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The Crystal Structures of Tetramethylammonium Tetrachloro-cobaltate (II), -nickelate (II), and -zincate (II)

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The crystal structures of the isomorphous tetramethylammonium tetrachloro-cobaltate(II), -nickelate(II), and -zincate(II) are reported. The space group is *Pnma* with $Z=4$. The cell dimensions are $a=12\cdot276$, $b=9\cdot001$, $c=15\cdot539$ Å for the cobalt isomorph; $a=12\cdot264$, $b=8\cdot982$, $c=15\cdot486$ Å for the nickel isomorph; and $a=12\cdot276$. $b=8\cdot998$, $c=15\cdot541$ Å for the zinc isomorph. The structures were determined from three-dimensional X-ray diffraction data and were refined by the full-matrix least-squares technique. There is some disordering in the orientation of both the $[MCl_4]^{2-}$ and the $[N(CH_3)_4]^+$ tetrahedra. The $[MCl_4]^{2-}$ tetrahedron appears to be disordered in the same manner in the three compounds.

Introduction

As an extension of investigations carried out in this laboratory into the distortion of the tetrahedral $[CuCl_4]^{2-}$ ion (Morosin & Lingafelter, 1961), we have studied the distortion of the $[NiCl_4]^{2-}$ ion in the crystal structure of tetramethylammonium tetrachloronickelate(II), $[N(CH_3)_4]_2NiCl_4$. For comparison with this structure we also report the crystal structure determination of the cobalt(II) analog and the redetermination of the crystal structure of the zinc(II) analog (Morosin & Lingafelter, 1959), which are isomorphous with it.

While simple crystal-field theory predicts a distortion of tetrahedrally coordinated copper(II) in the form of a flattened tetrahedron, it predicts a distortion of tetrahedrally coordinated nickel(II) in the form of an elongated tetrahedron (Orgel, 1960). However, it has been shown by Liehr & Ballhausen (1959) that spin orbit forces can remove the degeneracy of the ground state and leave a species which is not subject to this Jahn–Teller distortion. The present series of compounds is excellent for testing these theories since the nickel is surrounded by four identical ligands, eliminating any distortion due to asymmetric ligand fields; also, any distortion due to asymmetric crystal packing forces would be detectable in the isomorphous zinc(II) and cobalt(II) compounds since these ions are not susceptible to a Jahn–Teller distortion.

The crystal structure of tetramethylammonium tetrachlorozincate(II) was previously determined (Morosin & Lingafelter, 1959; hereafter referred to as ML) from three-dimensional film data and refined (with isotropic thermal parameters) to a final reliability index ($\Sigma\,||F_o|-|F_c||/\Sigma\,|F_o|$) of 0·155 by a series of difference syntheses. As noted by them, the structure exhibited high temperature factors for the lighter atoms. Attempts in this laboratory to refine the structure further by the full-matrix least-squares method with anisotropic temperature factors resulted in unusually high temperature factors. Since this behavior is typical of refinement attempts in which some systematic errors have been encountered in the collection of the data used, it was decided to collect a new, more accurate, set of data on a single-crystal X-ray diffractometer.

Preparation of the compounds

Crystals of $[N(CH_3)_4]_2ZnCl_4$ and $[N(CH_3)_4]_2CoCl_4$ were prepared, as described by ML, by evaporation of an aqueous solution containing the appropriate stoichiometric amounts of $N(CH_3)_4Cl$ and MCl_2. Attempts to prepare the nickel compound by this method resulted in deposition of a tan polycrystalline solid and not a blue compound [the color attributed to the $[NiCl_4]^{2-}$ ion (Gruen & McBeth, 1959)]. Tetramethylammonium tetrachloronickelate(II) was finally prepared in this laboratory by M. Kellerman and B. J. Schein. Appropriate stoichiometric amounts of solid $N(CH_3)_4Cl$ and $NiCl_2.6H_2O$ were placed in a crystallizing dish and heated on a steam bath until a uniform tan paste was obtained. Heating in an oven at 80 °C for several hours resulted in the blue solid, $[N(CH_3)_4]_2NiCl_4$, which is deliquescent and must be stored in a desiccator. Suitable crystals were obtained by evaporation of a nitromethane (Eastman Organic Chemicals, spectro grade) solution in a vacuum desiccator containing Drierite. Since the compound is deliquescent, unlike the zinc and cobalt analogs, the crystals were mounted in Lindemann glass capillaries for collection of the X-ray data.

Space group and cell dimensions

Preliminary Weissenberg and oscillation photographs showed the three compounds to be isomorphous and showed systematic absences of $hk0$ for $h=2n+1$ and $0kl$ for $k+l=2n+1$, confirming the possible space groups to be $Pn2_1a$ or *Pnma* as reported by ML. Accurate cell parameters were determined from the least-squares fit to 2θ values measured on a Picker diffractometer equipped with a General Electric single-crystal orienter. The cell dimensions, along with the details of the experimental conditions, are given in Table 1. The estimated standard deviations are as obtained from the least-squares refinement. The cell parameters for the cobalt and zinc isomorphs agree with those given by ML.

Data collection

Intensity data for the zinc isomorph were collected from a prismatic crystal approximately $0{\cdot}31 \times 0{\cdot}26 \times 0{\cdot}28$ mm in size. It was mounted with the c axis parallel to the φ axis of a Picker diffractometer equipped with a General Electric single-crystal orienter and data were collected, with the use of Mo $K\alpha$ ($\lambda = 0{\cdot}71069$ Å) radiation, by the $\omega - 2\theta$ scan method (moving-crystal moving-counter). Before scanning through the reflection, a background count (B_1) was taken for a time equal to one half the scan time. The scan (S) was then taken and another background count (B_2) was taken at the end of the scan, again for one half the scan time. The intensity of each reflection was calculated as: $I = S - B_1 - B_2$, and the standard deviation of this intensity was calculated as: $\sigma_I = (S + B_1 + B_2)^{\frac{1}{2}}$. Reflections were examined in shells of 2θ to a maximum of 47°, at which point the intensities were falling off so rapidly that it was deemed not worthwhile to collect data at any higher 2θ values. Of the 1283 reflections examined, 433 had $I < 2{\cdot}7\ \sigma_I$ and were coded as unobserved reflections. The factor of $2{\cdot}7\ \sigma_I$ assures that all of the reflections coded as observed have intensities significantly different from the background at greater than the 99% confidence level.

The crystal chosen for intensity measurements for the cobalt isomorph was a rod-like prism approximately $0{\cdot}6 \times 0{\cdot}12 \times 0{\cdot}20$ mm in size. It was mounted with a as the rotation axis and integrated equi-inclination Weissenberg photographs were taken on multiple films in a Nonius camera with Fe $K\alpha$ ($\lambda = 1{\cdot}93728$ Å) radiation. The photographs were integrated in one direction only (perpendicular to the rotation axis); the diffraction spots were then scanned normal to the direction of the camera integration, using a Moll-type densitometer feeding into a Leeds and Northrup amplifier and recorder with a logarithmic slide wire. The tracings thus obtained were then planimetered and the area under each peak taken as the relative intensity. Only those spots appearing within the linear response range of the film were measured. Data were collected for levels $0kl$ through $7kl$. The total number of reflections examined was 802, of which 315 were coded as unobserved and 487 were coded as observed. The unobserved reflections were given an intensity equal to the minimum observable intensity for that particular level. No cross level photographs were taken.

Intensity data for the nickel isomorph were taken in the same manner as described for the cobalt isomorph with a crystal which was an approximately cylindrical rod about 0·12 mm in diameter and 0·56 mm in length and with rather poorly defined faces. It was mounted in a capillary with the rod axis (the a axis) parallel to the rotation axis. Levels $0kl$ through $9kl$ were taken, using Cu $K\alpha$ ($\lambda = 1{\cdot}54178$ Å) radiation. Individual level scale factors were determined using data for about 13 reflections per level collected on a diffractometer with Cu $K\alpha$ radiation as described for the zinc isomorph. Of the 1039 reflections which were examined, 436 were coded as unobserved and given an intensity equal to the minimum observable intensity for that particular level. The density measured by the flotation technique was 1·35 g.cm^{-3} and that calculated on the basis of four molecules in the cell is 1·358 g.cm^{-3}.

Calculations

All calculations for this investigation were made on an IBM 7040–7094 Direct Couple System using the Crystal Structures Calculations System X-Ray 63 (Stewart, 1964). The scattering factors used were those for Zn^{2+}, Co^{2+}, Ni^{2+}, Cl^-, N, C (*International Tables for X-ray Crystallography*, 1962). The real part of the dispersion correction (−3·1) for the Ni^{2+} ion with Cu $K\alpha$ radiation was applied, but the imaginary part (0·7) was ignored. Lorentz and polarization factors were applied to the data for all three isomorphs, but no absorption corrections were made. For the radiation used in each case the linear absorption coefficients are 132, 71 and 21 cm^{-1} for the Co, Ni and Zn compounds, respectively. All full-matrix least-squares refinements were carried out with the modified version of ORFLS (Busing, Martin & Levy, 1962) included in X-ray 63. This program minimizes $\Sigma\, w(|F_o| - |F_c|)^2$. The reliability index is defined throughout as $R = \Sigma\, ||F_o| - |F_c|| / \Sigma\, |F_o|$, where the summation is over the observed unique reflections only.

Structure determination

Since problems had been encountered in an attempted least-squares refinement of the structure of the zinc isomorph with the data of ML with calculations made in the centric space group (*Pnma*), it was considered a distinct possibility that the correct space group might

Table 1. Cell parameters for $[N(CH_3)_4]_2MCl_4$

Estimated standard deviations are given in parentheses.

	Co	Ni	Zn
a	12·276 (1) Å	12·2639 (4) Å	12·276 (2) Å
b	9·001 (1)	8·9819 (8)	8·998 (2)
c	15·539 (2)	15·4861 (10)	15·541 (2)
Radiation used	Mo $K\alpha$	Cu $K\alpha$	Mo $K\alpha$
Number of reflections	14	15	14

be the acentric one ($Pn2_1a$). The essential difference between these two space groups is that, with four molecules in the cell, $Pnma$ requires the $[MCl_4]^{2-}$ and $[NCH_3)_4]^+$ tetrahedra to lie on mirror planes parallel to (010) and at $y=\frac{1}{4}$, while in $Pn2_1a$ the mirror planes are no longer present. If calculations were made assuming the absence of the mirror planes, and they actually were present, the structure should tend to exhibit this symmetry. Therefore, initial calculations were made with the new set of data assuming space group $Pn2_1a$. In the least-squares refinement of the structure of the zinc isomorph, unit weights were used, except that unobserved reflections with $|F_c| \le F_o$ were given a weight of zero.

The zinc and four chlorine positions were determined from a three-dimensional Patterson synthesis. Three cycles of isotropic least-squares refinement gave an R of 0·219. The R calculated with the final parameters of ML for the zinc and chlorine atoms (including the mirror related chlorine atom) was 0·229. Through a series of ΔF syntheses and subsequent least-squares refinement of the atoms that had been found, a set of parameters for all of the atoms was determined. Three cycles of isotropic least-squares refinement gave an R of 0·122; however, the temperature factors of some of the carbon atoms were unusually high and the tetramethylammonium tetrahedra were quite distorted. This was the same behavior which had been noted in the attempted refinement using ML's film data. A fresh attempt was therefore made to determine the positions of the lighter atoms. A ΔF synthesis phased on the zinc and chlorine parameters showed the positions of all of the nitrogen and carbon atoms. These were refined by a series of ΔF syntheses, reducing R to 0·127. Three cycles of isotropic least-squares refinement gave an R of 0·115, but, again, the temperature factors were high and the tetrahedra were distorted. Nevertheless, the refinement was continued with four cycles of anisotropic least-squares, resulting in an R of 0·090 and large temperature factors and distorted tetrahedra. The positions of the atoms were essentially the same as those given by ML.

