

# The Crystal Structure of *bis*-Salicylaldiminato-Nickel (II) and -Copper (II)

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The crystal structure of *bis*-salicylaldiminato-nickel (II) has been determined by 2-dimensional projections and the -copper (II) compound has been shown to be isomorphous. The cell dimensions of the nickel compound are  $a_0 = 12.96$ ,  $b_0 = 5.83$ ,  $c_0 = 8.11$  Å,  $\beta = 95^\circ 35'$ ,  $Z = 2$ . The space group is  $P2_1/c$ . The molecule is found to be planar (standard deviation = 0.022 Å) and to have a *trans* configuration.

## Introduction

Tyson & Adams (1940) reported that *bis*-salicylaldiminato-nickel(II) is diamagnetic and that the nickel ion therefore presumably has a square coplanar coordination configuration, while *bis*-salicylaldehydato-nickel (II) is paramagnetic and presumably tetrahedral or octahedral. Stackelberg (1947) reported the cell dimensions and space group of *bis*-salicylaldiminato-copper (II), pointing out that the occurrence of two molecules in a cell of space group  $P2_1/c$  requires the molecule to have a center of symmetry and that the configuration of the 2 nitrogen and 2 oxygen atoms coordinated to copper must be *trans* planar.

He also reported that powder patterns indicated the nickel (II) compound to be isomorphous with the copper (II) compound. As a part of a study of the coordination compounds of nickel and copper we have now proven the isomorphism of their *bis*-salicylaldiminato-complexes and have determined the structure by two-dimensional projections.

## Experimental

The compounds were prepared by the method of Tyson & Adams (1940) and suitable crystals were obtained by slow evaporation from solutions in chloroform. The crystals of the nickel (II) and copper (II)

Table 1. Observed and calculated structure factors

<i>hkl</i>	$F_o$	$F_c$	<i>hkl</i>	$F_o$	$F_c$	<i>hkl</i>	$F_o$	$F_c$	<i>hkl</i>	$F_o$	$F_c$
000	—	3080	80 $\bar{2}$	92	059	904	< 36	1	10,0, $\bar{6}$	113	143
100	450	713	90 $\bar{2}$	296	269	90 $\bar{4}$	150	176	11,0, $\bar{6}$	143	138
200	195	-92	90 $\bar{2}$	< 58	72	10,0, $\bar{4}$	200	183	11,0, $\bar{6}$	171	176
300	423	406	10,0, $\bar{2}$	233	232	10,0, $\bar{4}$	143	151	12,0, $\bar{6}$	< 20	47
400	60	58	10,0, $\bar{2}$	332	311	11,0, $\bar{4}$	140	144	12,0, $\bar{6}$	200	214
500	479	454	11,0, $\bar{2}$	202	198	11,0, $\bar{4}$	165	156	13,0, $\bar{6}$	< 25	-9
600	< 22	62	11,0, $\bar{2}$	264	263	12,0, $\bar{4}$	177	165	14,0, $\bar{6}$	< 19	-3
700	197	-130	12,0, $\bar{2}$	< 76	79	12,0, $\bar{4}$	113	125	008	< 44	87
800	315	300	12,0, $\bar{2}$	202	195	13,0, $\bar{4}$	< 67	71	108	119	143
900	335	329	13,0, $\bar{2}$	119	123	13,0, $\bar{4}$	100	119	10 $\bar{8}$	247	267
10,0,0	300	268	13,0, $\bar{2}$	259	250	14,0, $\bar{4}$	75	77	208	< 90	110
11,0,0	372	352	14,0, $\bar{2}$	90	95	14,0, $\bar{4}$	< 54	64	20 $\bar{8}$	222	238
12,0,0	344	341	14,0, $\bar{2}$	153	167	15,0, $\bar{4}$	94	106	308	191	179
13,0,0	97	77	15,0, $\bar{2}$	< 49	60	006	504	490	30 $\bar{8}$	< 44	40
14,0,0	< 30	22	15,0, $\bar{2}$	< 27	5	106	323	302	408	218	223
15,0,0	96	89	16,0, $\bar{2}$	< 33	61	10 $\bar{6}$	196	185	40 $\bar{8}$	< 34	60
16,0,0	48	46	004	302	267	206	220	242	508	< 55	-45
002	127	101	104	367	342	206	< 71	89	50 $\bar{8}$	< 71	99
102	728	606	10 $\bar{4}$	335	318	306	274	282	608	< 30	28
10 $\bar{2}$	1274	1173	204	538	484	30 $\bar{6}$	121	121	60 $\bar{8}$	< 33	35
202	237	219	20 $\bar{4}$	124	114	406	186	178	708	121	131
20 $\bar{2}$	1390	1244	304	362	335	40 $\bar{6}$	< 34	6	708	< 39	58
302	303	282	30 $\bar{4}$	232	208	506	409	372	808	< 45	66
30 $\bar{2}$	< 37	18	404	508	454	50 $\bar{6}$	< 56	-22	80 $\bar{8}$	191	206
402	427	382	40 $\bar{4}$	171	190	606	49	80	908	106	116
40 $\bar{2}$	302	297	504	312	291	60 $\bar{6}$	241	234	90 $\bar{8}$	103	128
502	181	187	50 $\bar{4}$	367	357	706	274	-214	10,0, $\bar{8}$	< 44	81
50 $\bar{2}$	202	210	604	266	250	70 $\bar{6}$	334	334	11,0, $\bar{8}$	< 40	98
602	338	324	60 $\bar{4}$	318	329	806	< 88	109	0,0,10	< 42	79
60 $\bar{2}$	319	303	704	332	313	80 $\bar{6}$	140	170	1,0,10	< 34	39
702	281	267	70 $\bar{4}$	235	244	906	150	154	1,0, $\bar{10}$	< 21	41
70 $\bar{2}$	333	324	804	< 58	-46	90 $\bar{6}$	149	195	2,0,10	56	85
802	266	250	80 $\bar{4}$	300	304	10,0, $\bar{6}$	143	135	2,0, $\bar{10}$	< 29	66

