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

M. Calleri, G. Ferraris and D. Viterbo

*Bis(glyoximato)Pd(II), $(H_2C_2N_2OOH)_2Pd$, crystallizes
in the triclinic system with two molecules per unit cell
and belongs to space group $P\bar{1}$. Unit-cell parameters
are: $a_o = 3.5581$ Å, $b_o = 7.7720$ Å, $c_o = 14.0172$ Å,
$\alpha = 89°33'$, $\beta = 91°39'$, $\gamma = 89°54'$. The structural
analysis of this complex, based on all the reflexions
accessible with Cu K_α radiation and measured by an
automatic diffractometer (final R value 0.046), shows
that in the two crystallographically non equivalent
molecules Pd atoms coordinate four N atoms on a
plane and that the whole molecules are planar. The
intramolecular hydrogen bonds O-H- - -O, have to be
considered asymmetric. Pd atoms are not interested
in any contact, while some intermolecular contacts be-
tween C and O atoms are worth recording.*

Introduction

As a part of a programme of studies on the crystal
and molecular structure of glyoxime[1] and its derivatives,[2]
the authors performed this work on bis(glyoximato)-
Pd(II).

Experimental Section

Preparation and Crystal Data. Bis(glyoximato)Pd(II)
complex, $(H_2C_2N_2OOH)_2Pd$, was prepared by mixing
an alcoholic solution of glyoxime with a hot hydro-
chloric solution of $PdCl_2$ and then nearly neutralizing it
with dilute sodium hydroxide.

By recrystallization of the precipitate from water or
dilute acetic acid, we obtained yellow-orange acicular
crystals of low transparency and luster. Their cross-
section is very small and they are always elongated and
streaked in a preferential direction, which has been
chosen as [100], and do not show well defined faces.

From Weissenberg and precession photographs we
deduced that bis(glyoximato)Pd(II), (PdG), crystallizes
in the triclinic system; choosing for PdG a mor-
phological orientation similar to that of bis(glyoximato)-
Ni(II), (NiG), a primitive pseudo body-centered cell

results (the intensities of reflexions with h+k+l odd
are actually very weak).

The unit-cell parameters were refined by a least-
squares procedure, using an adequate number of ϑ_{hkl}
values measured with a single crystal on the diffracto-
meter, with Cu K_α radiation ($\lambda_{\alpha_1} = 1.54050$ Å); the
following values, with their standard deviations, were
obtained : $a_o = 3.5582 \pm 0.0030$ Å, $b_o = 7.7720 \pm
0.0012$ Å, $c_o = 14.0172 \pm 0.0034$ Å, $\alpha = 89°33' \pm 1'$,
$\beta = 91°39' \pm 1'$, $\gamma = 89°54' \pm 1'$.

In order to have a unit cell oriented in accordance
with the recommendations of the Commission on
Crystallographic Data[3] it is sufficient to apply to our
crystallographic axes the following transformation:

$$\begin{vmatrix} \mathbf{a_2} \\ \mathbf{b_2} \\ \mathbf{c_2} \end{vmatrix} = \begin{vmatrix} 0 & 1 & 0 \\ 0 & 0 & -1 \\ -1 & 0 & 0 \end{vmatrix} \begin{vmatrix} \mathbf{a_1} \\ \mathbf{b_1} \\ \mathbf{c_1} \end{vmatrix} \quad (1)$$

In this way it results that $\alpha_2 = \beta_1$, $\beta_2 = 180° - \gamma_1$ and
$\gamma_2 = 180° - \alpha_1$.

We chose $P\bar{1}$ as space group and the choice was
confirmed by the subsequent structural analysis.

