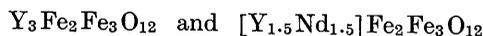


the Y.I.G., as observed by Cunningham & Anderson (1960) in the Sm substituted Y.I.G. These dimensions varied from 12.380 Å in $Y_3Fe_2Fe_3O_{12}$ to 12.530 Å in $[YNd_2]Fe_2Fe_3O_{12}$, 12.478 in $[Y_2Pr]Fe_2Fe_3O_{12}$ and 12.434 in $[Y_{2.5}La_{0.5}]Fe_2Fe_3O_{12}$. These data were found for the maximum amount of Nd, Pr and La substituted for the Y in iron garnets. If higher proportions of these rare earths are introduced, one obtains a mixture of garnets, perovskites and in some cases also hematite. Cerium ions did not substitute for the yttrium in the iron garnets. No shift of the lines of the Y.I.G. were found in these samples and besides the garnet lines, perovskite and hematite, CeO_2 lines were also identified there. Dillon & Nielsen (1960), arrive at the same conclusion.

The cell dimensions of



measured by us are in fair agreement with the data obtained by Bertaut & Forrat (1956, 1957) and Geller & Gilileo (1957).

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The Crystal Structure of the α -Form of *bis*-(N-methylsalicylaldiminato)-Copper

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The crystal structure of the α -form of *bis*-(N-methylsalicylaldiminato)-copper has been determined. The unit cell has

$$a_0 = 24.71 \pm 0.02, \quad b_0 = 9.25 \pm 0.01, \quad c_0 = 6.66 \pm 0.02 \text{ \AA},$$

space group *Ibam*, and contains 4 molecules. Intramolecular distances and angles are essentially the same as those reported for the nickel compound, except that the molecule of the copper compound is completely planar and the metal-ligand distances are 0.1 Å longer. The packing of the molecules is quite similar to that found for *bis*-dimethylglyoximato-nickel and involves chains of Cu atoms with a Cu-Cu separation of 3.33 Å.

Introduction

Stackelberg (1947) described the cell dimensions and space groups of three forms of *bis*-(N-methylsalicylaldiminato)-copper, which he called α , β , and γ . Since it appeared from his results that the structure of the α -form is somewhat similar to that found by Godycki and Rundle (1953) for *bis*-dimethylglyoximato-nickel, we have determined its structure.

The determination of the structure was carried out independently in both laboratories and preliminary reports have appeared (Methuen & v. Stackelberg,

1960; Lingafelter, Morosin & Simmons, 1960). Since the results of the two determinations are in quite satisfactory agreement, and since the refinement was carried somewhat further at the University of Washington, the present report has been written in terms of that determination.

Experimental

bis-(N-methylsalicylaldiminato)-copper was prepared by the reaction between methylamine and *bis*-salicylaldehydato-copper in ethyl alcohol, and recrystal-

lized twice from chloroform. Suitable crystals were obtained by slow evaporation of a solution in chloroform. The crystals are green orthorhombic needles on [001], as described by Stackelberg.

Cell dimensions were obtained from rotation and zero-level Weissenberg photographs with the NaCl pattern ($a_0=5.6394$ Å) superimposed for calibration. All photographs were taken with Cu $K\alpha$ radiation ($\lambda=1.5418$ Å). The cell dimensions are:

$$a_0=24.71 \pm 0.02 \text{ \AA}, \quad b_0=9.25 \pm 0.01 \text{ \AA}, \\ c_0=6.66 \pm 0.02 \text{ \AA}.$$

The density calculated for 4 molecules/cell is 1.45 g./ml.; measured by flotation, 1.47 g./ml. Systematic absence of hkl for $h+k+l$ odd, of $0kl$ for k odd, and of $h0l$ for h odd indicate the space groups $Ibam$ or Iba . On the basis of the great similarity in intensity distribution between $hk0$ and $hk2$ reflections the space group was assumed to be $Ibam$.

$hk0$ and hkl intensities were obtained with a Nonius Integrating Weissenberg camera, integrating in one direction only and using multiple films and several exposure times. The crystal used had dimensions of $0.1 \times 0.05 \times 5$ mm. Each diffraction spot in the linear response range of each film was scanned normal to the direction of camera integration with a Moll type densitometer feeding into a Leeds and Northrup recorder having a logarithmic slide wire. The areas under the densitometer tracings were measured with a planimeter and used as relative intensities. The several films for a given level were placed on the same scale by comparison of common diffraction spots and the two levels were scaled together by comparison of calculated and observed intensities during the structure determination.

