Acta Cryst. (1961). **14**, 888

The Crystal Structure of *Di*aqua*bis*(salicylaldehydato) Nickel

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(*Received* 25 *May* 1960 *and in revised form* 26 *October* 1960)

The crystal structure of *di*aqua*bis* (salicylaldehydato) nickel has been determined by 2-dimensional projections. The cell dimensions are

$$a_0 = 12{\cdot}93,\quad b_0 = 7{\cdot}32,\quad c_0 = 7{\cdot}41 \text{ Å},\quad \beta = 90°15',\quad Z = 2.$$

The space group is $A2/m$. The molecule has a trans octahedral configuration with Ni–O distances 2·03 Å.

Introduction

Tyson & Adams (1940) have reported that the green *bis*-(salicylaldehydato) nickel prepared by them is paramagnetic and therefore presumably has a tetrahedral configuration. However, they mention that their analysis indicates their compound to be a dihydrate. It would seem most likely that the two water molecules are coordinated to the nickel ion, leading to an octahedral configuration. In connection with our study of the coordination compounds of nickel, we have determined the crystal structure of this complex and find it to be *trans*-*di*aqua*bis*(salicylaldehydato) nickel, $Ni(C_6H_4OCHO)_2.2\,H_2O$.

Experimental

The compound was prepared by the method of Tyson & Adams (1940). Because of its insolubility in all solvents tested, it was not possible to grow suitable crystals by recrystallization. However, when salicylaldehyde was allowed to diffuse through a 55% water–ethanol medium into a very dilute solution of nickel acetate in the same solvent, usable crystals were formed. The crystals are thin, square, monoclinic plates on (100), outlined by (011), sometimes also exhibiting small (111) faces.

The cell dimensions were determined from rotation and Weissenberg photographs taken with Cu radiation ($\lambda = 1{\cdot}5418$ Å):

$$a_0 = 12{\cdot}93,\ b_0 = 7{\cdot}32,\ c_0 = 7{\cdot}41 \text{ Å};\ \beta = 90°\ 15'.$$

The cell contains two molecules; calculated density, 1·60 g.cm.$^{-3}$; observed, 1·60 g.cm.$^{-3}$.

The absence of (hkl) reflections with $k+l$ odd indicates space groups $A2$, Am or $A2/m$. The morphology of the crystals suggests $A2/m$, which was confirmed by the successful determination of the crystal structure.

Intensities of ($h0l$) reflections were determined with Cu $K\alpha$ radiation using multiple films and a range of exposure times on a Nonius Integrating Weissenberg camera, integrating in one direction only. The diffraction spots were then scanned normal to the direction of integration with a Moll type microphotometer feeding into a Leeds & Northrup amplifier and recorder. The areas under the peaks in the photometer tracing were measured with the integrator described by Brathovde & Breazeale (1955) and used as relative intensities.

Intensities of ($0kl$) reflections were determined in the same manner with Mo $K\alpha$ radiation on an Integrating Precession camera (Stewart & Lingafelter, 1960), except that peak heights were taken as relative intensities.

All intensities were corrected for Lorentz and polarization effects and the observed structure factors were placed on an absolute scale by comparison with calculated values during the refinement of the structure.

Determination of structure

If the assumption of the space group $A2/m$ is correct, the projection on (010) is centrosymmetric and the nickel atoms are phase-determining for most of the ($h0l$) reflections. Accordingly, this Fourier projection was calculated assuming all phase angles to be zero. The molecule was clearly recognizable and the projection was refined by a series of difference syntheses, using an IBM 650, to a final value of $R = 0{\cdot}061$. Structure factors were calculated using scattering factors for oxygen, carbon and hydrogen from McWeeny (1951) and for nickel from the *International Tables* (1935). No correction for dispersion was made at this time.