Goniometric measurements on PdG crystals are
almost impossible, at any rate we were able to see that
the elongation zone exhibits the same faces as in NiG.
Examination under the polarizing microscope showed
that the crystals are nearly always lying on a face, (011)
or (01$\bar{1}$), which exhibits an extinction direction making
with the x axis an angle of $\simeq 10°$; seldom the crystals
orientation is such that they show an extinction angle
close to 0°. PdG crystals, lying as explained above,
exhibit an appreciable pleochroism; their colour is
canary-yellow for light vibrating in the extinction direc-
tion nearly parallel to [100], while it is brown-orange
in the direction perpendicular to the former.

Other physical data are: $V = 387.456$ Å^3; M.W. =
280.524; $D_{calc.} = 2.405$ g cm^{-3}; Z = 2; F(000) =
272 e; linear absorption coefficient for Cu K_α
radiation: $\mu = 199.60$ cm^{-1}.

Intensity Measurement. Intensities, all on the same
relative scale, were measured by a General Electric
automatic three-circle diffractometer, equipped with a

(1) M. Calleri, G. Ferraris and D. Viterbo, *Acta Cryst.*, **20**, 73 (1966).
(2) M. Calleri, G. Ferraris and D. Viterbo, *Acta Cryst.*, **22**, 468 (1967).
(3) O. Kennard, J. C. Speakman and J. D. H. Donnay, *Acta Cryst.*, **22**, 445 (1967).

Na(Tl)I scintillation counter, using nickel-filtered Cu K_α radiation. The crystal selected for the measurements, 0.6 mm long with a mean cross-section of about 0.02×0.02 mm, was mounted with its elongation direction, [100], parallel to the φ axis of the goniostat and integrated intensities were collected by the ϑ-2ϑ scanning method, with a scanning speed of 1° per minute. Background was measured for a 0.5° interval on both sides of each peak. It has been possible to measure 1687 reflexions, corresponding to $\simeq 97\%$ of those accessible with Cu K_α radiation; about 550 reflexions had a relative integrated intensity, after subtracting the background, of about 10 counts against a maximum value of about 26,000 counts for reflexion 002.

The correction for the Lorentz-polarization effect was performed by standard formulae; the computation of atomic scattering factors was done by linearly interpolating the values recommended in the International Tables.[4] The real part of the correction for the anomalous scattering of palladium atoms ($\Delta f' = -0.5$) was introduced; the imaginary part was neglected since only at high ϑ values its contribution to the modulus of the amplitude scattered by palladium atoms rises to $\simeq 2\%$. No absorption correction was used.

Determination of the Structure. PdG structure has been solved by projections of the Patterson and electron-density functions along the three crystallographic axes. The examination of these projections showed that palladium atoms occupy the two sets of positions 0,0,0 and ½,½,½ of symmetry $\bar{1}$, in agreement with the fact that the reflexions with $h+k+l$ odd are weak; it was also possible to draw approximate coordinates for the other atoms. It resulted that the structure of PdG consists of two families of molecules, crystallographically non equivalent, and that the asymmetric unit is formed by two half molecules. The y and z coordinates were sensibly refined by successive cycles of electron-density and difference projections along [100]; the section $b_0 c_0 \sin\beta$, with the largest area, is in fact the best resolved.

The values of x coordinates were less reliable owing to the overlappings which happen in the other two projections. At this stage a computation of structure factors for all the 1687 reflexions yielded $R = 0.21$; the molecular configuration was clear, with palladium atoms coordinating on a plane four nitrogen atoms.

At a later stage, when the structure had been sufficiently refined, we computed a three-dimensional difference synthesis which showed, in the positions where the hydrogen atoms were to be expected, rather broadened positive peaks. The coordinates tentatively assigned to the hydrogen atoms were refined and the values so obtained implied C-H and O-H distances ranging from 0.7 Å to 1.05 Å. Since coordinates for hydrogen atoms which yield bond distances of such an uncertainty seem to us of doubtful physical meaning, we neglected the hydrogen atoms in the final stage of refinement and do not report the relative coordinates. In any case it is important to remember that a rather broad positive peak appeared in the difference synthesis near both to oxygen atoms O(1) and O(4) (cf. Fig. 1),

thus indicating the presence of asymmetrical hydrogen bonds (for the discussion of this point cf. the last paragraphs).

