

## X-ray Studies on the Metal Complexes with the Glyoximes.

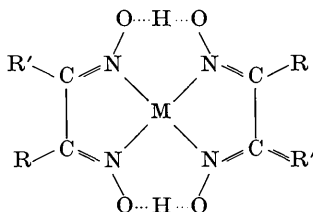
### IV. Structure of the Ni-Methyl-Ethyl-Glyoxime

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In the course of the examination of the metal-complexes of the *R-R*-glyoximes of general formula:



the crystal structure of Ni-methyl-ethyl-glyoxime has been determined by two-dimensional projections.

The unit cell is monoclinic with the following lattice constants:

$$a = 4.75, b = 11.75, c = 11.97 \text{ \AA}, \beta = 92^\circ, Z = 2.$$

The space group is  $P2_1/c$ . The molecule is found to be planar and to have a *trans* configuration. In this structure an intermolecular Ni-Ni bond is not present as in Ni-dimethyl-glyoxime. The intramolecular hydrogen bond is very short 2.33 \AA.

#### Introduction

In a series of papers devoted to the structure of the metal-complexes with dimethyl-glyoxime, Frasson, Bardi & Bezzi (1959) have recently described the structure of Cu-dimethyl-glyoxime and Frasson, Panattoni & Zannetti (1959*a, b*) the structures of Pt- and Pd-dimethyl-glyoxime.

Pt- and Pd-dimethyl-glyoxime are isomorphous with the Ni-dimethyl-glyoxime studied by Godycki & Rundle (1953). In these structures the metal exhibits a sixfold coordination through four short intramolecular  $M-N$  bonds and two long intermolecular  $M-M$  bonds and the molecule is planar.

The structure of the Cu-dimethyl-glyoxime is in a certain sense anomalous with respect to the other metal-complexes of this series: the molecule is not planar; the Cu atom bound to the four nitrogen atoms of the chelate rings is also bound to one oxygen atom of another molecule giving rise to a pyramidal coordination.

The Cu- and Ni-complexes of methyl-ethyl-glyoxime have been examined by Cox *et al.* (1936). On the basis of the powder diagrams they stated that the two compounds are isomorphous and different from the corresponding complexes of dimethyl-glyoxime. But from the examination of the powder with a high-angle spectrometer, Frasson, Panattoni & Zannetti (1959*c*) have found some differences and have therefore analyzed the structures of both complexes.

In this note we shall report the determination of the structure of the Ni-methyl-ethyl-glyoxime.

#### Experimental and crystal data

Crystals of Ni-methyl-ethyl-glyoxime were prepared by the method described by Cox *et al.* (1936). The determination of the space group was carried out using precession photographs. Systematic absence of ( $h0l$ ) for  $l$  odd and of ( $0k0$ ) for  $k$  odd indicate the space group  $C_{2h}^5-P2_1/c$ . The unit cell contains two molecules and has the following lattice constants:

$$a = 4.75 \pm 0.01, b = 11.75 \pm 0.03, c = 11.97 \pm 0.03 \text{ \AA}, \\ \beta = 92^\circ 00' \pm 40'.$$

Observed density = 1.61 g.cm.<sup>-3</sup>; calculated density = 1.57 g.cm.<sup>-3</sup>.

The  $h0l$  and  $0kl$  diffractions were obtained by the multiple-film technique with Cu  $K\alpha$  radiation in a Weissenberg camera. The intensities were evaluated by means of a photometric recorder and corrected by means of the usual Lorentz and polarization factors.