Individual anisotropic temperature factors were used in the form $\exp[-(A_i + C_i \cos^2 \Phi_i) \sin^2 \theta/\lambda^2]$, where A_i and C_i are characteristic of the atom and Φ_i is the angle between the direction of maximum vibration and the normal to the reflection plane. The hydrogen atoms were introduced in calculated positions at $R \sim 0{\cdot}15$, assuming a C–H distance of 1·075 Å and, because of the probable hydrogen bonding, the same distance for O–H.

Table 1. *Atomic coordinates and temperature factors*

				$h0l$			$0kl$
Atom	x	y	z	E*	A	C	B_y
Ni	0·0000	0·0000	0·0000	9°	1·30	2·0	1·70
O_1	0·0000	0·2788	0·0000	11	2·20	2·0	1·60
O_2	0·1267	0·0000	0·1603	0	1·70	1·2	5·40
O_3	0·0870	0·0000	−0·2262	14	1·45	1·1	7·02
C_1	0·2163	0·0000	0·1076	20	2·00	1·0	8·05
C_2	0·2495	0·0000	−0·0784	59	1·50	0·5	8·50
C_3	0·3604	0·0000	−0·0964	63	2·60	1·1	12·10
C_4	0·4048	0·0000	−0·2671	−63	2·80	0·8	7·50
C_5	0·3416	0·0000	−0·4161	63	2·70	0·3	8·50
C_6	0·2343	0·0000	−0·4035	0	2·00	1·0	7·40
C_7	0·1878	0·0000	−0·2330	0	1·60	0·6	3·30
H_1	0·0331	0·3629	0·1042	11	2·20	2·0	1·60
H_2	−0·0331	0·3629	−0·1042	11	2·20	2·0	1·60
H_3	0·2759	0·0000	0·2093	20	2·00	1·0	8·05
H_4	0·4085	0·0000	0·0222	63	2·60	1·1	12·10
H_5	0·4874	0·0000	−0·2818	−63	2·80	0·8	7·50
H_6	0·3761	0·0000	−0·5478	63	2·70	0·3	8·50
H_7	0·1880	0·0000	−0·5232	0	2·00	1·0	7·40

* E is the angle between the direction of maximum vibration and C*, measured toward $-a$*.

