

The Crystal and Molecular Structure of Bis(glyoximato)platinum(II)

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Bis(glyoximato)platinum(II), $(\text{H}_2\text{C}_2\text{N}_2\text{OOH})_2\text{Pt}$, crystallizes in the monoclinic system, prismatic class, with two molecules per unit cell and belongs to space group $P2_1/n$. Unit-cell parameters are: $a_0 = 3.5039$, $b_0 = 7.892$, $c_0 = 14.093$ Å; $\beta = 92^\circ 43'$. The X-ray study of this complex, based on 611 reflexions measured with Cu $K\alpha$ radiation on an automatic diffractometer (final R value 0.043), shows that its molecular and crystal structure is similar to those of the analogous complexes of Ni^{II} and Pd^{II} . Pt atoms coordinate with four N atoms, and the whole molecule is planar; the intramolecular hydrogen bond O—H---O is considered to be asymmetric. Asymmetry in bond lengths of glyoxime complexes is discussed and the effects of absorption are considered.

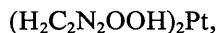
Introduction

As a part of a programme of studies on the crystal and molecular structures of glyoxime complexes with transition metals (Calleri, Ferraris & Viterbo, 1967*a,b*), the authors performed this work on bis(glyoximato)platinum(II).

Experimental

Preparation and crystal data

The bis(glyoximato)platinum(II) complex,



was prepared by mixing a hot aqueous solution of glyoxime with a PtCl_2 solution and neutralizing the mixture with ammonia. By recrystallization of the precipitate from dilute acetic acid at 80–90°C brown-violet acicular crystals of very small cross-section were obtained.

From Weissenberg photographs and single-crystal diffractometry it was deduced that bis(glyoximato)platinum(II) (PtG hereinafter) crystallizes in the monoclinic system, prismatic class. A morphological orientation similar to that of the analogous Ni and Pd complexes (NiG and PdG) was chosen for PtG, *i.e.* the x axis coincident with the elongation direction, and from the systematic extinctions ($0k0$, k odd; $h0l$, $h+l$ odd) the assignment of PtG to space group $P2_1/n$ is unambiguous.

Crystals of PtG present identifiable faces only in zone [100]; forms always present are $\{011\}$ and $\{001\}$ and form $\{010\}$ is also occasionally present. Examination under the polarizing microscope showed that the crystals were always so placed as to present an extinction angle close to 0° . PtG crystals, lying as described above, exhibit an appreciable pleochroism: for light vibrating in the extinction direction 'parallel' to

[100] the light is almost completely absorbed even when the crystals are only about 0.1 mm thick, while in the direction normal to this they are blood-red in colour. The pleochroism found in PtG crystals is much more marked than in the crystals of either NiG or PdG ; in addition, while the last two complexes show the least absorption in the extinction direction which makes the smallest angle with [100], PtG crystals strongly absorb light vibrating along [100].

The unit-cell parameters were refined by a least-squares procedure, with an adequate number of θ_{hkl} values measured on the diffractometer at room temperature from a single crystal, with Cu $K\alpha$ radiation ($\lambda_{\alpha_1} = 1.54050$, $\lambda_{\alpha_2} = 1.54434$ Å); the following values with their standard deviations were obtained: $a_0 = 3.5039(7)$, $b_0 = 7.892(1)$, $c_0 = 14.093(3)$ Å; $\beta = 92^\circ 43'(1')$.

Other physical data are: $V = 398.27$ Å³; M.W. = 369.214; $D_{\text{calc}} = 3.150$ g.cm⁻³; $Z = 2$; $F(000) = 336e$; linear absorption coefficient for Cu $K\alpha$ radiation, $\mu = 345.0$ cm⁻¹.

