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The Crystal Structure of Bis(diethyldithiophosphato)nickel(II), Ni $[(C_2H_5O)_2PS_2]_2$

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Bis(diethyldithiophosphato)nickel(II) is monoclinic, space group $P2_1/c$, with two molecules per unit cell. Unit-cell dimensions, determined with the use of standardized silicon powder and computed by the method of least-squares, are $a = 10{\cdot}493 \pm 0{\cdot}005$, $b = 10{\cdot}300 \pm 0{\cdot}003$, $c = 8{\cdot}76 \pm 0{\cdot}01$ Å, $\beta = 102{\cdot}59 \pm 0{\cdot}05°$.

The structure has been determined from a three-dimensional Patterson synthesis and a series of three-dimensional Fourier syntheses. Refinement was by the method of full-matrix least-squares, using data of the type $h0l - h7l$, to the final residual of 0·115. The molecule itself is centrosymmetric with nickel at the centre of symmetry. The nickel and four sulphur atoms are in square planar configuration, with nickel–sulphur bonds of 2·23 and 2·24 Å, which are well within the range 2·1–2·3 Å found for other square planar nickel(II) complexes. The nickel atom shows no tendency to coordinate to any atom in other molecules.

Introduction

This diamagnetic compound was first prepared by Malatesta & Pizzotti (1945) and since then consideration has been given to its probable molecular structural formula together with the structural formulae of similar complexes. Quite recently Lopez-Castro & Truter (1963) observed that in diamagnetic nickel(II) complexes the Ni–S distance is 2·1–2·3 Å, whereas in six-coordinate complexes it is 2·4–2·6 Å. They have commented that this is in accordance with ligand-field theory which predicts that the stronger field produced by the ligands closer to the nickel will cause the d_γ electrons to pair in the d_{z^2} orbitals, so producing a diamagnetic complex with no close neighbours in the z direction. Hence the most likely structural configuration for this compound would be one shown in Fig. 1(*a*) with a nickel atom and four sulphur atoms in square planar configuration. Other configurations, shown in Fig. 1(*b*), (*c*) and (*d*), were considered possible but less likely.

This compound has, however, a few rather unusual properties:

(i) Four-membered rings like Ni–S–P–S in Fig. 1(*a*) are comparatively rare. When this investigation was commenced, only one such structure was fully determined (Barclay & Hoskins, 1962) but since then another similar structure (Franzini, 1963) has been reported.

(ii) Its deep purple colour is unusual, as most diamagnetic square-planar nickel compounds are yellow, brown or red.

(iii) It has a high solubility in most solvents including non-polar light petroleum.

These properties have raised doubts about the correctness of the theoretical predictions, and an investigation of its structure by X-ray methods was undertaken in order to resolve any uncertainties.

Since the completion of the structure determination we have learned of a preliminary communication regarding $Ni[(OEt)_2PS_2]_2$ by Glinskaya & Porai-Koshits (1959) which gave a space group, a unit cell, and the Ni–S distance and configuration in good agreement with the present work. Their report appears, however, to have been based solely on a Patterson synthesis and a single electron-density projection. This is scarcely conclusive, particularly in view of the difficulty in distinguishing in projection between sulphur, phosphorus and two superimposed oxygen atoms.

Experimental

Crystal data

Bis(diethyldithiophosphato)nickel(II)
$Ni[(C_2H_5O)_2PS_2]_2$
Colour: deep purple, almost opaque.
Solubility: highly soluble in most organic solvents both polar and non-polar;
soluble also in water and very slightly in oils.
Unit-cell dimensions at 20°C:

$$a = 10{\cdot}493 \pm 0{\cdot}005 \text{ Å}$$
$$b = 10{\cdot}300 \pm 0{\cdot}003$$
$$c = 8{\cdot}76 \pm 0{\cdot}01$$
$$\beta = 102{\cdot}59 \pm 0{\cdot}05°$$

The errors quoted are four times the standard deviations.

Space group extinctions from Weissenberg photographs are

$$h0l:\ l = 2n+1$$
$$0k0:\ k = 2n+1\,,$$

indicating the monoclinic space group $P2_1/c$.

Because of the high solubility of the substance, its density was estimated by measuring the dimensions and mass of a well-developed crystal. This gave a value of 1·4 g.cm^{-3}. The calculated density for $Z=2$ is 1·54 g.cm^{-3}. With $Z=2$, the nickel must be in a special position at the centre of symmetry; the molecule itself is centrosymmetric with one-half of each molecule occupying one of the four general positions of the space group.

For Cu $K\alpha$ radiation the linear absorption coefficient $\mu = 71{\cdot}4$ cm^{-1}.

Accurate unit-cell dimensions were obtained from $h0l$ and $hk0$ Weissenberg photographs obtained with crystals sprinkled with silicon powder* as a calibrating substance. The cell parameters and their standard deviations were obtained by a least-squares program written by Sanger (1964), and 45 reflexions with resolved α_1 and α_2 spots lying between the 533 and 444 powder lines of silicon provided 90 measurements for least-squares computations.

Standards used:

$$\lambda(\text{Cu } K\alpha_1) = 1{\cdot}54051 \text{ Å}$$
$$\lambda(\text{Cu } K\alpha_2) = 1{\cdot}54433 \text{ Å}$$

For Si line 533:

$$\theta(\text{Cu } K\alpha_1) = 68{\cdot}446°,\ \theta(\text{Cu } K\alpha_2) = 68{\cdot}811°$$

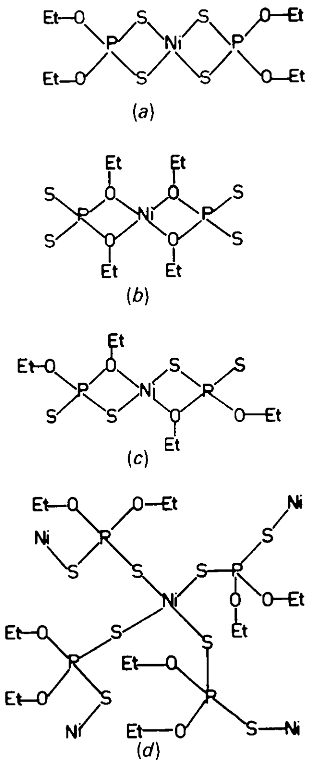

Fig. 1. Possible structural configurations for $Ni[(C_2H_5O)_2PS_2]_2$. (*a*) is considered most likely on chemical grounds.

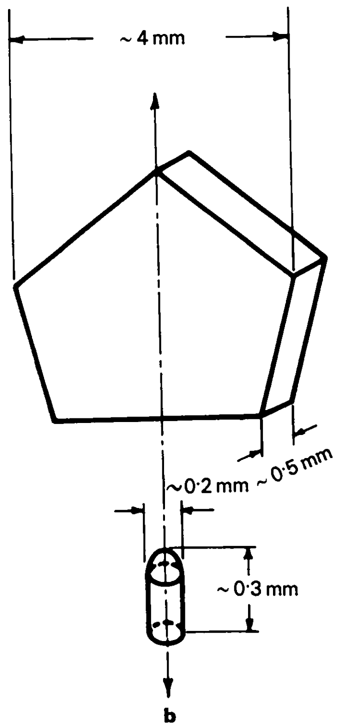

Fig. 2. The shape and size of the initial and final crystals.