Lorentz and polarization factors were applied, but no correction was made for absorption. Three reflections, 200, 110 and 211 were found to be considerably affected by secondary extinction. They were therefore omitted from all difference syntheses and in calculations of R .

146 out of a possible 155 $hk0$ reflections and 58 out of a possible 135 hkl reflections were observed. All calculations were carried out on an IBM-650. Structure factors were calculated using atomic scattering factors from Berghuis *et al.* (1955). For comparison of observed and calculated structure factors and for all difference syntheses except the first two, the observed structure factors were corrected for dispersion by the method of Templeton (1955).

Determination of Structure

Assuming the four Cu to occupy a 4-fold set of equivalent positions in $Ibam$, they may be placed in (4c) without loss of generality. The contribution of the Cu to all observed $hk0$ reflections is then $+4f_{Cu}$. Therefore a Fourier projection on (001) was calculated, assuming all phase angles to be zero. A

reasonable trial structure was immediately apparent from an examination of the projection.

Table I. Atomic positions and temperature factors

	x/a	y/b	z/c	B
Cu	0000	0000	0000	4.2
O	0435	1695	0000	4.0
C ₁	0965	1870	0000	4.6
C ₆	1330	0690	0000	4.9
C ₂	1170	3285	0000	4.9
C ₃	1725	3515	0000	6.0
C ₅	1885	0955	0000	5.2
C ₄	2085	2340	0000	5.8
C ₇	1155	-0795	0000	4.5
C ₈	0590	-2885	0000	4.1
N	0655	-1250	0000	4.0
H ₁	0880	4200	0000	5.0
H ₂	1880	4700	0000	5.0
H ₃	2550	2375	0000	5.0
H ₄	2125	-0050	0000	5.0
H ₅	3500	3325	0000	5.0
H ₆	4050	1500	0000	5.0
H ₇	4700	1750	1200	5.0
H ₈	4700	1750	-1200	5.0

Because of the visual identity of the intensity distribution of $hk0$ and $hk2$ reflections, it was decided to attempt the refinement of the structure by means of Fourier sections $\rho_0(x, y, 0)$ and difference synthesis sections at $z=0$, calculated from the $hk0$ and hkl data alone. These proceeded quite satisfactorily. At $R=0.15$, the hydrogen atoms were introduced in calculated positions, assuming a C-H distance of 1.075 Å and individual isotropic temperature factors were used. The final values of the discrepancy factor, omitting the three reflections strongly affected by secondary extinction and also omitting unobserved reflections, are $R_{hk0}=0.080$ and $R_{hkl}=0.078$.

The final values of the position and thermal parameters are given in Table 1, and observed (cor-

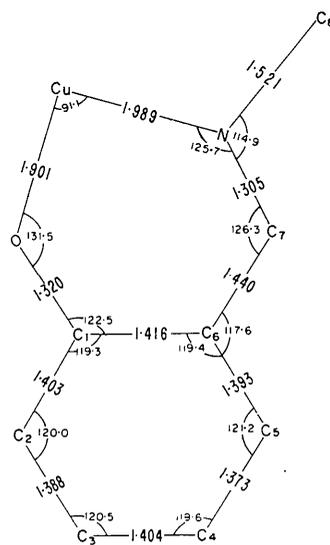


Fig. 1. Bond lengths and angles.

Table 2. *Observed and calculated structure factors* ($\times 10$)