Since it appeared that a successful refinement was not being obtained in the acentric space group, calculations were continued in space group $Pnma$. Furthermore, since the trial structure was the same as that reported by ML, their parameters were used as a starting point. These parameters gave an initial R of 0·158. Five cycles of least-squares refinement of an overall scale factor, positions, and isotropic temperature factors resulted in a decrease of R to 0·128. Again, the temperature factors were high, reaching a maximum of $B=17{\cdot}5$ Å^2 for a carbon atom, and the tetrahedra were quite distorted. In these refinements some of the correlation coefficients between the scale factor and the various temperature factors were rather large, ranging from 0·09 to 0·72. Therefore, another set of three cycles of least-squares refinements was carried out, in which the temperature factors were set back to 'reasonable' fixed values, refining only positions and the overall scale factor. This reduced R only from 0·147 to 0·140. Three more cycles varying the isotropic temperature factors and the positions, but not the scale factor, reduced R to 0·127. The resulting structure was essentially the same as before these six cycles were carried out. Even though the temperature factors still were not reasonable, it was decided to continue the least-squares refinement with anisotropic temperature factors. Four cycles reduced R to 0·062. After correcting errors in the data, two further cycles brought R to the final value of 0·056. For the final cycle of refinement, the average ratio of the change in any parameter to its estimated standard deviation was 0·05 and the maximum ratio was 0·22. The data were examined for secondary extinction effects by plotting $\ln(F_o/|F_c|)$ against I_c, where $I_c=\mathrm{Lp}F_c^2$ (Housty & Clastre, 1957). This plot showed no trend for $\ln(F_o/|F_c|)$ to become negative as I_c increases; therefore, no correction was made. Observed and calculated structure factors are given in Table 2.

Although the crystal structure will be discussed in a later section, it will be of interest to mention here that the temperature factors were still unusually high and the tetrahedra were still distorted.

As an independent check on the least-squares refinement, a series of difference syntheses were calculated phased on the final parameters, but omitting a different carbon atom each time. These ΔF maps showed, in the vicinity of the omitted carbon atom, an electron density that appeared to match the final least-squares parameters quite closely.

We have also refined the structure using the data of ML to a final R of 0·094. This structure agrees quite satisfactorily with that determined with the use of the diffractometer data, both with respect to the positions of the atoms and the sizes and orientations of the thermal ellipsoids.

The final parameters for the zinc isomorph were used as a trial structure for the refinement of the cobalt isomorph. The weighting scheme used in the least-squares refinements was a modified Hughes scheme in which $\sqrt{w}=1$ for all reflections with $F_o<40$; $\sqrt{w}=40/F_o$ when $F_o \ge 40$; $\sqrt{w}=0$ for those unobserved reflections with $|F_c| \le F_o$. Since no data had been taken to scale the individual levels together experimentally, initial individual level scale factors were determined by comparison between the observed structure factors and the structure factors calculated for the trial structure. The R for this calculation was 0·131. Holding the scale factors constant, but refining positions and anisotropic temperature factors for two cycles, then two cycles refining only the scale factors, and, finally two cycles of refinement of only the positions and temperature factors, gave a final R of 0·111. For the final cycle, the average ratio of the change in a parameter to its estimated standard deviation was 0·03 and the maximum ratio was 0·26. The data were examined for secondary extinction effects as described for the zinc compound.

Although there were some large differences between observed and calculated structure factors, these did not show a systematic trend in the plot and therefore no corrections were made. The final list of observed and calculated structure factors is given in Table 3.

The determination of the structure of the nickel isomorph was carried out completely independently from that of the zinc isomorph in order to eliminate any bias that might occur. Because of space limitations, the details will not be given here; however, the two determinations proceeded along quite similar lines, with one exception. The refinement seemed to have halted at an R of 0·115; however, up to that point the individual level scale factors had been held constant at their experimentally determined values. One cycle of least-squares refinement of only these scale factors reduced R to 0·088. The changes in the scale factors on this cycle varied from 0·07% to 11·8%. It thus seems that some of the experimentally determined scale factors were in error. Two further cycles of anisotropic refinement resulted in the final R of 0·075. During the final cycle the average ratio of the change in a parameter to its estimated standard deviation was 0·26 and the maximum ratio was 1·16. The weighting scheme used was a modified Hughes scheme in which $\sqrt{w}=1$ for those reflections with $F_o<20$; $\sqrt{w}=20/F_o$ for those reflections with $F_o \geq 20$; and $\sqrt{w}=0$ for those unobserved reflections for which $|F_c| \leq F_o$. Prior to the final

Table 2. Observed and calculated structure factors for tetramethylammonium tetrachlorozincate(II)

Unobserved reflections are indicated by an asterisk.