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* Standardized Si powder was obtained from Dr W. Parrish, Philips Laboratories, Irvington-on-Hudson, New York, U.S.A.

For Si line 444:

$$\theta(\mathrm{Cu}\ K\alpha_1)=79{\cdot}314^\circ,\ \theta(\mathrm{Cu}\ K\alpha_2)=80{\cdot}100^\circ$$

Crystals used for the collection of intensity data were obtained by slow evaporation of an acetone solution at a few degrees below 0 °C and had a plate-like habit with one dimension an order of magnitude smaller than the other two. Such a habit and the considerable value of μ tended to produce doubling of some spots. This effect was minimized by dissolving a large crystal down to a roughly cylindrical shape. The shapes and sizes of the initial and final crystals are shown in Fig. 2. The spots still showed a trace of doubling and it was decided to integrate the intensities in one direction (rotation of the film cassette) in order to facilitate visual measurements. (This procedure does not, of course, correct the absorption error.)

Using a Nonius integrating Weissenberg camera and the multiple film technique, 8 layers of intensity photographs, *h*0*l* through *h*7*l*, were measured visually with the aid of a calibration strip and corrected for Lorentz and polarization effects. Another similar crystal was used to obtain *hk*0 intensities to provide approximate inter-layer scale factors for a Patterson synthesis.

All photographs were taken at room temperature (20 °C). A total 1411 reflexions were measured, including 214 unobserved.

No corrections were made for absorption or extinction, but a few strong reflexions were omitted from the least-squares refinement. During an early stage of investigation, rotation and zero-layer Weissenberg photographs about the same crystallographic direction were prepared both for $\mathrm{Ni[(OEt)_2PS_2]_2}$ and also for $\mathrm{Pd[(OEt)_2PS_2]_2}$. The diffraction patterns coincided on superposition, confirming chemical opinion that these two compounds are isomorphous. No attempt was made to pursue this aspect any further.

Structure determination

From a three-dimensional unsharpened Patterson synthesis, peaks consistent with a square-planar Ni–S–P–S arrangement were found. Structure factors calculated up to $\sin^2\theta=0{\cdot}3$, using the coordinates of these four atoms, gave a reliability index $R=0{\cdot}46$. A three-dimensional Fourier synthesis based upon these structure factors appeared encouraging and gave more satisfactory coordinates for the Ni, S and P atoms. Initially an isotropic temperature factor $B=2{\cdot}0$ Å^2 was assumed, which was later adjusted to 3·5 Å^2. The oxygen atoms were located by correlation of the peaks in successive Fourier syntheses with Patterson peaks; the carbon atoms were located with less certainty. The reliability index was 0·34 at this stage. The positions of the carbon atoms were not located with any certainty until the refinement stage, when the full range of intensity data was being used, and the heavier atoms were near to their final positions. After several three-dimensional difference syntheses and one cycle of a differential synthesis, R was reduced to 0·25 for all reflexions excluding unobserved.

At this stage refinement by least-squares was commenced. Unobserved reflexions where F_c was less than the minimum observable were excluded from the refinement, as were other reflexions affected by extinction or whose observed values were considered unreliable. These are indicated by an asterisk in Table 1. Computations were carried out on UTECOM, a DEUCE computer, using a least-squares program written by Rollett (1961), modified by B. McHugh and R. Vowels of the University of New South Wales Computing Department.

Eleven cycles of refinement reduced the R index to 0·124 excluding unobserved reflexions and those marked with an asterisk in Table 1, which lists observed

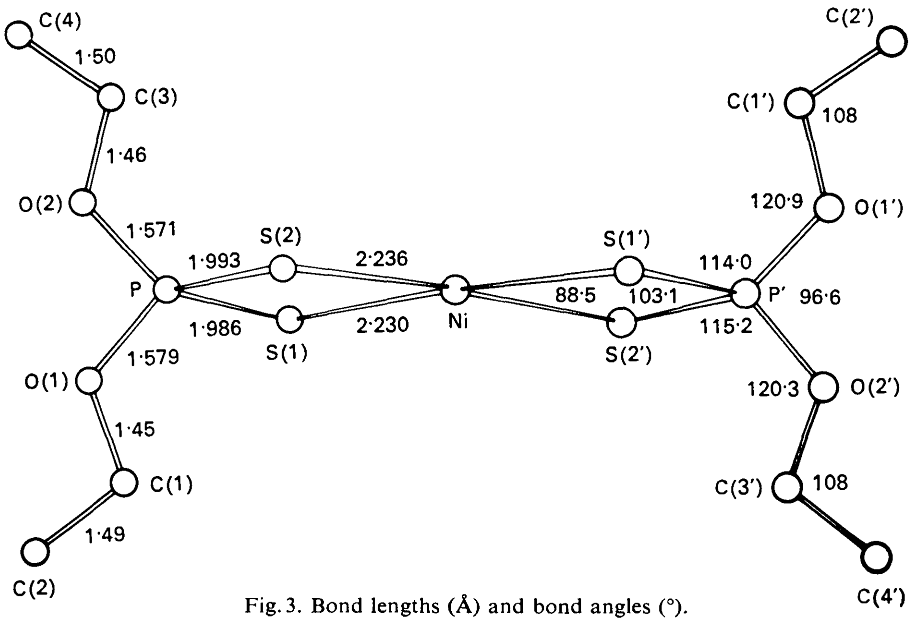

Fig. 3. Bond lengths (Å) and bond angles (°).

Table 1. *Values of* F_o *and* F_c (×25)

Reflexions not included in the refinement are indicated by an asterisk.