Intensity measurement

Intensities, all on the same relative scale, were measured by a General Electric automatic three-circle diffractometer, equipped with a Na(Tl)Cl scintillation counter, with the use of nickel-filtered Cu $K\alpha$ radiation. The crystal selected for the measurements, 0.45 mm long with a cross-section of 0.10×0.10 mm², was mounted with its elongation direction, [100], parallel to the ϕ axis of the goniostat and integrated intensities were collected by the $\theta - 2\theta$ scanning method, with a scanning speed of 1° per minute. The background was measured for a 0.5° interval on both sides of each peak. It was possible to measure 820 independent reflexions; for 209 reflexions the intensity was zero or only slightly greater than the background (I_{meas} about 15 counts against a value of about 100,000 counts for

a few strong reflexions). After checking that the corresponding F_c 's had values not greater than $2e$ these reflexions were considered 'unobserved' and excluded from the refinement. They are not listed in Table 1.

The computation of atomic scattering factors, with both the real and imaginary corrections for the anomalous scattering of Pt, was done by linearly interpolating the values reported in *International Tables for X-ray Crystallography* (1962). Lorentz and polarization and absorption corrections were applied, the latter being done by the program *GON09* by Hamilton (1966).

99.00. Rotation and refinement of the structure

The intensities and unit-cell parameters of PtG are similar to those of PdG, so a structure factor calculation

based on a set of coordinates derived from those of the triclinic PdG was carried out. In PdG the relative positions of the non-equivalent molecules are very close to those required by the $P2_1/n$ space group. The coordinates so derived yielded an $R=0.23$, with an overall temperature factor $B=3 \text{ \AA}^2$; a subsequent three-dimensional synthesis of electron density confirmed the hypothesis of isostructuralism.

Two least-squares cycles, refining only the coordinates, and with unit-weight for all reflexions, reduced R to 0.16; a refinement including individual isotropic thermal parameters, as well, with the weighting scheme illustrated below, lowered R to 0.08. During the last and subsequent cycles, some reflexions (generally weak and marked with an asterisk in Table 1) were given zero weight because their intensities were probably af-

Table 1. *Moduli of observed and calculated structure amplitudes with the corresponding phase angles (absolute scale)*

Phase angles differing from 0° or 180° result from the introduction of the imaginary part of the atomic scattering factor of Pt.