0,0,L		
2	455	464
4	2057	-1991
6	284	-313
8	165	-139
10	322	314
12	437	420
14	293	-285
16	310	-316
0,1,L		
1	796	-821
3	1799	-1671
5	281	250
7	1186	1220
9	900	882
11	76	-83
13	451	-445
15	250	-283
0,2,L		
0	2296	-2182
2	1226	-1274
4	299	331
6	1451	1454
8	68	76
10	642	-654
12	148	-199
14	227	259
16	240	231
0,3,L		
1	111	-77
3	1154	1212
5	321	382
7	1190	-1191
9	653	-691
11	182	191
13	266	292
15	240	220
0,4,L		
0	1652	1728
2	440	507
4	620	-663
6	654	-686
8	89	-32
10	334	330
12	259	252
14	155	-144
0,5,L		
1	737	-726
3	852	-827
5	206	202
7	445	406
9	387	411
11	74*	32
13	269	-287
0,6,L		
0	891	-877
2	193	-205
4	407	370
6	413	414
8	118	96
10	303	-298
12	169	-193
0,7,L		
1	70*	30
3	413	416
5	271	247
7	345	-413
9	298	-292
11	132	125
0,8,L		
0	293	303
2	149	173
4	201	-197
6	289	-306
8	88*	44
10	159	157
0,9,L		
1	162	-149
3	261	-255
5	79*	12
7	135	158
1,0,L		
2	1269	1363
3	459	362
4	339	-366
5	539	509
6	784	-759
7	203	177
8	601	-601
9	118	-75
10	496	-479
11	182	-207
12	705	218
13	78*	-4
14	370	388
15	83*	-6
16	85*	69
17	83*	-15
1,1,L		
1	1206	1233
2	477	-304
3	102	-77
4	763	787
5	575	-555
6	164	158
7	541	-530
8	272	-271
9	67*	-11
10	115	117
11	262	289
12	76*	-11
13	76*	-27
14	76*	-4
15	244	-279
16	83*	-10
1,2,L		
1	346	358
2	83	126
3	661	-697
4	842	-818
5	365	-307
6	476	450
7	60*	15
8	1099	1093
9	67*	-56
10	197	178
11	195	195
12	253	-293
13	77*	41
14	245	-244
15	73*	-16
16	101	-77
1,3,L		
1	567	-634
2	664	-553
3	502	-520
4	127	-134
5	863	856
6	87	76
7	553	564
8	64*	6
9	298	-320
10	70*	-37
11	180	-205
12	75*	30
13	75*	47
14	77*	-27
15	148	175
16	81*	10
1,4,L		
1	63	-91
2	880	889
3	129	138
4	202	173
5	134	169
6	474	-479
7	112	75
8	416	-412
9	70*	-28
10	205	-205
11	155	-125
12	118	130
13	75*	7
14	263	249
15	81*	5
1,5,L		
1	775	776
2	62*	-5
3	426	-414
4	253	210
5	351	-346
6	66*	12
7	115	-121
8	119	-118
9	72*	-19
10	75*	57
11	247	242
12	76*	2
13	81*	66
14	80*	-5
1,6,L		
1	90	72
2	372	-412
3	98	-73
4	187	-167
5	81	-76
6	83	86
7	72*	10
8	318	322
9	75*	-0
10	154	189
11	78*	32
12	170	-156
13	82	12
1,7,L		
1	179	-192
2	70*	-62
3	130	-141
4	72*	-36
5	314	312
6	74*	16
7	250	266
8	76*	10
9	175	-178
10	92	-7
11	163	-165
12	79*	14
1,8,L		
1	74*	-55
2	146	142
3	74*	79
4	247	245
5	76*	-19
6	78*	-101
7	78*	-4
8	205	-228
9	104	41
1,9,L		
1	194	147
2	77*	-17
3	104	-75
4	79*	35
5	178	-165
6	77*	10
2,0,L		
0	1348	-1344
1	285	-101
2	703	-604
3	959	-950
4	660	643
5	864	-862
6	429	408
7	394	383
8	165	173
9	65*	9
10	238	-212
11	172	-207
12	177	-189
13	77*	-65
14	165	136
15	80*	38
16	231	242
17	84*	44
2,1,L		
0	423	-319
1	1166	1029
2	142	-115
3	519	461
4	452	468
5	364	-389
6	164	187
7	611	-591
8	92	-101
9	593	-568
10	329	-325
11	72*	-26
12	167	-171
13	390	394
14	107	-87
15	146	166
16	82*	-5
2,2,L		
0	145	88
1	938	978
2	967	990
3	693	724
4	148	-117
5	55*	20
6	993	-1008
7	61*	55
8	63*	-3
9	66*	72
10	393	403
11	71*	-21
12	73*	44
13	104	107
14	109	-112
15	79*	3
16	176	-185
2,3,L		
0	373	437
1	64	-87
2	94	-72
3	411	-438
4	351	-363
5	270	-234
6	61*	25
7	706	713
8	65*	-52
9	479	474
10	199	184
11	98	-100
12	190	184
13	272	-272
14	78*	34
15	130	-128
16	80*	-16
2,4,L		
0	902	-468
1	127	-158
2	352	-344
3	281	-266
4	540	544
5	308	-290
6	387	361
7	79	70
8	69*	-19
9	115	103
10	182	-173
11	85	-58
12	125	-142
13	77*	-83
14	78*	53
15	81*	20
2,5,L		
0	183	231
1	640	638
2	200	-226
3	415	418
4	64*	-10
5	227	-219
6	348	361
7	180	-193
8	72*	-53
9	274	-272
10	193	-212
11	76*	-57
12	76*	-3
13	260	250
14	80*	-13
2,6,L		
0	325	360
1	70	82
2	206	193
3	203	200
4	197	-191
5	70*	80
6	333	-315
7	143	-129
8	93	-65
9	75*	-1
10	224	226
11	77*	29
12	108	116
13	80*	14
2,7,L		
0	247	214
1	110	-96
2	70*	5
3	246	-236
4	200	-180
5	143	-130
6	75*	4
7	223	232
8	75*	32
9	201	214
10	78*	1
11	79*	-59
2,8,L		
0	127	-127
1	99	-119
2	142	-167
3	74*	-61
4	132	123
5	83	35
6	254	257
7	78*	-14
8	79*	-50
9	78*	27
2,9,L		
0	77*	-21
1	167	151
2	77*	-15
3	155	168
4	77*	6
5	77*	-28
6	77*	38
3,0,L		
1	1501	-1503
2	965	-935
3	724	750
4	333	309
5	185	-201
6	247	259
7	321	-310
8	286	245
9	413	405
10	249	241
11	72*	25
12	218	-197
13	75*	58
14	310	-322
15	103	112
16	82*	-44
17	85*	12
3,1,L		
1	863	-819
2	112	114
3	53*	42
4	296	-231
5	436	427
6	333	-347
7	201	208
8	355	-313
9	135	-151
10	80	-67
11	316	-319
12	74*	-28
13	76*	-28
14	85	66
15	188	169
16	81*	64
3,2,L		
1	178	247
2	73	-38
3	774	699
4	369	397
5	65	-61
6	115	-104
7	281	-257
8	579	-568
9	67*	7
10	104	-102
11	72*	-3
12	221	226
13	143	-159
14	231	233
15	82*	-48
16	80*	49
3,3,L		
1	426	421
2	394	406
3	206	192
4	254	-278
5	467	-458
6	234	204
7	296	-283
8	416	402
9	214	198
10	105	-88
11	264	257
12	74*	19
13	75*	26
14	79*	-0
15	131	-132
3,4,L		
1	358	-367
2	382	-336
3	63	61
4	221	-258
5	64	33
6	182	156
7	66*	-61
8	325	350
9	128	105
10	125	124
11	74*	24
12	144	-146
13	76*	29
14	195	-206
15	80*	41
3,5,L		
1	475	-481
2	290	266
3	222	226
4	149	-171
5	278	265
6	149	-137
7	162	136
8	72*	20
9	73*	-40
10	74*	-59
11	243	-247
12	77*	-37
13	78*	-48
14	83	54
3,6,L		
1	160	159
2	281	245
3	113	-112
4	226	241
5	70*	56
6	85	-80
7	74*	-10
8	286	-299
9	78*	-79
10	92	-83
11	82	59
12	134	136
13	80*	-29
3,7,L		
1	160	180
2	155	153
3	72*	53
4	140	-136
5	253	-262
6	74*	-14
7	178	-169
8	148	146
9	136	139
10	79*	-41
11	141	140
3,8,L		
1	73*	-3
2	178	-177
3	75*	-54
4	172	-164
5	84	47
6	78*	99
7	77*	18
8	153	154
9	78*	-31
3,9,L		
1	132	-152
2	76*	36
3	88	64
4	76*	12
5	127	130
4,0,L		
0	838	861
1	954	-959
2	100	53
3	102	-108
4	691	-696
5	715	706
6	539	-543
7	120	162
8	173	-189
9	102	78
10	337	345
11	186	161
12	254	269
13	116	-107
14	103	-94
15	80*	-76
16	156	-169
4,1,L		
0	1014	-990
1	328	-275
2	397	-385
3	808	-783
4	157	139
5	255	-257
6	130	-133
7	607	597
8	201	189
9	383	372
10	128	126
11	118	-109
12	87	96
13	264	-277
14	81*	74
15	110	-129
4,2,L		
0	623	-631
1	251	-283
2	240	-207
3	68	-84
4	527	517
5	205	199
6	637	636
7	472	-465
8	90	102
9	200	-193
10	350	-366
11	74*	65
12	208	-212
13	76*	37
14	80*	83
15	80*	26
4,3,L		
0	190	-210
1	383	352
2	544	545
3	751	735
4	226	232
5	112	108
6	333	-340
7	509	-522
8	67*	-12
9	251	-251
10	74*	29
11	79	80
12	153	-167
13	344	210
14	79*	-26
15	136	121
4,4,L		
0	742	768
1	270	-273
2	62*	84
3	61*	-44
4	459	-488
5	254	248
6	309	-313
7	93	92
8	86	-75
9	74*	-16
10	239	244
11	80*	86
12	211	202
13	79*	-19
14	80*	-69
4,5,L		
0	424	-377
1	235	-231
2	64*	-5
3	437	-420
4	161	135
5	109	-91
6	168	-158
7	279	284
8	75*	83
9	224	224
10	89	89
11	86	-37
12	78*	-14
13	179	-170
4,6,L		
0	388	-400
1	69*	77
2	94	-91
3	77	-55
4	216	229
5	71*	-26
6	243	240
7	75*	27
8	75*	57
9	99	-75
10	190	-196
11	78*	-21
12	126	-127
4,7,L		
0	156	-131
1	85	54
2	74*	95
3	258	258
4	97	91
5	127	123
6	100	-116
7	218	-229
8	77*	-5
9	146	-138
10	79*	53
4,8,L		
0	250	238
1	82	80
2	75*	60
3	75*	-7
4	140	-147
5	76*	-60
6	148	-130
7	78*	79
8	78*	-15
4,9,L		
0	77*	-45
1	81	-89
2	77*	1
3	160	-144
4	78*	45
5,0,L		
1	464	466
2	1033	1038
3	290	-278
4	966	970
5	84*	110
6	238	-229
7	64*	34
8	692	-623
9	253	-270
10	208	-181
11	138	-170
12	324	346
13	80*	-44
14	269	245
15	82*	-54
16	82*	-1
5,1,L		
1	810	861
2	112	91
3	246	-249
4	384	393
5	985	-963
6	172	143
7	493	-471
8	67*	25
9	427	406