(K = 0,L = 0)		
1	1825	2140
2	-1527	1104
3*	-650	-247
4	1754	1704
5	1715	1669
6*	-86	-40
7	-940	-803
8	333	406
9	142	120
10	404	432
11	390	507
12	417	495
13	231	276
(K = 0,L = 2)		
1	2897	3054
2	854	886
3	121	201
4	870	951
5	2989	2892
6	1373	1209
7	-700	-660
8	-682	-679
9	535	504
10	353	418
11	112	144
12	-115	-171
(K = 0,L = 4)		
1	1226	1151
2	148	15
3	519	393
4	614	562
5	1162	1137
6	1230	1277
7	203	187
8*	-110	-10
9*	100	60
10	321	368
11	225	305
(K = 0,L = 6)		
1	-128	-103
2	328	342
3	341	294
4	-286	-320
5	142	144
6	519	669
7	221	297
8	110	101
(K = 0,L = 8)		
1	200	195
2	-198	-210
3	190	147
4	176	166
5*	89	61
6*	-75	-52
7	110	133
(K = 0,L = 10)		
1	200	180
2	-86	-55
(K = 0,L = -2)		
0	2825	3124
1	1098	854
2	-1824	-1292
3	324	254
4	-679	-504
5	903	913
6	691	656
7	371	321
8	1015	1005
9	531	517
10	498	485
11	941	979
12	629	638
13	165	119
(K = 0,L = -4)		
0	729	761
1	-1255	-817
2	-131	-55
3	1096	902
4	638	559
5	731	719
6	1484	1354
7	1769	1654
8	625	585
9	-142	-89
10	489	506
11	984	1075
12	154	48
13	-426	530
(K = 0,L = -6)		
0	336	368
1	278	318
2	1380	1251
3	176	170
4	181	219
5	1607	1645
6	1391	1394
7	244	185
8	-380	-328
9	-240	-249
10	639	593
11	321	271
12	-216	-227
(K = 0,L = -8)		
0	774	796
1	662	648
2	142	109
3	142	154
4	203	165
5	743	811
6	423	324
7	-305	-284
8	-315	-318
9*	-91	-95
10	445	366
11	290	268
(K = 0,L = -10)		
0	262	355
1	157	240
2*	-90	-38
3	-162	-192
4	159	165
5	218	262
6*	-79	-40
7	-126	-190
8	148	105
(K = 1,L = 0)		
1*	431	891
2	-493	-385
3	1386	1315
4	1645	1403
5	757	651
6	355	290
7	-1078	-909
8	-433	-343
9*	113	81
10*	-112	-27
11	-228	314
12	-206	283
(K = 1,L = 1)		
1*	2475	3176
2	1179	1080
3*	-200	-60
4	1024	1055
5	2342	2139
6	414	450
7	-582	-492
8	193	218
9	473	564
10	246	286
11	96	125
12	109	159
(K = 1,L = 2)		
1	-1819	-1769
2	-324	-399
3	477	427
4	657	661
5	265	258
6	558	518
7	151	146
8*	113	20
9	112	140
10	148	149
11	-89	-104
12	-154	-235
(K = 1,L = 3)		
1	1522	1522
2	1207	1043
3	463	492
4*	88	128
5	1289	1167
6	1619	1529
7	103	218
8	-256	-320
9	109	108
10	363	492
11	189	272
(K = 1,L = 4)		
1	-616	-510
2	-987	-898
3	-126	-56
4*	98	14
5	-209	-204
6	-156	-145
7	228	209
8*	111	46
9	227	292
(K = 1,L = 5)		
1	580	585
2	462	409
3	175	203
4*	-107	-88
5	538	633
6	785	874
7	221	242
8*	-103	-11
9*	-86	-4
10	154	242
(K = 1,L = 6)		
1*	104	-72
2	371	-382
3*	111	50
4	253	252
5	-278	335
6	-154	173
7	-143	-168
(K = 1,L = 7)		
1	-356	-351
2*	-113	-4
3	64[illegible]	589
4	222	101
5*	-106	-60
6*	97	135
7	165	267
8	106	90
(K = 1,L = 8)		
1*	113	112
2*	-111	-62
3*	107	59
4	140	168
5*	89	77
6	-74	-102
(K = 1,L = 9)		
1	101	102
2*	-96	-50
3	176	128
4	231	239
(K = 1,L = -1)		
0*	2093	3787
1	-334	-129
2	-450	-191
3	1800	1640
4	645	651
5	903	888
6	390	425
7	96	106
8	606	571
9	359	357
10	468	495
11	472	580
12	331	395
13	184	219
(K = 1,L = -2)		
0	928	923
1	1422	1146
2	-903	-820
3	1017	827
4	675	609
5	-271	-250
6	-959	-858
7	-1153	-1035
8	-742	-601
9	451	471
10*	-113	-29
11*	106	10
12*	-90	-65
13	143	183
(K = 1,L = -3)		
0	1437	1437
1	393	370
2	-375	-240
3	96	313
4	586	650
5	1185	1072
6	1116	956
7	838	809
8	770	742
9*	113	63
10	319	348
11	875	988
12	410	460
13	-156	-218
(K = 1,L = -4)		
0	1078	893
1	-982	-910
2	-888	-804
3	-324	-373
4	206	155
5	-807	-613
6	-756	-657
7	-502	-496
8	431	399
9	537	535
10	315	316
11	143	121
12	170	179
(K = 1,L = -5)		
0	394	349
1	212	236
2	1457	1337
3	369	426
4	-418	-318
5	958	996
6	1679	1766
7	913	919
8	-341	-330
9	-278	-261
10	749	709
11	757	697
(K = 1,L = -6)		
0	-303	-343
1	-775	-718
2	-773	-671
3	390	384
4*	-103	-113
5*	-106	-9
6	221	196
7	196	145
8	362	400
9	313	300
10	179	161
11*	89	77
12	-206	-213
(K = 1,L = -7)		
0	531	590
1	915	1024
2	527	589
3	-221	-154
4	112	37
5	1100	1120
6	667	684
7*	-113	-57
8	-193	-212
9*	-104	-28
10	494	448
11	299	278
(K = 1,L = -8)		
0	-198	-222
1*	-114	79
2	-115	-80
3	228	262
4	198	211
5	196	176
6	221	261
(K = 1,L = -9)		
0	299	384
1	303	383
2	109	107
3	107	-95
4	151	101
5	405	476
6	202	218
7	-189	-251
8*	-85	-61
9	241	238
10	205	292
(K = 1,L = -10)		
0*	84	61
1*	88	16
2*	90	108
3*	90	16
4*	89	72
5*	85	87
6*	80	6
7	-175	-204
8	-129	-166
(K = 1,L = -11)		
1*	51	43
2*	-57	-114
3*	-58	-42
4	167	234
5	118	147
(K = 2,L = 0)		
1*	712	1533
2	-2447	-1895
3	502	538
4	1963	2035
5	1877	1837
6	419	417
7	873	780
8	952	748
9	700	637
10	154	94
11	137	174
12	110	157
(K = 2,L = 1)		
1	-165	-135
2	-396	-315
3	935	810
4	687	647
5	1078	944
6	827	791
7	-485	-543
8	-485	-451
9	246	290
10	238	262
11	-184	-243