Table 1 (cont.)

<i>hkl</i>	<i>F<sub>o</sub></i>	<i>F<sub>c</sub></i>	<i>hkl</i>	<i>F<sub>o</sub></i>	<i>F<sub>c</sub></i>	<i>hkl</i>	<i>F<sub>o</sub></i>	<i>F<sub>c</sub></i>	<i>hkl</i>	<i>F<sub>o</sub></i>	<i>F<sub>c</sub></i>
3,0, $\overline{10}$	81	112	13,2,0	136	152	150	<30	2	061	80	31
4,0, $\overline{10}$	<38	69	14,2,0	96	101	250	174	-145	012	192	-177
5,0, $\overline{10}$	<33	79	15,2,0	118	130	350	195	-177	022	203	201
6,0, $\overline{10}$	<39	79	130	<22	-3	450	<30	-23	032	107	111
110	<12	1	230	392	324	550	<30	4	042	354	321
210	131	-124	330	244	204	650	<30	27	052	<56	-18
310	49	-68	430	58	-39	750	37	36	062	91	68
410	37	37	530	111	-97	850	37	28	013	185	173
510	38	36	630	37	99	950	139	120	023	59	81
610	66	-65	730	152	127	10,5,0	76	58	033	521	522
710	161	-163	830	<29	-28	11,5,0	50	-59	043	122	-98
810	<25	-3	930	243	-230	12,5,0	17	-19	053	276	269
910	69	84	10,3,0	93	-103	060	105	111	063	35	37
10,1,0	<29	4	11,3,0	71	79	160	40	56	014	140	147
11,1,0	61	42	12,3,0	82	70	260	205	194	024	225	217
12,1,0	58	65	13,3,0	<25	11	360	204	205	034	142	-129
13,1,0	<29	-26	14,3,0	<21	3	460	<27	3	044	384	368
14,1,0	<26	-25	15,3,0	<14	6	560	62	86	054	<52	-7
15,1,0	<23	-14	040	291	280	660	108	131	015	254	246
16,1,0	<17	-4	140	223	196	760	79	98	025	55	-62
020	143	-133	240	305	286	860	89	106	035	167	142
120	114	127	340	248	250	960	79	103	045	<55	52
220	567	538	440	175	176	170	<21	00	055	<43	63
320	326	322	540	206	227	270	39	42	016	79	-89
420	488	466	640	119	119	370	49	45	026	158	147
520	573	564	740	211	224	470	36	40	036	64	75
620	308	332	840	131	166	570	16	10	046	108	117
720	392	435	940	<30	25	011	604	609	017	221	233
820	214	225	10,4,0	126	138	021	83	86	027	<55	38
920	119	147	11,4,0	118	135	031	218	210	037	145	148
10,2,0	224	254	12,4,0	120	133	041	81	-68	018	<51	31
11,2,0	34	-16	13,4,0	74	100	051	<56	84	028	95	96
12,2,0	<30	27									