Table 2. *Observed and calculated structure factors*

h	k	l	Obs.	Calc.
0	0	2	438	401
0	0	4	420	421
0	0	6	< 184	49
0	0	8	269	245
1	0	0	964	1021
1	0	2	200	131
1	0	−2	763	756
1	0	4	553	540
1	0	−4	517	515
1	0	6	500	512
1	0	−6	232	241
1	0	8	204	184
1	0	−8	265	255
2	0	0	156	166
2	0	2	195	190
2	0	−2	628	650
2	0	4	676	673
2	0	−4	767	735
2	0	6	614	634
2	0	−6	249	272
2	0	8	102	97
2	0	−8	306	303
3	0	0	658	603
3	0	2	1050	980
3	0	−2	873	892
3	0	4	457	465
3	0	−4	334	363
3	0	6	212	211
3	0	−6	213	251
3	0	8	75	71
3	0	−8	< 264	226
4	0	0	355	359
4	0	2	1025	1018
4	0	−2	729	764
4	0	4	307	301
4	0	−4	341	369
4	0	6	172	206
4	0	−6	199	201
4	0	8	117	136
4	0	−8	195	195
5	0	0	733	736
5	0	2	747	690
5	0	−2	539	570
5	0	4	336	322
5	0	−4	403	430
5	0	6	215	220
5	0	−6	119	84
5	0	8	302	268
6	0	−8	191	166
6	0	0	213	256
6	0	2	671	652
6	0	−2	502	532
6	0	4	166	173
6	0	−4	351	384
6	0	6	333	352
6	0	−6	245	272
6	0	8	244	220
6	0	−8	58	78
7	0	0	120	139
7	0	2	382	375
7	0	−2	290	341
7	0	4	245	234
7	0	−4	396	434
7	0	6	367	384
7	0	−6	350	378
7	0	8	139	151
7	0	−8	61	76
8	0	0	591	559
8	0	2	512	520
8	0	−2	360	390
8	0	4	219	222
8	0	−4	51	−53
8	0	6	123	123
8	0	−6	270	277
8	0	8	78	91
8	0	−8	69	68
9	0	0	472	479
9	0	2	329	328
9	0	−2	378	376
9	0	4	247	238
9	0	−4	52	−47
9	0	6	90	107
9	0	−6	171	169
10	0	0	290	256
10	0	2	148	−169
10	0	−2	261	258
10	0	4	369	373
10	0	−4	335	320
10	0	6	175	189
10	0	−6	171	141
11	0	0	216	209
11	0	2	67	88
11	0	−2	179	209
11	0	4	286	281
11	0	−4	211	227
11	0	6	72	94
11	0	−6	67	68
12	0	0	226	244
12	0	2	254	238
12	0	−2	69	61
12	0	4	220	215
12	0	−4	243	205
12	0	6	< 93	25
12	0	−6	7	−6
13	0	0	123	106
13	0	2	187	203
13	0	−2	94	91
13	0	4	89	104
13	0	−4	75	112
14	0	0	133	106
14	0	2	163	174
14	0	−2	102	80
14	0	4	< 125	25
14	0	−4	81	73
15	0	0	132	112
15	0	2	< 124	20
15	0	−2	61	83
15	0	−4	138	140
16	0	0	79	77
16	0	2	67	74
16	0	−2	90	81
0	2	0	1952	1938
0	4	0	1150	1141
0	6	0	445	425
0	8	0	213	234
0	1	1	702	739
0	3	1	694	689
0	5	1	282	250
0	7	1	256	254
0	9	1	72	77
0	0	2	398	401
0	2	2	63	−80
0	4	2	251	254
0	6	2	77	96
0	8	2	80	108
0	1	3	< 30	27
0	3	3	184	184
0	5	3	66	70
0	7	3	159	172
0	9	3	47	50
0	0	4	361	421
0	2	4	134	144
0	4	4	310	314
0	6	4	173	149
0	8	4	138	128
0	1	5	293	347
0	3	5	294	341
0	5	5	203	175
0	7	5	206	189
0	9	5	43	67
0	0	6	64	49
0	2	6	< 42	−66
0	4	6	104	97
0	6	6	82	52
0	8	6	107	72
0	1	7	138	157
0	3	7	153	175
0	5	7	81	92
0	7	7	105	115
0	0	8	235	245
0	2	8	155	151
0	4	8	188	179
0	6	8	109	101
0	1	9	158	148
0	3	9	169	149
0	5	9	125	87
0	0	10	184	149
0	2	10	117	93

In order to determine the position of the water molecules, the ($0kl$) data were used to calculate a Fourier projection on (100) and the position of the oxygen atom of the water molecule was refined by difference syntheses. Holding the C^*-component of the temperature factors constant at the values required for ($h0l$), the $0kl$ reflections could be refined to $R=0{\cdot}102$; allowing the C^*-component to vary, R_{0kl} could be reduced to 0·061, with a final C^*-component of $B=1{\cdot}21$ Å^2 for the nickel ion, compared with the value 2·32 from the $h0l$ refinement.

Therefore, a new program was written to permit calculation of structure factors, including the dispersion correction by the method suggested by Templeton (1955), and a final series of refinement cycles of both projections was carried out.

In the refinement including the dispersion correction, there were no significant changes in coordinates and the corresponding R values are $R_{h0l}=0{\cdot}056$, $R_{0kl}(\text{compatible})=0{\cdot}071$, $R_{0kl}(\text{independent})=0{\cdot}062$, while the C^*-components of the Ni temperature factor are $B_{h0l}=1{\cdot}35$ and $B_{0kl}=1{\cdot}10$. Thus the discrepancy due to neglect of the difference in dispersion correction between Cu $K\alpha$ and Mo $K\alpha$ radiation is largely 'taken up' by the temperature factors and scale factors, as reported by Geller & Gilleo (1959), with no significant changes in atomic positions.