12	-325	-476
(K = 2,L = 2)		
1	999	1130
2	171	287
3	-979	-760
4	535	572
5	1341	1380
6	1050	995
7	-258	-277
8	221	267
9	619	707
10	570	701
(K = 2,L = 3)		
1	-1223	-1336
2	-1016	-977
3	175	143
4	491	451
5	-134	-96
6	145	145
7	266	251
8*	-110	-2
9	181	247
10	131	166
(K = 2,L = 4)		
1	1111	1194
2	664	690
3	219	280
4	272	250
5	494	480
6	265	287
7	154	158
8*	-107	-5
9	137	170
10	296	362
11	151	278
(K = 2,L = 5)		
1	-572	-581
2	-601	-620
3	198	220
4	296	308
5	-525	-538
6	-221	-218
7*	-107	-83
8	198	89
9	164	200
(K = 2,L = 6)		
1	510	520
2	873	869
3	614	598
4*	-110	-1
5	190	154
6	259	308
7	216	260
(K = 2,L = 7)		
1	107	99
2	-350	-382
3	154	175
4	340	368
5*	-101	-53
6	-208	-289
7	-109	-186
(K = 2,L = 8)		
1	107	92
2*	106	39
3	178	203
4	269	345
5*	85	66
6	68	69
(K = 2,L = 9)		
1*	97	68
2*	-92	-14
3*	-82	-15
4	71	125
(K = 2,L = -1)		
0	830	1105
1	1793	1655
2	-1461	-1220
3	1360	1033
4	1871	1670
5	303	316
6	-412	-382
7	-1596	-1548
8	-502	-503
9	492	515
10	109	24
11	-246	-301
12	-262	-344
(K = 2,L = -2)		
0	1924	1708
1	756	721
2	1576	1580
3	1359	1316
4	1542	1608
5	1188	1115
6	848	727
7	612	663
8	663	633
9	109	104
10*	-109	-90
11	101	123
12	371	389
13	165	170
(K = 2,L = -3)		
0	1257	1142
1	-475	-296
2	-1446	-1254
3*	-68	-50
4	873	838
5	-393	-335
6	-1385	-1151
7	-1514	-1309
8*	106	8
9	917	966
10	153	172
11*	-101	-107
12*	84	52
13	140	163
(K = 2,L = -4)		
0	1388	1248
1	466	524
2	1241	1071
3	1825	1669
4	801	792
5	-198	-146
6	384	367
7	706	705
8	240	232
9	-350	-367
10	303	310
11	619	656
12	303	349
(K = 2,L = -5)		
0	419	358
1	-1427	-1326
2	-1436	1390
3	562	458
4	318	253
5	-336	-298
6	-488	-475
7*	-107	93
8	625	599
9	492	505
10	209	232
11	184	171
(K = 2,L = -6)		
0*	99	79
1	761	773
2	669	631
3	196	163
4	-227	-222
5	431	494
6	538	577
7	190	172
8	-154	-139
9	413	401
10	470	594
11	479	494
12	88	101
(K = 2,L = -7)		
0	-375	-391
1	-340	-386
2	-303	-329
3	418	405
4	107	112
5	153	158
6	350	402
7*	-109	-64
8	106	120
9	139	146
(K = 2,L = -8)		
0	426	428
1	221	208
2	109	16
3	-154	-122
4	271	256
5	344	374
6	340	406
7	179	184
8	137	138
9	246	293
10	350	414
(K = 2,L = -9)		
0*	-101	-36
1*	103	8
2	104	70
3	104	127
4	143	149
5	140	124
6	165	161
(K = 3,L = 0)		
1	352	299
2	-1825	-1403
3	-261	241
4	438	625
5	1054	839
6	-182	-127
7	-1182	-1090
8	-309	-287
9	895	819
10	431	413
11	-234	-182
12	397	465
(K = 3,L = 1)		
1	984	1039
2	150	213
3	126	37
4	1228	1026
5	654	649
6	537	540
7	688	760
8	989	1141
9	863	910
10	209	258
(K = 3,L = 2)		
1	-745	-722
2	-126	-209
3	954	978
4*	-114	-37
5	-315	-298
6*	140	91
7*	-152	-69
8	-387	-406
9*	154	156
10	280	334
11*	114	118
12	-215	278
(K = 3,L = 3)		
1	667	750
2	1062	1079
3	328	292
4	-359	-294
5*	-139	-36
6	258	258
7	472	471
8	271	241
9	359	359
10	400	476
(K = 3,L = 4)		
1	-630	-721
2*	-122	-15
3	527	489
4	564	534
5	-562	-512
(K = 3,L = 5)		
1	911	936
2	1063	1236
3	412	375
4	262	279
5*	156	199
6*	156	41
7	259	190
(K = 3,L = 6)		
1	-505	-482
2	-611	-693
3	494	536
4	500	529
5	-154	-121
6	-296	-329
7*	132	11
8*	110	116
9	72	94
(K = 3,L = 7)		
1*	-156	-31
2	387	466
3	531	642
4	431	457
5*	-142	-8
6*	126	120
7	182	211
(K = 3,L = 8)		
1*	153	3
2	-336	-325
3*	-142	-85
4	262	294
(K = 3,L = 9)		
1*	-134	33
2*	126	45
3	225	178
4	134	189
(K = 3,L = -1)		
0	-1015	1056
1	-372	-189
2	1654	1599
3	2272	2114
4	2675	2340
5	925	802
6	900	814
7	1321	1290
8	679	626
9	500	464
10*	-154	-56
11	-240	-241
(K = 3,L = -2)		
0	1174	1028
1	-1172	-1003
2	-1779	-1640
3	126	44
4	1629	1436
5	321	243
6	-313	-222
7	-1169	-1152
8	215	175
9	766	809
10	218	256
11	-399	-420
12	-281	-304
(K = 3,L = -3)		
0	834	832
1	1294	1433
2	1890	1927
3	1599	1697
4	1563	1576
5	586	584
6*	132	55
7	576	503
8	218	206
9	-227	-180
10*	-153	-138
11*	139	65
12	397	405
13	173	221
(K = 3,L = -4)		
0	443	368
1	-744	-672
2	-1338	-1412
3	813	787
4	1142	1061
5	184	147
6	-961	-900
7	-365	-365
8	443	446
9	447	505
10	-302	-324
(K = 3,L = -5)		
0	362	384
1	1047	1131
2	970	1073
3	995	808
4	300	280
5	-400	-422
6	363	401
7	311	281
8*	-157	-70
9	219	201
10	461	484
11	401	455
12	343	321
(K = 3,L = -6)		
0	-290	-225
1	-833	-848
2	142	59
3	842	875
4	200	162
5	-371	-403
6*	-155	-68
7*	-157	-51
8*	146	21
9*	-148	-78
10*	136	32
11	162	139
(K = 3,L = -7)		
0*	155	15
1	620	637
2	311	217
3	-312	-267
4	156	91
5*	157	0
6	353	333
7	312	359
8	365	384
9	551	643
10	340	371
11	212	190
(K = 3,L = -8)		
0*	-155	-162
1*	-156	-85
2*	156	34
3*	156	125
4*	-155	-31
5*	-154	-58
6*	150	122
7	-203	-218
8	-190	-171
9*	-118	-13
10	193	207
(K = 3,L = -9)		
0*	-139	-7