H	K	L	FO	FC	ALPHA	H	K	L	FO	FC	ALPHA	H	K	L	FO	FC	ALPHA	H	K	L	FO	FC	ALPHA													
2	0	0	77.9	76.2	8.5	3	3	2	44.1	41.3	9.7	4	2	4	17.4	19.7	12.8	3	1	-6	37.6	39.9	10.1	1	4	-8	7.5	7.9	0.0	1	2	-11	42.5	42.0	10.7	
4	0	0	26.7	27.8	10.5	3	3	-2	40.9	40.7	10.1	4	2	-4	23.4	26.3	10.5	3	2	4	8	93.8	95.7	7.3	2	4	8	36.9	37.9	10.5	3	2	11	21.5	21.2	11.1
1	0	0	159.6	156.3	5.3	5	3	2	5.5	6.4	180.0	0	3	5	15.4	16.6	180.0	0	3	2	-6	45.8	45.5	9.6	3	2	-6	45.8	45.5	9.6	3	2	-6	45.8	45.5	9.6
2	1	0	29.1	26.0	180.0	0	4	4	103.0	98.6	7.1	1	3	4	86.5	83.0	8.0	1	2	-6	28.1	28.7	180.0	3	4	8	4.9	5.7	180.0	0	3	11	42.8	46.4	9.5	
3	1	0	53.1	56.0	8.3	1	4	1	16.4	16.5	180.0	0	5	4	83.4	81.1	2	2	5	8	60.3	58.1	9.6	2	5	8	5.8	5.8	180.0	0	3	11	42.8	46.4	9.5	
0	2	0	104.9	96.9	8.4	7	-2	5	0	4.7	180.0	0	3	4	86.5	81.1	11.1	2	2	-6	55.9	58.1	9.2	1	5	8	4.7	4.7	0.3	1	4	-11	37.2	37.2	10.1	
1	2	0	10.3	10.0	0.0	2	4	2	60.8	56.5	9.1	3	3	-4	46.7	45.0	8.8	4	2	6	21.6	22.3	10.2	1	5	-8	53.4	49.8	9.1	1	4	-11	39.5	38.7	10.7	
2	2	0	93.8	91.8	8.3	2	4	-2	62.9	62.5	8.4	4	3	-6	4.5	4.5	180.0	0	2	5	23.2	23.2	9.8	2	5	8	5.8	5.8	180.0	0	3	11	42.8	46.4	9.5	
3	2	0	9.5	10.6	180.0	0	4	4	2	17.3	19.6	12.2	0	4	4	91.7	87.4	7.5	0	3	6	15.7	15.1	0.0	3	5	8	21.6	21.0	12.1	0	5	11	37.4	34.4	10.8
4	2	0	23.6	27.7	10.1	4	4	-2	26.2	19.4	12.8	1	4	4	62.7	6.8	180.0	1	3	6	73.2	73.4	8.1	3	5	-8	28.6	25.8	11.0	2	5	11	27.1	26.8	10.4	
5	2	0	110.0	105.1	5.9	5	4	2	11.0	11.0	180.0	0	5	4	8.2	8.2	180.0	0	4	5	10.0	10.0	0.0	4	5	8	36.7	36.7	10.9	3	5	11	27.1	26.8	10.4	
3	3	0	43.3	43.1	9.6	1	5	2	68.5	68.8	8.9	2	4	4	56.2	53.2	9.1	2	3	6	3.0	3.0	0.0	1	6	8	6.3	6.3	180.0	1	6	11	27.1	27.6	11.0	
0	4	0	105.0	106.0	8.7	1	5	-2	71.8	73.4	7.9	2	4	-4	55.9	54.1	9.1	3	3	6	36.8	36.2	9.4	1	6	-8	3.4	3.4	0.0	0	6	-11	33.0	30.9	10.3	
1	4	0	18.4	18.0	0.0	2	5	2	33.8	32.1	10.8	0	5	4	52.7	7.8	180.0	1	4	8	18.0	17.1	0.0	1	7	8	31.6	32.0	10.3	0	7	11	24.7	27.1	9.3	
2	4	0	64.8	62.8	8.5	2	5	-2	4.3	3.4	180.0	0	4	-4	19.9	19.2	12.5	0	4	6	82.0	81.3	7.3	2	6	-8	37.0	33.3	10.2	0	7	11	24.7	27.1	9.3	
3	4	0	19.2	19.9	12.4	3	5	2	33.8	32.1	10.8	0	5	4	52.7	7.8	180.0	1	4	8	18.0	17.1	0.0	1	7	8	31.6	32.0	10.3	0	7	11	24.7	27.1	9.3	
4	4	0	70.6	70.1	8.4	3	5	-2	37.1	34.4	10.1	1	5	4	69.3	65.4	8.3	2	4	6	48.0	46.1	9.6	1	7	8	34.6	33.2	10.5	2	7	11	24.7	27.1	9.3	
5	4	0	8.7	8.7	180.0	0	6	2	64.0	64.6	8.4	1	5	-4	62.3	62.8	8.8	2	4	-6	51.4	49.6	9.4	0	7	8	26.5	30.8	10.5	1	7	11	24.7	27.1	9.3	
6	4	0	36.4	35.0	10.0	1	6	2	81.1	84.9	180.0	2	5	4	6.0	6.0	180.0	0	6	8	34.0	33.7	180.0	0	8	8	37.5	37.5	9.1	3	7	11	24.7	27.1	9.3	
0	6	0	60.9	63.5	8.7	2	6	2	41.7	40.4	10.3	2	5	-4	9.2	9.2	180.0	0	3	4	6	61.0	61.0	0.0	1	0	-9	79.7	76.6	7.4	3	7	11	24.7	27.1	9.3
2	6	0	42.2	40.2	7.7	2	6	-2	45.6	44.1	9.6	3	5	4	31.8	31.1	10.3	0	5	6	5.5	5.0	0.0	3	0	-9	27.7	27.7	10.9	3	7	11	24.7	27.1	9.3	