compounds are identical in appearance except for color (Ni: orange-red, Cu: dark green), six-sided monoclinic plates, tabular on (100), outlined by (001) and (011).

The cell dimensions and space group were determined from rotation, equi-inclination Weissenberg, and precession photographs, using Cu  $K\alpha$  radiation ( $\lambda=1.5418$  Å). Dimension measurements on photographs of the two compounds were essentially the same and visual examination revealed no detectable differences in intensities. (Initial determination of cell dimensions and space group were made by Curtiss (1947) and an initial Fourier projection on (010) was made by Breazeale (1955)). The cell dimensions are:

$$a_0=12.96, \quad b_0=5.83, \quad c_0=8.11 \text{ \AA}; \quad \beta=95^\circ 35'.$$

Observed density = 1.62 g.cm.<sup>-3</sup>; calculated for 2 molecules per cell = 1.64 g.cm.<sup>-3</sup>. Systematic absence of (*h*0*l*) for *l* odd and of (0*k*0) for *k* odd indicate the space group to be  $P2_1/c$ . These values agree with those reported by Stackelberg (1947) and by Simonsen & Pfluger (1957).

Intensities of reflections for all three axial zones of the nickel compound were obtained from integrated photographs using multiple films and a range of exposure times. (*h*0*l*) and (*h**k*0) data were obtained with Cu  $K\alpha$  radiation 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 and Northrup Amplifier and a recorder containing a logarithmic slide wire. Intensities were taken to be proportional to the areas under the photometer tracings. (0*kl*) data were obtained with Mo  $K\alpha$  radiation on an Integrating Precession Camera (Stewart, 1958) using an identical procedure. Intensities were measured for 97 of the 135 unique (*h*0*l*) reflections in the accessible portion of the sphere of reflection, 82 of the 104 (*h**k*0) reflections, and 33 of the 42 (0*kl*) reflections. All intensities were corrected for Lorentz and polarization effects.

#### Determination of the structure

Since the presence of only two nickel atoms in a cell of space group  $P2_1/c$  requires these atoms to lie at centers of symmetry; and since they can be placed at (0, 0, 0) and (0,  $\frac{1}{2}$ ,  $\frac{1}{2}$ ) without loss of generality, it was possible to begin with the calculation of the Fourier projection  $\rho(x, z)$ , assuming all phase angles to be determined by the contribution of the nickel atoms (i.e.,  $\alpha=0$ ). This calculation clearly showed the positions of the other atoms and the projection was quickly refined by ( $F_o - F_c$ ) difference syntheses. (After the final refinement, only 4 of the 97 observed reflections were found to have  $\alpha \neq 0$ .)

From the *x* and *z* coordinates obtained from the projection on (010) and the assumption of molecular planarity and reasonable bond lengths and angles,

trial structures were readily obtained for the other two projections and in the final stages of refinement the three projections were refined simultaneously by difference syntheses, using an overall isotropic temperature factor (final value) of  $B=2.430 \times 10^{16}$ .