#### Electron-density projections and refinement of the atomic coordinates

Owing to the presence of only two molecules in the unit cell, the metal atoms must be on symmetry centres. Therefore the Fourier projections on the three

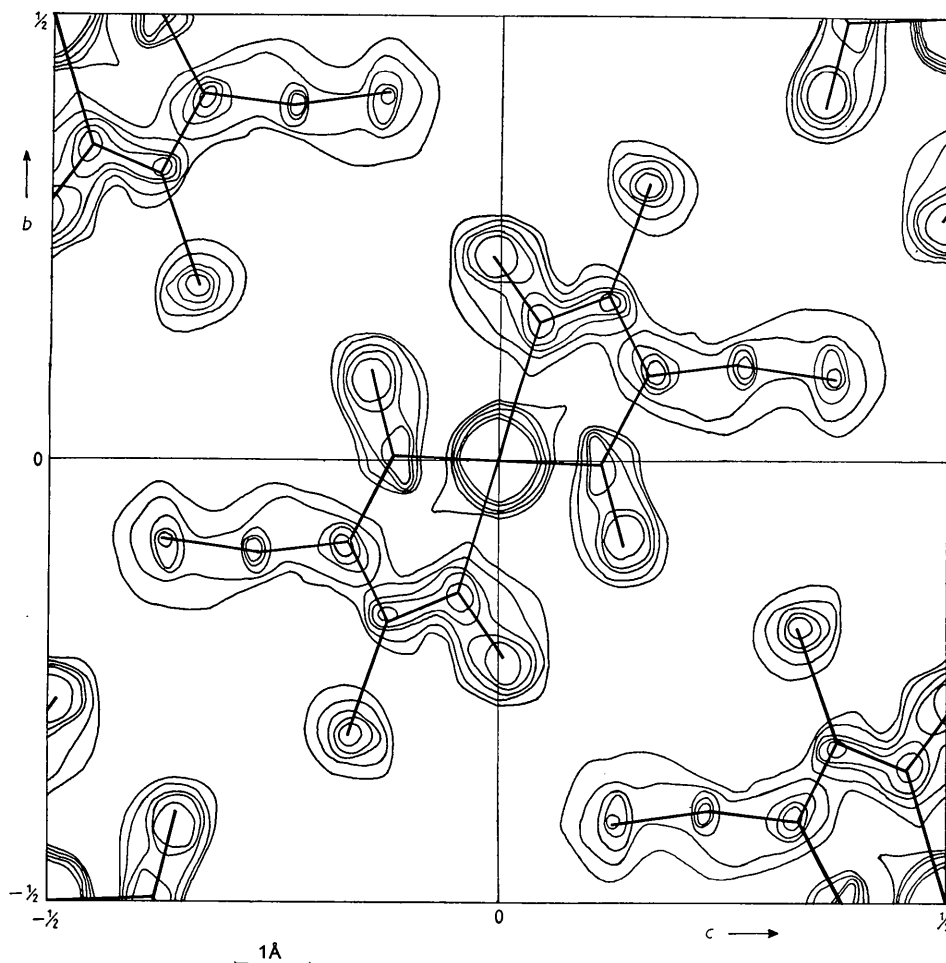


Fig. 1. Electron-density projection on (100). Contours at 2, 3, 4, 5, 6 e.Å<sup>-2</sup>. Upper levels for the Ni atom are omitted.