3	6	0	15.8	15.8	0.0	3	6	2	180.0	180.0	0.0	3	5	4	31.8	31.1	10.3	1	5	6	59.4	56.1	9.6	3	0	-9	27.7	27.7	10.9	3	7	11	24.7	27.1	9.3	
1	7	0	41.8	43.7	10.3	1	7	2	44.2	46.7	9.4	0	6	4	54.8	53.4	9.6	1	5	-6	61.3	60.9	8.3	0	1	9	67.8	74.9	7.8	0	8	11	33.7	35.8	11.4	
2	7	0	25.6	23.8	11.5	1	7	-2	46.7	48.6	9.1	1	6	4	5.1	5.6	180.0	2	5	7	46.8	47.7	10.1	1	5	-6	5.9	5.9	180.0	2	7	11	24.7	27.1	9.3	
3	7	0	38.4	36.6	9.4	2	7	2	44.2	46.7	9.4	0	6	4	54.8	53.4	9.6	2	5	7	46.8	47.7	10.1	1	5	-6	5.9	5.9	180.0	2	7	11	24.7	27.1	9.3	
2	8	0	30.5	29.5	10.8	2	7	2	25.3	23.8	11.2	2	6	4	44.2	43.6	9.0	3	5	6	25.8	24.5	11.8	2	1	9	42.7	42.5	9.8	1	8	11	32.2	33.4	10.9	
1	8	0	18.5	18.5	11.3	3	7	2	25.6	23.8	11.4	2	6	-4	43.9	43.0	9.5	3	5	6	25.5	24.9	11.2	2	1	-9	45.6	45.9	8.5	1	8	11	32.2	33.4	10.9	
0	10	0	19.8	23.1	17.1	0	8	2	39.1	41.8	9.6	3	6	4	3.2	3.2	180.0	0	6	6	43.4	42.1	11.3	0	2	9	82.9	9.1	180.0	1	9	11	24.7	27.1	9.3	
*1	0	1	144.9	170.3	4.8	2	8	2	36.8	29.5	10.5	1	7	4	41.0	43.1	9.7	1	6	6	5.4	4.5	180.0	1	2	9	57.5	62.1	8.2	0	4	12	36.4	38.3	9.7	
3	0	1	146.0	155.3	5.3	2	8	-2	28.4	28.9	10.9	1	7	-4	44.1	45.2	9.8	1	6	6	4.8	4.8	180.0	1	2	-9	46.6	46.3	8.3	2	4	12	24.9	23.9	10.8	
3	0	1	43.4	42.9	10.5	1	9	2	28.6	29.1	10.8	3	7	4	21.9	22.7	11.0	2	6	8	39.9	37.1	9.7	2	2	9	5.2	4.3	180.0	2	4	12	24.9	23.9	10.8	
3	0	1	46.8	44.2	10.3	1	9	-2	28.9	28.7	11.0	3	7	-4	25.7	23.8	11.0	2	6	-6	45.5	42.7	8.8	2	2	-9	3.7	4.9	0.0	1	5	12	24.9	23.9	10.8	
0	1	1	131.1	115.1	6.9	1	9	2	21.9	22.3	10.9	2	6	4	31.2	31.8	10.4	2	6	8	39.9	37.1	9.7	2	2	9	5.2	4.3	180.0	2	4	12	24.9	23.9	10.8	
1	1	1	69.2	61.9	180.0	1	0	3	81.4	81.0	9.6	2	8	4	26.1	25.0	11.5	1	7	-6	36.6	38.8	10.1	3	2	-9	34.6	34.4	9.6	0	6	12	27.7	29.8	10.1	
1	1	-1	40.2	42.2	180.0	1	0	3	89.9	82.5	9.8	2	8	-4	26.1	25.0	11.5	0	8	6	35.3	36.7	9.6	0	3	6	61.0	64.7	7.8	0	6	12	27.7	29.8	10.1	
1	1	0	36.2	37.1	180.0	1	0	3	72.3	63.0	11.6	1	9	-4	27.6	27.6	10.8	0	8	6	35.3	36.7	9.6	0	3	6	61.0	64.7	7.8	0	6	12	27.7	29.8	10.1	
2	1	1	86.3	86.9	7.4	3	0	-3	47.3	46.8	9.5	1	9	-4	27.6	26.4	11.5	2	8	-6	23.8	22.3	12.6	1	3	-9	11.8	11.0	0.0	1	7	12	24.3	22.8	11.1	
1	1	1	55.5	56.4	9.9	2	1	3	84.9	84.9	9.7	1	7	1	17.0	17.0	10.9	1	7	1	17.0	17.0	10.9	1	7	1	17.0	17.0	10.9	1	7	1	17.0	17.0	10.9	
4	1	1	22.9	26.3	11.0	1	1	3	13.4	14.4	180.0	0	1	0	-5	11.6	10.6	4.9	1	9	-6	25.7	23.7	11.8	2	3	-9	47.7	46.7	9.0	0	10	13	42.1	42.4	9.6
*0	2	1	6.8	7.9	11.0	1	-3	6.0	7.1	0.0	3	0	5	36.8	38.0	10.4	1	1	0	87.4	86.7	7.1	3	3	-9	4.7	4.9	180.0	0	10	13	42.1	42.4	9.6		
2	2	1	115.4	116.4	6.2	2	2	4	62.6	62.6	9.0	2	2	4	43.9	44.9	10.1	1	1	0	87.4	86.7	7.1	3	3	-9	4.7	4.9	180.0	0	10	13	42.1	42.4	9.6	
1	2	1	97.6	93.6	8.3	2	1	-3	62.5	70.9	8.8	0	1	5	125.3	131.7	5.8	3	0																	