1*	143	80
2*	144	127
3*	144	89
4	200	202
5	277	296
6	262	270
7	243	266
8	218	223
9	302	349
(K = 3,L = -10)		
0*	106	-21
1*	113	58
2*	-115	-21
3*	-116	-92
4*	-113	-105
5*	108	185
6	200	87
7*	-84	-233
8	-146	194
(K = 4,L = 0)		
1*	319	614
2	885	873
3	989	813
4	2084	1929
5	-162	-84
6	522	462
7	1095	1020
8	1072	981
9	517	445
10*	145	43
11*	-125	-122
12	228	238
(K = 4,L = 1)		
1	731	814
2	637	466
3	-1474	-1118
4	-1414	-1227
5	-99	-26
6	219	183
7	-658	574
8	-616	577
9	371	420
10	627	637
11*	116	134
12	-190	-231
(K = 4,L = 2)		
1	675	827
2	758	736
3	862	762
4	524	528
5	522	406
6*	-141	-2
7	481	542
8	488	542
9	604	665
10	184	184
(K = 4,L = 3)		
1	139	204
2	551	556
3	804	752
4	181	91
5	-631	-494
6	-120	-95
7*	-154	-178
8	-212	-259
9	-259	-327
10*	82	19
11	221	237
(K = 4,L = 4)		
1	680	613
2	990	1017
3	642	609
4	687	676
5*	149	4
6	-215	-220
7	330	341
8	231	328
9	203	238
(K = 4,L = 5)		
1	-787	-757
2	198	190
3	1028	999
4	429	374
5*	-154	-57
6	-123	-144
(K = 4,L = 6)		
1	362	392
2	1028	974
3	375	356
4	377	342
5*	149	10
6*	139	125
7	205	188
8	198	140
(K = 4,L = 7)		
1	333	-334
2	375	-435
3*	150	57
4	374	426
5*	133	83
6	-330	-214
(K = 4,L = 8)		
1	293	210
2	200	174
3	107	239
4	281	131
5	240	85
(K = 4,L = -1)		
0	352	443
1	519	579
2	-1904	-1725
3	1336	-1321
4	312	281
5	941	757
6	-181	-190
7	-306	-375
8	479	473
9	874	892
10	417	454
11	-261	-267
12	-321	369
(K = 4,L = -2)		
0	-506	-469
1	1060	1230
2	2221	1922
3	1295	1494
4	1155	1273
5	330	230
6	181	160
7	964	978
8	679	585
9	518	505
10	-120	-126
11	-262	-268
12	224	277
(K = 4,L = -3)		
0	-153	175
1	-768	717
2	-1255	-1172
3	291	313
4	1310	1356
5	1019	1107
6	190	-166
7	-407	-454
8	608	607
9	616	574
10	-416	-322
11	-583	-645
12	-206	-280
(K = 4,L = -4)		
0	318	285
1	846	785
2	927	948
3	1412	1553
4	839	826
5	-447	376
6	-230	230
7	669	685
8	616	533
9	330	375
10*	142	77
11*	125	20
12	105	242
(K = 4,L = -5)		
0	368	372
1	-524	-507
2	-256	-258
3	1087	1060
4	1127	1136
5	-231	-216
6	-469	-530
7*	153	77
8*	154	-34
9	365	406
10	388	-479
11	-95	29
(K = 4,L = -6)		
0	-118	-181
1	353	365
2	469	535
3	460	460
4	417	467
5	302	-283
6	126	208
7	215	251
8	602	555
9	568	607
10	176	185
(K = 4,L = -7)		
0*	-153	-72
1*	153	14
2	435	367
3	126	68
4	-252	-253
5	-309	-282
6	-126	-172
7	-211	-204
8	-400	-358
9	-181	-217
10*	109	190
11	195	263
(K = 4,L = -8)		
0*	-149	-49
1*	150	112
2*	151	106
3	371	347
4	368	356
5*	-147	-28
6*	142	112
7	429	462
8	303	306
9	316	368
(K = 4,L = -9)		
0*	-130	-30
1*	134	30
2*	-135	-57
3*	-135	-161
4	-266	-303
(K = 4,L = -10)		
0*	94	9
1	81	103
2	148	154
3	211	193
4	142	139
5	78	69
6	120	76
7	131	130
(K = 5,L = 0)		
1	212	190
2	-118	-129
3	-1935	1793
4	-697	-551
5	516	471
6	-176	-147
7	-365	-339
8	160	75
9	495	480
10	455	486
(K = 5,L = 1)		
1	960	1243
2	2163	2217
3	1878	1816
4	1010	860
5	-507	-353
6	-259	245
7	695	660
8	587	588
9	193	215
(K = 5,L = 2)		
1	143	33
2	1278	1260
3	359	296
4	-833	-768
5	-889	-809
6	190	121
7	-148	-18
8	-343	-337
9	-262	-306
10	203	263
11	160	244
(K = 5,L = 3)		
1	418	353
2	1427	1406
3	1392	1385
4	884	864
5*	-157	-19
6	159	143
7	651	711
8	439	482
9	195	182
(K = 5,L = 4)		
1	128	49
2	731	665
3	904	910
4	-189	-201
5*	-145	-73
6	-198	-157
7	250	247
8*	129	59
9	-241	-321
10	-179	-258
(K = 5,L = 5)		
1	181	173
2	552	450
3	432	310
4	585	566
5	160	153
6	156	134
7	338	340
8	315	370
9	190	232
(K = 5,L = 6)		
1	-792	-744
2	-159	157
3	283	337
4	278	359
5*	-138	-62
6*	127	-107
7	146	188
8	209	255
(K = 5,L = 7)		
1*	146	102
2	321	234
3	244	234
(K = 5,L = 8)		
1*	-154	-8
2	247	-255
3	-268	-211
4	167	128
(K = 5,L = 9)		
1	243	114
2	246	271
3	225	90
(K = 5,L = -1)		
0	-231	-366
1	637	776
2	1588	1799
3	1219	1312
4	344	364
5	785	-740
6	140	58
7	675	613
8	606	550
9	605	560
10	303	302
11*	116	103
12	159	274
(K = 5,L = -2)		
0	101	114
1	-760	-777
2	-966	-986
3	-318	-294
4	228	117
5	1096	987
6*	115	0
7	311	252
8	443	397
9	413	353
10*	-136	-4
11	-334	-367
12	-167	-246
(K = 5,L = -3)		
0	-462	387
1	554	609
2	572	601
3	470	445
4	547	550
5*	123	37
6	231	203
7	769	804
8	830	853
9	819	906
10	259	267
11*	-116	-29
12	165	185
(K = 5,L = -4)		
0	268	261
1	-195	-140
2	-159	71
3	470	393
4	1159	1092
5	131	100
6	-328	-294
7	195	87
8	487	482
9	-404	-425
10	581	-697
11	-262	-283
12	148	182
(K = 5,L = -5)		
0	-227	-208
1	225	176
2	533	553
3	718	742
4	786	768
5	244	201
6	437	425
7	652	686
8	798	754
9	573	604
10*	123	1
11	-237	350
(K = 5,L = -6)		
0	-274	-297
1	-271	-207
2	626	697
3	569	534
4	-193	-142
5	-582	-662
6	-198	-222
