Acta Cryst. (1953). **6**, 487

The Structure of Nickel Dimethylglyoxime*

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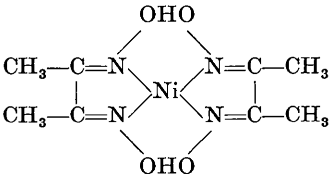
(*Received* 15 *October* 1952 *and in revised form* 4 *November* 1952)

Nickel dimethylglyoxime is orthorhombic, $a_0 = 16{\cdot}68$, $b_0 = 10{\cdot}44$, $c_0 = 6{\cdot}49$ Å, $Z = 4$, space group *Ibam*. The molecules are required to have symmetry $2/m$, and, within our limits of error, have the higher symmetry *mmm*.

The expected structure is confirmed. The intramolecular O.H.O bonds are the shortest yet observed, 2·44 Å. An explanation is advanced to explain the difference in solubilities of copper and nickel dimethylglyoximes in water, and the unusually small pleochroism.



Crystallographic data are given for the corresponding palladium compound, and for nickel cyclohexanedionedioxime.

Introduction

It has seemed valuable to try to understand in some detail the specificity of certain analytical reagents. One of the most promising for study is the selective precipitation of Ni^{++} and Pd^{++} from aqueous solution by dimethylglyoxime and certain related compounds.

Both Ni^{++} and Pd^{++} form square, quadricovalent complexes, and part of the specificity of dimethylglyoxime can be accounted for by the relatively few divalent ions with square covalence. Mellor (1943) lists known square complexes of Pt^{++}, Fe^{++}, Co^{++}, Mn^{++}, Cu^{++} and Ag^{++}. However, for most of these it is easy to keep the metal in another oxidation state, and for some the tendency to form octahedral complexes is so great that square complexes are obtainable only under special circumstances. It is not, however, easy to account for the difference in solubility of Cu^{++} and Ni^{++} complexes of dimethylglyoxime. The work reported here was undertaken to see if a detailed structural study would aid in understanding this difference.

A previous study of nickel dimethylglyoxime has been reported by Miloné (1938) and Miloné & Tappi (1940). However, Miloné's observed density, 1·49 g.cm.$^{-3}$, was far greater than his X-ray density, 1·31 g.cm.$^{-3}$, while both were much less than our observed density, 1·61 g.cm.$^{-3}$. We suspect that Miloné had solvated crystals, though his method of crystallization was similar to ours. In any case, previous data were insufficient to provide an accurate structure.

Experimental procedure

Preparation and properties of nickel dimethylglyoxime

The molecular complex was prepared by reacting dilute solutions of dimethylglyoxime and nickel chloride. Recrystallization of the resulting precipitate from nitrobenzene yielded long, red needles of very small cross-section. Only four prismatic faces were found by optical goniometery and the face development at the end of the needles was not observable. Assuming the prism planes to be (110) an axial ratio, $a:b = 1{\cdot}598$, was obtained, in good agreement with that found subsequently from diffraction photographs.

In polarized light the crystals exhibit a slight pleochroism. For maximum absorption the electric vector was perpendicular to the needle axis (c_0 axis), while differences, if any, within the (001) plane were too small to be observed.

Diffraction data

The X-ray diffraction data were obtained by means of the usual single-crystal techniques. In order to photograph a large portion of the sphere of reflection, the following photographs were taken:

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* Contribution No. 226 from the Institute of Atomic Research and the Department of Chemistry, Iowa State College, Ames, Iowa. Work supported in part by the Industrial Science Research Institute, Iowa State College, and in part by the Ames Laboratory of the Atomic Energy Commission.

Based on a thesis submitted by L. E. Godycki to the Iowa State College in partial fulfilment of the requirements for the PhD. degree.

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Cu K radiation—Weissenberg—($hk0$) to ($hk4$)
Mo K radiation—Precession—($h0l$) to ($h3l$) and ($0kl$) to ($3kl$).

The multiple-film technique was employed in obtaining Weissenberg data, while the Mo $K\alpha$ photographs were taken with a General Electric XRD-3 voltage- and current-stabilized diffraction unit as a series of timed exposures, using a factor of two between exposures in each set.

The intensities of the observed reflections were estimated by visual-comparison procedures and were corrected for Lorentz and polarization factors. The resulting F^2 were correlated so that all observed data were on the same relative intensity scale.