Table 1. Observed and calculated structure factors for the Ni-dimethylglyoxime

$h0l$	$F_o$	$F_c$	$h0l$	$F_o$	$F_c$	$h0l$	$F_o$	$F_c$	$h0l$	$F_o$	$F_c$
1 0	31.8	31.6	3 6	11.6	12.4	0 4	2.8	2.4	3 $\bar{6}$	28.0	30.8
2 0	26.4	24.8	4 6	3.6	6.4	0 6	52.8	56.8	4 $\bar{6}$	4.8	5.2
3 0	26.0	25.2	5 6	3.6	4.8	0 8	52.0	49.2	5 $\bar{6}$	12.6	12.0
4 0	18.0	17.6				0 10	9.2	7.2			
5 0	6.4	7.2	1 8	10.8	9.6	0 12	11.2	10.4	1 $\bar{8}$	2.4	3.2
6 0	4.6	4.4	2 8	6.8	10.0	0 14	5.6	5.2	2 $\bar{8}$	12.4	15.2
			3 8	4.8	8.0				3 $\bar{8}$	6.8	4.0
			4 8	4.4	7.2	1 $\bar{2}$	29.6	28.4	4 $\bar{8}$	14.8	12.0
1 2	136.8	140.4				2 $\bar{2}$	21.6	16.4	5 $\bar{8}$	6.4	8.4
2 2	23.6	19.6				3 $\bar{2}$	29.2	27.2			
3 2	30.4	33.2	1 10	19.6	20.8	4 $\bar{2}$	22.8	27.2	1 $\bar{10}$	16.4	19.6
4 2	14.8	15.6	2 10	4.4	2.0	5 $\bar{2}$	15.2	14.4	2 $\bar{10}$	1.2	2.4
5 2	10.4	13.2	3 10	4.9	4.8	6 $\bar{2}$	5.6	6.4	3 $\bar{10}$	7.6	7.2
6 2	1.8	1.6	4 10	2.8	4.4				4 $\bar{10}$	12.0	15.2
						1 $\bar{4}$	56.0	64.4			
1 4	41.2	40.4	1 12	9.2	12.4	2 $\bar{4}$	51.2	44.4	1 $\bar{12}$	2.0	6.8
2 4	34.4	33.2	2 12	6.9	6.8	3 $\bar{4}$	20.0	20.8	2 $\bar{12}$	4.6	4.4
3 4	2.8	2.8	3 12	1.6	1.2	4 $\bar{4}$	31.6	26.8	3 $\bar{12}$	7.2	7.6
4 4	17.2	21.6				5 $\bar{4}$	9.6	8.4			
5 4	7.6	6.4	1 14	6.0	5.6				1 $\bar{14}$	3.0	2.8
			2 14	2.0	4.0	1 $\bar{6}$	44.0	43.6	2 $\bar{14}$	4.4	8.4
1 6	16.4	17.2				2 $\bar{6}$	12.0	13.2			
2 6	2.8	5.2	0 2	54.8	54.4						

Table 1 (cont.)