7	278	284
8	-311	-362
9	-483	-545
10*	-111	-125
11	165	212
(K = 5,L = -7)		
0*	147	-83
1	346	352
2	462	473
3	610	712
4	552	607
5*	146	51
6*	143	2
7	387	323
8	437	443
9	221	230
10	-160	-271
(K = 5,L = -8)		
0*	-138	-144
1	140	53
2	193	198
3	-190	-196
4	-424	-429
5	-213	-149
6*	-130	-51
7*	121	128
8	-209	200
9	-181	-135
(K = 5,L = -9)		
0*	-117	-8
1	189	121
2	288	323
3	346	385
4	129	157
5	-125	-163
(K = 5,L = -10)		
0*	-73	-96
1*	83	82
2*	88	16
3	-193	-240
4	-129	-172
5	134	117
(K = 6,L = 0)		
1*	656	1350
2	1507	1702
3	1631	1566
4	-167	-140
5*	-406	-427
6	-298	137
7	536	506
8	159	172
9	151	29
10	134	79
11	211	361
(K = 6,L = 1)		
1	877	958
2	1488	1530
3	-911	-918
4	-1184	-1068
5	447	373
6	832	807
7	159	131
8	-422	-361
9	-258	231
10	126	138
(K = 6,L = 2)		
1	474	442
2	1819	1734
3	1751	1642
4	1205	1204
5*	149	37
6	221	160
7	545	444
8	527	405
9*	-140	64
10	-228	-240
(K = 6,L = 3)		
1	115	87
2	568	518
3	195	74
4	-593	-645
5	-219	-51
6	322	260
7	536	505
8*	-146	31
9	-400	432
(K = 6,L = 4)		
1*	-136	-9
2	249	227
3	835	880
4	858	946
5	275	221
6	250	181
7	468	442
8	384	505
9	344	291
(K = 6,L = 5)		
1	-482	-505
2	442	469
3	222	204
4	-275	309
5	250	216
6	148	9
7	228	244
8	151	160
9	-53	-189
(K = 6,L = 6)		
1	393	305
2*	160	40
3	157	85
4*	154	30
5	143	196
6	128	81
(K = 6,L = 8)		
1	300	285
2	346	335
(K = 6,L = 9)		
1	209	173
(K = 6,L = -1)		
0	418	635
1	780	992
2	372	479
3	837	-790
4	-262	-226
5	452	424
6	-206	-193
7	156	132
8*	160	21
9	-218	-165
10*	-140	-110
11	-228	-223
(K = 6,L = -2)		
0	253	194
1	613	724
2	664	769
3	106	132
4	387	307
5	-359	-317
6	418	368
7	444	406
8	722	761
9	858	837
10	447	487
11	231	248
(K = 6,L = -3)		
0	381	319
1	443	361
2	278	242
3	-487	-468
4*	-131	-91
5	200	172
6	-431	-424
7	-222	-45
8	275	283
9*	-154	-108
10	-309	-293
11	-228	-224
(K = 6,L = -4)		
0	-184	-179
1*	-129	-26
2	184	125
3	384	341
4	815	870
5	476	446
6	470	449
7	663	677
8	910	1007
9	779	909
10	187	190
11	211	-283
(K = 6,L = -5)		
0	208	167
1	206	194
2	-146	93
3*	150	15
4*	-154	1
5	497	-539
6	-275	-245
7	543	568
8	216	207
9	-431	-476
10	-173	-234
11	184	250
(K = 6,L = -6)		
0*	-159	-16
1*	-158	49
2	418	390
3	1090	1019
4	919	938
5	508	531
6*	-159	-25
7	381	388
8	486	571
9	293	281
10	-213	-337
(K = 6,L = -7)		
0	-316	-304
1	159	51
2	358	376
3	-275	-279
4	-387	-428
5	-218	89
6	262	219
7	348	440
8*	-129	-140
9	-221	-258
(K = 6,L = -8)		
0	203	180
1	206	41
2	365	385
3	593	662
4	356	373
5	196	167
6*	-134	-121
7	120	85
8	234	224
(K = 6,L = -9)		
0*	-114	-73
1	118	114
2	120	158
3	-120	-142
4	167	-170
5*	113	14
6	203	213
7	143	170
(K = 7,L = 0)		
1	782	1224
2	926	1081
3	-120	123
4	143	46
5	718	632
6	314	289
7	179	49
8	-308	-277
9	-460	-409
10	433	374
(K = 7,L = 1)		
1	362	253
2	1324	1436
3	1333	1391
4	262	230
5	-290	-158
6	498	342
7	802	636
8	387	324
9	-221	167
(K = 7,L = 2)		
1	236	-254
2	718	659
3	256	170
4	-725	-640
5	120	147
6	801	684
7	793	792
8*	-165	-6
9	-286	339
(K = 7,L = 3)		
1	101	76
2	512	434
3	1117	1007
4	689	614
5*	179	5
6	309	248
7	508	463
8	481	482
(K = 7,L = 4)		
1	-228	-170
2	293	338
3	-493	534
4	-506	-608
5	-309	-296
6	243	203
7	443	472
8	263	263
(K = 7,L = 5)		
1	430	365
2	-218	-255
3	283	264
4	331	311
5	294	284
6*	155	103
7*	132	106
8	343	327
(K = 7,L = 6)		
1*	179	111
2*	178	17
3*	-173	11
4	-283	-267
5	-211	-264
(K = 7,L = 7)		
1	476	358
2	162	194
3*	-152	75
4*	135	23
5	157	181
(K = 7,L = 8)		
1	349	293
(K = 7,L = -1)		
0	250	357
1	552	748
2	941	1126
3	718	711
4	481	422
5	420	338
6	707	691
7	309	277
8	176	117
9	234	197
10	454	455
11	443	420
(K = 7,L = -2)		
0	749	994
1	747	885
2	807	943
3	263	-315
4	416	-445
5	-645	-497
6	-299	234
7*	-179	-42
8	-397	-323
9	-469	-555
10	-205	-196
(K = 7,L = -3)		
0	426	413
1	598	648
2	309	312
3*	-146	-5
4	386	312
5	917	796
6	704	715
7*	179	52
8	431	394
9	555	596
10	491	390
(K = 7,L = -4)		
0	333	239
1	362	379
2*	-156	19
3	-508	-619
4	-629	-832
5	-579	-641
6	-488	-469
7	505	564
8	322	363
9	-224	-241
10	-187	-191
11	258	312
(K = 7,L = -5)		
0	587	634
1	271	186
2*	171	87
3	390	377
4	707	794
5	717	765
6	178	52
7*	175	125
8	464	489
9	390	458
(K = 7,L = -6)		
0	400	-493
1	-359	-416
2	253	257
3*	-179	-104
4	-538	-607
5	-353	-411
6	387	442
7	897	845
8	213	225
9	-225	243
(K = 7,L = -7)		
0	404	399
1	-171	-64
2	246	252
3	548	557
4	400	422
5*	167	119
6*	-159	-172
7	208	123
8	387	412
(K = 7,L = -8)		
0	-259	-282
1	218	86
2	268	275
3*	-155	-53
4*	-150	-60
5*	144	52
6*	132	327
7	262	346
(K = 7,L = -9)		
0*	-104	-8
1*	-114	-18
2	236	176
3	263	289