Nickel dimethylglyoxime is orthorhombic. The lattice constants, determined from precession pictures on which the diffraction pattern of quartz was simultaneously recorded, are

$$a_0 = 16{\cdot}68,\ b_0 = 10{\cdot}44,\ c_0 = 6{\cdot}49\ \text{Å}\,.$$

For $Z = 4$, $\varrho_c = 1{\cdot}70$ g.cm.$^{-3}$ as compared with $\varrho_o = 1{\cdot}61$ g.cm.$^{-3}$.

The occurrence of systematic absences among the observed reflections can be summarized as follows:

(hkl) present only if $h+k+l$ is even,
($0kl$) present only if k and l are even,
($h0l$) present only if h and l are even.

The possible space groups are, therefore, D_{2h}^{26}–$Ibam$ and C_{2v}^{21}–Iba.

Structural investigation

The ($00l$) reflections were the most intense in the entire reciprocal lattice, suggesting a layer structure. Moreover, for a given h and k, structure factors depended upon whether l was even or odd, but appeared to be otherwise independent of l. (For ($h0l$) and ($0kl$) data, l was observable to $l = 8$ for this relatively short axis, and good comparisons were effectively limited to $l = 6$.) This suggests an absence of z parameters, and completely planar molecules. In this case the nickel positions are 4(c) of $Ibam$; all light atoms, aside from hydrogens, lie in mirror planes, and the minimum molecular symmetry is $2/m$. The alternative is that the nickels lie in 4(a) of Iba, the molecule is only pseudoplanar, and the minimum molecular symmetry is C_2. As noted, the molecules are planar within the limits detectable by the X-ray data. The liquid-air test of the crystals was negative, which is also consistent with a centrosymmetric structure, and consequently the higher space group was assumed.

The Patterson projection onto (001) (Fig. 1) is very similar to a Fourier projection, since nickel atoms at 0, 0, 0; 0, 0, $\frac{1}{2}$ (and body-centering) make nearly all signs of ($hk0$) reflections positive. The five-membered rings of the complex are quite apparent, confirming the structure of Brady & Muers (1930), based on five-membered rings as originally proposed by Pfeiffer & Richarz (1928) and by Hieber & Leutert (1929). Molecules centered at 0, 0, 0 and 0, 0, $\frac{1}{2}$ must, however, be rotated 90° with respect to each other, so that ring carbons from one molecule overlap, approximately, the oxygen atoms from the other. Nitrogen atoms from the two also overlap. There is no reason for the nitrogen atoms to lie precisely on the axes as they appear to do in the Patterson. The apparent special positions are due to superposition. The Fourier projection, $\varrho(x, y)$, does nothing to resolve these superimposed peaks. Hence only rough parameters could be obtained from two-dimensioned work.

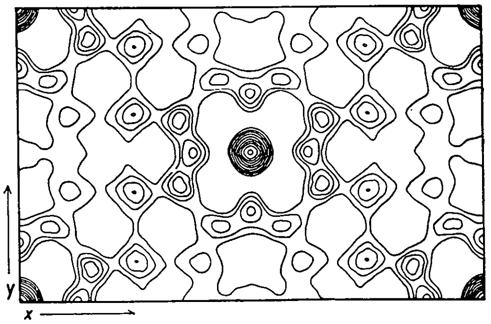

Fig. 1. Patterson projection onto (001).

Refinement of coordinates

In order to resolve the super-imposed peaks, the three-dimensional Fourier section, $\varrho(x, y, 0)$, was calculated. The determination of the signs of the F's consisted of several steps which are summarized in Table 1. The progress of the structure-factor calculations was followed by calculating the value of the reliability index,

$$R(hkl) = \sum_{hkl} \big||F_o| - |F_c|\big| \div \sum_{hkl} |F_o|$$

for at least the (hkl) data.

In trial 1 the structure factors were computed with parameters from the two-dimensional Fourier. The atom form factors were determined from a graph made with the data of James & Brindley (*Internationale Tabellen*, 1935). An isotropic temperature factor, $\exp(-B \sin^2\theta/\lambda^2)$, was used, where B was found to have the value 6·46 Å^2. The reliability index for odd layer-line data, to which nickel atoms make no contribution, was quite large at this stage.

In trial 2 the nitrogen atoms were arbitrarily displaced 0·15 Å away from the axes. Trial-and-error methods showed that they must be displaced in such a manner as to decrease the N–Ni–N angles in the carbon ring. Such a displacement made a very notable improvement in R for the odd layer lines (Table 1, trial 2).

