-12	203	221
H, 2, 3		
0	980	918
1	1234	1121
-1	517	450
2	592	519
-2	334	285
3	350	-433
-3	162	58
-4	194	197
5	289	-325
-5	1188	1204
7	179	212
-7	448	421
-8	223	160
-10	301	277
-11	428	361
H, 2, 4		
1	318	370
-1	403	-413
2	1172	-1124
-2	2620	-2177
4	763	-774
-4	1941	-1652
-5	919	994
6	477	439
-6	292	273
7	182	162
-7	215	192
-8	175	-263
-10	305	-320
-11	305	222
H, 2, 5		
0	371	-473
1	1098	-1090
-1	2162	-1825
2	559	-531
3	240	262
-3	388	-372
4	231	-267
-4	326	-275
5	240	-240
-5	975	-851
6	240	-249
-6	220	-259
-7	620	-594
-8	179	213
-9	342	303
-13	138	-131
H, 2, 6		
0	489	401
1	289	-324
-1	264	252
2	816	817
-2	677	555
-3	481	512
-4	1512	1298
-5	281	-268
6	223	-203
-6	388	329
8	146	242
-9	318	321
-10	158	208
H, 2, 7		
1	489	514
-1	800	719
-2	390	-357
3	776	803
-3	959	794
-4	289	-267
5	539	511
-7	281	222
-8	211	-211
H, 2, 8		
0	375	-364
1	390	346
2	170	-208
-3	330	-305
6	297	-304
-6	522	-457
-8	400	-340
-9	444	-475
-10	162	-137
H, 2, 9		
0	211	235
1	527	-532
-1	129	237
2	289	358
3	570	-597
7	223	-256
9	223	-255
-9	159	-230
-11	281	-228
H, 2, 10		
0	416	426
1	416	-403
2	326	311
-2	166	125
4	464	496
-4	211	-262
6	244	269
-6	277	234
-8	400	315
-12	220	201
-14	289	235
H, 2, 11		
1	203	212
-1	231	-278
-3	268	-283
-4	379	333
7	264	239
-10	305	260
-11	293	322
H, 2, 12		
0	203	-226
1	248	293
-1	223	-172
2	264	-223
-2	436	-508
4	293	-273
-5	240	360
8	117	-118
-8	199	-262
-14	264	-287
H, 2, 13		
-1	203	-189
-4	330	-371
-5	383	-491
7	88	-80
-7	420	-421
-8	199	280
-11	191	-222
-13	182	-195
H, 2, 14		
-3	284	319
-4	203	248
-8	318	188
H, 2, 15		
-1	314	325
-3	293	381
5	105	124
-5	141	241
-7	293	284
-9	211	277
H, 2, 16		
-6	162	-211
-8	256	-235
H, 2, 18		
0	105	161
-1	134	-132
-2	129	232
-3	122	-159
-8	154	168
H, 3, 0		
1	397	508
2	187	264
3	814	-994
4	252	334
5	172	-182
6	203	-221
8	443	-475
9	641	-569
H, 3, 1		
0	443	347
-1	243	147
-2	247	150
2	610	716
-3	321	414
3	421	-505
-6	263	221
6	227	188
-7	279	-232
7	421	505
-8	515	522
8	236	93
-10	341	285
H, 3, 2		
-1	866	-671
1	1079	923
-3	830	851
3	1023	1036
-4	314	-322
-5	909	921
-7	279	-278
7	452	446
-8	373	387
-9	236	320
9	341	300
-10	263	180
-11	416	435
H, 3, 3		
-1	361	352
1	586	-584
-2	1239	-1117
2	310	226
-4	759	-799
4	287	202
-5	354	382
-6	443	-495
6	467	-405
-7	266	161
7	318	-245
-8	826	-834
-10	330	-357
H, 3, 4		
0	408	-457
-1	1023	-903
1	1228	-1195
-2	459	-461
-3	711	-661
3	452	-431
-5	976	-919
5	483	-442