ected by casual measurement errors. The refinement was completed in a few cycles after the introduction of anisotropic vibrational parameters for all the atoms: the final R value was 0.049 (0.043 excluding the reflexions marked with an asterisk in Table 1). The final weighted R was 0.053 and the standard error of an observation of unit weight was 0.807.

The program used for least-squares refinement was that of Busing, Martin & Levy (1962) with minor modifications to take into account the imaginary part of the atomic scattering factors. The weighting scheme employed was of the type:

$$w_{hkl} = A/(BF_o^2 + |F_o| + C), \quad \text{if } |F_o| \geq C; \quad (1)$$

$$w_{hkl} = DF_o^2, \quad \text{if } |F_o| < C. \quad (2)$$

The constants C and D were given such values as to have $0 < w_{hkl} < 1$ and to make the two weighting systems coincide when $|F_o| = C$; C and B were varied slightly during the refinement in order to give a satisfactory constancy to $\Sigma w\Delta^2$ for the amplitudes in various groups. The values assumed by C were around $2|F_{\min}|$ and those of B around $4/|F_{\max}|$.

The 611 values of F_o , calculated with the final parameters, are reported in Table 1. The final fractional coordinates and vibrational anisotropic parameters are listed in Table 2, the latter are the B_{ij} coefficients of the function:

$$\exp\left(-\frac{1}{4} \sum_{i=1}^3 \sum_{j=1}^3 B_{ij} h_i h_j a_i^* a_j^*\right). \quad (3)$$

Because of the overwhelming contribution to the structure factors from Pt, the standard deviations of the light-atom parameters are higher than those which could be expected from the value of R .

Description and discussion of the structure

The PtG molecule (Fig. 1) is planar and its best mean plane (Schomaker, Waser, Marsh & Bergman, 1959), in fractional coordinates and referred to the cell axes, has the following equation:

$$3.3277 X - 2.2927 Y + 0.9328 Z = 0. \quad (4)$$

Table 3 reports the distances, d , of the atoms from plane (4), with their standard deviations, σ , and the ratios $|d/\sigma|$. On the basis of the t test, only atom N(2) is possibly out of plane (4); on the other hand the application of the χ^2 test shows that the whole molecule does not deviate significantly from planarity (Cruickshank & Robertson, 1953). The angle between the molecular and the (100) planes is small (about 18°) as in the analogous complexes of Ni and Pd, while the molecular packing (Fig. 2) is very similar to that of PdG; there is also a correspondence in the intermolecular contacts. The oxygen atom O(2) at $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$ (that is, O(2) belonging to the molecule at the 'centre' of the cell) is involved in two contacts: with C(2) (3.11 Å) and with C(2') [the same C(2) translated by a_0] (3.21 Å).