The next stage of refinement involved the application of Booth's (1949) method of steepest descents, as modified by Vand (1951). In order to simplify the calculations, it was assumed that the molecule exhibited D_{2h} symmetry. The parameters used were chosen from those of trial 2, and the value of φ_0, +231·7, was calculated from the (hkl) data of that step. Again a very significant decrease in R for odd layer lines was obtained. Parameters obtained by one steepest-descents refinement are listed as trial 3 of Table 1.

In the final parameter refinement no assumptions were made about the symmetry of the molecule. Signs of F's were derived from the parameters obtained from the steepest-descents refinement, except that it was assumed that the even layer lines, where the parameterless nickel set is most important, had signs as previously determined from trial 2. A Fourier section, $\varrho(x, y, 0)$, was prepared (Fig. 2). Since the molecules lie on planes at $z = 0, \frac{1}{2}$, this one section is all that is required to determine the structure.

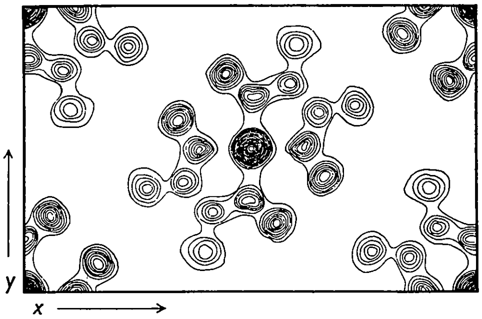

Fig. 2. Fourier section, $\varrho(x, y, 0)$.

The location of maxima in the projection was accomplished with Booth's method (1948). This process yielded the trial-4 parameters with which the F's were recalculated. The R factors indicated good agreement between the observed and calculated structure factors. A linear absorption coefficient was also considered at this step, but this proved to be small enough to ignore.

The trial-4 coordinates were further improved by using the back-shift method of Booth (1946). On the synthetic Fourier the maximum correction due to non-convergence was 0·04 Å, and the average was 0·02 Å.

Application of the back-shift corrections yielded the trial-5 parameters with which the F's were recalculated. The R factors for the last step of refinement indicated satisfactory agreement between F_o and F_c. Since no sign changes occurred in the last set of calculations, the trial-5 parameters were considered to be the best which could be obtained from the data.

The observed and final calculated structure amplitudes are listed in Table 2.

Determination of errors

The errors in the final coordinates were estimated by varying Cruickshank's procedure (1949). In order

Table 1. *Summary of refinement process for nickel dimethylglyoxime*

		Trial number				
		1	2	3	4	5
N_I	x	0·117	0·121	0·121	0·113	0·114
	y	0·000	0·986	0·988	0·989	0·986
N_{II}	x	0·000	0·991	0·993	0·990	0·988
	y	0·183	0·192	0·192	0·181	0·178
O_I	x	0·163	0·155	0·159	0·158	0·158
	y	0·105	0·092	0·091	0·098	0·098
O_{II}	x	0·066	0·057	0·058	0·053	0·053
	y	0·261	0·247	0·253	0·260	0·260
C_I	x	0·072	0·081	0·076	0·081	0·082
	y	0·779	0·765	0·768	0·775	0·778
C_{II}	x	0·139	0·146	0·146	0·148	0·146
	y	0·883	0·868	0·879	0·883	0·883
C_{III}	x	0·095	0·104	0·101	0·101	0·102
	y	0·635	0·624	0·627	0·640	0·636
C_{IV}	x	0·228	0·236	0·235	0·232	0·232
	y	0·850	0·829	0·839	0·856	0·854
$R(hk0)$		0·21	0·23	—	0·15	0·14
$R(hk1)$		0·52	0·38	0·28	0·21	0·18
$R(hk2)$		0·18	0·21	—	0·12	0·12
$R(hk3)$		0·47	0·33	—	0·22	0·20
$R(hk4)$		—	—	—	0·16	0·15
$R(hkl)$		—	—	—	—	0·14

1. Parameters from two dimensional Fourier.
2. Parameters from trial-and-error procedure with nitrogen atoms off axes.
3. Parameters from steepest-descents method.
4. Parameters from three-dimensional Fourier.
5. Parameters from back-shift method.

Table 2. *Observed and calculated structure factors*

The three columns comprising each section are, from left right, the h index, the observed and the calculated structure factors respectively. Unless noted otherwise the signs of the calculated factors are positive.