<i>hk</i>	F_o	F_c	<i>hk</i>	F_o	F_c	<i>hk</i>	F_o	F_c	<i>hk</i>	F_o	F_c
	$l=0$		29,3	71	77	14,8	266	286	2,3	< 31	18
2,0	1010	1518	0,4	< 52	42	16,8	177	176	4,3	318	343
4,0	117	-141	2,4	418	403	18,8	143	129	6,3	< 35	-34
6,0	394	433	4,4	993	1029	20,8	89	85	8,3	447	-437
8,0	129	100	6,4	576	594	22,8	< 64	42	10,3	177	167
10,0	672	725	8,4	705	771	1,9	144	152	12,3	< 45	31
12,0	28	-26	10,4	642	651	3,9	145	106	14,3	< 49	53
14,0	336	288	12,4	398	416	5,9	209	239	16,3	< 53	-27
16,0	723	796	14,4	555	578	7,9	168	165	18,3	103	-105
18,0	562	599	16,4	244	189	9,9	239	226	20,3	174	189
20,0	390	352	18,4	238	248	11,9	245	249	22,3	< 57	-45
22,0	275	247	20,4	326	322	13,9	146	162	24,3	88	-92
24,0	246	209	22,4	200	189	15,9	146	157	26,3	< 50	-4
26,0	178	129	24,4	223	187	17,9	136	125	28,3	< 41	12
28,0	159	142	26,4	81	78	19,9	< 52	75	1,4	< 37	8
30,0	117	113	28,4	86	82	0,10	165	172	3,4	539	491
1,1	1385	2016	1,5	286	304	2,10	176	173	5,4	813	775
3,1	729	694	3,5	737	764	4,10	137	138	7,4	52	76
5,1	606	655	5,5	690	679	6,10	90	102	9,4	65	-63
7,1	586	666	7,5	489	487	8,10	118	108	11,4	< 48	28
9,1	745	831	9,5	514	544	10,10	152	151	13,4	< 51	-22
11,1	382	389	11,5	451	461	12,10	137	125	15,4	< 54	-46
13,1	332	364	13,5	470	429	14,10	110	97	17,4	295	-261
15,1	722	713	15,5	< 204	52	16,10	93	108	19,4	91	-93
17,1	455	442	17,5	< 16	8	1,11	132	153	21,4	67	91
19,1	313	308	19,5	317	298	3,11	95	98	23,4	< 54	26
21,1	366	352	21,5	271	284	5,11	94	102	25,4	< 50	26
23,1	255	212	23,5	259	274	7,11	83	100	27,4	< 42	6
25,1	214	178	25,5	150	154	9,11	70	76	2,5	168	168
27,1	197	174	27,5	61	81	11,11	98	101	4,5	175	181
29,1	125	121	0,6	575	565				6,5	< 46	-35
31,1	142	113	2,6	678	760				8,5	140	152
0,2	73	-73	4,6	479	499				10,5	< 50	48
2,2	471	546	6,6	397	365	2,1	856	-925	12,5	191	178
4,2	512	556	8,6	308	306	4,1	811	852	14,5	57	-4
6,2	1175	1268	10,6	246	211	6,1	116	-78	16,5	302	-305
8,2	1132	1229	12,6	351	353	8,1	75	76	18,5	68	-52
10,2	817	797	14,6	< 104	111	10,1	350	-338	20,5	< 56	3
12,2	690	726	16,6	125	111	12,1	588	-549	22,5	< 54	-21
14,2	544	574	18,6	279	276	14,1	< 45	23	24,5	< 49	-5
16,2	554	564	20,6	214	214	16,1	126	154	26,5	< 41	38
18,2	286	212	22,6	225	197	18,1	268	267	1,6	203	-218
20,2	197	161	24,6	143	159	20,1	197	199	3,6	316	-293
22,2	278	256	26,6	96	104	22,1	105	117	5,6	221	-214
24,2	184	164	1,7	397	360	24,1	74	-71	7,6	55	-72
26,2	230	215	3,7	614	702	26,1	87	-87	9,6	57	74
28,2	125	129	5,7	374	334	28,1	< 46	-42	11,6	175	161
30,2	95	93	7,7	127	120	30,1	38	-54	13,6	113	134
1,3	528	563	9,7	< 180	58	1,2	< 24	5	15,6	60	5
3,3	336	302	11,7	220	173	3,2	148	130	17,6	< 57	-2
5,3	674	768	13,7	295	345	5,2	451	-454	19,6	57	-61
7,3	1111	1247	15,7	278	254	7,2	448	-455	21,6	54	-55
9,3	779	880	17,7	196	202	9,2	145	-143	23,6	< 46	-33
11,3	646	670	19,7	182	207	11,2	230	-217	25,6	40	-29
13,3	490	529	21,7	178	153	13,2	67	68	2,7	222	-226
15,3	485	482	23,7	< 67	64	15,2	< 49	-18	4,7	279	-314
17,3	552	554	0,8	159	131	17,2	56	77	6,7	< 55	58
19,3	251	231	2,8	213	182	19,2	412	412	8,7	< 56	-21
21,3	135	76	4,8	368	415	21,2	135	113	10,7	< 57	-47
23,3	216	170	6,8	282	284	23,2	140	-162	12,7	< 57	13
25,3	198	157	8,8	144	76	25,2	92	-90	14,7	< 57	32
27,3	101	107	10,8	204	203	27,2	< 48	-26	16,7	96	120
			12,8	317	295	29,2	< 39	18			

rected for dispersion) and calculated structure factors in Table 2.