6	164	123
-7	180	-183
7	325	-325
-11	310	-313
H, 3, 5		
0	298	-335
-1	448	-469
1	428	450
-2	1110	1106
2	338	-330
-4	735	808
-5	203	-323
-8	370	400
-9	220	267
-12	266	-209
H, 3, 6		
0	282	389
-1	913	1032
-2	456	506
-3	148	590
3	448	409
-4	215	181
4	252	-59
5	495	450
-7	488	506
-9	243	295
H, 3, 7		
-2	196	-221
2	330	277
3	203	311
-4	254	-292
4	341	370
-6	298	268
6	270	237
-8	262	252
-9	220	-215
-12	231	181
H, 3, 8		
0	227	146
-2	145	-138
2	298	202
-3	254	-261
3	483	-526
-4	191	141
4	266	-230
-7	333	-317
-8	287	-342
-9	432	-430
H, 3, 9		
0	345	-380
-2	231	249
3	185	133
-4	270	-303
4	298	-295
-6	357	-313
H, 3, 10		
0	341	-330
-1	239	-250
1	258	356
-2	290	228
2	185	-109
3	294	312
-4	212	-194
4	223	265
-5	392	487
-6	491	-499
-8	196	207
-9	373	316
-11	314	266
H, 3, 11		
1	279	-312
-2	467	-477
-3	252	232
3	270	-296
4	274	254
-10	282	-222
-11	294	211
H, 3, 12		
-1	408	-399
1	504	-513
-5	467	-496
-6	381	366
-7	365	-388
-10	263	-104
H, 3, 13		
0	239	186
-7	290	192
-8	321	342
H, 3, 14		
-1	534	507
-3	282	255
-6	381	181
-7	385	351
H, 4, 0		
3	192	-177
4	289	-215
H, 4, 1		
-1	516	408
1	1175	-978
-2	365	402
-3	1323	1276
3	1155	-1125
-4	482	544
5	373	301
-6	192	-87
-7	314	-375
-9	289	311
9	163	-351
H, 4, 2		
0	149	-182
-1	213	206
1	373	380
-2	407	-260
2	415	406
4	495	484
5	247	216
-6	440	-457
6	271	260
7	352	305
-8	339	-343
H, 4, 3		
0	651	-655
-1	651	-534
1	999	878
2	263	-287
-3	445	-256
3	411	384
-4	373	-365
-5	490	-504
5	482	566
-7	285	-322
7	625	680
-9	289	-343
H, 4, 4		
0	276	192
-1	276	-333
-2	243	162
2	217	-189
-6	285	364
-8	297	281
H, 4, 5		
0	297	336
-1	259	242
-3	318	-296
3	411	-374
-4	230	159
5	881	-933
-7	583	637
7	208	-358
-9	373	424
H, 4, 6		
0	239	-260
2	230	-208
3	179	-172
-4	226	195
4	365	-322
-6	297	236
6	268	-256
H, 4, 7		
0	335	298
-1	247	-296
1	499	-493
-2	356	-369
-3	415	-425
3	243	253
4	230	188
-5	380	322
5	402	386
-9	427	-449
H, 4, 8		
0	171	185
1	217	181
-3	271	-332
-6	347	-329
H, 4, 9		
0	217	-247
-2	377	414
-3	1049	1139
3	259	-290
-4	297	-281
-5	271	361
-6	243	-259
-9	415	476
H, 4, 10		
0	234	177
-3	243	229
H, 4, 11		
-1	385	-409
1	440	485
-3	544	-524
-4	188	139
-5	562	-671
-6	289	228
-7	323	-471
-9	289	-337
H, 4, 13		
-1	402	434
-7	234	277
H, 5, 0		
1	825	790
2	278	323
3	852	795
4	183	202
9	234	222
H, 5, 1		
1	354	-349
-1	276	315
-2	364	303
3	563	-581
-3	610	667
-4	172	-167
-5	278	231
-7	190	-252
-8	276	281
H, 5, 2		
0	217	240