	$h00$	
4	21	26
6	39	58
8	83	76
10	24	24
12	43	37
14	22	21
16	8	7
18	13	13
20	6	7

	$h10$	
3	12	21
5	81	87
7	109	102
9	55	49
11	26	23
13	34	33
15	11	10
17	13	11
19	7	6

	$h20$	
0	16	32
2	7	14
4	7	12
6	85	87
8	71	80
10	46	44
12	22	19
14	9	11
16	10	10
18	8	8
20	3	4

	$h30$	
1	61	65
3	47	54
5	9	−1
7	30	36
9	37	43
11	30	30
13	4	−3
15	9	11
17	10	11
19	7	8

	$h40$	
0	36	51
2	120	118
4	58	62
6	4	11
8	8	14
10	42	31
12	9	7
14	6	10
16	16	17
18	7	6

	$h50$	
1	76	67
3	81	82
5	17	25
7	20	23
9	61	56
11	40	35
13	8	7
15	12	10
17	9	9

	$h60$	
0	36	36
2	41	39
4	45	49
6	30	25
8	58	49
10	47	39
12	12	12
14	6	6
16	9	8
18	5	5

	$h70$	
1	30	30
3	30	29
5	32	32
7	27	22
9	28	20
11	< 6	2
13	7	8
15	8	7
17	9	7

	$h80$	
0	55	46
2	22	20
4	< 6	5
6	< 6	8
8	16	14
10	< 6	6
12	6	6
14	6	4
16	3	3

	$h90$	
1	22	20
3	< 6	1
5	< 6	6
7	16	15
9	12	7
11	9	8
13	8	7

	$h,10,0$	
0	15	13
2	12	11
4	4	4
6	18	16
8	13	12
10	9	6
12	8	6

	$h,11,0$	
1	17	14
3	10	8
5	8	7
7	14	9
9	5	5
11	6	4

	$h,12,0$	
0	12	6
2	10	7
4	9	7
6	8	4
8	3	3

	$h11$	
2	33	30
4	3	2
6	21	−23
8	32	−37
10	15	17
12	8	13
14	13	16
16	6	7

	$h21$	
1	10	11
3	34	−20
5	45	43
7	9	−4
9	18	15
11	6	5
13	4	−5

	$h31$	
2	14	11
4	37	35
6	11	13
8	1	−7
10	16	15
12	4	−4
14	12	−12

	$h41$	
1	25	−24
3	8	−5
5	11	−14
7	20	−18
9	3	−7
11	6	8
13	4	−4

	$h51$	
2	26	−22
4	7	−11
6	15	−19
8	6	−7
10	6	−9
12	5	6

	$h61$	
1	9	10
3	31	31
5	9	4
7	< 5	−2
9	5	−9

	$h71$	
2	11	13
4	6	6
6	12	9
8	13	9

	$h81$	
1	5	8
3	11	−11
5	9	−8
7	< 5	1
9	6	8

Table 2 (*cont.*)

	*h*91	
2	9	9
4	9	−7
6	9	−9

	h,10,1	
1	5	5
3	4	4

	*h*02	
0	275	329
2	106	114
4	20	26
6	45	51
8	61	59
10	23	20
12	32	31
14	19	18
16	6	6
18	12	10
20	5	6

	*h*12	
1	111	130
3	15	21
5	60	65
7	78	77
9	43	38
11	22	18
13	26	28
15	10	9
17	10	9
19	6	5

	*h*22	
0	23	29
2	10	17
4	12	13
6	63	66
8	59	61
10	35	35
12	17	16
14	7	9
16	8	8
18	8	7

	*h*32	
1	49	51
3	43	43
5	< 6	4
7	25	29
9	32	34
11	25	25
13	4	−3
15	8	9
17	10	9
19	8	6

	*h*42	
0	39	41
2	88	90
4	48	48
6	< 6	10
8	10	12
10	31	27
12	8	6
14	6	9
16	14	14
18	8	5

	*h*52	
1	58	51
3	66	63
5	19	20
7	20	19
9	52	46
11	30	28
13	8	6
15	11	9
17	10	7

	*h*62	
0	34	29
2	37	31
4	38	39
6	25	20
8	48	40
10	37	31
12	11	10
14	6	5
16	8	7
18	4	4