$OkI$	$F_o$	$F_c$	$OkI$	$F_o$	$F_c$	$OkI$	$F_o$	$F_c$	$OkI$	$F_o$	$F_c$
2 0	30.4	40.8	11 3	1.2	0.8	12 6	6.8	8.0	8 9	3.2	2.4
4 0	11.6	13.2	13 3	8.8	9.2	14 6	4.0	4.4	10 9	1.2	1.6
6 0	23.6	19.2							12 9	1.2	0.8
8 0	24.4	27.6	2 3	4.2	4.0	1 6	9.6	7.6			
10 0	30.4	35.6	4 3	22.0	20.8	3 6	24.8	27.2	0 10	8.8	7.2
12 0	16.8	20.8	6 3	7.6	6.4	5 6	4.0	4.0	2 10	14.8	12.4
14 0	4.0	4.0	8 3	10.4	11.6	7 6	8.8	9.6	4 10	32.4	31.2
			10 3	5.2	5.6				6 10	16.8	15.6
1 1	105.6	105.2	12 3	3.2	2.8	11 6	2.6	2.4	8 10	12.4	11.2
3 1	20.0	22.0				13 6	2.4	2.0	10 10	6.0	6.0
5 1	46.8	50.8	0 4	2.9	2.8						
7 1	27.2	29.6	2 4	3.6	2.8	1 7	37.2	40.4	1 10	4.4	8.4
9 1	27.6	28.0	4 4	40.0	42.4	3 7	19.6	21.6	3 10	10.8	9.6
11 1	12.4	11.6	6 4	18.4	19.6	5 7	16.0	17.6	5 10	8.4	5.6
13 1	14.0	14.4	8 4	24.0	26.8	7 7	9.2	8.8	7 10	9.4	9.2
15 1	3.6	3.2	10 4	3.4	3.2	9 7	21.2	20.4	9 10	4.4	4.8
			12 4	1.2	0.4	11 7	10.0	9.6	11 10	1.2	1.6
2 1	28.8	32.4	14 4	6.9	6.8						
4 1	16.0	12.8				2 7	4.4	3.6	1 11	13.6	11.2
6 1	11.2	10.0	1 4	3.2	2.0	4 7	8.2	8.0	3 11	14.8	16.8
8 1	3.2	3.6	3 4	8.8	8.4	6 7	9.6	8.4	5 11	12.0	10.4
10 1	1.2	1.6	5 4	12.2	12.0	8 7	7.2	6.0	7 11	6.4	5.2
12 1	1.4	1.2	7 4	1.2	0.4	10 7	1.2	0.4	9 11	10.4	10.8
14 1	1.6	2.4	9 4	7.4	7.2	12 7	6.4	6.0			
			11 4	4.8	3.2				2 11	3.2	2.4
0 2	49.6	54.6	13 4	1.2	0.8	0 8	48.8	55.2	4 11	10.2	10.0
2 2	13.6	13.2				2 8	24.8	24.0	6 11	4.2	4.0
4 2	57.6	72.8	1 5	23.2	21.6	4 8	23.2	21.6	8 11	3.2	3.6
6 2	37.2	40.8	3 5	21.2	24.4	6 8	10.4	5.2	10 11	3.4	3.2
8 2	26.9	26.8	5 5	14.4	16.0	8 8	16.6	16.4			
10 2	1.6	2.4	7 5	10.4	6.8	10 8	18.6	18.4	0 12	8.4	8.8
12 2	10.8	20.4	9 5	16.2	16.0	12 8	8.0	8.4	2 12	9.2	5.6
14 2	9.6	10.8	11 5	1.2	1.6				4 12	12.4	11.6
			13 5	10.2	10.0	1 8	5.6	8.8	6 12	3.2	2.4
1 2	31.6	24.4				3 8	4.8	4.0	8 12	7.6	6.4
3 2	35.6	32.8	2 5	24.0	22.4	5 8	8.0	7.6			
5 2	21.2	20.0	4 5	7.6	6.8	7 8	4.8	4.0	3 12	5.8	5.6
7 2	22.0	25.6	6 5	9.2	10.0	9 8	1.2	0.8	5 12	1.2	0.8
9 2	4.8	4.4	8 5	4.6	4.4				7 12	1.2	1.6
11 2	1.2	1.6	10 5	1.4	1.2	1 9	20.4	20.0	9 12	2.6	2.4
13 2	1.1	1.2	12 5	1.2	1.6	3 9	21.6	18.4			
15 2	1.6	2.4	14 5	1.2	0.8	5 9	33.6	35.6	1 13	6.4	5.2
						7 9	10.8	9.6	3 13	11.2	10.0
1 3	31.6	27.6	0 6	50.4	54.4	9 9	14.0	12.0	5 13	1.4	1.2
3 3	6.8	10.8	2 6	10.8	6.8	11 9	7.2	7.2	7 13	1.2	0.8
5 3	54.4	53.6	4 6	27.6	28.8						
7 3	18.6	18.4	6 6	7.2	7.6	2 9	8.8	5.6	0 14	6.0	4.4
9 3	14.0	13.6	8 6	11.6	9.2	4 9	1.2	0.8	2 14	6.4	4.8
			10 6	13.2	12.8	6 9	3.2	2.8	4 14	7.4	7.2

fundamental planes of the structure may be directly calculated using the heavy-atom method.

The small inclination of the molecule with respect to (100) results in good resolution and this projection was therefore examined first.

With the first location of all the light atoms a new set of signs was calculated for all the  $OkI$  reflections followed by a new calculation of the electron-density projection. The comparison of the experimental structure factors  $F_o$  and of the calculated  $F_c$  enabled us to put the  $F_o$  on an absolute scale and to calculate the thermal factor. For the calculation of the  $F_c$ , the atomic form factors of Berghuis *et al.* (1955) were used for the light atoms and that of Viervoll & Øgrim (1949) for the Ni atom.

For the refinement of the atomic coordinates

Cochran's method of difference synthesis (1951) was followed.

Fig. 1 shows the electron-density projection on (100).

In the projection on (010) some atoms are unresolved; therefore, at first, the  $z/c$  coordinates found on the (100) projection was used and the  $x/a$  coordinate was calculated on the basis of both the bond lengths and the supposed inclination of the molecule with respect to this plane. The treatment followed for this projection is the same that has been described for the (100) projection.