10	171	173
11	485	474
12	75*	-2
13	150	146
14	79*	-40
15	129	-145
5,2,L		
1	69	84
2	1125	-1103
3	586	-571
4	724	-719
5	166	169
6	276	267
7	275	262
8	536	527
9	78	-85
10	188	188
11	185	174
12	272	-280
13	107	121
14	257	-244
15	79*	-8
5,3,L		
1	733	-730
2	344	-320
3	235	223
4	63*	48
5	803	769
6	106	-109
7	365	367
8	166	-169
9	306	-302
10	74*	-4
11	355	-392
12	78*	10
13	122	-120
14	79*	-14
15	155	139
5,4,L		
1	198	184
2	825	821
3	69	-62
4	501	473
5	67*	-52
6	182	-193
7	90	83
8	428	-410
9	81	-64
10	178	-176
11	149	-143
12	221	224
13	80*	0
14	209	197
5,5,L		
1	479	451
2	279	-305
3	74	-40
4	326	340
5	554	-545
6	75*	74
7	309	-314
8	167	-166
9	255	251
10	78*	122
11	276	280
12	80*	17
13	81*	47
5,6,L		
1	71*	20
2	418	-414
3	87	-58
4	366	-362
5	74*	-57
6	116	137
7	91	57
8	322	324
9	77*	26
10	79	80
11	79*	6
12	140	-143
5,7,L		
1	321	-319
2	105	-121
3	76*	95
4	75*	30
5	340	325
6	77*	49
7	126	120
8	79	-62
9	106	-124
10	79*	-2
5,8,L		
1	76*	-43
2	271	269
3	81	97
4	145	147
5	76*	-53
6	109	-85
7	77*	-9
5,9,L		
1	147	157
2	78*	-38
3	78*	-52
6,0,L		
0	546	-557
1	258	247
2	347	-340
3	211	-206
4	514	528
5	488	-518
6	884	868
7	161	169
8	97	-122
9	76*	94
10	477	-503
11	78*	-84
12	259	-271
13	78*	6
14	83*	15
15	83*	42
6,1,L		
0	215	178
1	539	529
2	58*	-11
3	929	917
4	198	190
5	270	281
6	265	224
7	296	-289
8	105	-80
9	328	-335
9	328	-335
10	166	-165
11	110	127
12	80	-61
13	240	264
14	80*	-17
15	106	99
6,2,L		
0	882	885
1	515	498
2	161	166
3	295	289
4	683	-674
5	124	-102
6	545	-545
7	122	104
8	87	97
9	73*	1
10	343	343
11	76*	-77
12	281	286
13	81	46
14	81*	-4
6,3,L		
0	251	248
1	573	-606
2	108	-103
3	707	-698
4	250	-261
5	66*	-50
6	72*	4
7	140	149
8	71*	-9
9	293	292
10	112	95
11	77*	-32
12	106	95
13	245	-250
14	80*	-9
6,4,L		
0	411	-411
1	71	-71
2	204	-204
3	134	-138
4	323	314
5	163	-134
6	500	503
7	73*	52
8	74*	-17
9	119	72
10	331	-309
11	78*	-32
12	200	-192
13	79*	-27
6,5,L		
0	163	168
1	223	207
2	145	-116
3	431	427
4	72*	-10
5	182	179
6	218	220
7	224	-230
8	76*	-60
9	246	-260
10	107	-115
11	83	78
12	79*	14
6,6,L		
0	207	201
1	86	51
2	202	193
3	102	107
4	178	-183
5	78*	16
6	353	-375
7	76*	-53
8	76*	57
9	79*	8
10	210	192
11	80*	-8
6,7,L		
0	194	176
1	210	-216
2	78	-36
3	256	-279
4	114	-116
5	75*	8
6	77*	50
7	122	125
8	78*	-8
9	148	112
6,8,L		
0	223	-239
1	77*	-53
2	77*	-53
3	76*	-20
4	154	157
5	77*	0
6	125	114
7,0,L		
1	237	236
2	200	-219
3	181	157
4	696	-687
5	498	-499
6	79*	-47
7	185	-194
8	435	428
9	304	307
10	75*	-4
11	146	154
12	156	-166
13	80*	13
14	116	-119
15	82*	-24
7,1,L		
1	144	-119
2	488	-454
3	134	113
4	311	-316
5	505	504
6	86	77
7	253	258
8	220	231
9	213	-209
10	112	92
11	330	-346
12	78*	-58
13	107	-95
14	80*	-37
7,2,L		
1	418	-412
2	646	662
3	212	223
4	331	325
5	320	321
6	97	-82
7	64*	29
8	195	-199
9	135	-123
10	93	-68
11	147	-148
12	115	111
13	81*	-50
14	81*	156
7,3,L		
1	363	382
2	487	476
3	388	-397
4	85	99
6	69*	-37
7	71*	-87
8	73	-120
9	75*	65
10	142	-132
11	305	297
12	82*	67
13	81*	107
7,4,L		
1	141	132
2	322	-320
3	116	97
4	337	-328
5	291	-277
6	72*	10
7	154	-146
8	298	280
9	177	176
10	78*	64
11	92	99
12	120	-136
7,5,L		
1	142	-149
2	175	-174
3	73*	-34
4	195	-185
5	311	323
6	92	59
7	185	195
8	142	148
9	165	-167
10	79*	16
11	183	-194
7,6,L		
1	144	-129
2	216	217
3	73*	19
4	222	232
5	177	170
6	77*	-79
7	75*	19
8	200	-193
9	79*	-68
10	77*	-17
7,7,L		
1	206	190
2	212	199
3	93	-94
4	76*	-11
5	172	-178
6	79*	-33
7	87*	-46
8	77*	-7
7,8,L		
1	77*	64
2	185	-196
3	76*	-25
4	78*	-55
8,0,L		
0	72*	-10
1	89	-68
2	111	118
3	75*	51
4	165	-156
5	72*	74
6	374	-373
7	95	-93
8	92*	47
9	80*	-24
10	344	360
11	76*	2
12	150	172
13	87*	-13
14	82*	-0
8,1,L		
0	62*	51
1	100	-113
2	63*	15
3	407	-415
4	67*	32
5	263	-262
6	70*	48
7	219	220
8	72*	-0
9	113	111
10	75*	23
11	86	-63
12	79*	25
13	121	-118
8,2,L		
0	480	-461
1	67*	-66
2	70	69
3	67*	-34
4	370	371
5	69*	25
6	71*	61
7	71*	0
8	72*	9
9	73*	30
10	216	-208
11	78*	31
12	216	-225
13	81*	-12
8,3,L		
0	84	-79
1	263	280
2	66*	13
3	334	334
4	70*	-10
5	71*	51
6	72*	-48
7	96	-91
8	73*	30
9	128	-106
10	78*	-25
11	79*	-3
12	79*	-32
8,4,L		
0	175	181
1	71*	-83
2	71*	43
3	71*	6
4	147	-146
5	88	96
6	207	-192
7	75*	-62
8	76*	-41
9	78*	-48
10	247	224
11	76*	19
8,5,L		
0	71*	-22
1	71*	47
2	73*	44
3	219	-217
4	74*	7
5	217	-227
6	76*	-45
7	235	226
8	78*	22
9	125	128
10	77*	70
8,6,L		
0	212	-170
1	81	-63
2	75*	-70
3	75*	-39
4	160	152
5	77*	27
6	143	151
7	78*	12
8	77*	-27
9	78*	-2
8,7,L		
0	82	-55
1	129	140
2	76*	11
3	166	171
4	77*	22
5	76*	-23
6	77*	-17
9,0,L		
1	67*	-45
2	117	119
3	70*	19
4	382	393
5	85*	-27
6	77*	33
7	80*	-4
8	231	-229
9	85*	12
10	80*	-37
11	82*	4
12	95	117
13	82*	29
9,1,L		
1	131	120
2	70*	-52
3	70*	-37
4	71*	1
5	305	-302
6	73*	-69
7	134	-132
8	74*	-61
9	195	202
10	77*	-25
11	186	190
12	80*	-17
9,2,L		
1	69*	50
2	445	-452
3	70*	-40
4	115	-112
5	72*	45
6	72*	47
7	71*	-5
8	73*	49
9	74*	-21
10	103	101
11	79*	18
12	117	-75
9,3,L		
1	224	-214
2	77	62
3	194	187
4	73*	-33
5	176	181
6	79*	39
7	98	72
8	75*	73
9	113	-85
10	79*	6
11	194	-184
9,4,L		
1	72*	-25
2	152	167
3	73*	5
4	208	200
5	75*	-1
6	75*	0
7	76*	4
8	174	-166
9	79*	-9
10	86	-62
9,5,L		
1	92	63
2	75*	-10
3	78	78
4	75*	23
5	205	-208
6	77*	-43
7	122	-141
8	77*	-76
9	146	147
9,6,L		
1	76*	47
2	151	-136
3	78*	-61
4	118	-145
5	79*	16
6	92	61
7	77*	19
9,7,L		
1	144	-141
2	77*	-11
3	103	91
10,0,L		
0	259	-262
1	71*	-14
2	236	-237
3	103	85
4	254	254
5	92	121
6	437	495
7	80*	-8
8	86	-68
9	80*	26
10	301	-298
11	80*	44
10,1,L		
0	71*	-9
2	73*	-33
4	75*	-64
5	119	122
6	74*	-38
7	283	-271
8	76*	-7
9	225	-245
10	79*	21
11	80*	35
10,2,L		
0	517	521
1	73*	-57
2	121	109
3	74*	-89
4	365	-371
5	73*	-32
6	281	-281
7	74*	-12
8	76*	32
9	78*	-50
10	219	208
10,3,L		
0	92	-82
1	337	-354
2	79	55
3	401	-410
4	97	90
5	73*	-10
6	76*	-36
7	94	160
8	79*	8
9	211	209
10	80*	16
10,4,L		
0	244	-25
1	74*	23
2	158	-147
3	75*	21
4	183	186
5	78*	25
6	310	313
7	79*	29
8	78*	-20
9	79*	15
10,5,L		
0	77*	-46
1	119	115
2	76*	-3
3	281	278
4	78*	18
5	83*	100
6	78*	-19
7	206	-196
10,6,L		
0	228	213
1	77*	36
2	98	94
3	76*	-1
4	154	-160
11,0,L		
1	178	198
2	270	-266
3	75*	-42
4	329	-341
5	81*	-97
6	96	85
7	91	-9
8	282	291
9	81*	6
10	83*	59
11,1,L		
1	297	-304
2	151	-162
3	77	63
4	75*	3
5	295	290
6	93	85
7	109	126
8	106	91
9	108	-126
11,2,L		
1	92	-99
2	365	370
3	76*	-74
4	180	201
5	93	107
6	79*	-90
7	80*	64
8	198	-196
9	80*	-51
11,3,L		
1	276	276
2	78*	49
3	74*	-103
4	78*	58
5	224	-213
6	79*	-47
7	120	-103
8	103	-109
11,4,L		
1	79*	83
2	181	-185
3	78*	17
4	202	-216
5	88	-87
6	80*	48
7	79*	-21
11,5,L		
1	155	-154
2	128	-113
3	77*	-6
4	78*	16
12,0,L		
0	232	234
1	149	140
2	102	106
3	162	153
4	145	-139
5	80*	-40
6	185	-190
7	119	-121
8	81*	-2
12,1,L		
0	262	256
1	128	-110
2	85	77
3	205	-231
4	135	-120
5	78*	-59
6	78*	-104
7	160	168
12,2,L		
0	287	-293
1	76*	-28
2	78*	-61
3	135	-128
4	149	162
5	78*	-55
6	114	124
7	153	153
12,3,L		
0	137	-138
1	100	110
2	106	-94
3	180	190
4	81*	71
5	78*	43
12,4,L		
0	140	164
1	78*	72
2	106	73
3	120	122
13,0,L		
1	123	-149
2	81*	86
3	80*	72
4	80*	58
5	83*	54
13,1,L		
1	80*	83
2	86	81
3	78*	7
4	78*	44
13,2,L		
1	78*	75
2	79*	-99
3	78*	23