	*h*72	
1	29	25
3	26	24
5	28	27
7	22	17
9	23	17
11	< 6	1
13	7	6
15	7	6
17	6	6

	*h*82	
0	44	38
2	19	16
4	< 6	4
6	< 6	7
8	13	12
10	< 6	5
12	5	5
14	6	4
16	4	3

	*h*92	
1	23	17
3	< 6	1
5	< 6	4
7	14	13
9	8	6
11	8	6
13	7	6

	h,10,2	
0	14	10
2	10	9
4	5	3
6	15	14
8	12	8
10	8	5
12	7	5

	h,11,2	
1	15	11
3	9	7
5	9	6
7	12	9
9	8	4

	h,12,2	
0	8	5
2	8	6
4	8	6
6	6	4

	*h*13	
2	14	9
4	< 6	0
6	12	−13
8	20	−21
10	10	10
12	6	7
14	9	11
16	5	5

	*h*23	
1	5	3
3	7	−19
5	21	24
7	3	−2
9	10	10
11	6	2
13	4	−4

	*h*33	
2	3	5
4	18	20
6	8	7
8	< 6	−3
10	11	10
12	5	−3
14	8	−8

	*h*43	
1	15	−13
3	4	−3
5	8	−8
7	12	−10

	*h*53	
2	16	−13
4	< 6	−6
6	9	−11
8	5	−4

	*h*63	
1	3	6
3	19	20
5	3	3

	*h*73	
2	7	8
4	5	3
6	7	7
8	7	5

	*h*83	
1	4	5
3	9	−8
5	6	−5

	*h*93	
2	6	10
4	5	−4
6	6	−6

	h,10,3	
1	3	4
3	3	4

Table 2 (*cont.*)

	*h*04	
0	131	130
2	45	50
4	14	16
6	27	24
8	32	30
10	16	12
12	20	18
14	14	11
16	< 5	3
18	8	6
	*h*14	
1	47	56
3	12	14
5	28	32
7	37	38
9	22	20
11	12	10
13	17	16
	*h*24	
0	16	17
2	12	12
4	11	11
6	29	33
8	25	31
10	16	19
12	12	9
	*h*34	
1	18	26
3	18	23
5	< 5	5
7	12	16
9	15	18
11	12	14
	*h*44	
0	21	21
2	35	43
	*h*54	
1	27	27
3	27	33
	*h*64	
0	18	17
2	18	17
	*h*74	
1	14	13
3	12	13
	*h*84	
0	24	22
2	13	9
	*h*94	
1	9	10
	h,10,4	
0	10	6
2	14	5

to compute the quantities, F, and, therefore, the values of $\sigma(A_h)$ and $\sigma(A_k)$, it was necessary to apply a temperature factor to the F_o. The resulting values of $\sigma(A_h)$ and $\sigma(A_k)$ were 0·652 e.Å^{-4} and 1·07 e.Å^{-4} respectively. The values of p for each of the atoms were obtained from the peaks in the $\varrho(x, y, 0)$ map calculated with the F_o and the signs from trial 5. The errors, together with the standard deviations in the radial coordinates, are listed in Table 3.

Discussion

The final structure for the nickel dimethylglyoxime molecule, including bond lengths and bond angles, is shown in Fig. 3. The important intramolecular and intermolecular distances, with the calculated standard errors, σ, and the bond angles, are also listed in Table 4.

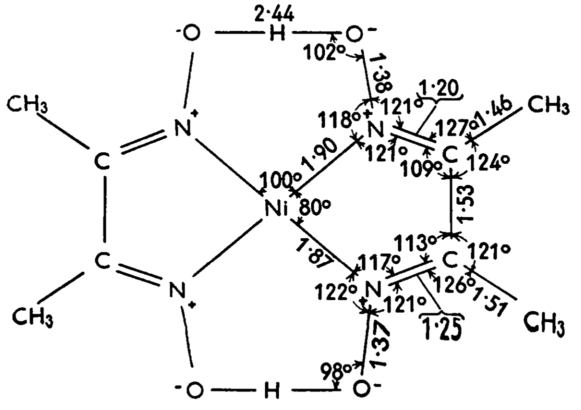

Fig. 3. Molecular structure of nickel dimethylglyoxime.

The molecule is planar and contains four five-membered rings. The molecule is required by the space group to have the symmetry C_{2h}. There is no obvious reason why it should not have the higher symmetry, D_{2h}, but discrepancies as large as 0·05 Å in the observed distances for the N–C and C–CH_3 bonds suggest the lower symmetry. Application of the significance test suggested by Cruickshank (1949), however, indicates that these deviations are not significant. The molecular symmetry, then, may be as high as D_{2h}.