Final values of observed and calculated structure factors are listed in Table 1. They give values of  $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$  of 0.080 for  $(h0l)$ , 0.102 for  $(hk0)$ , 0.066 for  $(0kl)$  and 0.083 for all three zones combined.

All calculations in the final stages of refinement were made on an IBM Type 650 machine, using scattering factors from the *Internationale Tabellen zur Bestimmung von Kristallstrukturen* (1935) for nickel and from McWeeny (1951) for the other atoms.

Table 2. Atomic coordinates  
*Bis* (salicylaldiminato) nickel (II)

Atom	$x$	$y$	$z$
Ni	0.0000	0.0000	0.0000
C <sub>1</sub>	0.1807	-0.2811	0.0378
C <sub>2</sub>	0.2370	-0.1125	0.1400
C <sub>3</sub>	0.3413	-0.1585	0.1984
C <sub>4</sub>	0.3999	-0.0100	0.3025
C <sub>5</sub>	0.3540	0.1979	0.3431
C <sub>6</sub>	0.2533	0.2500	0.2870
C <sub>7</sub>	0.1924	0.0950	0.1860
N	0.0866	-0.2452	-0.0245
O	0.0963	0.1563	0.1391
H <sub>1</sub>	0.0557	-0.3713	-0.0981
H <sub>2</sub>	0.2178	-0.4406	0.0127
H <sub>3</sub>	0.3764	-0.3146	0.1605
H <sub>4</sub>	0.4778	-0.0524	0.3505
H <sub>5</sub>	0.3987	0.3194	0.4200
H <sub>6</sub>	0.2206	0.4109	0.3206

The final atomic positions are given in Table 2, and the three final Fourier projections are shown in Fig. 1(a), (b) and (c). Standard deviations of the coordinates, calculated by the method of Cruickshank (1949) are given in Table 3. The larger values for  $\sigma(y)$

Table 3. Standard deviations of coordinates

	$\sigma(x)$ (Å)	$\sigma(y)$ (Å)	$\sigma(z)$ (Å)
O	0.015	0.024	0.015
N	0.017	0.041	0.016
C <sub>2, 3, 4, 5, 7</sub>	0.018	0.029	0.017
C <sub>1, 6</sub>	0.021	0.045	0.016

for N, C<sub>1</sub>, and C<sub>6</sub> are due to overlap in the projection on [100], so that the  $y$  values were obtained only from the projection on [001].

### Discussion of structure

The molecules of *bis*-salicylaldiminato-nickel (II) are planar and the structure of the crystal involves a packing of these planar molecules in essentially the same arrangement as has been reported for other planar molecules such as naphthalene (Cruickshank, 1957). The planarity of the molecules has been checked by calculating the least-squares plane through a