During the refinement of both projections, for the Ni atom the temperature factor  $B$  was found to be  $3.4 \text{ \AA}^{-2}$  which is smaller than for the light atoms, for which  $B \approx 4.2 \text{ \AA}^{-1}$ .

Table I lists the experimental and the calculated

Table 2. Atomic coordinates for Ni-methyl-ethyl-glyoxime

	$x/a$	$y/b$	$z/c$
Ni	0.000	0.000	0.000
C <sub>1</sub>	0.136	0.185	0.120
C <sub>2</sub>	0.330	0.092	0.165
C <sub>3</sub>	0.136	0.311	0.164
C <sub>4</sub>	0.500	0.106	0.256
C <sub>5</sub>	0.342	0.090	0.371
N <sub>1</sub>	-0.030	0.152	0.045
N <sub>2</sub>	0.222	-0.001	0.112
O <sub>1</sub>	-0.231	0.228	-0.008
O <sub>2</sub>	0.422	-0.097	0.136

structure factors for the  $0kl$  and the  $h0l$  zones;  $R=0.11$  for both projections. Table 2 lists the final coordinates for one half of the molecule of Ni-methyl-ethyl-glyoxime, the other half being related to the first one by the symmetry centre on the Ni atom.

### Estimation of accuracy

For both projections the accuracy of the proposed coordinates has been calculated by the method of Cruickshank (1949). On the projection on (100) the values of  $p$  and  $\rho_0$  introduced in the formula of

Table 3. Standard errors of the atomic coordinates

	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	$\sigma(r)$
C <sub>1</sub>	0.020 Å	0.005 Å	0.034 Å	0.038 Å
C <sub>2</sub>	0.020	0.016	0.026	0.038
C <sub>3</sub>	0.020	0.022	0.032	0.044
C <sub>4</sub>	0.001	0.028	0.048	0.056
C <sub>5</sub>	0.003	0.036	0.021	0.042
N <sub>1</sub>	0.005	0.005	0.004	0.010
N <sub>2</sub>	0.005	0.018	0.008	0.020
O <sub>1</sub>	0.002	0.010	0.007	0.012
O <sub>2</sub>	0.002	0.009	0.009	0.013
Aver. value	0.009 Å	0.017 Å	0.021 Å	0.030 Å

Cruickshank has been calculated for all the atoms. On the projection on (010) the values of  $p$  and  $\rho_0$  have been calculated only for the well resolved maxima. For the calculation of  $\sigma$  on this projection, the same values of  $p$  and  $\rho_0$  of the resolved maxima have been attributed to the unresolved maxima. In Table 3 the values of  $\sigma$  for the atoms and along the various directions are listed.

### Shape of the molecule and description of the structure

To simplify the study of the shape of the molecule a new set of atomic coordinates has been calculated with respect to the mean plane of the molecule. It was evident that the ethyl group does not lie on the same plane as the remaining part of the molecule. Therefore the ethyl-group has not been considered in calculating the mean plane, of which the equation is:

$$-1.048x - 0.379y + z = 0.$$

In Table 4(a) the new atomic coordinates on the three orthogonal axes  $\xi, \eta, \zeta$  originating from one nickel atom are listed;  $\xi$  and  $\eta$  lie in the mean plane of the molecule,  $\zeta$  being normal to this plane. It is seen that the ethyl group is noticeably out of the mean plane of the molecule. On Table 4(b) the  $\xi, \eta, \zeta$  coordinates for an underlying molecule are listed with the intention of simplifying the calculation of the intermolecular distances. From the  $\zeta$  coordinates it can be seen that the spacing between two molecules of successive layer is  $3.32 \pm 0.02$  Å. Fig. 2 shows the shifting of the molecules of successive layers.