The bond distances (Table 4) suggest that the principal electronic form contributing to the ground state is one in which all except C–N bonds are essentially single bonds, while these are essentially double bonds. All bonds are, however, somewhat short for this interpretation, indicating conjugation with other structures which give some double-bond character to the bonds. Since methyl carbons are located with a relatively poor accuracy, the apparent shortening of the C–CH_3 bonds may be exaggerated. The length of the Ni–N bond in nickel phthalocyanine (Robertson & Woodward, 1937) is 1·83 Å, considerably shorter than we find, 1·87–1·90 Å. The difference appears to be larger than the experimental error of the two determinations. A likely explanation is the compression of the Ni–N bonds by the six-membered ring framework of the phthalocyanine, and a slight tension on the Ni–N bonds due to the larger requirements of the five-membered rings in the case of dimethylglyoxime.

Of special interest is the very short O–H–O bond, 2·44 Å, shorter than any O–H–O bond, heretofore reported.* It is noteworthy that the O–H stretching

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* Prof. E. G. Cox has called to our attention the short O–H–O bond, 2·48 Å, reported for boehmite (Reichert & Yost, 1946), but the accuracy of this powder determination was only 0·07 Å, so its significance is questionable. Shahat (1951) has reported an intramolecular hydrogen bond in maleic acid of 2·46 Å. Three-dimensional refinement is still to be reported.

Table 3. *Standard deviations of final parameters*

Atom	p	$(\partial^2\varrho/\partial r^2)_{r=0}$	$\sigma(x)$ (Å)	$\sigma(y)$ (Å)	$\sigma(r)$ (Å)
N_I	4·38	−101	0·006	0·011	0·013
N_{II}	3·90	−75·8	0·009	0·014	0·017
O_I	4·68	−136	0·005	0·008	0·009
O_{II}	4·58	−129	0·005	0·008	0·009
C_I	4·50	−92·3	0·007	0·012	0·014
C_{II}	4·57	−96·4	0·007	0·011	0·013
C_{III}	3·20	−39·6	0·016	0·027	0·031
C_{IV}	3·34	−43·7	0·015	0·025	0·029

Table 4. *Intramolecular and intermolecular distances and bond angles in nickel dimethylglyoxime*

Atoms*	Distance	Standard error, σ	Angles	
Ni–N_I	1·90 Å	0·01 Å	N_I–Ni–N_{II}	80°
Ni–N_{II}	1·87	0·02	N_{II}–Ni–N_I	100
N_I–O_I	1·38	0·02	Ni–N_I–C_{II}	121
N_{II}–O_{II}	1·37	0·03	Ni–N_{II}–C_I	117
N_I–C_{II}	1·20	0·03	N_I–C_{II}–C_I	109
N_{II}–C_I	1·25	0·03	N_{II}–C_I–C_{II}	113
C_I–C_{II}	1·53	0·03	C_{II}–C_I–C_{III}	121
C_{II}–C_{IV}	1·46	0·04	C_I–C_{II}–C_{IV}	124
C_I–C_{III}	1·51	0·04	Ni–N_I–O_I	118
O_I–O_{II}	2·44	0·02	Ni–N_{II}–O_{II}	122
O_I–C'_{IV}	3·25	0·04	N_I–O_I–O_{II}	102
O_{II}–C'_{IV}	3·72	0·04	N_{II}–O_{II}–O_I	98
O_{II}–C'_{III}	4·01	0·04		
C_{III}–C'_{IV}	4·04	0·06		
O_{II}–C'_I	3·31	0·02		
O_I–C'_I	3·27	0·02		
Ni–Ni″	3·25	0·005		
C'_{IV}–C''_{IV}	3·99	0·06		
C'_{III}–C''_{IV}	4·27	0·06		
C'_{IV}–C''_{III}	4·27	0·06		

* Unprimed symbols refer to the molecule at the origin of the unit cell. Those with one prime refer to molecules in the $(x, y, 0)$ plane. Symbols with two primes refer to the molecule directly above the one at the origin.

frequency for this hydrogen bond is only 1800 cm.$^{-1}$, about half the normal 3500 cm.$^{-1}$, and that spectroscopic arguments have been presented indicating that the hydrogen lies symmetrically between the two oxygens in this case (Rundle & Parasol, 1952).

The short hydrogen bond is in keeping with chemical observations that these hydrogens are very difficult to replace. It seems possible that the short hydrogen bond is in part responsible for the low solubility of nickel dimethylglyoxime in water. The hydrogen appears to be held so tightly that the O–H group does not interact appreciably with water, and hence loses its usual solubilizing power.

Contrary to some of our earlier speculations, spectroscopic study of crystalline copper dimethylglyoxime indicates that it also has a short and probably symmetrical hydrogen bond. It seems unlikely that the difference in solubility of copper and nickel compounds can be due to any difference in this feature. However, a difference in packing and the pleochroism deserve comment.