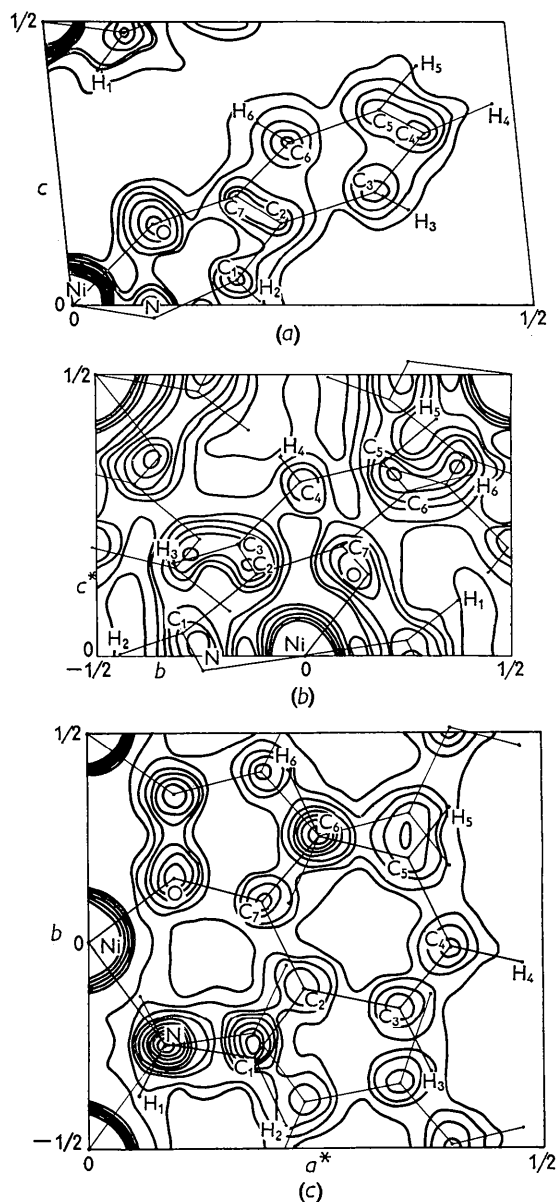


Fig. 1. (a) Fourier projection on (010). (b) Fourier projection on (100). (c) Fourier projection on (001). Contours at intervals of  $2 e \cdot \text{Å}^{-2}$ . Zero and negative contours and central contours at Ni omitted.

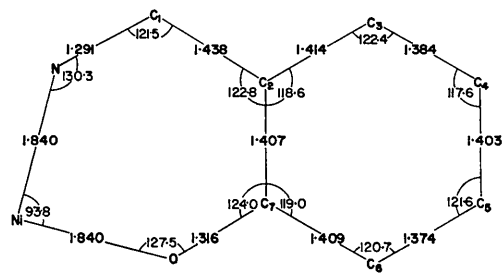


Fig. 2. Bond distances and angles.

molecule and the deviations of the atoms therefrom. The standard deviation,  $[\sum d_i^2/n]^{1/2}$  of the perpendicular distances of the atoms from the plane is 0.022 Å, with no regularity or trend of the distances along the molecule.

The bond distances and angles within the molecule are given in Fig. 2.

It is noticed that, although the set of four ligand atoms bonded to the nickel atom is exactly planar and the bond distances are all equal, the configuration is not exactly 'square', but rectangular, the intrachelate bond angle being 93.8°, somewhat larger than the 90° required for a square.

The Ni-N and Ni-O bond distances, 1.84 Å, agree satisfactorily with distances reported for other diamagnetic nickel (II) complexes: 1.86 Å in *bis*-salicylaloximate-nickel (Merritt *et al.*, 1956); 1.87 and 1.90 Å in *bis*-dimethylglyoximate-nickel (Godycki & Rundle, 1953); and are considerably shorter than the distances found in paramagnetic nickel (II) compounds: 2.10 Å in nickel (II) acetate tetrahydrate (Van Niekirk & Schoening, 1953); 2.08 and 2.09 Å in nickel (II) glycinate dihydrate (Stosick, 1945); 2.03 Å in diaquo-*bis*-salicylaldehydato-nickel (II) (Stewart, Lingafelter & Breazeale, 1959).

It may be pointed out that this structure for the copper compound, with its green color, contradicts the suggestion of Waters, Hall & Llewellyn (1958) that copper complexes of this type are green in color only when 'coordination occurs in the octahedral posi-

tion'. Outside of the bonded N and O atoms, the closest atom to the metal atom is an oxygen atom at 3.85 Å, much too far to be considered as coordinated.

Other contact distances between atoms from different molecules are given in Table 4, which gives the shortest distances found between atoms of different types.

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Table 4. *Shortest intermolecular distances*

Ni-Ni	4.99 Å	N-N	4.06
Ni-O	3.85	N-C	3.49, 3.60
Ni-N	4.18, 4.55	N-CH	3.87, 4.00
Ni-C	4.42, 4.98		
Ni-CH	4.12, 4.78	C-C	4.36, 4.63
		C-CH	3.41, 3.43
O-O	4.20		
O-N	3.64, 3.73	CH-CH	3.48, 3.58
O-C	4.25, 4.64		
O-CH	3.58, 3.71		