1	923	-849
-1	288	-239
3	306	-412
-3	476	-429
-4	200	-231
-5	473	-498
7	493	-506
H, 5, 3		
-1	302	315
-2	443	-470
4	248	189
-8	484	-458
-10	214	-221
H, 5, 4		
0	408	-425
1	346	323
-1	217	201
2	220	-192
-2	350	-300
-3	190	-286
5	623	575
-5	252	206
7	484	491
-7	336	328
H, 5, 5		
0	227	174
1	344	352
-1	276	-299
-2	265	270
-3	224	-226
-4	306	381
5	280	-240
-8	306	266
-9	272	247
-10	217	163
H, 5, 6		
-1	391	-459
-2	149	213
5	518	-506
-5	278	272
-7	356	-534
-9	316	-331
H, 5, 7		
-2	142	-114
3	286	288
-3	179	-230
-4	272	-254
-9	255	-298
H, 5, 8		
0	276	189
-1	310	350
-2	255	193
3	336	290
-3	582	649
-7	313	401
-9	408	450
H, 5, 9		
0	316	-366
-1	241	235
-2	449	411
-6	169	-205
H, 5, 10		
1	350	-279
-1	252	-296
-3	651	-632
-5	541	-585
-7	313	-298
-9	276	-276
H, 5, 11		
-2	453	-425
4	248	237
H, 5, 12		
1	323	264
-3	190	183
-5	306	248
H, 6, 0		
1	262	160
2	156	-135
3	396	370
6	306	316
7	124	-155
H, 6, 1		
0	193	-103
1	228	-209
-1	134	101
3	447	-465
-3	303	-289
-4	274	244
5	380	-359
-5	340	-330
6	187	-125
7	387	-401
8	181	-105
9	134	-192
-9	161	-200
-11	130	-125
H, 6, 2		
0	124	-124
-1	124	56
2	202	236
-2	450	-398
3	259	-252
-4	171	-189
-6	415	-404
-8	503	-454
10	183	-162
H, 6, 3		
0	212	209
1	544	535
2	143	175
-2	193	-229
3	136	83
-4	228	-207
5	140	119
-5	306	241
6	212	194
-6	196	-165
7	262	289
-8	177	-180
-9	109	-89
-11	202	204
H, 6, 4		
1	93	-51
2	174	115
-2	750	666
-3	174	-85
4	183	223
-4	497	482
8	146	74
-8	359	346
10	146	129
-10	181	166
-11	79	81
H, 6, 5		
0	130	-149
1	265	-244
-1	456	-471
2	111	75
-2	208	163
3	171	143
4	140	94
-4	202	205
5	140	-87
-5	274	-276
-7	199	-226
-9	156	121
-11	143	-102
H, 6, 6		
0	183	-306
2	355	-408
-2	239	-300
3	190	-189
-3	174	-137
4	171	-146
-4	205	-226
5	143	-179
8	124	-108
-9	136	-183
-11	127	-90
H, 6, 7		
0	146	-193
1	150	122
-1	262	261
2	218	-261
3	150	163
-3	243	303
4	174	-124
-5	362	404
-7	434	478
-11	143	114
H, 6, 8		
0	363	419
1	136	107
2	177	169
-2	167	191
3	143	179
-3	150	173
4	127	158
-5	234	184
6	152	202
-11	68	-1
H, 6, 9		
0	156	198
1	300	-308
3	246	-257
-3	124	-165
-5	243	-263
7	127	-129
-7	239	-263
-9	143	-225
H, 6, 10		
0	134	-111
-2	274	-211
3	136	123
4	228	-226
-5	140	-140
6	99	-127
-8	187	-187
H, 6, 11		
1	327	348
3	177	180
-4	120	136
5	86	93
-5	93	92
H, 6, 12		
0	118	-113
-1	111	88
3	93	-96
4	89	130
-7	128	170
-8	143	210
-10	161	195
H, 6, 13		
1	183	-152
-1	93	-139
-8	183	211
H, 6, 14		
-1	136	-156