and calculated structure factors (25 × absolute scale). During this stage of refinement the results were rescaled, layer by layer, after each cycle. The final calculations were carried out on the IBM 7040 computer at the Australian Atomic Energy Research Establishment at Lucas Heights. Two more cycles of a full-matrix least-squares refinement, using a program prepared by Mrs Hogg (Hogg, 1965) reduced the residual

Table 2. *Positional and thermal parameters for the atoms in the asymmetric unit*

The temperature factors are in the form:
$T_i = \exp\,[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$
All parameters have been multiplied by 10^4

	$x(\sigma_x)$	$y(\sigma_y)$	$z(\sigma_z)$	$B_{11}(\sigma_{B_{11}})$	$B_{22}(\sigma_{B_{22}})$	$B_{33}(\sigma_{B_{33}})$	$B_{12}(\sigma_{B_{12}})$	$B_{13}(\sigma_{B_{13}})$	$B_{23}(\sigma_{B_{23}})$
Ni	0	0	0	71 (2)	56 (4)	174 (5)	3 (2)	34 (3)	−9 (3)
S(1)	1876 (3)	1024 (4)	21 (5)	61 (3)	23 (6)	211 (8)	−11 (3)	52 (4)	−28 (5)
S(2)	771 (4)	−1707 (4)	−1093 (6)	81 (4)	21 (6)	221 (8)	1 (3)	66 (4)	−25 (5)
P	2337 (3)	−586 (4)	−983 (4)	49 (3)	34 (5)	128 (6)	16 (3)	30 (3)	5 (4)
O(1)	2689 (8)	−357 (10)	−2625 (11)	70 (9)	76 (14)	111 (14)	28 (8)	25 (9)	31 (11)
O(2)	3673 (9)	−1221 (11)	−166 (11)	71 (9)	48 (14)	140 (16)	34 (9)	34 (10)	25 (11)
C(1)	1758 (17)	255 (19)	−3882 (22)	116 (18)	68 (27)	187 (32)	44 (17)	0 (19)	33 (23)
C(2)	2333 (20)	291 (20)	−5293 (21)	186 (25)	95 (27)	157 (27)	0 (20)	33 (21)	24 (21)
C(3)	3972 (17)	1497 (19)	1507 (18)	130 (20)	110 (27)	133 (24)	65 (17)	54 (18)	33 (19)
C(4)	5095 (15)	−2426 (18)	1840 (21)	72 (15)	109 (27)	198 (30)	29 (15)	9 (17)	81 (21)

Table 3. *Interatomic distances and bond angles, and their standard errors*

Ni —S(1)	2·230 ± 0·004 Å	S(1)–Ni —S(2)	88·5 ± 0·1°
Ni —S(2)	2·236 ± 0·004	S(1)–P —S(2)	103·1 ± 0·2
S(1)–P	1·986 ± 0·006	S(1)–P —O(1)	114·0 ± 0·4
S(2)–P	1·993 ± 0·005	S(2)–P —O(2)	115·2 ± 0·5
P —O(1)	1·579 ± 0·009	O(1)–P —O(2)	96·6 ± 0·5
P —O(2)	1·571 ± 0·009	P —O(1)–C(1)	120·9 ± 0·9
O(1)–C(1)	1·45 ± 0·02	O(1)–C(1)–C(2)	108 ± 1
C(1)–C(2)	1·49 ± 0·02	P —O(2)–C(3)	120·3 ± 0·8
O(2) C(3)	1·46 ± 0·02	O(2)–C(3)–C(4)	108 ± 1
C(3)–C(4)	1·50 ± 0·02		

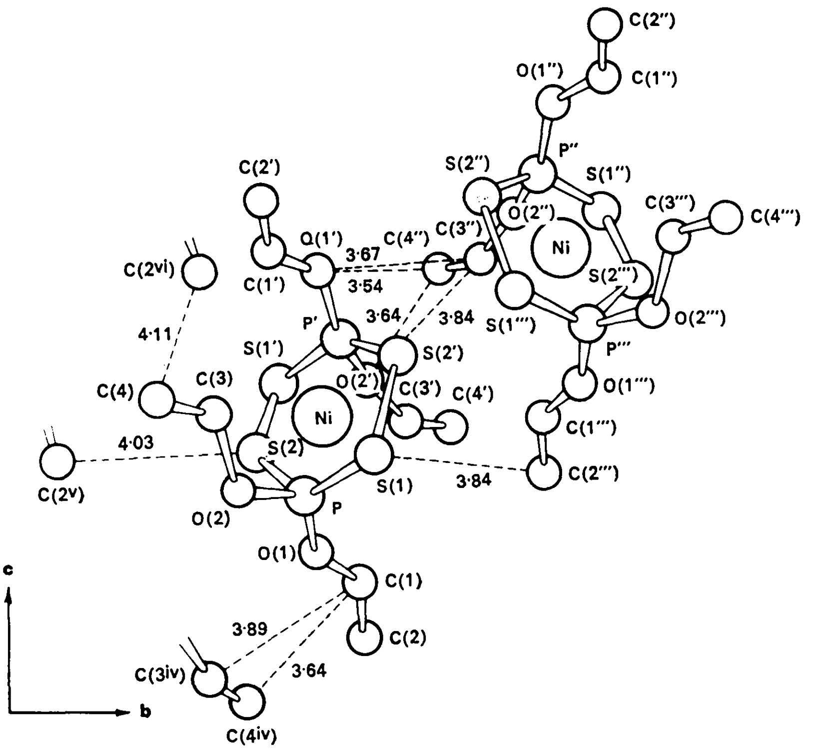

Fig. 4. Intermolecular distances and the relative positions of the two molecules in the unit cell. (Lines joining sulphur atoms do not represent bonds.)

to 0·115. The function minimized in the least-squares refinement was $\Sigma\, w(|F_o(hkl)|-|F_c(hkl)|)^2$. Two weighting schemes were used. For the earlier cycles

$$\sqrt{w}=|F_o|/|F^*| \text{ for } |F_o|\le|F^*|$$
$$\sqrt{w}=|F^*|/|F_o| \text{ for } |F_o|>|F^*|$$

where $|F^*|$ is a selected value. In this case, the value of $|F^*|$ chosen was 60 electrons, which is approximately one-half of the maximum structure factor observed, and so this scheme gives highest weight to reflexions of moderate intensity. For the last cycles, the weighting was

$$\sqrt{w}=1 \quad \text{ for } |F_o|\le|F^*|$$
$$\sqrt{w}=|F^*|/|F_o| \text{ for } |F_o|>|F^*| .$$

which increased the weight for weaker reflexions.