Fig. 3 shows bond lengths and angles in the molecule. In Table 5 the bond lengths and the most

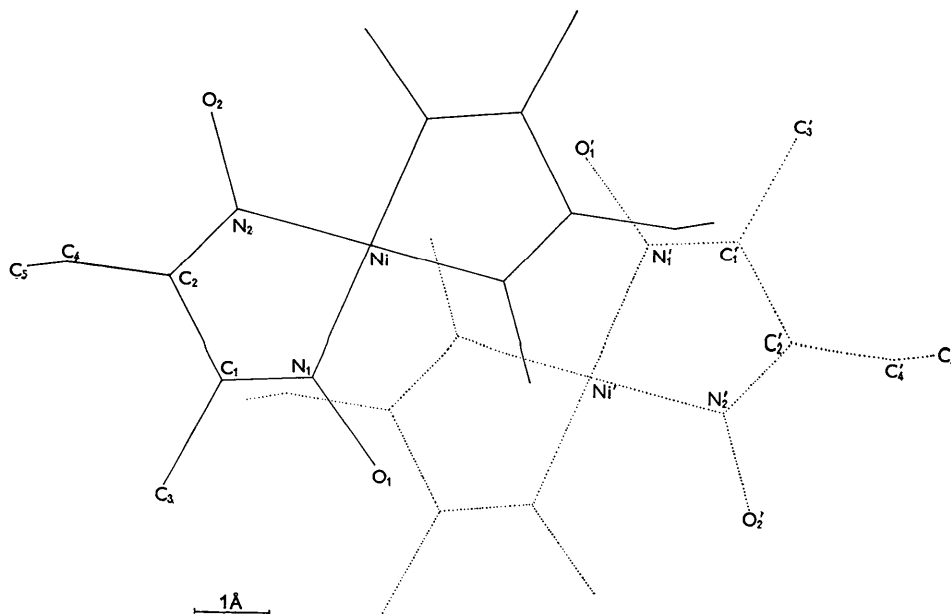


Fig. 2. Relative positions of the molecules of successive layer.

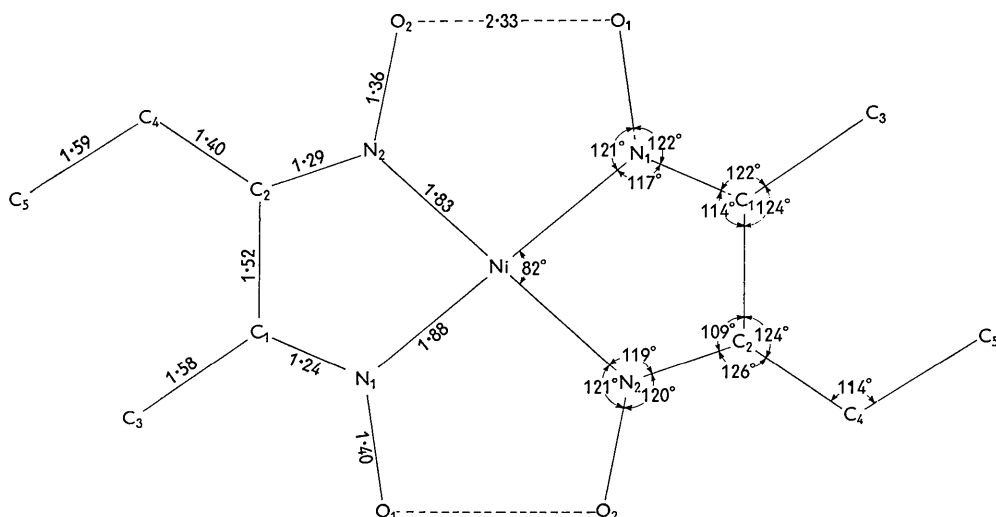


Fig. 3. Bond distances and angles in Ni-methyl-ethyl-glyoxime.