cycles of refinement, examination of the data as described for the zinc compound revealed a secondary extinction effect. The nine reflections with the largest values of I_c were therefore given a weight of zero in subsequent refinements. Observed and calculated structure factors are given in Table 4.

Discussion

Information on the three isomorphous compounds is collected in Tables 5 through 9. Positional parameters are given in Table 5 and the thermal parameters are given in Table 6.

A most exceptional feature exhibited by the structures is the unusually large values of the thermal parameters. It is unlikely that these temperature factors describe actual thermal motion of the atoms since they are much larger than any that are reported in other normal structures. We feel that they indicate a rotational disordering of the structures. This point will now be discussed.

Normally, when difficulties such as these are encountered in a crystal structure determination, the cause may be found in a systematic error in the intensity data. For the large values of the thermal parameters to have been caused by systematic errors, it would be necessary for these errors to be similar in all cases, since (as will be shown later) all of the structures show similar patterns in the thermal ellipsoids. It is difficult to see how this could have occurred, since the four different sets of data were collected by four different investigators from crystals of different sizes and shapes using a variety of experimental techniques. A disordering (randomness) in the positions of the atoms would give rise to the large temperature factors that are observed.

Examination of the thermal parameters reveals a number of differences between the values for the three structures. As has been noted by other authors (Srivastava & Lingafelter, 1966; Werner, 1964), the temperature factors can compensate for errors in the data due to absorption and dispersion effects, and can therefore be in error by amounts much larger than indicated by the estimated standard deviations. It is therefore not surprising that there are some differences in the temperature factors. However, the same general pattern in the temperature factors exists in the structures. This can be seen more clearly from Table 7, which gives the root mean square displacements along the principal axes of the thermal ellipsoids and the direction of these axes relative to the cell edges. The axes are listed in order of increasing size, axis 1 being the smallest, axis 2 intermediate, and axis 3 the largest.

The thermal ellipsoids of all the chlorine atoms show similar orientations, except for axes 2 and 3 of Cl(1). However, the ellipsoids for this atom are essentially isotropic in the plane defined by axes 2 and 3, and therefore, any orientation calculated for them has no

*Table 3. Observed and calculated structure factors for tetramethylammonium tetrachlorocobaltate(*II*)*

Unobserved reflections are indicated by an asterisk.

0,0,L		
2	466	434
4	2014	-1994
6	182	-203
8	214	-150
10	233	216
12	410	438
14	280	-268
0,1,L		
1	676	-763
3	1626	-1534
5	429	313
7	1247	1184
9	936	845
11	178*	-77
13	381	-432
15	241	-252
0,2,L		
2	1338	-2001
4	1057	-1343
6	1479	1528
8	157*	34
10	637	-647
14	245	244
0,3,L		
1	110	-105
3	955	1069
5	341	352
7	1293	-1160
9	656	-693
11	214	201
13	288	278
0,4,L		
0	1481	1721
2	508	475
4	547	-643
6	605	-625
8	175*	-79
10	303	295
12	226	240
14	101	-150
0,5,L		
1	754	-682
3	813	-768
5	265	228
7	461	410
9	389	391
11	146*	49
13	223	-284
0,6,L		
0	451	-876
2	248	-222
4	373	379
6	402	401
8	164*	87
10	242	-274
12	166	-170
0,7,L		
1	175*	-12
3	423	410
5	232	259
7	473	-456
9	307	-279
0,8,L		
0	319	329
2	207	170
4	261	-201
6	357	-294
0,9,L		
1	171	-173
3	234	-240
1,0,L		
1	41*	-48
2	1091	1266
3	534	375
4	576	-473
5	646	543
6	796	-701
7	211	134
8	483	-434
9	150*	-109
10	505	-470
11	166*	-226
12	164	153
13	153*	-22
14	313	308
15	106*	7
1,1,L		
1	754	1114
2	474	-260
3	60*	-36
4	838	770
5	436	-451
6	198	186
7	473	-455
8	302	-259
9	152*	-74
10	161*	100
11	166*	175
12	153*	37
13	152*	-25
14	132*	7
15	231	-234
1,2,L		
1	317	366
2	265	233
3	658	-666
4	700	-755
5	348	-364
6	445	428
7	116*	-0
8	966	1076
9	157*	-17
10	154*	131
11	203	207
12	226	-253
13	146*	63
14	124	-175
15	71*	-35
1,3,L		
1	463	-576
2	620	-591
3	553	-550
4	120	-121
5	709	735
6	138*	64
7	491	530
8	156*	-10
9	263	-285
10	166*	-11
11	163	-125
12	152*	7
13	135*	73
14	109*	-50
1,4,L		
1	125	-126
2	751	840
3	210	151
4	138*	43
5	178	202
6	442	-441
7	159*	83
8	385	-325
9	166*	-67
10	263	-213
11	154	-142
12	138*	101
13	115*	-4
14	241	228
1,5,L		
1	659	758
2	149*	-2
3	439	-417
4	215	263
5	282	-254
6	164*	2
7	166*	-73
8	165*	-144
9	160*	-84
10	150*	61
11	226	193
12	114*	21
13	80	66
1,6,L		
1	163*	102
2	270	-325
3	165*	-116
4	166*	-156
5	106*	-67
6	164*	104
7	160*	-2
8	247	295
9	141*	1
10	125	155
11	103*	60
1,7,L		
1	163*	-149
2	162*	-68
3	243	-189
4	157*	-57
5	264	283
6	145*	15
7	257	255
8	122*	20
9	165	-171
10	75*	1
1,8,L		
1	138*	-65
2	136*	101
3	131*	85
4	217	215
5	116*	-7
6	104*	-86
7	87*	3
1,9,L		
1	203	179
2	77*	-23
3	64*	-87
2,0,L		
1	316	-268
2	749	-545
3	1086	-963
4	632	559
5	951	-831
6	311	267
7	452	443
8	227	209
9	127*	70
10	134*	-42
11	289	-241
12	135*	-157
13	125*	-61
14	109*	117
15	84*	41
2,1,L		
0	339	-298
1	810	977
2	168	-134
3	384	382
4	519	504
5	466	-411
6	212	197
7	535	-479
8	133	-133
9	536	-459
10	342	-346
11	136*	-61
12	150	-189
13	271	318
14	107*	-65
15	170	151
2,2,L		
0	132	-47
1	765	1043
2	774	951
3	685	754
4	88*	11
5	96*	13
6	855	-923
7	115*	42
8	124*	-20
9	137*	14
10	295	320
11	137*	-29
12	131*	-32
13	119*	134
14	100*	-87
15	70*	11
2,3,L		
0	313	361
1	88*	4
2	91*	-48
3	277	-316
4	376	-400
5	240	-252
6	116*	-28
7	613	641
8	131*	-18
9	395	414
10	224	200
11	150	-107
12	229	213
13	211	-194
14	86*	20
2,4,L		
0	746	-794
1	192	-142
2	264	-297
3	287	-331
4	511	443
5	355	-327
6	314	249
7	133*	129
8	137*	19
9	154	124
10	134*	-81
11	126*	-84
12	112*	-109
13	92*	-88
14	58*	37
2,5,L		
0	218	216
1	554	620
2	213	-210
3	294	323
4	131*	25
5	289	-278
6	384	392
7	138*	-98
8	136*	-65
9	203	-217
10	225	-243
11	150	-94
12	90*	-18
13	114	213
2,6,L		
0	246	269
1	136*	112
2	232	199
3	228	241
4	138	-132
5	137*	87
6	314	-282
7	131*	-138
8	174*	-46
9	114*	-24
10	170	164
11	80*	38
2,7,L		
0	278	270
1	134*	-43
2	133*	-15
3	180	-180
4	144	-211
5	134	-125
6	118*	1
7	190	207
8	98*	18
9	181	180
2,8,L		
0	126	-81
1	125	-136
2	134	-148
3	119	-100
4	100*	77
5	93*	33
6	246	225
7	65*	6
2,9,L		
0	63*	-29
1	83	154
2	54*	-29
3,0,L		
1	1535	-1569
2	953	-813
3	888	829
4	573	496
5	213	-224
6	247	223
7	365	-334
8	126*	42
9	498	430
10	222	213
11	144*	33
12	139*	-92
13	127*	20
14	282	-248
15	161	145
3,1,L		
1	660	-736
2	64*	85
3	74*	12
4	253	-208
5	311	290
6	425	-395
7	117*	117
8	302	-312
9	137*	-68
10	143*	-77
11	179	-205
12	138*	9
13	125*	-14
14	106*	78
15	75*	107
3,2,L		
1	253	287
2	217	-233
3	699	709
4	261	371
5	104*	-99
6	114*	-67
7	351	-298
8	488	-462
9	140*	67
10	144*	-29
11	142*	-24
12	134*	147
13	119	-175
14	98*	135
15	58*	-48
3,3,L		
1	255	313
2	387	418
3	252	240
4	287	-270
5	352	-348
6	221	227
7	270	-244
8	456	429
9	151	147
10	143*	-75
11	138*	161
12	126*	-19
13	108*	-1
14	87*	-0
3,4,L		
1	351	-406
2	195	-237
3	177	95
4	126*	-131
5	131*	-0
6	137*	115
7	141*	-29
8	225	232
9	151	120
10	138*	100
11	127*	13
12	111*	-89
13	89*	28
3,5,L		
1	406	-402
2	245	268
3	144	207
4	161	-167
5	164	186
6	186	-173
7	144*	73
8	141*	5
9	134*	15
10	124*	-75
11	217	-167
12	87*	-18
3,6,L		
1	179	187
2	214	173
3	144*	-99
4	144*	166
5	142*	22
6	139*	-58
7	134*	-17
8	238	-222
9	114*	-61
10	98*	-63
11	74*	47
3,7,L		
1	178	121
2	194	157
3	135*	86
4	151	-163
5	214	-220
6	119*	17
7	115	-141
8	175	173
9	88	124
3,8,L		
1	111*	-27
2	115	-128
3	105*	-42
4	114	-125
5	90*	53
6	77*	76
4,0,L		
1	1080	-942
2	46*	-53
3	57*	-72
4	675	-647
5	818	720
6	458	-399
7	116	170
8	181	-205
9	109*	101
10	229	233
11	178	168
12	203	243
13	113	-144
14	78*	-65
15	48*	-96
4,1,L		
0	764	-896
1	214	-206
2	429	-400
3	667	-677
4	185	141
5	278	-269
6	152	-146
7	557	505
8	224	164
9	298	307
10	113	127
11	112*	-104
12	105*	72
13	201	-221
14	76*	91
4,2,L		
0	381	-462
1	215	-296
2	164	-161
3	72	-92
4	432	427
5	215	210
6	540	560
7	534	-537
8	108*	99
9	224	-230
10	266	-295
11	110*	118
12	154	-159
13	88*	38
14	68*	53
4,3,L		
0	182	-205
1	272	272
2	535	550
3	596	626
4	226	232
5	136	120
6	375	-354
7	456	-444
8	112*	-1
9	221	-188
10	111*	51
11	105*	78
12	158	-178
13	124	152
14	52*	-44
4,4,L		
0	605	684
1	281	-293
2	96*	38
3	99*	-22
4	347	-421
5	300	283
6	254	-214
7	113	99
8	113*	-84
9	111*	21
10	205	173
11	95*	84
12	175	176
13	60*	-47
4,5,L		
0	483	-435
1	177	-211
2	108*	4
3	356	-354
4	177	152
5	113*	-61
6	251	-180
7	233	219
8	108*	95
9	199	166
10	146	98
11	78*	-74
12	57*	-34
4,6,L		
0	339	-374
1	113*	46
2	113*	-68
3	113*	-32
4	219	179
5	110*	-30
6	194	182
7	102*	-32
8	94*	58
9	84*	-74
10	130	-147
4,7,L		
0	164	-139
1	105*	11
2	195	118
3	174	196
4	99*	98
5	94	130
6	167	-146
7	222	-187
8	67*	5
4,8,L		
0	224	189
1	81*	70
2	79*	48
3	75*	-10
4	161	-114
5	61*	-47
5,0,L		
1	484	464
2	959	951
3	380	-316
4	928	864
5	91	47
6	202	-196
7	112*	33
8	662	-585
9	297	-321
10	255	-146
11	123*	-131
12	343	302
13	99*	-78
14	227	211
5,1,L		
1	638	757
2	64	46
3	271	-267
4	472	432
5	707	-806
6	104	139
7	452	-377
8	121*	16
9	395	355
10	127	161
11	448	422
12	113*	6
13	97*	125
14	72*	-68
5,2,L		
1	75*	101
2	874	-960
3	600	-617
4	697	-671
5	223	235
6	230	215
7	309	299
8	470	465
9	127*	-106
10	126*	155
11	119	159
12	246	-248
13	127	142
14	219	-217
5,3,L		
1	533	-614
2	316	-334
3	204	188
4	107*	30
5	689	683
6	119*	-81
7	324	323
8	180	-209
9	263	-284
10	122*	8
11	335	-352
12	97*	22
13	107	-101
5,4,L		
1	278	275
2	710	730
3	116*	-79
4	469	453
5	123*	-48
6	126*	-170
7	127*	76
8	386	-365
9	121*	-95
10	112*	-141
11	99*	-118
12	183	199
5,5,L		
1	416	412
2	285	-374
3	126*	-69
4	381	365
5	530	-493
6	126*	81
7	318	-274
8	157	-168
9	202	227
10	95*	140
11	228	263
5,6,L		
1	126*	-3
2	453	-398
3	125*	-73
4	355	-339
5	120*	-27
6	114*	131
7	107*	56
8	269	245
9	83*	22
10	61*	62
5,7,L		
1	337	-292
2	111*	-142
3	108*	42
4	104*	56
5	291	301
6	89*	36
7	77*	117
8	56*	-87
5,8,L		
1	80*	-44
2	282	267
3	130	113
4	152	137
6,0,L		
1	340	290
2	365	-296
3	289	-229
4	498	430
5	663	-600
6	909	794
7	271	231
8	97*	-139
9	99*	131
10	487	-488
11	92*	-122
12	222	-226
13	68*	17
6,1,L		
0	192	143
1	438	457
2	54*	17
3	865	807
4	249	231
5	302	233
6	313	256
7	277	-234
8	97*	-69
9	289	-256
10	163	-178
11	91*	107
12	81*	-59
13	206	213
6,2,L		
0	570	771
1	452	538
2	68	124
3	319	311
4	563	-588
5	85	-112
6	477	-474
7	96*	124
8	99*	138
9	99*	-13
10	312	313
11	124	-136
12	235	256
6,3,L		
0	242	244
1	518	-524
2	81*	-123
3	553	-614
4	306	-319
5	93*	-34
6	96*	18
7	99*	88
8	99*	-6
9	251	270
10	90*	87
11	60*	-16
12	66*	125
6,4,L		
0	293	-324
1	91*	-54
2	220	-164
3	94	-171
4	331	277
5	159	-171
6	440	449
7	98*	80
8	45*	-41
9	89*	87
10	314	-280
11	66*	-39
12	146	-157
6,5,L		
0	165	176
1	98*	161
2	99	-123
3	243	366
4	99*	-14
5	107	169
6	207	251
7	213	-180
8	85*	-60
9	236	-207
10	110	-143
6,6,L		
0	167	157
1	96*	69
2	135	148
3	94	120
4	159	-153
5	88*	27
6	375	-319
7	76*	-48
8	66*	47
9	50*	-8
6,7,L		
0	235	189
1	254	-198
2	79*	-40
3	298	-239
4	205	-122
5	66*	13
6	57*	50
7	40*	88
6,8,L		
0	146	-193
1	46*	-69
2	40*	-43
7,0,L		
1	225	207
2	122	-124
3	272	236
4	681	-590
5	563	-521
6	123*	-108
7	251	-234
8	345	316
9	347	353
10	128*	-21
11	203	185
7,1,L		
1	70*	53
2	455	-430
3	93*	100
4	312	-285
5	433	389
6	125*	75
7	228	232
8	256	246
9	133*	-140
10	127*	86
11	280	-253
7,2,L		
1	332	-431
2	442	561
3	236	242
4	281	235
5	356	316
6	130*	-19
7	134*	18
8	134*	-73
9	131*	-107
10	122*	-66
11	188	-186
12	87*	57
7,3,L		
1	216	243
2	444	498
3	384	-362
4	127*	71
5	256	-248
6	134*	-45
7	134*	-48
8	131*	-113
9	124*	8
10	113*	-143
11	246	226
12	65*	71
7,4,L		
1	130	130
2	228	-240
3	133*	115
4	300	-291
5	289	-306
6	133*	-25
7	129	-159
8	233	197
9	226	203
10	96*	41
11	69*	120
7,5,L		
1	134*	-71
2	134	-153
3	133*	-50
4	253	-217
5	267	256
6	123*	51
7	163	167
8	216	187
9	178	-145
7,6,L		
1	124*	-144
2	174	162
3	120*	28
4	197	193
5	186	184
6	100*	-34
7	87*	32
8	113	-136
7,7,L		
1	181	155
2	293	245
3	88*	-107
4	79*	-14
5	112	-121