Four hydrogen atoms attached to C(1) and C(3) (for numbering see Fig. 3) were placed in the expected tetrahedral positions, and reduced R by 0·004, but when they were included in a least-squares cycle their indicated shifts were meaningless. It was concluded that the data were not sufficiently good to locate hydrogen atoms and they were removed from the final calculations. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962) for all atoms. Anisotropic temperature factors were used for the last 8 cycles of refinement on UTECOM and the 2 cycles on the IBM 7040 computer. Positional and thermal parameters together with their standard deviations are listed in Table 2. The B_{ij}'s are coefficients in the expression

$$\exp\left[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+2B_{12}hk+2B_{13}hl+2B_{23}kl)\right]$$

Interatomic distances, bond angles and thermal ellipsoids were calculated on the IBM 7040 computer using the ORFFE program by W.R.Busing, K.O. Martin and M.A.Levy of Oak Ridge National Laboratory, U.S.A. The interatomic distances and bond angles are shown in Fig. 3 and are listed in Table 3.

Discussion

A difference synthesis calculated with the use of the final parameters showed a negative peak of 3·00 e.Å^{-3} at the site of the nickel atom, perhaps owing to the neglect of the rather large anomalous dispersion correction ($\Delta f'=-3{\cdot}2$ electrons; Cromer, 1965). Elsewhere the maximum variation was $\pm 0{\cdot}6$ e.Å^{-3}. At the sites of all atoms (excluding nickel) the value of $\Delta\varrho$ was approximately zero.

Bond lengths agree very well with similar lengths reported in other structures. For example the Ni–S distances obtained in this work (2·23 and 2·24 Å) are in exact agreement with those in nickel(II) xanthate (Franzini, 1963) and are in the range 2·1–2·3 Å found for other square-planar nickel(II) complexes. In the organic part of the molecule, the mean O–C and C–C distances of 1·45 and 1·49 Å are normal for this type of compound. For example, in $[C_2H_5O_4S]^-$ reported by Jarvis (1953) the corresponding distances were 1·44 and 1·51 Å.

The intermolecular distances as well as the relative positions of the two molecules in the unit cell are shown in Fig. 4. These are consistent with packing by van der Waals forces, and show no tendency for the nickel atom to coordinate to any atoms in another molecule.

The anisotropic temperature coefficients, B_{ij} show no unexpected features. However, Lingafelter & Donohue (1966) have pointed out that interaction occurs between temperature and scale factors when data about one axis only are being used, so that caution is required when interpreting the thermal parameters, particularly B_{22}. However, the favorable correlation matrix, and the fact that the scale factor was not freely variable, have convinced the authors that the thermal ellipsoids shown in Fig. 5 are of semi-quantitative significance. These indicate that the largest r.m.s. vibrational components are in the directions of smallest constraint and *vice versa*. For example, Ni, S and P all have a large component normal to their plane; the C and O atoms tend to vibrate least along the bond direction.

The phosphorus atom is practically in the Ni–S plane, its calculated distance from the plane being 0·03 Å. The plane through O(1), O(2) and P is almost at right angles to the Ni–S plane, the calculated angle being 87·9°. This plane also passes through the Ni atom, within the limits of observational error. The bond distribution around P is therefore approximately tetrahedral. Atoms C(2) and C(4) also lie in the O–P–O plane within the limits of experimental error, the calculated distances from the plane being 0·02 Å and 0·04 Å respectively.

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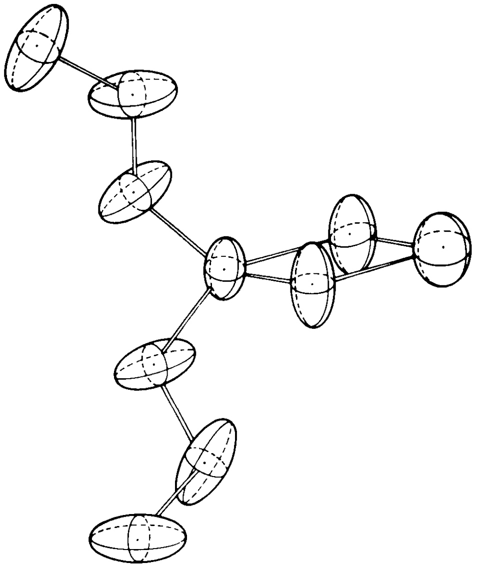

Fig. 5. Vibrational ellipsoids.

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A Refinement of the Parameters of α Manganese

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The atomic parameters of α manganese, first determined by Bradley & Thewlis (1927), have been refined from an R index of 0·093 to a final R of 0·029 for fifty reflections. This refinement was based on an analysis of the integrated intensities of X-ray diffracted powder peaks measured independently at two laboratories. The lattice constant of α manganese was determined from liquid helium temperature up to room temperature and a change in the thermal expansion coefficient was found in the vicinity of the Néel temperature (95°K) although no structural change was observed in this region.

The structure of α manganese as determined by Bradley & Thewlis (1927) is as follows:

Space group $I\bar{4}3m$ no. 217 in *International Tables for X-ray Crystallography* (1952).

2 Mn(1)	in 2(*a*)	000, *etc.*	
8 Mn(2)	in 8(*c*)	*xxx*, *etc.*	$x(2)=0{\cdot}317$
24 Mn(3)	in 24(*g*)	*xxz*, *etc.*	$x(3)=0{\cdot}356$, $z(3)=0{\cdot}042$
24 Mn(4)	in 24(*g*)	*xxz*, *etc.*	$x(4)=0{\cdot}089$, $z(4)=0{\cdot}278$

This result is based on X-ray intensities read from Phragmén-camera photographs taken by Westgren & Phragmén (1925). Kasper & Roberts (1956) checked Bradley & Thewlis's parameters with neutron diffraction data and found them to be accurate enough ($\pm 0{\cdot}003$) to establish the magnetic structure at 4·2, 77, and 298°K.

In an attempt by Gazzara, Middleton & Weiss to determine the characteristic temperature Θ of α-Mn it was found desirable to refine the structural parameters by applying modern experimental X-ray diffraction techniques. A refinement was performed on twenty-one Cr $K\alpha$ diffraction peaks from powder specimens. During this same time, a similar refinement was performed by E. O. Hall on α-Mn powders using Cu $K\alpha$ radiation. This report presents the best values of the structural parameters obtained from the two investigations.

Although many powder samples were examined in this X-ray diffraction analysis, the data from only four sources were eventually used:

(1) A pure, carbon-free, electrolytic −400 mesh powder. This showed some diffraction peak broadening and gave intensities identical with those of sample (2).

(2) Electrolytic plate, ground mortar and pestle and sifted to −400 mesh particle size. Although the cold working increased the diffraction peak widths, it reduced extinction effects. The integrated intensity of the Cr $K\alpha$ diffraction peak $\Sigma h^2=18$, for example, was increased 4% through cold working. All calculations involving Cr $K\alpha$ radiation are based on measurements performed on this material.

(3) A portion of powder sample (2) annealed at 440°C for 90 hours in vacuum. All of the diffraction peaks obtainable with Cr $K\alpha$ radiation from this sample could be resolved and accurately measured with Mo $K\alpha$ radiation; many of the high-angle Mo $K\alpha$ diffraction peaks were resolved sufficiently well to be integrated. All results obtained with Mo $K\alpha$ radiation were taken