Table 4

 (a) Atomic coordinates of the Ni-methyl-ethyl-glyoxime referred to the axes  $\xi$ ,  $\eta$ ,  $\zeta$ 

	$\xi$	$\eta$	$\zeta$
Ni	0.000 Å	0.000 Å	0.000 Å
C <sub>1</sub>	+1.842	-1.935	-0.008
C <sub>2</sub>	+0.507	-2.654	-0.004
C <sub>3</sub>	+3.239	-2.650	-0.018
C <sub>4</sub>	+0.366	-4.045	+0.075
C <sub>5</sub>	+0.447	-4.551	+1.571
N <sub>1</sub>	+1.734	-2.174	+0.020
N <sub>2</sub>	-0.434	-1.776	+0.026
O <sub>1</sub>	+2.892	+0.154	+0.028
O <sub>2</sub>	-1.734	-2.174	+0.011

 (b) Atomic coordinates  $\xi$ ,  $\eta$ ,  $\zeta$  of a molecule underlying the one described on (a)

	$\xi$	$\eta$	$\zeta$
Ni'	-1.615 Å	-2.983 Å	-3.325 Å
C <sub>1</sub> '	+0.226	-4.918	-3.333
C <sub>2</sub> '	-1.109	-5.637	-3.329
C <sub>3</sub> '	+1.624	-5.633	-3.343
C <sub>4</sub> '	-1.249	-7.028	-3.250
C <sub>5</sub> '	-1.168	-7.534	-1.754
N <sub>1</sub> '	+0.119	-3.687	-3.305
N <sub>2</sub> '	-2.049	-4.759	-3.299
O <sub>1</sub> '	+1.275	-2.833	-3.301
O <sub>2</sub> '	-3.349	-5.157	-3.315

significant intermolecular distances are listed with standard errors.

### Discussion of the structure

It follows from theoretical considerations as well as from experimental evidence that the Ni(II) cation in structures of this type prefers to an octahedral coordination.

In Ni-dimethyl-glyoxime this is realised by four short intramolecular Ni-N bonds and two long intermolecular Ni-Ni bonds of length 3.24 Å. Godycki & Rundle (1953) suggest that this Ni-Ni bond is the

cause of the specificity of the dimethyl-glyoxime as an analytical reagent for Ni. On the contrary for Ni-methyl-ethyl-glyoxime Cox *et al.* have pointed out that 'a remarkable feature of this substance is its ready solubility in alcohols and benzene, in which it was about 50 times as soluble as Ni-dimethyl-glyoxime.'

In Ni-methyl-ethyl-glyoxime the molecule assumes a packing system completely different from that in the dimethyl-complex; the direction Ni-Ni is no longer perpendicular to the plane of the molecule and the distance Ni-Ni is increased to 4.75 Å. Table 5 shows that, outside the bonded N and O atoms, the closest atom to Ni is an oxygen of an overlying molecule at 3.44 Å, much too far to be considered as coordinated.

Table 5. Intermolecular and intramolecular distances in Ni-methyl-ethyl-glyoxime

(a) Intramolecular distances

Ni-N <sub>1</sub>	1.88 ± 0.01 Å	C <sub>1</sub> -C <sub>2</sub>	1.52 ± 0.05 Å
Ni-N <sub>2</sub>	1.83 ± 0.02	C <sub>1</sub> -C <sub>3</sub>	1.58 ± 0.06
N <sub>1</sub> -O <sub>1</sub>	1.40 ± 0.02	C <sub>2</sub> -C <sub>4</sub>	1.40 ± 0.06
N <sub>2</sub> -O <sub>2</sub>	1.36 ± 0.02	C <sub>4</sub> -C <sub>5</sub>	1.59 ± 0.06
N <sub>1</sub> -C <sub>1</sub>	1.24 ± 0.04	O <sub>1</sub> -O <sub>2</sub>	2.33 ± 0.02
N <sub>2</sub> -C <sub>2</sub>	1.29 ± 0.04		

(b) Intermolecular distances

Ni <sub>0,0,0</sub> -Ni <sub>1,0,0</sub>	4.75 ± 0.01 Å	N <sub>2</sub> -N <sub>2</sub> '	4.75 ± 0.03 Å
Ni <sub>0,0,0</sub> -Ni <sub>0,½,½</sub>	3.39 ± 0.02	C <sub>2</sub> -O <sub>1</sub> '	3.39 ± 0.04
Ni <sub>1,0,0</sub> -O <sub>1</sub>	6.44 ± 0.02	C <sub>4</sub> -N <sub>1</sub> '	3.41 ± 0.06
Ni <sub>1,0,0</sub> -O <sub>2</sub>	3.44 ± 0.02		

The separation of the molecules in successive layers is 3.32 Å. This distance, although sufficient to avoid interaction between the two planar molecules, does not permit the co-planarity of the ethyl-group with the rest of the molecule. If the ethyl-group and the rest of the molecule are coplanar, the atoms C<sub>5</sub> and C<sub>3</sub> of an overlying molecule are only 3.37 Å apart. This

is too small in comparison to the 4 Å required for two methyl-groups in contact.