Table 4. *Observed and calculated structure factors for tetramethylammonium tetrachloronickelate* (II)

Unobserved reflections are indicated by an asterisk. Reflections removed because of secondary extinction effects are indicated by *E*.

	0,0,L	
2	337	411
4	1334E	-1816
6	94	-115
8	82	-76
10	153	155
12	268	251
14	189	-187
16	175	-165
	0,1,L	
1	552	-713
3	1343E	-1419
5	341	343
7	915	1034
9	641	636
11	68*	-59
13	255	-239
15	168	-157
17	65*	-3
	0,2,L	
0	1398E	-1838
2	971E	-1165
4	88	125
6	1075	1176
8	57*	62
10	436	-455
12	73*	-86
14	175	177
16	119	108
	0,3,L	
1	136	-136
3	803	949
5	213	257
7	893	-943
9	441	-475
11	146	137
13	127	138
15	130	110
	0,4,L	
0	1220	1458
2	352	401
4	456	-526
6	441	-461
8	65*	10
10	177	169
12	135	121
14	90	-82
16	103	-95
	0,5,L	
1	564	-562
3	580	-597
5	228	211
7	288	264
9	233	240
11	75*	30
13	155	-139
15	64*	-73
	0,6,L	
0	623	-633
2	111	-122
4	253	240
6	232	232
8	74	65
10	172	-151
12	109	-96
14	63*	67
	0,7,L	
1	71*	-29
3	250	241
5	192	171
7	260	-252
9	177	-161
11	84	78
	0,8,L	
0	177	170
2	75*	96
4	121	-104
6	180	-159
8	72*	27
10	66*	68
	0,9,L	
1	102	-80
3	163	-131
5	70*	20
7	66*	73
	0,10,L	
0	115	-120
2	63*	-0
	1,0,L	
1	20	-39
2	945E	1198
3	451	416
4	405	-477
5	465	461
6	670	-681
7	155	148
8	353	-383
9	64*	-65
10	356	-343
11	146	-148
12	82	84
13	81*	-1
14	223	210
15	82*	-1
	1,1,L	
1	834E	1057
2	394	-291
3	78	-49
4	628	629
5	324	-348
6	98	42
7	329	-357
8	205	-197
9	83	-76
10	120	134
11	107	114
12	79*	-0
13	83*	-55
14	83*	-19
15	157	-150
	1,2,L	
1	301	335
2	231	269
3	671	-651
4	557	-632
5	317	-295
6	329	348
7	59*	15
8	775	823
9	67*	-41
10	121	132
11	128	124
12	140	-161
13	82*	25
14	123	-111
15	81*	-9
	1,3,L	
1	447	-473
2	567	-550
3	460	-508
4	93	-95
5	546	616
6	111	96
7	381	436
8	66*	-20
9	192	-205
10	75*	-54
11	74*	-58
12	81*	21
13	83*	62
14	82*	-7
	1,4,L	
1	53*	-75
2	621	692
3	136	132
4	58*	36
5	103	139
6	369	-374
7	68*	50
8	228	-227
9	75*	-23
10	117	-123
11	98	-91
12	83*	39
13	82*	7
14	139	116
	1,5,L	
1	564	570
2	63*	-23
3	342	-324
4	173	163
5	186	-160
6	71*	18
7	74*	-33
8	77*	-86
9	80*	-58
10	82*	47
11	101	103
12	82*	7
13	80*	30
	1,6,L	
1	71*	60
2	203	-223
3	73	-75
4	74*	-76
5	76*	-49
6	78*	28
7	80*	20
8	170	177
9	83*	-4
10	119	110
11	82*	15
12	83	-78
	1,7,L	
1	76*	-82
2	79*	-36
3	130	-127
4	80*	-30
5	163	163
6	82*	15
7	175	158
8	83*	7
9	90	-95
10	80*	-15
	1,8,L	
1	83*	-34
2	83*	53
3	83*	54
4	155	133
5	82*	-17
6	82*	-55
7	80*	-6
8	126	-107
	1,9,L	
1	107	92
2	80*	-13
3	79*	-47
	2,0,L	
0	954E	-1186
1	277	-228
2	589	-506
3	897	-998
4	461	480
5	738	-742
6	201	215
7	336	345
8	157	156
9	60*	21
10	65	-55
11	167	-170
12	73*	-76
13	76*	-59
14	90	72
15	76*	24
	2,1,L	
0	407	-323
1	950E	847
2	113	-87
3	291	261
4	418	461
5	330	-351
6	146	161
7	371	-391
8	97	-108
9	347	-411
10	266	-280
11	70*	-72
12	133	-128
13	229	217
14	77*	-57
15	90	86
	2,2,L	
0	150	-129
1	816	897
2	803	873
3	643	671
4	42	56
5	46*	11
6	728	-771
7	54*	14
8	59*	-29
9	63*	68
10	222	229
11	71*	-2
12	75*	-23
13	77*	75
14	77*	-60
15	75*	4
	2,3,L	
0	294	350
1	78	46
2	71	-44
3	208	-237
4	313	-339
5	214	-220
6	55*	-6
7	467	503
8	63*	-8
9	314	327
10	146	152
11	74*	-45
12	133	125
13	137	-133
14	76*	25
	2,4,L	
0	671	-647
1	123	-154
2	248	-260
3	228	-238
4	374	379
5	231	-231
6	216	195
7	64*	64
8	67*	-9
9	78	75
10	74*	-50
11	76*	-46
12	77*	-56
13	76*	-60
	2,5,L	
0	141	161
1	502	497
2	144	-180
3	238	247
4	62*	22
5	209	-212
6	258	278
7	70*	-73
8	72*	-46
9	126	-143
10	155	-153
11	77*	-64
12	76*	-4
13	150	120
	2,6,L	
0	168	176
1	77	79
2	130	129
3	163	162
4	70*	-71
5	71*	52
6	196	-179
7	107	-99
8	76*	-56
9	77*	1
10	115	111
11	76*	23
	2,7,L	
0	196	169
1	74*	-29
2	74*	-0
3	107	-103
4	146	-142
5	106	-90
6	77*	8
7	106	113
8	77*	24
9	102	113
	2,8,L	
0	77*	-39
1	77*	-76
2	77*	-96
3	77*	-42
4	77*	53
5	77*	19
6	144	132
7	74*	-5
	2,9,L	
0	74*	-12
1	96	79
3	87	73
	3,0,L	
1	1297E	-1347
2	807	-739
3	689	666
4	428	426
5	156	-163
6	171	186
7	286	-304
8	94	90
9	302	301
10	180	187
11	60*	41
12	84	-89
13	66*	49
14	164	-168
15	76	79
16	61*	-32
	3,1,L	
1	683	-659
2	88	68
3	70	-39
4	263	-229
5	210	223
6	302	-326
7	114	143
8	284	-261
9	53*	-54
10	57	-42
11	164	-170
12	64*	-26
13	66*	-23
14	66*	29
15	97	77
16	61*	36
	3,2,L	
1	150	175
2	255	-252
3	669	621
4	236	288
5	40*	-9
6	44*	-27
7	190	-200
8	379	-399
9	55*	5
10	65	-65
11	62*	-0
12	122	121
13	110	-120
14	105	104
15	64*	-43
	3,3,L	
1	230	255
2	339	364
3	254	244
4	174	-203
5	248	-270
6	176	179
7	217	-200
8	333	314
9	108	105
10	68	-66
11	120	121
12	66*	13
13	66*	15
14	65*	6
15	62*	-53
	3,4,L	
1	275	-315
2	177	-191
3	46*	69
4	114	-142
5	51*	29
6	96	102
7	56*	-71
8	163	169
9	82	68
10	71	73
11	66*	27
12	68	-56
13	65*	27
14	103	-93
	3,5,L	
1	304	-327
2	226	202
3	145	168
4	110	-130
5	119	123
6	134	-121
7	77	63
8	63*	12
9	65*	16
10	66*	-28
11	123	-117
12	65*	-27
13	63*	-29
	3,6,L	
1	121	120
2	142	127
3	90	-93
4	114	126
5	62*	47
6	63*	-30
7	65*	5
8	148	-153
9	66*	-56
10	66*	-49
11	64*	35
12	62*	60
	3,7,L	
1	64*	73
2	122	111
3	65*	66
4	86	-86
5	135	-136
6	66*	-9
7	116	-98
8	103	92
9	75	72
10	62*	-25
11	73	54
	3,8,L	
1	66*	-0
2	90	-80
3	66*	-33
4	84	-77
5	65*	24
6	65*	48
7	63*	11
8	82	62
	3,9,L	
1	83	-70
2	63*	24
3	62*	35
4	61*	4
5	60*	52
	4,0,L	
0	682	715
1	792	-838
2	37	-28
3	140	-116
4	517	-500
5	613	619
6	282	-273
7	133	161
8	148	-156
9	57*	28
10	141	136
11	130	111
12	134	132
13	70*	-50
14	70*	-47
15	67*	-43
	4,1,L	
0	837	-863
1	203	-191
2	302	-315
3	506	-529
4	123	118
5	164	-169
6	152	-163
7	383	372
8	102	98
9	203	200
10	104	94
11	66*	-62
12	95	92
13	123	-121
14	69*	58
15	67*	-59
	4,2,L	
0	350	-383
1	195	-227
2	178	-156
3	91	-91
4	310	317
5	119	135
6	406	420
7	358	-360
8	75	80
9	134	-136
10	180	-182
11	67*	44
12	98	-85
13	70*	13
14	69*	40
15	66*	9
	4,3,L	
0	178	-172
1	182	198
2	416	432
3	463	482
4	199	194
5	80	77
6	213	-226
7	318	-334
8	59*	11
9	122	-108
10	66*	23
11	68*	48
12	122	-130
13	70*	74
14	68*	-27
	4,4,L	
0	494	538
1	190	-212
2	49*	16
3	51*	-20
4	308	-317
5	221	213
6	134	-126
7	85	75
8	64	-57
9	66*	-33
10	88	91
11	70*	54
12	103	92
13	68*	-0
	4,5,L	
0	306	-283
1	129	-132
2	57*	2
3	219	-215
4	121	102
5	61*	-42
6	151	-136
7	136	125
8	67*	41
9	99	100
10	70*	66
11	70*	-9
12	68*	2
13	79	-63
	4,6,L	
0	211	-206
1	63*	34
2	63*	-35
3	64*	-52
4	116	98
5	67*	-15
6	108	103
7	69*	12
8	70*	47
9	70*	-40
10	77	-83
11	67*	-10
	4,7,L	
0	102	-88
1	68*	-6
2	69*	57
3	121	115
4	69*	61
5	94	80
6	70*	-62
7	107	-113
8	69*	-3
9	67*	-52
	4,8,L	
0	125	96
1	70*	51
2	70*	27
3	69*	-2
4	69*	-59
5	68*	-30
6	67*	-51
7	66*	49
	4,9,L	
0	65*	-25
1	65*	-39
	5,0,L	
1	320	349
2	682	756
3	238	-233
4	608	606
5	127	119
6	176	-164
7	53	63
8	382	-383
9	191	-201
10	92	-93
11	120	-144
12	186	174
13	65*	-40
14	133	105
15	61*	-37
16	56*	-7
	5,1,L	
1	451	573
2	118	113
3	193	-208
4	337	356
5	567	-607
6	137	119
7	288	-268
8	52*	-12
9	248	236
10	108	108
11	264	237
12	64*	8
13	65*	59
14	64*	-14
15	61*	-50
16	56*	-14
	5,2,L	
1	102	112
2	662	-684
3	418	-467
4	460	-489
5	77	83
6	181	180
7	198	185
8	306	305
9	65	-52
10	86	76
11	128	127
12	144	-135
13	80	89
14	119	-99
15	59*	2
	5,3,L	
1	430	-445
2	290	-275
3	134	127
4	45*	4
5	492	484
6	80	-76
7	199	206
8	97	-105
9	178	-182
10	62*	0
11	200	-178
12	65*	6
13	64*	-46
14	61*	-16
15	57*	45
	5,4,L	
1	115	126
2	523	527
3	49*	-49
4	266	268
5	53*	-19
6	111	-132
7	78	79
8	212	-196
9	63*	-42
10	88	-78
11	110	-106
12	107	97
13	62*	-6
14	90	79
	5,5,L	
1	286	276
2	188	-207
3	55*	-61
4	246	260
5	309	-288
6	60	55
7	150	-151
8	132	-124
9	128	118
10	65*	71
11	129	124
12	62*	15
13	58*	14
	5,6,L	
1	60*	29
2	225	-214
3	61*	-42
4	195	-188
5	63*	-58
6	64*	71
7	65*	32
8	163	149
9	64*	20
10	63*	26
11	61*	7
12	68	-58
	5,7,L	
1	170	-154
2	91	-100
3	65*	50
4	65*	17
5	176	149
6	65*	37
7	64*	48
8	63*	-37
9	66	-55
10	58*	-0
11	59	-47
	5,8,L	
1	64*	-27
2	138	117
3	64*	55
4	76	62
5	62*	-25
6	61*	-40
7	59*	-2
8	56*	-48
	5,9,L	
1	67	61
2	58*	-18
3	57*	-23
4	56*	18
5	54*	-45
	6,0,L	
0	407	-399
1	194	199
2	192	-197
3	194	-178
4	324	330
5	399	-403
6	517	494
7	139	127
8	66	-73
9	62	52
10	270	-255
11	77	-69
12	124	-126
13	70*	-0
14	68*	-6
	6,1,L	
0	118	105
1	312	354
2	31*	3
3	532	565
4	169	168
5	141	145
6	182	167
7	126	-130
8	70	-60
9	151	-144
10	125	-114
11	69*	74
12	70*	-34
13	114	109
14	68*	-12
	6,2,L	
0	473	534
1	395	409
2	95	107
3	268	255
4	390	-404
5	99	-93
6	312	-317
7	81	67
8	73	81
9	64*	27
10	163	160
11	70*	-44
12	139	117
13	69*	26
	6,3,L	
0	226	239
1	353	-356
2	76	-93
3	385	-401
4	222	-221
5	54*	-14
6	57*	14
7	61*	55
8	64*	-5
9	130	115
10	69*	59
11	70*	-19
12	70*	57
13	102	-95
	6,4,L	
0	208	-207
1	53*	-45
2	100	-102
3	101	-101
4	171	159
5	121	-102
6	266	250
7	65*	34
8	67*	-14
9	69*	42
10	162	-129
11	70*	-22
12	92	-75
	6,5,L	
0	112	112
1	128	104
2	87	-73
3	210	204
4	64*	-11
5	97	88
6	150	143
7	93	-84
8	70*	-30
9	121	-111
10	70*	-73
11	68*	34
	6,6,L	
0	67*	75
1	67*	24
2	98	92
3	68*	72
4	69*	-74
5	69*	17
6	185	-174
7	70*	-39
8	70*	31
9	69*	10
10	88	74
	6,7,L	
0	128	111
1	111	-89
2	70*	-22
3	123	-121
4	70*	-72
5	70*	6
6	69*	29
7	68*	50
	6,8,L	
0	102	-39
1	69*	-32
2	68*	-15
3	68*	-13
4	78	66
	7,0,L	
1	144	150
2	32	-42
3	132	119
4	386	-338
5	383	-359
6	84	-91
7	156	-148
8	182	166
9	227	200
10	60*	-10
11	99	92
12	76	-65
	7,1,L	
1	25*	30
2	350	-317
3	38	41
4	239	-275
5	223	220
6	63	61
7	119	124
8	161	141
9	73	-58
10	60*	39
11	150	-134
12	62*	-34
	7,2,L	
1	297	-245
2	296	314
3	184	187
4	153	146
5	229	220
6	50*	-8
7	53*	9
8	56*	-51
9	67	-69
10	61*	-13
11	87	-82
	7,3,L	
1	143	154
2	351	337
3	218	-209
4	48	55
5	132	-148
6	53*	-30
7	56*	-18
8	59*	-59
9	61*	3
10	88	-72
11	107	105
	7,4,L	
1	91	84
2	126	-135
3	66	54
4	143	-129
5	184	-173
6	58*	-27
7	99	-92
8	91	93
9	118	102
10	62*	25
	7,5,L	
1	56*	-31
2	102	-97
3	58*	-29
4	127	-125
5	115	119
6	61*	37
7	85	83
8	85	88
	7,6,L	
1	82	-80
2	63	59
3	62*	23
4	98	89
5	116	97
6	62*	-15
	7,7,L	
1	74	52
2	131	110
	8,0,L	
0	104	-82
1	56	-59
2	40	36
3	42	43
4	45	-37
5	83	84
6	166	-153
7	64	-61
8	56*	9
9	59*	-27
10	153	143
11	62*	8
12	72	65
13	59*	-4
	8,1,L	
0	25*	18
1	27*	-23
2	31*	23
3	173	-169
4	40*	16
5	161	-148
6	49*	6
7	73	67
8	56*	6
9	59*	29
10	61*	19
11	62*	-20
12	61*	21
13	59*	-29
	8,2,L	
0	194	-178
1	69	-80
2	63	57
3	45	-40
4	164	161
5	48*	24
6	52*	-4
7	55*	-12
8	56*	5
9	60*	20
10	72	-65
11	62*	21
12	100	-84
13	57*	-9
	8,3,L	
0	69	-66
1	110	116
2	46*	10
3	141	127
4	50*	7
5	53*	25
6	55*	-26
7	58*	-8
8	60*	19
9	61*	-20
10	62*	-13
11	61*	-10
12	59*	-26
	8,4,L	
0	52	38
1	52*	-45
2	53*	4
3	54*	8
4	56*	-40
5	60	68
6	63	-61
7	60*	-30
8	61*	-28
9	62*	-36
10	88	76
11	59*	10
	8,5,L	
0	58*	-30
1	56*	41
2	58*	39
3	83	-69
4	60*	10
5	118	-106
6	61*	-47
7	76	74
8	61*	14
9	60*	40
10	58*	16
	8,6,L	
0	61	-46
1	61*	-23
2	61*	-24
3	62*	-30
4	62	51
5	62*	9
6	61*	48
7	60*	12
8	59*	-12
9	56*	-1
	8,7,L	
0	61*	-42
1	61*	52
2	61*	5
3	64	54
4	60*	21
5	59*	-17
6	57*	-10
	8,8,L	
0	68	51
	9,0,L	
1	15	-7
2	21*	-10
3	26*	-21
4	182	162
5	34*	3
6	49	45
7	41*	19
8	80	-61
9	45*	-0
10	45*	2
11	45*	-2
12	44*	32
	9,1,L	
1	21*	11
2	41	-25
3	28*	-8
4	32*	22
5	103	-94
6	38*	-16
7	48	-45
8	43*	-31
9	71	69
10	45*	-19
11	45*	58
12	44*	-10
	9,2,L	
1	48	37
2	191	-176
3	33*	-36
4	35*	-25
5	38*	23
6	40*	9
7	43*	-4
8	44*	-22
9	45*	-21
10	45*	23
11	45*	14
	9,3,L	
1	69	-69
2	36*	10
3	98	91
4	39*	-10
5	41*	41
6	43*	4
7	44*	10
8	45*	26
9	46*	-15
10	45*	16
11	67	-52
	9,4,L	
1	41*	-6
2	41*	34
3	42*	-10
4	76	66
5	44*	0
6	45*	18
7	45*	15
8	45*	-39
9	45*	-4
10	44*	-16
	9,5,L	
1	44*	-5
2	44*	-14
3	45*	46
4	45*	21
5	66	-56
6	46*	-11
7	45*	-51
8	44*	-16
	9,6,L	
1	46*	17
2	46*	-29
3	45*	-19
4	45*	-49
5	45*	4
6	44*	16
	9,7,L	
1	44*	-40

Table 5. *Positional parameters* (× 10⁴)

Estimated standard deviations are given in parentheses.