Nickel dimethylglyoxime molecules are planar with all molecules exactly parallel to (001) planes, and stacked with nickel atoms directly above each other separated by $\frac{1}{2}c_0 = 3{\cdot}245$ Å. The methyl groups form the thickest portion of the molecule, so that alternate molecules are rotated 90° about c_0; the packing along c_0 resembles interlocking blocks. The copper compound has a more complex type of packing, not yet fully known, but there are no chains of copper atoms as there are in the nickel compound.

As noted above, nickel dimethylglyoxime is pleochroic; light with its electric vector in the plane of the molecule is absorbed more than light with its electric vector normal to the molecular plane. The pleochroism is, however, very slight, which is quite surprising for a large molecule containing conjugated double bonds. This suggests rather important intermolecular interactions along the c_0 axis.

It is to be noted that the bonding to nickel is square, which should mean that nickel uses dsp^2 orbitals, and possesses a vacant $4p$-orbital. We suggest that the first excited state consists essentially of the electronic configuration derived from promoting a non-bonding $3d$-electron to the $4p$-level and forming Ni–Ni bonds. This configuration would be octahedral, using the well-known d^2sp^3 octahedral orbitals. If some of this configuration contributes to the ground state, with some of the ground configuration mixed into the first excited state, then there will be a small but important Ni–Ni contribution to the ground state, stabilizing the particular packing noted in the crystal. This proposal will also account for the unusual pleochroism. On the other hand, the extra electron of copper would

Table 5. *Crystallographic data of metal–dioxime complexes*

Compound*	Crystal class	Space group	Lattice constants (Å) a_0	b_0	c_0
$Ni(HD)_2$	Orthorhombic	*Ibam*	16·68	10·44	6·50
$Pd(HD)_2$	Orthorhombic	*Ibam*	16·9	10·6	6·50
$Ni(HC)_2$	Orthorhombic	*Iba*	20·3	10·2	6·41

* HD refers to the dimethylglyoxime derivative.
HC refers to the cyclohexanedionedioxime derivative.

prevent this type of interaction, and would, in part, explain the choice of a different packing arrangement for the copper compound.

The long Ni–Ni distance, 3·245 Å, implies that the Ni–Ni bonds contribute only slightly to the ground state. On the other hand, even a few Kcal. can play an important role in determining solubility.

It seems quite likely that the type of metal–metal interaction proposed here is fairly general. In a large number of nickel, palladium and platinum square complexes the metal atoms form chains. In several of these, abnormal pleochroic effects have been observed, *e.g.* in magnus green salts $[Pt(NH_3)_4^{++}(PtCl_4)]^{--}$ (Cox, Pinkard, Wardlaw & Preston, 1932) light with its electric vector parallel to the Pt–Pt chains, and normal to the plane of the ions, is absorbed more readily than light with its electric vector in the planes of the ions. Furthermore, a cursory survey of square copper complexes reveals different types of packings, with little or no tendency to form copper chains.*

The proposal made here is consistent with Mulliken's (1951) acid–base theory of intermolecular complexes. It is to be noted that he has suggested that the packing of aromatic molecules is influenced by the small contribution to the ground state of intermolecular bonded structures not unlike that proposed here.

Related compounds

Crystallographic data have been obtained for palladium dimethylglyoxime and for nickel cyclohexanedionedioxime (Table 5). The unit cells and symmetry are closely related in these compounds. Odd layer lines of the palladium compound, to which there is no palladium scattering, are so nearly identical with those of the nickel compound that it is clear that the molecular shape and type of packing is nearly identical. Though it shows the same absences, the cyclohexane ring can hardly be planar, so the space group for nickel cyclohexanedionedioxime is undoubtedly *Iba* rather than *Ibam*. In all cases OH and NO frequencies suggest short and symmetrical hydrogen bonding. We have not examined these crystals further.

A preliminary account of the structure of copper dimethylglyoxime has now been given (Bezzi, Bua & Schiavinato, 1951). The packing in this monoclinic crystal is entirely different. In particular, the coppers are at very great distances from each other, and with the organic part of the molecules interposed, so that no copper–copper bonding is possible. Fouriers seem to suggest a molecular structure identical with that of the nickel compound. If this is true, the intramolecular distances can differ by only a few hundredths of an Ångström unit from those in nickel dimethylglyoxime. In spite of the close correspondence of the molecular sizes and shapes, dimethylglyoxime will precipitate Ni^{++} quantitatively without carrying down Cu^{++} with it! We consider this to be excellent evidence that weak nickel–nickel binding, such as suggested here, is a fundamental feature of the nickel dimethylglyoxime crystal.