In Ni-dimethyl-glyoxime, Godycki & Rundle (1953) have found an exceptionally short hydrogen bond of 2.44 Å. Recently Williams, Wohlauer & Rundle (1959) in a least-squares refinement of the structure of the Ni-dimethyl-glyoxime have reduced this bond length to 2.40 Å. In the Ni-methyl-ethyl-glyoxime the hydrogen bond is a few hundredths of an Ångström shorter.

At present we are working on the structure of the Cu-methyl-ethyl-glyoxime to clarify the reasons for non-isomorphism of the two complexes.

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## The Crystal Structure of *mono*-Thiourea-Lead(II) Acetate

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*mono*-Thiourea-lead(II) acetate,  $\text{Pb}[\text{SC}(\text{NH}_2)_2](\text{C}_2\text{H}_3\text{O}_2)_2$ , is monoclinic,

$$a = 4.55, b = 15.81, c = 14.28 \text{ \AA}, \beta = 106.4^\circ;$$

the space group is  $P2_1/c$ , and there are four formula units in the unit cell. The structure was determined by X-ray analysis, the final parameters being refined from  $F_o - F_c$  syntheses of  $0kl$ ,  $1kl$  and  $2kl$  data (856 observed reflections). The structure consists of chains of coordination polyhedra joined by sulphur atoms, each forming two coordinative bonds of 3.10 Å with adjacent Pb atoms. These chains, running along [100], are linked in pairs through weaker Pb-S bonds (3.34 Å). The coordination polyhedra can be described as distorted pentagonal bipyramids with three sulphur and four oxygen atoms at the vertices.

#### Introduction

Lead(II) acetate forms two different coordination compounds with thiourea ( $\text{SC}(\text{NH}_2)_2 = \text{tu}$ ):  $\text{Pbtu}(\text{C}_2\text{H}_3\text{O}_2)_2$  and  $\text{Pbtu}_6(\text{C}_2\text{H}_3\text{O}_2)_2$ . Crystals suitable for X-ray analysis can be grown from aqueous solutions (Nardelli & Chierici, 1959). A short account of the structure of *mono*-thiourea-lead(II) acetate has been given previously (Nardelli & Fava, 1959a), in which the orientation and lengths of the Pb-S bonds were reported only. The present paper gives a full account of this structure, including the positions of the light C, N and O atoms, which were located satisfactorily in spite of the presence of the heavy Pb atom.

#### Crystal data

$\text{Pbtu}(\text{C}_2\text{H}_3\text{O}_2)_2$ : colourless monoclinic needles, elongated along [100].

$$a = 4.55 \pm 0.01, b = 15.81 \pm 0.03, c = 14.28 \pm 0.07 \text{ \AA}, \\ \beta = 106.4 \pm 0.1^\circ.$$

The unit cell ( $V = 986 \text{ \AA}^3$ ) contains four formula units (density: observed 2.66, calculated 2.70 g.cm.<sup>-3</sup>). Space group:  $P2_1/c$ . Absorption coefficient for Cu  $K\alpha$  radiation:  $\mu = 358 \text{ cm.}^{-1}$ .

#### Experimental

Multiple-film integrated (Wiebenga & Smits, 1950) and non-integrated equi-inclination Weissenberg photographs (Cu  $K\alpha$  radiation) were taken of the  $0kl$ ,  $1kl$  and  $2kl$  layers, using a slender, nearly cylindrical crystal (mean radius: 0.003 cm.). In addition, the  $h0l$  reflections were recorded using an irregular fragment cut from one of the larger needles. The intensities were determined photometrically. Absorption in the  $0kl$ ,