		Co	Ni	Zn
M	*x*	2447 (3)	2429 (2)	2459 (1)
	y	2500 (*)	2500 (*)	2500 (*)
	z	4070 (2)	4070 (1)	4068 (1)
Cl(1)	*x*	631 (7)	620 (3)	631 (3)
	y	2500 (*)	2500 (*)	2500 (*)
	z	4055 (6)	4020 (3)	4062 (3)
Cl(2)	*x*	3035 (5)	3018 (3)	3061 (2)
	y	432 (6)	440 (3)	456 (3)
	z	3386 (4)	3401 (2)	3388 (2)
Cl(3)	*x*	3145 (8)	3122 (4)	3142 (4)
	y	2500 (*)	2500 (*)	2500 (*)
	z	5400 (5)	5404 (2)	5414 (2)
N(1)	*x*	1515 (24)	1463 (10)	1508 (8)
	y	2500 (*)	2500 (*)	2500 (*)
	z	960 (14)	958 (6)	954 (7)
N(2)	*x*	4936 (19)	4940 (9)	4914 (8)
	y	2500 (*)	2500 (*)	2500 (*)
	z	8269 (15)	8260 (6)	8256 (6)
		Table 5 (*cont.*)		
C(1)	*x*	2614 (36)	2678 (12)	2686 (12)
	y	2500 (*)	2500 (*)	2500 (*)
	z	992 (24)	1006 (12)	1012 (13)
C(2)	*x*	1118 (28)	1063 (17)	1098 (17)
	y	2500 (*)	2500 (*)	2500 (*)
	z	43 (26)	53 (11)	84 (11)
C(3)	*x*	1103 (34)	1046 (16)	1046 (13)
	y	3737 (39)	3805 (20)	3708 (18)
	z	1430 (25)	1407 (13)	1421 (12)
C(4)	*x*	4370 (38)	4418 (20)	4436 (20)
	y	2500 (*)	2500 (*)	2500 (*)
	z	7378 (27)	7397 (11)	7377 (11)
C(5)	*x*	4117 (36)	4119 (20)	4111 (20)
	y	2500 (*)	2500 (*)	2500 (*)
	z	8943 (30)	8964 (15)	8880 (15)
C(6)	*x*	5404 (38)	5500 (18)	5330 (16)
	y	3906 (44)	3873 (18)	3756 (18)
	z	8434 (21)	8417 (10)	8415 (10)

* Required by symmetry to be identically equal to 0·25; therefore, e.s.d. is zero.

Table 6. *Thermal parameters* ($\times 10^2$)

The temperature factor is defined by:

$$\exp\left[-\tfrac{1}{4}\sum_{i=1}^{3}\sum_{j=1}^{3} B_{ij}h_ih_ja_i^*a_j^*\right].$$

Estimated standard deviations are given in parentheses.

		Co	Ni	Zn
M	B_{11}	483 (29)	842 (12)	382 (5)
	B_{22}	431 (14)	610 (8)	453 (5)
	B_{33}	395 (14)	526 (7)	367 (5)
	B_{12}	*	*	*
	B_{13}	3 (17)	−3 (8)	8 (6)
	B_{23}	*	*	*
Cl(1)	B_{11}	421 (62)	797 (24)	378 (15)
	B_{22}	745 (43)	1149 (26)	931 (24)
	B_{33}	709 (42)	1233 (26)	958 (24)
	B_{12}	*	*	*
	B_{13}	43 (39)	60 (19)	33 (18)
	B_{23}	*	*	*
Cl(2)	B_{11}	717 (41)	1235 (18)	802 (15)
	B_{22}	611 (26)	839 (14)	680 (14)
	B_{33}	882 (33)	1239 (18)	1075 (19)
	B_{12}	144 (25)	181 (13)	186 (13)
	B_{13}	55 (28)	94 (15)	65 (15)
	B_{23}	−181 (32)	−333 (16)	−314 (15)
Cl(3)	B_{11}	828 (73)	1354 (29)	865 (26)
	B_{22}	1407 (75)	1788 (38)	1670 (41)
	B_{33}	427 (35)	542 (16)	424 (17)
	B_{12}	*	*	*
	B_{13}	−177 (38)	−170 (17)	−186 (18)
	B_{23}	*	*	*
N(1)	B_{11}	525 (192)	1158 (88)	434 (46)
	B_{22}	330 (89)	605 (47)	504 (49)
	B_{33}	496 (103)	638 (49)	612 (54)
	B_{12}	*	*	*
	B_{13}	−147 (127)	19 (51)	37 (47)
	B_{23}	*	*	*
N(2)	B_{11}	403 (154)	1120 (72)	465 (49)
	B_{22}	357 (93)	642 (48)	499 (49)
	B_{33}	597 (125)	533 (44)	431 (46)
	B_{12}	*	*	*
	B_{13}	−64 (106)	−174 (48)	−95 (40)
	B_{23}	*	*	*
C(1)	B_{11}	323 (323)	522 (99)	379 (74)
	B_{22}	2340 (506)	2652 (227)	2155 (205)
	B_{33}	856 (221)	1523 (137)	1203 (128)
	B_{12}	*	*	*
	B_{13}	−79 (200)	−64 (83)	−12 (83)
	B_{23}	*	*	*
C(2)	B_{11}	229 (255)	1565 (142)	1163 (148)
	B_{22}	3163 (656)	2700 (238)	2367 (239)
	B_{33}	870 (230)	722 (76)	664 (96)
	B_{12}	*	*	*
	B_{13}	−242 (176)	−395 (88)	−389 (96)
	B_{23}	*	*	*
C(3)	B_{11}	1690 (305)	1959 (126)	1468 (120)
	B_{22}	1194 (220)	1861 (127)	1566 (124)
	B_{33}	1920 (320)	2717 (177)	2237 (160)
	B_{12}	566 (205)	965 (102)	546 (101)
	B_{13}	−82 (237)	−270 (121)	−204 (113)
	B_{23}	−731 (246)	−1227 (135)	−1126 (121)
C(4)	B_{11}	1319 (368)	2593 (207)	2102 (202)
	B_{22}	1341 (318)	1161 (110)	1090 (120)
	B_{33}	908 (261)	1116 (110)	780 (104)
	B_{12}	*	*	*
	B_{13}	−440 (237)	−1021 (123)	−931 (121)
	B_{23}	*	*	*
C(5)	B_{11}	657 (322)	1492 (184)	1136 (165)
	B_{22}	2529 (570)	3920 (490)	3505 (379)
	B_{33}	1071 (312)	1467 (164)	1052 (151)
	B_{12}	*	*	*
	B_{13}	355 (241)	430 (141)	142 (132)
	B_{23}	*	*	*
C(6)	B_{11}	2636 (451)	3778 (242)	2945 (201)
	B_{22}	1492 (271)	1661 (114)	1679 (127)
	B_{33}	1098 (215)	1618 (108)	1516 (119)
	B_{12}	−1035 (291)	−1698 (146)	−1749 (140)
	B_{13}	−582 (250)	−1087 (132)	−942 (131)
	B_{23}	124 (233)	761 (98)	747 (105)

* Required by symmetry to be zero.

physical significance. The thermal ellipsoids for the carbon atoms of the three compounds are oriented similarly, except for axes 1 and 2 of C(2) and axes 1 and 2 of C(6) in the cobalt isomorph. Axes 1 and 2 of C(6) are essentially the same length; therefore, directions calculated for them also have no physical significance. The orientations of the thermal ellipsoids for the metal atoms and the two nitrogen atoms do not generally agree in the three isomorphs. For the zinc and cobalt isomorphs, these are the atoms which are, to a large extent, isotropic. Again this would give the directions of the axes no physical meaning.

Table 8 gives the orientation of the thermal ellipsoids of the chlorine and carbon atoms with respect to the bond between them and the central atom of their respective tetrahedra. In every case, with the exception of C(2) in the cobalt isomorph, the axis with the smallest displacement is the one that is nearly parallel to the bond direction. The other two axes are then, of course, approximately perpendicular to the bond direction. This indicates that the disorder is of the form of a rotation or oscillation of the tetrahedron about its central atom – any translation of the tetrahedron would cause some of the larger axes of the thermal ellipsoids to lie in directions other than perpendicular to the bonds. The thermal ellipsoids of the metal and nitrogen atoms are also consistent with this description, since the temperature parameters for these atoms are not excessively large, indicating that they are not disordered.

Thus, with the exception of only C(2) of the cobalt isomorph, all of the atoms which appear to be disordered in the structures have their thermal ellipsoids oriented in similar directions. It is interesting to note that the cobalt isomorph is the only one in which experimental cross-level scaling was not available; this causes the B_{11} values (those associated with the direction of the rotational axis) and the individual level scale factors to be completely degenerate (Lingafelter & Donohue, 1966) and could, therefore, cause the temperature factors to be rather unrealistic. However, the initial scale factors were determined on the basis of a structure factor calculation using the final zinc parameters; thus, if the two structures are as isomorphous

Table 7. R.M.S. displacements along the principal axes of the thermal ellipsoids and the angles between these axes and the cell edges

Reading across each line the numbers are: the r.m.s. displacement (with e.s.d. given in parentheses) in Å and the angles (°) which the axis makes with the *a*, *b*, and *c* axes. Semicolons separate the three axes. Axis 1 (shortest) is listed first, then axis 2 (intermediate) and then axis 3 (longest). The different lines for each atom give the values for the cobalt, nickel, and zinc isomorphs in that order. For M, Cl(1), Cl(2), Cl(3) the r.m.s. displacements have been multiplied by 10 . For the remaining atoms they have been multiplied by 10^2. An asterisk indicates an axis required to be perpendicular to the *b* axis. A dagger indicates an axis required to be parallel to the *b* axis.