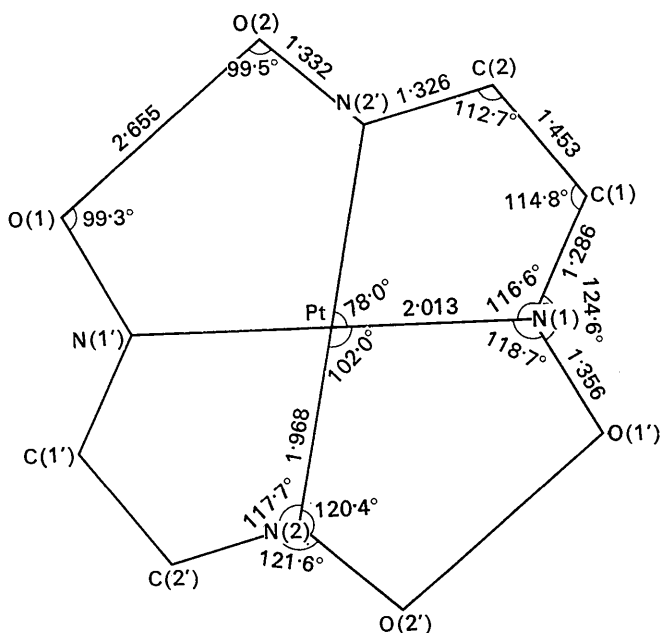


Fig. 1. Molecular bonds and angles and atom labelling.

Table 2. Fractional atomic coordinates and vibrational parameters (\AA^2) with, below, the significant figures of the estimated standard deviations

	x/a_0	y/b_0	z/c_0	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Pt	0	0	0	3.12 3	2.65 3	3.33 3	0.40 3	0.23 2	0.20 3
C(1)	0.1956 44	0.3130 23	0.0876 17	2.8 6	5.1 9	9.0 1.0	0.2 6	0.0 7	-2.8 8
C(2)	0.0984 56	0.2032 33	0.1655 15	3.6 7	7.7 1.5	6.5 1.0	0.5 8	-0.3 7	-2.8 1.0
N(1)	0.1605 43	0.2448 18	0.0048 12	3.2 5	4.2 6	8.6 1.1	-0.8 5	0.4 5	0.9 7
N(2)	0.0132 37	-0.0505 22	-0.1365 9	3.2 5	6.4 8	3.5 6	0.6 5	0.2 4	-0.5 5
O(1)	-0.2451 33	-0.3230 15	0.0772 10	4.1 5	5.1 5	9.0 9	-0.4 4	0.5 6	3.0 6
O(2)	-0.1003 45	-0.0703 22	0.1978 10	6.1 8	8.4 7	4.8 6	0.2 7	0.8 5	2.4 6

The short distance (3.26 Å) between C(1) and the oxygen atom O(1), translated by b_0 (Fig. 2) is also noteworthy.

Table 3. Distances, d , of the atoms from plane (4) with their standard deviations, σ , and $|d/\sigma|$

Pt	d	σ	$ d/\sigma $
Pt	0	0	0
C(1)	0.015 Å	0.016 Å	0.94
C(2)	0.016	0.020	0.80
N(1)	-0.022	0.015	1.47
N(2)	0.032	0.013	2.46
O(1)	-0.003	0.012	0.25
O(2)	0.012	0.016	0.75