The pseudosymmetry $\bar{4}$ axes of the two VS$_8$ chromophores are in planes parallel to (010). The axis of the V(1) complex, bisecting the S(1)–V(1)–S(4) angle, is nearly parallel to the a^* reciprocal axis; that of V(2), bisecting the S(5)–V(2)–S(7) angle is almost parallel to the axis c^*.

According to the notation of Hoard & Silverton (1963), in the V(1) complex, chelation is along the dodecahedral edges labelled *m*, as in Ti(S$_2$CNEt$_2$)$_4$ (Colapietro *et al.*, 1970) and in V(dtpa)$_4$ (Bonamico *et al.*, 1970). This complex thus belongs to the *Id* dodecahedral (D_{2d}–$\bar{4}2m$ symmetry) sub-class of M(X$_2$)$_4$ stereoisomers. In the V(2) complex, chelation is along two *m* and two *g* edges, and this is probably the cause of the major distortion. The resulting stereoisomer belongs to the *Vd* sub-class, with C_2–2 symmetry. To date, the V(2) complex is the first MS$_8$ cromophore found to have this configuration, which is energetically unfavourable (Hoard & Silverton, 1963).

The V–S distances are of two kinds: the average V–S$_A$ distance is 2·50 Å, V–S$_B$ is 2·46 Å, with an $(M–A)/(M–B)$ ratio of 1·02. V–S$_A$ and V–S$_B$ bond lengths can be compared with the corresponding distances in V(dtpa)$_4$, 2·524 and 2·470 Å respectively. Assuming a mean distance of 2·48 Å as a unit length, the shape parameters computed for the V(1) dodecahedron are: $a=1{\cdot}17$, $m=1{\cdot}11$, $g=1{\cdot}27$, $b=1{\cdot}44$, $\theta_A=35{\cdot}4°$, $\theta_B=77{\cdot}0°$. Those computed for the V(2) dodecahedron are: $a=1{\cdot}25$, $m=1{\cdot}17$, $g=1{\cdot}21$, $b=1{\cdot}47$, $\theta_A=38.2°$, $\theta_B=70{\cdot}2°$. These parameters can be compared with the 'most favourable' parameters of Hoard & Silverton for the $D2_d$–$\bar{4}2m$ coordination polyhedron: $a=m=1{\cdot}17$, $g=1{\cdot}24$, $b=1{\cdot}49$, $\theta_A=35{\cdot}2°$, $\theta_B=73{\cdot}5°$, $(M–A)/(M–\mathrm{B})=1{\cdot}03$. The lengths of the dodecahedral edges in the two complexes are listed in Table 5.

The high estimated standard deviation in the positions of lighter atoms make it difficult to assign physical significance to the differences found in the values of the bonds in the ligand molecule: the C–S average bond length is 1·64 Å; the C–C distance is 1·54 Å.

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Table 3. *Bond distances with e.s.d.'s*

Primed atoms are equivalent to those of Table 1 by the two-fold symmetry operation.

V(1)–S(1)	2·51 (2) Å (×2)	V(2)–S(5)	2·50 (2) Å (×2)
V(1)–S(2)	2·44 (1) (×2)	V(2)–S(6)	2·45 (1) (×2)
V(1)–S(3)	2·47 (1) (×2)	V(2)–S(7)	2·49 (1) (×2)
V(1)–S(4)	2·48 (1) (×2)	V(2)–S(8)	2·46 (1) (×2)
C(1)–S(1)	1·70 (3)	C(5)–S(5)	1·69 (3)
C(1)–S(2′)	1·64 (3)	C(5)–S(6′)	1·54 (3)
C(1)–C(3)	1·49 (4)	C(5)–C(7)	1·60 (4)
C(2)–S(3′)	1·67 (3)	C(6)–S(7′)	1·58 (3)
C(2)–S(4)	1·60 (3)	C(6)–S(8)	1·69 (3)
C(2)–C(4)	1·57 (4)	C(6)–C(8)	1·51 (4)

Table 4. *Bond angles with e.s.d.'s*

S(1)–V(1)–S(1′)	133·2 (5)°	S(5)–V(2)–S(5′)	132·8 (5)°
S(1)–V(1)–S(2)	80·6 (4)	S(5)–V(2)–S(6)	77·2 (3)
S(1)–V(1)–S(2′)	67·3 (3)	S(5)–V(2)–S(6′)	67·3 (3)
S(1)–V(1)–S(3)	78·2 (5)	S(5)–V(2)–S(7)	76·5 (4)
S(1)–V(1)–S(3′)	138·7 (4)	S(5)–V(2)–S(7′)	126·3 (4)
S(1)–V(1)–S(4)	70·7 (3)	S(5)–V(2)–S(8)	77·1 (5)
S(1)–V(1)–S(4′)	130·7 (3)	S(5)–V(2)–S(8′)	142·4 (3)
S(2)–V(1)–S(2′)	92·8 (4)	S(6)–V(2)–S(6′)	81·2 (4)
S(2)–V(1)–S(3)	153·9 (3)	S(6)–V(2)–S(7)	151·5 (4)
S(2)–V(1)–S(3′)	92·9 (3)	S(6)–V(2)–S(7′)	78·5 (4)
S(2)–V(1)–S(4)	79·4 (4)	S(6)–V(2)–S(8)	108·1 (4)
S(2)–V(1)–S(4′)	138·0 (4)	S(6)–V(2)–S(8′)	140·3 (4)
S(3)–V(1)–S(3′)	93·0 (5)	S(7)–V(2)–S(7′)	126·8 (4)
S(3)–V(1)–S(4)	79·4 (4)	S(7)–V(2)–S(8)	76·5 (5)
S(3)–V(1)–S(4′)	68·0 (5)	S(7)–V(2)–S(8′)	66·2 (5)
S(4)–V(1)–S(4′)	132·1 (4)	S(8)–V(2)–S(8′)	89·4 (5)
S(1)–C(1)–S(2′)	110 (2)°	S(5)–C(5)–S(6′)	116 (1)°
S(1)–C(1)–C(3)	117 (2)	S(5)–C(5)–C(7)	114 (2)
S(2′)–C(1)–C(3)	133 (2)	S(6′)–C(3)–C(7)	130 (2)
S(3′)–C(2)–S(4)	115 (2)°	S(7′)–C(6)–S(8)	112 (2)°
S(3)–C(2)–C(4)	121 (2)	S(7′)–C(6)–C(8)	128 (2)
S(4)–C(2)–C(4)	123 (2)	S(8)–C(6)–C(8)	120 (2)