M	224 (4)	92	*	2;	234 (4)	†		;	247 (8)	2	*	88
	258 (2)	89	*	1;	278 (2)	†		;	327 (2)	1	*	91
	215 (2)	113	*	23;	221 (2)	157	*	113;	240 (1)		†	
Cl(1)	229 (17)	8	*	98;	301 (9)	82	*	8;	307 (9)		†	
	316 (5)	8	*	98;	382 (4)		†	;	397 (4)	82	*	8
	218 (4)	3	*	93;	343 (5)		†	;	349 (4)	87	*	3
Cl(2)	235 (7)	119	38	68;	318 (8)	151	113	106;	351 (7)	94	118	28
	273 (3)	107	34	62;	406 (3)	162	104	101;	425 (3)	93	120	30
	228 (3)	116	38	65;	337 (3)	153	110	107;	398 (4)	95	120	30
Cl(3)	214 (10)	69	*	21;	337 (14)	159	*	69;	422 (11)		†	
	254 (4)	79	*	11;	419 (5)	169	*	79;	476 (5)		†	
	212 (5)	70	*	20;	344 (5)	160	*	70;	460 (6)		†	
N(1)	20 (3)		†	;	21 (4)	132	*	138;	29 (4)	138	*	48
	28 (1)		†	;	28 (1)	88	*	178;	38 (1)	2	*	88
	23 (1)	11	*	101;	25 (1)		†	;	28 (1)	79	*	11
N(2)	21 (3)		†	;	22 (4)	163	*	107;	28 (3)	107	*	17
	25 (1)	75	*	15;	29 (1)		†	;	38 (1)	15	*	105
	21 (1)	50	*	40;	25 (1)		†	;	26 (1)	140	*	50
C(1)	20 (10)	8	*	82;	33 (4)	82	*	172;	54 (6)		†	
	26 (2)	4	*	86;	44 (2)	86	*	176;	58 (2)		†	
	22 (2)	1	*	89;	39 (2)	89	*	179;	52 (2)		†	
C(2)	14 (11)	18	*	71;	35 (5)	71	*	161;	63 (7)		†	
	27 (2)	68	*	22;	47 (2)	158	*	68;	58 (3)		†	
	24 (2)	61	*	29;	42 (2)	151	*	61;	55 (3)		†	
C(3)	27 (4)	112	35	65;	46 (4)	145	95	125;	57 (4)	116	124	45
	28 (1)	120	39	67;	50 (2)	141	101	127;	70 (2)	113	127	46
	28 (2)	112	38	61;	43 (2)	152	98	116;	64 (2)	106	127	41
C(4)	28 (5)	57	*	33;	41 (5)		†	;	45 (5)	33	*	123
	27 (2)	63	*	27;	38 (2)		†	;	63 (2)	27	*	117
	19 (2)	63	*	27;	37 (2)		†	;	57 (3)	27	*	117
C(5)	24 (7)	150	*	60;	40 (6)	120	*	150;	57 (6)		†	
	36 (2)	134	*	44;	49 (3)	136	*	134;	70 (4)		†	
	35 (3)	127	*	37;	40 (3)	143	*	127;	67 (4)		†	
C(6)	30 (4)	59	53	52;	37 (4)	81	50	139;	65 (5)	32	119	104
	29 (1)	67	28	105;	38 (1)	115	94	154;	81 (2)	35	118	110
	24 (2)	57	34	96;	36 (2)	111	83	158;	77 (2)	40	123	111

Table 8. *Angles between principal axes of thermal ellipsoids and a vector defined by two atoms*

	Axis	Atoms defining vector	Angle between axis and vector Co	Ni	Zn
Cl(1)	1	M–Cl(1)	171°	170°	177°
	2		81	90	90
	3		90	100	93
Cl(2)	1	M–Cl(2)	169	179	173
	2		80	91	83
	3		93	90	91
Cl(3)	1	M–Cl(3)	2	11	2
	2		92	101	92
	3		90	90	96
C(1)	1	N(1)–C(1)	6	1	3
	2		84	89	93
	3		90	90	90
C(2)	1	N(1)–C(2)	127	178	172
	2		37	92	98

Table 8 (*cont.*)

	Axis	Atoms defining vector	Angle between axis and vector Co	Ni	Zn
	3		90	90	90
C(3)	1	N(1)–C(3)	6	9	2
	2		94	99	89
	3		86	91	88
C(4)	1	N(2)–C(4)	174	179	176
	2		90	90	90
	3		84	89	86
C(5)	1	N(2)–C(5)	164	1	9
	2		106	91	81
	3		90	90	90
C(6)	1	N(2)–C(6)	31	26	16
	2		60	115	105
	3		97	94	95

The e.s.d.'s range from 1 to 10°.

as they appear to be, these scale factors should be fairly accurate. Furthermore, if the B_{11} values are incorrect, it is difficult to explain why only one atom does not agree, while the others agree quite well.

The thermal parameters for the nickel isomorph are generally larger than for the other isomorphs. The cause for this is not apparent.

Analysis of the directions of the thermal ellipsoid axes of the chlorine atoms in the zinc isomorph reveals the probable mode of disorder of the $[ZnCl_4]^{2-}$ tetrahedra. There is a disorder caused by an oscillation of the tetrahedra in all directions about the central metal atom. Superimposed upon this is a disorder caused by an oscillation about the Zn–Cl(1) bond. It can be seen that the same general pattern exists throughout the three isomorphs.

It is well known that determination of parameters for carbon and nitrogen atoms cannot be accomplished with a great deal of accuracy in the presence of heavy atoms, as is the case in these structures. This is particularly true of the thermal parameters. For this reason, no analysis of the directions of the thermal ellipsoids for these atoms will be made.

Table 9 lists the bond lengths and angles for all three compounds. For the metal–chlorine bond lengths, the values are given both with and without correction for thermal motion, calculated with the program of Busing & Levy (1959) assuming the chlorine atoms to 'ride' on the metal atoms. It was not considered that the accuracy of the thermal parameters of the atoms in the tetramethylammonium ions is enough for the calculation of thermal motion corrections to be significant. The mean values of the metal–chlorine bond lengths, corrected for thermal motion, are Co–Cl 2·280, Ni–Cl 2·273, Zn–Cl 2·287 Å.* The Ni–Cl distance is in excellent agreement with the value 2·27 Å found in dichlorobis(triphenylphosphine)nickel (Garton, Henn, Powell & Venanzi, 1963) and in triphenylmethylarsonium tetrachloronickelate(II) (Pauling, 1966). In order to make the correction for thermal motion, we have extended the refinement of the triphenylmethylarsonium tetrachloronickelate(II) with anisotropic thermal parameters, using Pauling's data. This refinement reduced R from 0·074 to 0·064 but caused no significant changes in atomic positions. The mean Ni–Cl distance, corrected for thermal motion, is 2·275 Å.

The $[MCl_4]^{2-}$ tetrahedra appear to be distorted in all three of the isomorphs in the form of flattened tetrahedra. For nickel(II) this is contrary to what simple crystal-field theory predicts. It is true that the nickel isomorph has a distortion which is greater than the other two, but this is in the direction of greater flattening rather than in the direction of elongation. Since the observed distortions are similar, it would appear that they are caused by crystal packing forces and not by the Jahn–Teller effect. The $[NiCl_4]^{2-}$ ion in the crystal structure of bis(triphenylmethylarsonium)tetrachloronickel(II) is found to be regular tetrahedral (Pauling, 1966). This would seem to corroborate Liehr & Ballhausen's conclusion that tetrahedral nickel(II) is not subject to a Jahn–Teller distortion. Tetramethylammonium tetrachlorocuprate(II), which is approximately isomorphous with the present structures, contains a tetrahedral $[CuCl_4]^{2-}$ ion which is distorted in a similar manner to that of the present structure (Morosin & Lingafelter, 1961), although to a greater extent. This is quite compatible with crystal field theory which predicts a Jahn–Teller distortion for copper(II) complexes in the form of a flattened tetrahedron.

Table 9. *Bond lengths and angles*

Primed atoms are related to unprimed by reflection in mirror plane at $y=\frac{1}{4}$. The estimated standard deviations as obtained from the least-squares refinement are given in parentheses.

M–Cl(1)*	2·229 (9) Å	2·220 (4) Å	2·244 (4) Å
M–Cl(2)*	2·261 (6)	2·240 (3)	2·246 (3)
M–Cl(3)*	2·266 (9)	2·234 (4)	2·253 (4)
M–Cl(1)†	2·248	2·256	2·274
M–Cl(2)†	2·287	2·279	2·285
M–Cl(3)†	2·306	2·283	2·303
N(1)–C(1)	1·35 (5)	1·49 (2)	1·45 (2)
N(1)–C(2)	1·51 (5)	1·49 (2)	1·44 (2)
N(1)–C(3)	1·43 (4)	1·46 (2)	1·42 (2)
N(2)–C(4)	1·55 (5)	1·48 (2)	1·49 (2)
N(2)–C(5)	1·45 (5)	1·49 (3)	1·38 (3)
N(2)–C(6)	1·41 (4)	1·43 (2)	1·38 (2)
Cl(1)–M–Cl(2) Cl(1)–M–Cl(2′)	108·3 (2)°	107·8 (1)°	109·1 (1)°
Cl(1)–M–Cl(3)	112·8 (4)	114·4 (2)	112·1 (2)
Cl(3)–M–Cl(2) Cl(3)–M–Cl(2′)	108·3 (2)	107·8 (1)	108·4 (1)
Cl(2)–M–Cl(2′)	110·8 (4)	111·4 (2)	109·9 (2)
C(1)–N(1)–C(2)	111 (3)	112 (1)	114 (1)
C(1)–N(1)–C(3) C(1)–N(1)–C(3′)	110 (2)	109 (1)	111 (1)
C(2)–N(1)–C(3) C(2)–N(1)–C(3′)	112 (2)	110 (1)	110 (1)
C(3)–N(1)–C(3′)	103 (4)	107 (2)	99 (2)
C(4)–N(2)–C(5)	110 (3)	112 (1)	111 (1)
C(4)–N(2)–C(6) C(4)–N(2)–C(6′)	110 (2)	111 (1)	112 (1)
C(5)–N(2)–C(6) C(5)–N(2)–C(6′)	99 (2)	102 (1)	105 (1)
C(6)–N(2)–C(6′)	127 (4)	119 (2)	110 (2)

* Without correction for thermal motion.
† With correction for thermal motion ('riding' model assumed).

It is unfortunate that the structures are disordered since the only other reported structures of a non-chelated tetrahedral complex of nickel are those of dichlorobis(triphenylphosphine)nickel(II) (Garton,

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* B. Morosin has informed us that he has investigated the crystal structure of the manganese(II) compound, with experience quite similar to ours. Some of his results are: $a_0=12·33$, $b_0=9·06$, $c_0=15·64$ Å; 1248 reflections; refined in *Pnam* to $R=0·088$; mean Mn–Cl bond length 2·324 Å without correction for thermal motion, 2·372 Å with correction for thermal motion.

Henn, Powell & Venanzi, 1963) and bis(triphenylmethylarsonium)tetrachloronickel(II) (Pauling, 1966).

The phase diagram of the $CsCl–NiCl_2$ system has been determined (Iberson, Gut & Gruen, 1962) and it is found that below 50 mole% $NiCl_2$ there is a solid-to-solid color change from yellow to blue at 417°C caused by the formation of the compound Cs_3NiCl_5, which was shown to be isomorphous with Cs_3CoCl_5 by powder methods. Cs_3CoCl_5 is known to contain $[CoCl_4]^{2-}$ tetrahedra; therefore, Cs_3NiCl_5 presumably contains $[NiCl_4]^{2-}$ tetrahedra. We have prepared this compound in powder form and have found it to be stable at room temperature for long periods of time when stored in a desiccator. If single crystals of it can be prepared, it would probably provide a compound for an accurate structure determination of the tetrahedral $[NiCl_4]^{2-}$ ion.

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A Neutron Structure Analysis of $S_4N_4H_4$

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The hydrogen atoms in $S_4N_4H_4$ have been found to be covalently bonded to the nitrogen atoms in agreement with the inference of Sass & Donohue (*Acta Cryst.* (1958) **11**, 497] from an X-ray study. There is trigonal bonding about the nitrogen atom with coplanar SNHS groupings. The $S_4N_4H_4$ molecules are connected by N–H···N and N–H···S hydrogen bonds.

Introduction

A study of the structure of $S_4N_4H_4$ by X-ray methods was made by Sass & Donohue (1958) in an attempt to resolve conflicting chemical evidence regarding the molecular structure. Arnold (1938) and Goehring (1947) favoured a structure containing N–H bonds while Meuwsen (1929) and Sidgwick (1950) preferred a structure with S–H bonds. Measurements of the infrared and Raman spectra (Lippinscott & Tobin, 1953) showed strong absorption bands at 3220, 3285, and 3320 cm^{-1} which are characteristic of N–H bonds. Sass & Donohue located the sulphur and nitrogen atoms, and from considerations of ring angles and molecular packing, inferred that the hydrogen atoms were bound to nitrogen.

The present neutron structure analysis was carried out to obtain direct evidence for the location of the hydrogen atoms in the molecule and to study the nature of the intermolecular hydrogen bonding.

Experimental

The crystal, in the form of a rough cube of volume 0·92 mm^3, was supplied by Dr B. Dawson of the C.S.I.R.O. Division of Chemical Physics, Melbourne. The crystal data (taken from Sass & Donohue) are:

$$a=8{\cdot}010,\ b=12{\cdot}20,\ c=6{\cdot}727\ \text{Å}.$$

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