$\chi^2 = 10.35$

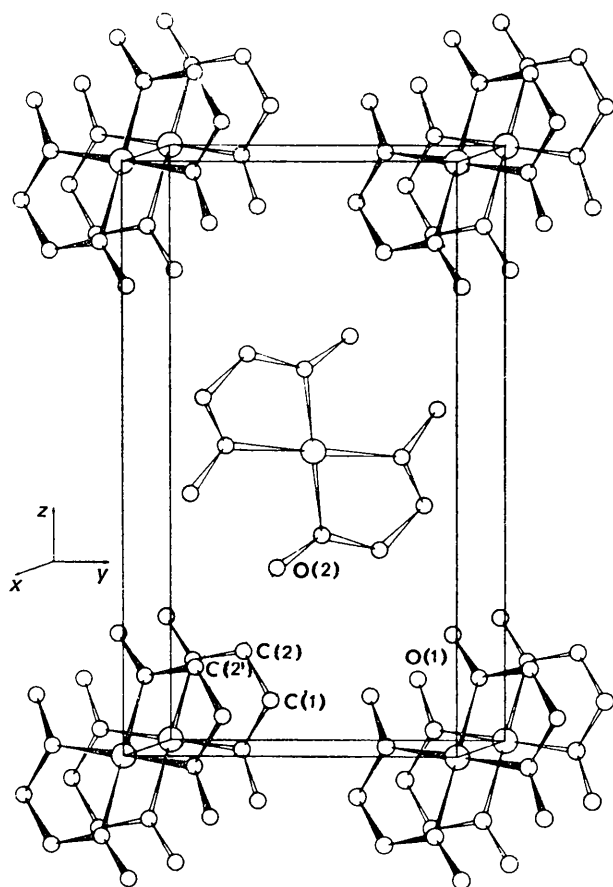


Fig. 2. Clinographic projection, along the x axis, of the contents of one unit cell.

Also, in PtG the intermetallic distance (equal to a_0 , *i.e.* 3.504 Å) is not of the same magnitude as that found in the corresponding complexes of dimethylglyoxime. It must be stressed that the Pt-Pt distance is a little shorter than the Pd-Pd distance in PdG (3.558 Å) and very much shorter than the Ni-Ni distance (4.196 Å) in NiG.

The degree of conjugation in the C-C and C=N bonds (see Table 4) is comparable with that found in NiG and PdG. The length of the bond O(1)-O(2) (2.66 Å) indicates that this intermolecular hydrogen bond should be considered to be asymmetric. A three-dimensional difference syntheses, based on final atomic parameters, was computed in order to attempt to locate the hydrogen atoms. Positive zones appeared in the positions possibly occupied by hydrogen atoms bound to carbon atoms, but without well-defined peaks; the zones in the neighbourhood of oxygen atoms offered no useful information at all. We therefore gave up the attempts to derive the hydrogen-atom coordinates since a tentative determination of coordinates from such broadened peaks had already proved unreliable in the case of the analogous complex of Pd^{II}.

The application of statistical tests (Cruickshank & Robertson, 1953) to the pairs of C=N, N-O and Pt-N bonds showed that only the difference between the two Pt-N bonds is possibly significant, although the trend of bond lengths is the same as that found in the other complexes formed by α -dioximes (Calleri, Ferraris & Viterbo, 1967*a,b*; Godycki & Rundle, 1953; Williams, Wohlaue & Rundle, 1959; Frasson, Bardi & Bezzi, 1959; Frasson, Panattoni & Zannetti, 1959; Panattoni, Frasson & Zannetti, 1959; Frasson & Panattoni, 1960; Murmann & Schlemper, 1967). The differences in question are, however, always less than, or at the limit of, statistical significance and it seems plausible that, if valid, they are a result not of a real asymmetry in the ligands, but rather of deformations caused by intermolecular contacts. This point of view is supported by the fact that in the PdG structure more significant differences between similar bonds were found in the molecule which is affected to the greater extent by intermolecular contacts. Certainly a factor to be taken into account in explaining these asymmetries is the role of the intramolecular hydrogen bond O-H---O, itself asymmetric. In fact, the differences in the lengths of the pairs of bonds in question in NiG, where the hydrogen bond is symmetric, are the least signi-