Structure Refinement. The structure refinement was carried out by the least-squares method using the well known full-matrix programme of Busing, Martin and Levy[5] with minor modifications.

Refinement of scaling factor, coordinates and isotropic vibrational parameters lowered R to 0.13 for all the 1687 reflexions. An examination of $|F_o\text{-}F_c|$ discrepancies pointed out however that the reflexions with a measured intensity smaller than $\simeq 10$ counts had merely the effect of badly affecting the scaling factor. In subsequent least-squares cycles the weights of these reflexions were made zero except when $|F_c| > |F_o|$; a measurement of 10-15 counts has, in fact, to be regarded as the minimum revealable.

The following weighting scheme was now introduced:

$$w_{hkl} = \frac{A}{(3/|F_{max}|)F_o{}^2 + |F_o| + 2|F_{min}|} \quad \text{if } |F_o| \geqslant 2|F_{min}| \quad (2)$$

$$w_{hkl} = a\, F_o{}^2 \qquad\qquad\qquad \text{if } |F_o| < 2|F_{min}| \quad (3)$$

To constant A was assigned such value as to have $0 < w_{hkl} < 1$; constant a was chosen in such a way as to make the two weighting functions coinciding when $|F_o| = 2|F_{min}|$; F_{max} and F_{min} have the obvious meaning of the greatest and smallest amplitudes chosen for the weighting functions.

The refinement of scaling factor, positional and anisotropic vibrational parameters for carbon, nitrogen, oxygen and palladium atoms, which involves 121 variables, was stopped when the variations of parameters were negligible and precisely of the order of $\sigma/10$.

The final R value for the 1109 reflexions, used throughout the last cycles of refinement and listed in Table I, is 0.046 (weighted R is 0.059). The reflexions of zero weight because «non observable» are not published; the 63 reflexions marked with an asterisk in Table I have been given zero weight in the course of the refinement because they are probably affected by casual measurement errors.

The final fractional coordinates and vibrational anisotropic parameters are listed in Table II; the latter are the B_{ij} coefficients of the function:

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

In Table III are reported the elements characterizing the vibrational ellipsoids referred to their own principal axes, i.e. in the form :

$$\sum_{i=1}^{3} q_i \sum_{j=1}^{3} g_{ij} h_j a_j{}^{*2} \quad (5)$$

(4) «International Tables for X-ray Crystallography», vol. III, Kynoch Press, Birmingham (1962).

(5) W. R. Busing, K. O. Martin and H. A. Levy, «Fortran Crystallographic Least Squares Program», ORNL-TM-305, Oak Ridge National Laboratory, Tennessee (1962).

Table I. Observed structure amplitudes and calculated structure factors (10 times the true values for the whole unit cell)

The tabulated data are arranged in repeating columns of the form: H K L $|F_o|$ F_c

Table II. Final fractional coordinates and vibrational parameters with (below) the significant figures of the standard deviations