Table 5. *Lengths of dodecahedral edges in* V(1) *and* V(2) *complexes*

V(1) complex			
a	S(1)–S(4)	2·89 (1) Å	(×2)
m	S(1)–S(2′)	2·74 (1)	(×2)
m	S(3)–S(4′)	2·77 (2)	(×2)
g	S(2)–S(4)	3·14 (2)	(×2)
g	S(1)–S(3)	3·14 (1)	(×2)
g	S(1)–S(2)	3·20 (2)	(×2)
g	S(3)–S(4)	3·16 (2)	(×2)
b	S(3)–S(3′)	3·58 (2)	
b	S(2)–S(2′)	3·53 (1)	
b	S(2)–S(3′)	3·56 (1)	(×2)
V(2) complex			
a	S(5)–S(7)	3·09 (1) Å	(×2)
m	S(7)–S(8′)	2·71 (2)	(×2)
m	S(5)–S(6)	3·09 (2)	(×2)
g	S(5)–S(6′)	2·74 (1)	(×2)
g	S(7)–S(8)	3·07 (2)	(×2)
g	S(5)–S(8)	3·10 (1)	(×2)
g	S(6)–S(7′)	3·13 (2)	(×2)
b	S(6)–S(6′)	3·19 (1)	
b	S(8)–S(8′)	3·46 (2)	
b	S(6)–S(8)	3·97 (2)	(×2)

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A Refinement of the Structure of Bis-(L-histidinato)zinc(II) Dihydrate*

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The crystal structure of bis-(L-histidinato)zinc(II) dihydrate, $Zn(C_6H_8N_3O_2)_2.2H_2O$, which was originally determined by Kretsinger, Cotton & Bryan [*Acta Cryst.* (1963), **16**, 651], has been further refined by full-matrix least-squares methods to a final *R* index of 0·071. Coordinates and individual anisotropic temperature parameters for Zn, C, N, and O were refined; hydrogen atoms were positioned on the basis of geometry. Contrary to the results of Kretsinger *et al.*, inclusion of the hydrogen atoms and anisotropic refinement have led to a significant improvement in the model.

Introduction

The crystal structure of bis-(L-histidinato)zinc(II) dihydrate was determined by Kretsinger, Cotton & Bryan (1963) (KCB). They obtained Cu *Kα* intensity data from equi-inclination Weissenberg photographs and determined the structure by Patterson and Fourier methods. Refinement of the structure by least-squares methods was normal through isotropic refinement (R=0·108). However, the introduction of the hydrogen atoms and anisotropic refinement of the heavy atoms caused an increase in *R* to 0·113 and significant changes in the dimensions of the histidine ligand. The most notable of these changes was in the C(3)–C(4) bond length (1·478 Å, isotropic without hydrogen atoms; 1·400 Å, anisotropic with hydrogen atoms). As previously noted by Donohue & Caron (1964), it is difficult to understand why the introduction of the hydrogen atoms and the allowance for anisotropy caused the large changes in the geometry and the increase in the *R* index.

Our recent interest in the geometry and dimensions of the histidine molecule (Kistenmacher & Marsh, 1971; Kistenmacher, Hunt & Marsh, 1971) led us to carry out further refinement of the structure of bis-(L-histidinato)zinc(II) dihydrate. Contrary to the experience of KCB, our refinement, including fixed hydrogen positions and individual anisotropic temper-

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