The authors are indebted to Dr Roger C. Voter for the preparation of the crystalline complexes, and to Prof. Charles V. Banks and Harry Diehl, as well as to Dr Voter, for helpful discussion. Mr R. Fitzwater helped obtain some of the lattice constants listed in Table 5.

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* *Note added in proof,* 24 *April* 1953.—The study of dichroism of planar complexes of the type $MPt(CN)_4 \cdot XH_2O$ by Yamada (1951) provides excellent support for the above proposal. Yamada also concluded that a direct interaction between planar molecules was necessary to account for the dichroism.

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Structures of the ReO_3-type with Recurrent Dislocations of Atoms: 'Homologous Series' of Molybdenum and Tungsten Oxides*

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(*Received* 24 *January* 1953)

The geometrical properties of structures of the ReO_3-type showing recurrent dislocations of atoms, analogous to those present in Mo_8O_{23}, Mo_9O_{26} and $W_{20}O_{58}$, are discussed. Two of the hypothetical atomic arrangements thus derived have been found to correspond to recently prepared molybdenum tungsten oxides $(Mo,W)_{10}O_{29}$ and $(Mo,W)_{11}O_{32}$. These compounds and the aforementioned molybdenum oxides are members of a 'homologous series', Me_nO_{3n-1}, based on a common structural principle. There is almost complete agreement between the experimentally derived structures of these homologues and the corresponding ideal structures. The same is also true for $W_{20}O_{58}$, the only hitherto known representative of the series Me_nO_{3n-2}.

Introduction

Investigations of molybdenum and tungsten oxides with an average valency of the metal atoms slightly less than six, namely Mo_8O_{23}, Mo_9O_{26} and $W_{20}O_{58}$, have shown that the crystal structures of these compounds are mutually closely related and based on structures of the ReO_3-type (*Strukturbericht*, 1937) containing dislocations of the atoms, suddenly occurring after long periods (Magnéli, 1948, 1950*a*, *b*). A geometrical discussion of hypothetical structures analogous to those derived for these oxides has proved to be valuable when investigating a number of double oxides of molybdenum and tungsten (Magnéli, 1952; Blomberg, Kihlborg & Magnéli, 1953) and will be described here. A comparison will be given between the crystal structures of the known oxides of this type and the corresponding hypothetical structures.

Structural principles of Mo_8O_{23}, Mo_9O_{26} and $W_{20}O_{58}$

The crystal structures of these oxides may be described as built up of metal–oxygen octahedra joined by corners to form blocks of the ReO_3-type, which extend infinitely through the crystals in two dimensions and have a finite, characteristic width in a third direction. The blocks are mutually joined along folded planes by octahedra having edges in common. These planes correspond to the recurrent dislocations of atoms occurring in the ReO_3-type structure.

The structures of Mo_8O_{23} and Mo_9O_{26} differ only in respect of the finite width of the ReO_3-type blocks, which extend through eight and nine MoO_6 octahedra respectively. The appearance of the planes joining the blocks is the same in both oxides and is characterized by the recurrent occurrence of groups of four MoO_6 octahedra joined by sharing edges (Figs. 1(*d*), 4(*a*), (*b*)). There is a regular, alternating displacement of the metal atoms in the octahedra, parallel to the *b* axes of the monoclinic unit cells (normal to the plane of the figures). The metal atoms thus form puckered layers parallel to the *ac* plane. There is a marked lengthening of the MoO_6 octahedra perpendicularly to this plane. The molybdenum atoms of the quadruplets of octahedra sharing edges are situated in planes characteristically tilted. The considerable distortion of the MoO_6 octahedra may suggest that the molybdenum atoms can be considered as co-ordinating five oxygen atoms in a square-pyramidal arrangement. For the following discussion, however, the simplified picture of distorted MoO_6 octahedra is more convenient.

The dislocation planes occurring in $W_{20}O_{58}$ are of a somewhat different appearance from those present in the molybdenum oxides, in showing groups of six metal–oxygen octahedra joined by sharing edges (Fig. 1(*e*)). The finite extension of the ReO_3-type blocks in this structure amounts to twenty octahedra. The metal atom layers are not puckered.

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* A survey of this investigation was presented at the meeting of the American Crystallographic Association in Camp Tamiment, Pa., June 1952.