Table 4. Bond lengths and angles, with their standard deviations in parenthesis

Pt—N(1)	2.013 (14) Å	N(1)—C(1)—C(2)	114.8 (1.7)°
Pt—N(2)	1.968 (14)	N(2)—C(2)—C(1)	112.7 (1.8)
C(1)—C(2)	1.453 (31)	C(1)—N(1)—Pt	116.6 (1.3)
C(1)—N(1)	1.286 (28)	C(1)—N(1)—O(1')	124.6 (1.5)
C(2)—N(2')	1.326 (30)	Pt—N(1)—O(1')	118.7 (1.1)
N(1)—O(1')	1.356 (21)	Pt—N(2)—O(2')	120.4 (1.2)
N(2)—O(2')	1.332 (22)	Pt—N(2)—C(2')	117.7 (1.3)
O(1)—O(2)	2.655 (21)	C(2')—N(2)—O(2')	121.6 (1.5)
N(1)—Pt—N(2)	102.0 (7)°	N(2')—O(2)—O(1)	99.5 (1.0)
N(1)—Pt—N(2')	78.0 (7)	N(1')—O(1)—O(2)	99.3 (9)

ficant of those observed among the complexes formed by glyoxime.

In Table 5 the root-mean-square displacements of the atoms along the three principal directions of thermal vibration are reported, together with the angles, $\varphi_x, \varphi_y, \varphi_z$ and φ_n , which these directions make with the crystallographic axes and with the normal to the molecular plane respectively. The thermal motion is rather high and markedly anisotropic for all the light atoms and also for platinum. From the values of Table 5 it can be seen that the direction of smallest vibration for carbon and nitrogen atoms is almost normal to the molecular plane, while for oxygen atoms the normal to this plane roughly coincides with the vibrational axis of intermediate magnitude. The three principal directions of vibration for the Pt atom are all out of the plane of the molecule. It was also possible to verify that the direction of largest vibration of carbon and oxygen atoms is nearly parallel to the C-C and O-O bonds respectively; nitrogen atoms have their direction of largest vibration nearly normal to the Pt-N bonds.

Table 5. *Parameters characterizing the principal directions of thermal vibration for all the atoms: root-mean-square displacements (r.m.s.d.) (Å) and angles which the principal directions make with the $x(\varphi_x), y(\varphi_y), z(\varphi_z)$ axes and the normal to the molecular plane (φ_n)*

	R.m.s.d.	φ_x	φ_y	φ_z	φ_n
Pt	0.201	133°	105°	44°	122°
	0.211	56	65	47	63
	0.174	118	30	97	135
C(1)	0.21	84	29	62	97
	0.36	94	118	28	82
	0.19	7	97	92	12
C(2)	0.23	98	51	40	105
	0.36	83	39	129	98
	0.21	11	91	82	18
N(1)	0.24	121	34	99	139
	0.33	92	79	11	91
	0.18	32	59	97	49
N(2)	0.21	74	84	20	73
	0.29	80	13	99	98
	0.20	19	102	107	20
O(1)	0.23	30	115	77	16
	0.37	92	61	29	96
	0.20	60	40	115	77
O(2)	0.28	11	99	87	9
	0.35	84	28	63	98
	0.21	100	116	27	89

Although the results reported in the present article are all based on intensities corrected for the absorption effect, a refinement was also carried out making use of

non-corrected intensities. In the second case the standard deviations, σ , for all the parameters turned out to be very slightly greater, while the two R values were practically the same. This fact could simply be ascribed to an insensibility of R and σ to systematic errors such as absorption, but it should be stressed that the positional parameters in the two cases never differ by more than the standard deviations. The vibrational parameters of light atoms show differences between σ and 2σ ; only the thermal parameters of the platinum atom change appreciably.

Therefore in the case of the crystal investigated here, with very small dimensions, and in other similar cases, the correction for the absorption effect does not seem to be essential, at least for the determination of positional parameters. Moreover, considering that the measurements of crystals with dimensions of 0.1–0.2 mm can be in error by at least 10–20%, and that the crystal surface may be very irregular, one may wonder if in many cases it would not be better to neglect the correction for absorption rather than make a correction based on crystal dimensions only roughly estimated.

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