Discussion

To estimate the standard deviations of the positional

parameters, the Cruickshank equation (1949) was used, multiplied by an additional factor to correct for the fact that only the $hk0$ and hkl reflections were used. This factor was the square root of the ratio of the total number of reciprocal lattice points

within the limiting sphere to the number in the $hk0$ and hkl levels. The standard deviations so calculated are $\sigma(x)=\sigma(y)=0.006$ Å, for oxygen, 0.007 Å for nitrogen and 0.008 Å for carbon.

Bond lengths and angles are given in Fig. 1 and listed in Table 3 along with the corresponding values for *bis*-(N-methylsalicylaldiminato)-nickel (Frasson, Panattoni & Sacconi, 1959) and *bis*-salicylaldiminato-nickel (Stewart & Lingafelter, 1959). None of the differences between corresponding bond lengths in different compounds are of statistical significance except for those involving the metal.

In both the nickel and copper chelates, the presence of the N-methyl group has caused an increase in the length of the metal-nitrogen bond by 0.10 Å over that of the metal-oxygen bond. That this increase is due to the steric effect of the methyl group is indicated by the equality of the *M*-N and *M*-O bond lengths in *bis*-salicylaldiminato-nickel (Stewart & Lingafelter, 1959), and by the very short

distance between the methyl group and the oxygen atom (2.68 Å in the nickel and 2.76 Å in the copper chelate).

The arrangement of the molecules of *bis*-(N-methylsalicylaldiminato)-copper in the crystal is essentially the same as that reported by Godycki & Rundle (1953) for *bis*-dimethylglyoximato-nickel. The planar molecules all lie parallel to (001), and the copper atoms form chains along the *c*-axis, with a Cu-Cu separation of 3.33 Å, only slightly larger than the Ni-Ni separation of 3.25 Å in *bis*-dimethylglyoximato-nickel, but considerably larger than the 2.64 Å separation found in copper (II) acetate (Van Niekirk & Schoening, 1953).

Understanding of the conditions for formation of this type of structure, involving weak metal-metal interactions must await further experimental data. It should be pointed out that Stackelberg's (1947) second crystal form of *bis*-(N-methylsalicylaldiminato)-copper probably does not have metal-metal interactions and that Ferguson (1960) has obtained an orthorhombic form of *bis*-(N-methylsalicylaldiminato)-nickel which is isomorphous with the copper chelate and therefore does have metal-metal interactions. We are at present examining this crystal.

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Table 3. *Interatomic distances and angles*

	(a)	(b)	(c)
<i>M</i> -O	1.90 Å	1.80 Å	1.84 Å
<i>M</i> -N	1.99	1.90	1.84
C ₁ -O	1.32	1.28	1.32
C ₇ -N	1.31	1.30	1.29
C ₆ -C ₇	1.44	1.46	1.44
C ₁ -C ₆	1.42	1.36	1.41
C ₁ -C ₂	1.40	1.41	1.41
C ₂ -C ₃	1.39	1.42	1.37
C ₃ -C ₄	1.40	1.38	1.40
C ₄ -C ₅	1.37	1.40	1.38
C ₅ -C ₆	1.39	1.40	1.41
N-C ₈	1.52	1.56	—
C ₈ -O'	2.76	2.68	—
O-M-N	91.1°	96°	93.8°
C ₁ -O-M	131.5	127	127.5
C ₆ -C ₁ -O	122.5	126	124.0
C ₁ -C ₆ -C ₇	123.0	124	122.8
N-C ₇ -C ₆	126.3	122	121.5
C ₇ -N-M	125.7	125	130.3
C ₂ -C ₁ -C ₆	119.3	119	119.0
C ₁ -C ₂ -C ₃	120.0	120	120.7
C ₂ -C ₃ -C ₄	120.5	121	121.6
C ₃ -C ₄ -C ₅	119.6	118	117.6
C ₄ -C ₅ -C ₆	121.2	122	122.4
C ₅ -C ₆ -C ₁	119.4	120	118.6
<i>M</i> -N-C ₈	119.4	125	—

(a) *bis*-(N-methylsalicylaldiminato)-copper.

(b) *bis*-(N-methylsalicylaldiminato)-nickel.

(c) *bis*-Salicylaldiminato-nickel.