	x/a_o	y/b_o	z/c_o	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Pd(1)	0.0	0.0	0.0	3.31	2.33	2.75	0.36	0.17	0.02
				9	7	8	3	3	2
Pd(2)	0.5	0.5	0.5	2.85	2.57	3.05	0.26	0.04	−0.04
				8	7	8	3	3	2
O(1)	−0.2770	−0.3053	0.0939	5.33	4.55	5.36	0.19	0.39	0.82
	26	11	6	40	36	40	15	16	15
O(2)	−0.1532	−0.0418	0.2033	6.11	6.98	3.34	0.57	0.32	0.88
	27	13	6	46	53	36	19	16	15
O(3)	0.5633	0.397?	0.3048	5.32	5.17	4.17	0.30	0.31	−0.92
	25	11	7	40	41	39	15	15	14
O(4)	0.7406	0.1587	0.4352	5.90	2.92	6.39	0.44	0.18	−0.81
	26	9	7	42	29	44	13	17	14
N(1)	−0.1641	−0.2393	0.0112	5.37	1.83	5.01	0.39	0.38	0.16
	28	9	7	47	26	42	13	17	12
N(2)	−0.0365	0.0702	0.1329	3.90	4.52	3.39	0.78	0.00	−0.06
	25	14	7	39	44	40	16	14	16
N(3)	0.4721	0.5224	0.3584	3.50	4.65	3.83	0.05	0.43	−0.08
	26	14	7	36	45	39	16	15	16
N(4)	0.3225	0.7380	0.4880	4.32	2.03	4.85	0.40	0.29	−0.18
	25	9	6	40	27	40	12	15	12
C(1)	0.1888	0.3263	0.0693	5.27	2.13	4.93	0.11	−0.17	−0.09
	32	12	8	52	32	47	15	19	14
C(2)	0.0630	0.2239	0.1511	3.97	4.62	4.37	0.21	−0.17	−0.79
	32	15	8	45	48	46	18	18	18
C(3)	0.3654	0.6760	0.3271	4.13	5.92	4.34	0.42	0.18	0.49
	34	17	8	49	60	48	21	19	21
C(4)	0.2785	0.8003	0.4041	4.84	3.66	5.56	0.27	0.12	0.40
	36	14	9	51	43	57	18	21	19

Table III. Parameters characterizing the vibrational ellipsoids referred to their own principal axes

	q_i	r.m.s.d.	g_{i1}	g_{i2}	g_{i3}
Pd(1)	0.683	0.186	0.108	0.043	−0.990
	0.860	0.209	0.942	0.314	0.141
	0.551	0.167	−0.318	0.949	−0.102
Pd(2)	0.745	0.194	0.696	0.415	0.602
	0.771	0.198	0.497	0.310	−0.798
	0.602	0.175	−0.519	0.856	−0.012
O(1)	1.299	0.256	−0.919	0.184	0.321
	1.509	0.276	0.392	0.498	0.780
	1.003	0.225	−0.034	0.848	−0.537
O(2)	1.462	0.272	−0.914	0.397	0.062
	1.867	0.307	0.405	0.888	0.217
	0.781	0.199	0.003	0.231	−0.974
O(3)	1.321	0.259	−0.894	0.286	−0.375
	1.443	0.270	0.416	0.813	−0.400
	0.895	0.213	−0.168	0.507	0.836
O(4)	1.488	0.274	0.981	0.099	0.196
	1.641	0.288	0.142	0.229	−0.960
	0.672	0.184	−0.136	0.968	0.199
N(1)	1.223	0.249	−0.423	−0.005	0.894
	1.382	0.265	0.901	0.113	0.444
	0.444	0.150	−0.108	0.994	−0.052
N(2)	0.858	0.208	−0.496	0.399	0.754
	1.266	0.253	0.566	0.821	−0.050
	0.829	0.205	−0.658	0.408	−0.656
N(3)	1.006	0.226	0.534	0.007	0.861
	1.163	0.243	0.041	0.999	−0.040
	0.820	0.204	−0.845	0.054	0.508
N(4)	1.089	0.235	0.949	0.185	−0.229
	1.222	0.249	−0.264	0.021	−0.972
	0.486	0.157	−0.175	0.983	0.056
C(1)	1.187	0.245	0.527	−0.001	0.864
	1.368	0.263	0.849	0.041	−0.503
	0.531	0.164	−0.037	0.999	0.013
C(2)	0.979	0.223	−0.901	0.417	0.097
	1.338	0.260	0.246	0.729	−0.637
	0.925	0.216	0.357	0.543	0.765
C(3)	1.053	0.231	0.342	0.195	−0.910
	1.541	0.279	0.204	0.939	0.274
	1.005	0.226	−0.918	0.283	−0.310
C(4)	1.224	0.249	0.978	0.187	−0.065
	1.415	0.268	0.051	0.214	0.975
	0.878	0.211	−0.204	0.959	−0.213

where q_i are the three principal vibrational semi-axes (in Å^2) and g_{ij} are their direction cosines with respect to the reciprocal unit-cell axes (j = 1,2,3 for a*, b*, c* respectively).