The final values of atomic coordinates and temperature factors are given in Table 1 and observed (corrected for dispersion) and calculated structure factors are given in Table 2.

Discussion

The space group $A2/m$ requires the *bis*(salicylaldehydato) nickel portion of the molecule to be exactly planar, parallel to (010), and to have a *trans* configuration. The two molecules in the cell are centered at (0, 0, 0) and at (0, ½, ½), with their 'long' axes quite close to the zone axis [1, 0, 1]. Two water molecules complete the coordination octahedron of each nickel atom. The water molecules are hydrogen-bonded to the phenolate oxygen atoms of adjacent molecules with OH–O distance of 2·83 Å.

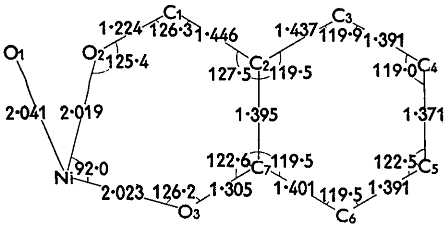

Fig. 1. Bond distances and angles.

Bond distances and angles are given in Fig. 1. Standard deviations, calculated by the method of Cruickshank (1949) are

$$\sigma_{\text{Ni–O}}=0{\cdot}02,\ \sigma_{\text{C–O}}=0{\cdot}03,\ \sigma_{\text{C–C}}=0{\cdot}035\ \text{Å};$$
$$\sigma_{\text{O–Ni–O}}=0{\cdot}7^\circ;\ \sigma_{\text{Ni–O–C}}=1{\cdot}8^\circ;$$
$$\sigma_{\text{O–C–C}}=\sigma_{\text{C–C–C}}=2{\cdot}3^\circ.$$

The coordination octahedron of the nickel atom is very close to regular, the intrachelate angle being 92·0°, slightly larger than 90°, as is also the case for the *bis*(salicylaldiminato) nickel (Stewart & Lingafelter, 1959). The bond distances to the three different types of oxygen atoms (carbonyl, phenolate, water) are essentially equal, with an average value of 2·03 Å. This distance agrees fairly well with values reported for other paramagnetic octahedral nickel complexes: *tetrakis* (aqua) *bis*(acetato) nickel, 2·10 Å (Van Niekirk & Schoening, 1953); *di*aqua*di*glycinatonickel, 2·08–2·12 Å (Stosick, 1945) and is considerably greater than the distance found in diamagnetic planar nickel complexes: *bis*(salicylaldiminato) nickel, 1·84 Å (Stewart & Lingafelter, 1959); *bis*(salicylaldoximato) nickel, 1·83 Å (Merritt, Guare & Lessor, 1956).

Closest contact distances between atoms in different molecules are given in Table 3.

Although the hydrogen atoms were introduced into calculated positions and these positions were not refined, the hydrogen atoms are clearly evident in a difference synthesis calculated from F_c values omitting the hydrogen atoms. This difference synthesis indicated C–H distances appreciably shorter than the assumed value of 1·075 Å and a trial calculation made with shortened C–H distances showed a very slight reduction in R, but it was not felt that the data warrant refinement of the hydrogen positions. The hydrogen atoms were therefore left in the calculated positions. A trial calculation with all hydrogen atoms omitted showed an increase in R_{h0l} from 0·060 to 0·078.

Table 3. *Closest intermolecular contact distances*

Atom	Contact in (010) plane		Contact out of (010) plane	
O_1	—		O	2·83 Å
O_2	CH	3·51 Å	O	3·79
O_3	O	4·58	O	3·79
C_1	CH	3·63	CH	3·67
C_2	—		CH	3·89
C_3	CH	3·88	CH	3·90
C_4	CH	4·04	CH	4·42
C_5	CH	3·88	CH	3·90
C_6	O	3·51	CH	3·67
C_7	—		O	3·83

This investigation was supported in part by the office of Ordnance Research (U.S. Army) under contract No. DA-04-200-ORD-668, and in part by the U.S. Public Health Service under Grant A-2241.