It can be seen from r.m.s.d. values (in Å) that the anisotropy of vibration of the atoms is considerable and that some of the ellipsoids are of revolution mostly around their shortest axis.
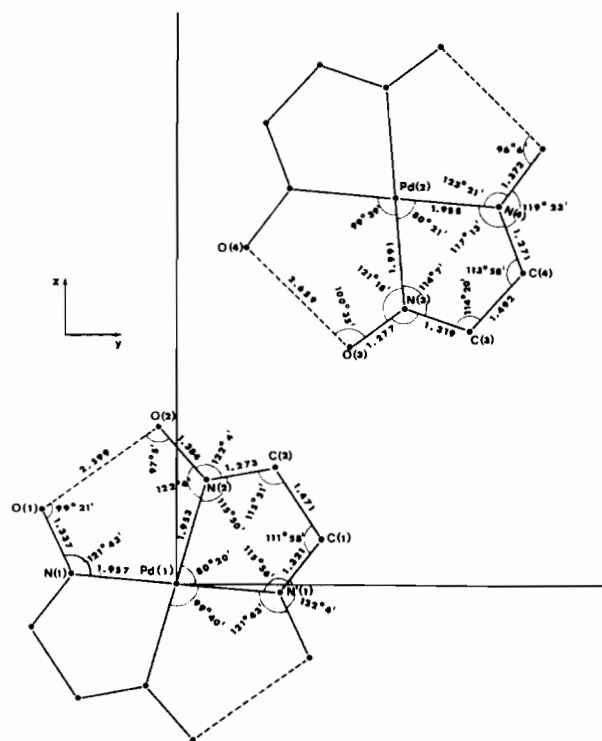
Figure 1. Molecular bonds and angles.

Results and Discussion

The best mean planes[6] for the two crystallographically non equivalent molecules of PdG, in fractional coordinates and referred to the cell axes, have the following equations:

$$3.3333 \, x - 2.3307 \, y + 2.0781 \, z = 0 \qquad (6)$$

$$3.3798 \, x + 2.4398 \, y - 0.1958 \, z = 2.8119 \quad (7)$$

In Table IV the distances of the atoms from their respective mean planes are reported; considering that the order of magnitude of the standard deviations is 0.010 Å, it can be concluded, on the basis of statistical tests[7] that only N(1) atom might be significantly out of the plane of equation (6); however both molecules have to be considered planar* in the light of χ^2 test.

Table IV. Distances of atoms from their respective mean planes

| Molecule at 0,0,0 | | Molecule at ½,½,½ | |
Atom	d (Å)	Atom	d (Å)
Pd(1)	0.000	Pd(2)	0.000
O(1)	−0.016	O(3)	0.003
O(2)	0.009	O(4)	−0.007
N(1)	0.034	N(3)	−0.012
N(2)	−0.009	N(4)	−0.017
C(1)	0.013	C(3)	0.008
C(2)	0.002	C(4)	0.003

A general view of the structure is given by Figure 2: both molecules are not greatly inclined on (100) plane ($\simeq 20°$) and the dihedral angle between their own planes is $\simeq 38°$.

The molecular packing is like that of NiG; this fact should be more manifest on choosing also for PdG a unit cell where the heavy atom centers (100) face. While between crystallographically equivalent molecules no contact occurs, there are some remarkable contacts between atoms of non-equivalent molecules and precisely between O(3) and C(2) (3.08 Å) and between O(3) and C(2) with a translation of a_0 (3.14 Å) (cf. Figure 2); analogous contacts occur in NiG structure, though no doubt weaker (3.19 and 3.22 Å). As in NiG, also in PdG no intermetallic contact takes place.

Coming back to the configurations of the two asymmetric units, the application of statistical tests[7] to bond lengths (cf. Table V), allows us to state the following considerations. About the molecule with Pd atom at 0,0,0, the difference between N-O bonds is significant and this fact may denote that the hydrogen
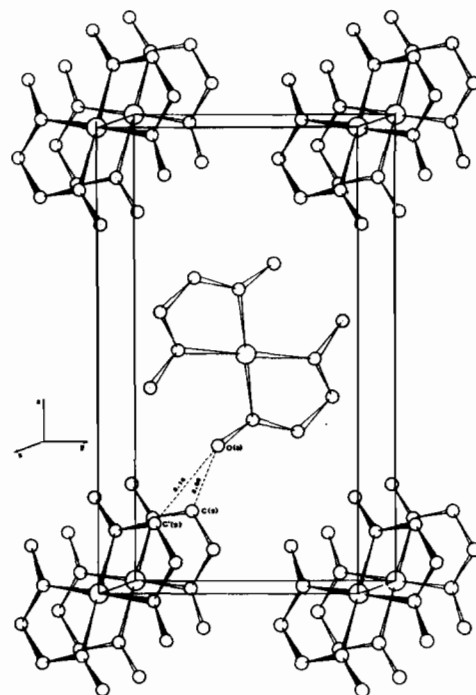
(6) V. Schomacher, J. Waser, R. E. Marsch and G. Bergman, *Acta Cryst.*, 12, 600 (1959).
(7) D. W. J. Cruickshank and A. P. Robertson, *Acta Cryst.*, 6, 698 (1953).
(*) The distances of PdG atoms from their relative mean planes are not, on the average, shorter than those found for NiG atoms. For the latter compound, however, statistical tests indicate that the molecule is probably non-planar; we have to point out at any rate that the standard deviations for NiG may be somewhat optimistic, since they were derived from a diagonal-blocks least-squares programme.

Figure 2. Clinographic projection, along the x axis, of the content of one unit cell

Table V. Bond lengths (in Å) and bond angles, with their standard deviations between brackets

Molecule at 0,0,0		Molecule at ½,½,½	
C(1)-C(2)	1.471 (14)	C(3)-C(4)	1.492 (16)
C(1)-N'(1)	1.321 (12)	C(3)-N(3)	1.319 (16)
C(2)-N(2)	1.273 (13)	C(4)-N(4)	1.271 (15)
N(1)-O(1)	1.337 (12)	N(3)-O(3)	1.277 (13)
N(2)-O(2)	1.384 (12)	N(4)-O'(4)	1.372 (12)
Pd(1)-N(1)	1.957 (7)	Pd(2)-N(3)	1.991 (8)
Pd(1)-N(2)	1.953 (9)	Pd(2)-N(4)	1.958 (7)
O(1)-O(2)	2.599 (12)	O(3)-O(4)	2.659 (12)
C(2)-C(1)-N'(1)	111.0° (9)	C(4)-C(3)-N(3)	114.3° (9)
C(1)-C(2)-N(2)	115.8° (9)	C(3)-C(4)-N(4)	114.0° (9)
C(1)-N'(1)-Pd(1)	115.9° (7)	C(3)-N(3)-Pd(2)	114.1° (7)
C(2)-N(2)-Pd(1)	115.8° (7)	C(4)-N(4)-Pd(2)	117.2° (7)
N(2)-Pd(1)-N'(1)	80.3° (4)	N(4)-Pd(2)-N(3)	80.3° (4)
Pd(1)-N(1)-O(1)	121.7° (6)	Pd(2)-N(3)-O(3)	121.3° (7)
C'(1)-N(1)-O(1)	122.1° (8)	C(3)-N(3)-O(3)	124.5° (9)
Pd(1)-N(2)-O(2)	122.1° (6)	Pd(2)-N(4)-O'(4)	123.3° (6)
C(2)-N(2)-O(2)	122.1° (8)	C(4)-N(4)-O'(4)	119.4° (8)
N(1)-Pd(1)-N(2)	99.7° (4)	N(3)-Pd(2)-N'(4)	99.7° (4)
N(1)-O(1)-O(2)	99.3° (5)	N(3)-O(3)-O(4)	100.6° (6)
N(2)-O(2)-O(1)	97.1° (6)	N'(4)-O(4)-O(3)	95.1° (5)