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Short Communications

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 1000 words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible. Publication will be quicker if the contributions are without illustrations.

Acta Cryst. (1961). **14**, 891

Low-temperature transitions in methyl ammonium alum.

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(*Received 8 December 1960*)

When Lipson (1935*a*) concluded that the room-temperature structure of methyl ammonium alum was cubic with space group *Pa*3 and unit-cell edge 12·479 kX. units (= 12·504 Å), one of his suggestions for the existence of the glide planes was that the methyl ammonium group might have spherical symmetry. Later, in the course of an investigation at microwave frequencies of the variation in dielectric loss with temperature, Griffiths & Powell (1952) observed that a number of compounds, one of which was methyl ammonium alum, exhibited marked anomalous effects and that with methyl ammonium alum the anomaly was of two kinds. Of these, one consisted of a peak in the dielectric loss at a temperature which was frequency-dependent, the peak occurring at temperatures higher than 300 °K. for wave lengths of 1·85 and 0·85 cm. respectively; the other was an abrupt transition in both the real and the imaginary parts of the dielectric constant at 170 °K., the transition temperature being independent of frequency. The present X-ray investigation was undertaken in an attempt to establish whether, on cooling, the abrupt transition at 170 °K. was associated with a cessation of rotation of the methyl ammonium group (as would be shown by disappearance of the glide planes) and, if so, to determine the crystal structure of the new phase.

Weissenberg photographs (Fig. 1) were first obtained at room temperature with the crystal of methyl ammonium alum oscillating about the [100] direction, and after the application of the standard corrections and the insertion of the appropriate scaling and temperature factors the agreement residual was 0·18 for the structural data published by Lipson (1935*a*). The crystal was then cooled progressively from room temperature to 100 °K. by subjecting it to a stream of cold nitrogen gas obtained by controlled boiling of liquid nitrogen in a Dewar vessel. Within this temperature range an abrupt transition to a structure of symmetry lower than cubic was observed optically to occur at 170 °K., and with further cooling the colours of the interference patterns changed gradually until a temperature of 150 °K. was reached after which the pattern remained constant. These observations were repeated with the temperature both increasing and decreasing during several successive temperature cycles until ultimately the 170 °K. transition disappeared and thereafter the sole transition observed was that at 150 °K. between a cubic and a non-cubic phase. The experiment was repeated and the same sequence was again observed.

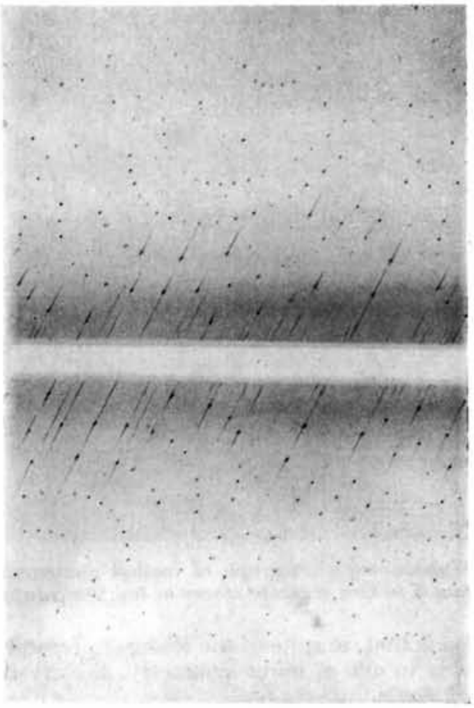

Fig. 1. Weissenberg photograph of methyl ammonium alum.

The existence of the non-cubic structures was confirmed by the use of X-ray diffraction techniques whereby