bond is asymmetric. As regards the molecule with Pd atom at ½,½,½, we could observe that the difference between N-O bonds is highly significant, in accordance with an asymmetric hydrogen bonding, that the difference between Pd-N bonds is significant (this fact will be considered below) and that the difference between C=N bonds is only possibly significant as it is also in the molecule at the origin. Looking at the difference between pairs of chemically similar bonds, it can be asserted that PdG molecules have symmetry C_{2h}.

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In both the two crystallographically equivalent molecules there is a modest degree of conjugation between C=N and C-C bonds, of about the same magnitude found in bis (dimethyl-glyoximato) Pd(II),[8,9] but smaller than in glyoxime[1] and in NiG.[2] We remember that in NiG too, a difference between C=N bonds has been observed, but the explanation of such difference is not a straightforward matter.

After examining the configuration of the molecules and having in mind the pseudo-symmetry which makes the packing of PdG molecules like that of NiG, the most significant comparison between the two molecules can be made, in our opinion, after orienting them so that atoms C(1) and C(2) correspond to C(3) and C(4). The comparison of the molecules so oriented shows that the pairs of significantly different bonds are: Pd(1)-N(1), Pd(2)-N(3); N(1)-O(1), N(3)-O(3) and O(1)-O(2), O(3)-O(4). These statistically significant differences, and also the difference between Pd-N ligands in the molecule with Pd atom at ½,½,½, have to be ascribed to the above illustrated intermolecular contacts.

While the molecule at the origin of the cell takes part in the contacts with its resonance stabilized portion and thus it is slightly influenced, the molecule at the center is more influenced and its bonds Pd(2)-N(3), N(3)-O(3) and O(3)- -O(4) are deformed. The

lenghtening of the hydrogen bonding, with respect to that of NiG, can possibly explain the intermolecular contacts and also the lowering to triclinic symmetry.

Looking also at the values of bond angles we can conclude that the differences between the two crystallographically independent molecules are due to the intermolecular contacts which take place in the crystalline state.

As regards the hydrogen bonding we repeat that O(1)- -O(2) and O(3)- -O(4) bonds have to be considered asymmetric for the following reasons. First of all by comparison of their lengths with the diagram, correlating O-H and O-H- -O distances, reported by Atoji and Rundle.[10] In the second place the significant difference between N-O bonds in the same molecule indicates that the hydrogen atom is nearer to one of the oxygen atoms than to the other; in NiG[2] where the hydrogen bridge has to be considered symmetric the difference between these bonds is not significant. Lastly we remember that the indications given by a three-dimensional difference syntheses suggested the presence of asymmetrical hydrogen bonds.

An inspection of the studies on the structures of Ni and Pd complexes with α-dioximes shows that Ni complexes[2,9,11] are characterized by short and most likely symmetrical hydrogen bonds, while in Pd complexes[8,9] much longer intramolecular hydrogen bonds take place.

(8) C. Panattoni, E. Frasson and R. Zannetti, *Gazz. Chim. Ital.*, 89, 2135 (1959).
(9) D. E. Williams, G. E. Wohlauer and R. E. Rundle, *J. Amer. Chem. Soc.*, 81, 755 (1959).

(10) M. Atoji and R. E. Rundle, *J. Chem. Phys.*, 29, 1306 (1958).
(11) E. Frasson and C. Panattoni, *Acta Cryst.*, 13, 893 (1960).