

## Structure Changes and Proton Transfer between O...O in Bis(dimethylglyoximato)platinum(II)<sup>†</sup> at Low Temperature (150 K) and at High Pressures (2.39 and 3.14 GPa)

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### Abstract

The structure of bis(dimethylglyoximato)platinum(II), at 300 and 150 K and at 2.39 and 3.14 GPa at 300 K, has been determined by X-ray diffraction. [Pt(C<sub>4</sub>H<sub>7</sub>N<sub>2</sub>O<sub>2</sub>)<sub>2</sub>],  $M_r = 425.30$ , *I*bam,  $Z = 4$  over the entire temperature and pressure range. At 300 K,  $a = 16.7735$  (14),  $b = 10.5790$  (15),  $c = 6.5175$  (5) Å,  $V = 1156.5$  (2) Å<sup>3</sup>,  $D_x = 2.443$  Mg m<sup>-3</sup>,  $\lambda(\text{Ag } K\alpha) = 0.5609$  Å,  $\mu = 69.5$  mm<sup>-1</sup>,  $F(000) = 800$ . The lengths of  $a$  and  $c$  decrease monotonically by 1.8 and 1.5% respectively with lowering of temperature from 300 to 150 K, whereas an elongation of 0.7% in  $b$  occurs. The structure was refined to  $R = 0.033$  and 0.029 at 300 and 150 K, and  $R = 0.044$  and 0.038 at 2.39 and 3.14 GPa respectively. A proton between O(1)...O(2) moves from O(1) to O(2) when the temperature is lowered from 300 to 150 K. Two methyl groups rotate by about 60° at 150 K from their position at 300 K and one of the two methyl groups has two orientational disorders with equal ratio at 150 K. Intermolecular contacts of O...H—C type are observed between the adjacent chains at 150 K. A metal–metal separation within the chain,  $c/2$ , decreases continuously from 3.2587 (3) Å at atmospheric pressure to 2.9745 (2) Å at 3.84 GPa. The crystal structure at high pressure is found to be similar to that observed at 150 K.

### Introduction

In the dimethylglyoxime (dmg) complexes of the divalent  $d^8$  metal ions, Ni<sup>II</sup>, Pd<sup>II</sup> and Pt<sup>II</sup>, and related compounds, electrical and optical properties have been studied at high pressures. Many of these complexes have chain structures with direct metal–metal contacts

along the chain direction. The decrease in the electrical resistance at high pressures has been interpreted by assuming that the shortening of the metal–metal separations increases interactions between filled  $(n-1)d_z$  and empty  $np_z$  orbitals on the metals of the adjacent complexes within the chain and that the increase in the band widths of the  $(n-1)d_z$  and  $np_z$  orbitals brings about a reduction of the band gap between them (Interrante & Messmer, 1971). In Pt(dmg)<sub>2</sub>, the electrical resistance decreases remarkably from  $ca$  10<sup>15</sup> Ω cm at atmospheric pressure (Atkinson, Day & Williams, 1968; Gomm, Thomas & Underhill, 1971) to 0.05 Ω cm at  $ca$  6.7 GPa (Hara, Shirovani & Onodera, 1976; Shirovani & Suzuki, 1986) and an absorption peak at 16 300 cm<sup>-1</sup>, assigned to the transition from the  $5d_z$  to the  $6p_z$  orbital (Ohashi, Hanazaki & Nagakura, 1970), shows a large red shift of 8700 cm<sup>-1</sup> at  $ca$  6.3 GPa (Zahner & Drickamer, 1960; Tkacz & Drickamer, 1986). At higher pressures, however, the electrical resistance increases slightly and the absorption peak shows a blue shift. Moreover, a new absorption peak appeared around 540 nm above 6.5 GPa (Shirovani & Suzuki, 1986). This reverse behavior was observed in Magnus' green salt, Pt(NH<sub>3</sub>)<sub>4</sub>PtCl<sub>4</sub>, dicarbonyl(acetylacetonato)iridium(I) (Interrante & Bundy, 1971), and several Pt<sup>II</sup> glyoxime complexes (Hara *et al.*, 1976; Hara & Nicol, 1978; Shirovani, Onodera & Hara, 1981; Tkacz & Drickamer, 1986). The reversal of the shift in the resistance was explained by the intermolecular back-bonding model (Miller, 1977). It was reported that  $d\pi-\pi^*$  back-bonding plays an important role in the resistance at high pressure in bis(benzil dioximato)platinum(II) (Hara & Nicol, 1978). In the present paper, we report the crystal structures at high pressures (2.39 and 3.14 GPa) with electrical resistance of  $ca$  10<sup>3</sup> Ω cm, the pressure dependence of lattice constants

<sup>†</sup> Bis(2,3-butanedione dioximato)platinum(II).

up to 3.84 GPa in Pt(dmg)<sub>2</sub>, and accurate crystal structures at 300 and 150 K, because previous data does not seem to be reliable enough for a discussion of the molecular structures and the bonding nature (Frasson, Panattoni & Zannetti, 1959). The proton transfer between O atoms and the rotation in two methyl groups at low temperatures and at high pressures will also be discussed.

### Experimental

#### Measurements at 300 and 150 K at atmospheric pressure

Dark-red needle crystals along *c*, 0.049 × 0.047 × 0.146 mm, with prominent faces {110} and {001}, were used for intensity measurements. A crystal specimen was cooled by a stream of cold N<sub>2</sub> gas surrounded by a warm N<sub>2</sub> gas curtain. The final unit-cell dimensions at four different temperatures were refined by the least-squares method based on reflections with 13 < θ < 20° (Ag Kα). Intensities at 300 and 150 K were collected on a Rigaku automated four-circle diffractometer using graphite-monochromated Ag Kα radiation (λ = 0.5609 Å) in order to avoid the large absorption of Pt for Mo Kα. Three standard reflections (002, 020, 200) were measured every 50 reflections and the variation in intensity was less than 0.6% throughout the whole experiment. The intensity data were corrected for Lorentz and polarization factors and an absorption correction was also made. Maximum and minimum transmission factors were 0.880 and 0.823 respectively (Busing & Levy, 1957). Crystal data and experimental conditions are summarized in Table 1.

#### Measurements at high pressures

The miniature diamond anvil cell for the single-crystal X-ray work described by Merrill & Bassett (1974) was modified because the beryllium disks used to support the diamonds give rise to large background counts and their easy transformation at the contact with the diamond at high pressures caused difficulties in centering the crystal on the diffractometer. The beryllium disks were replaced by two half spheres of rigid stainless steel cut in a cone of 35° half angle. A crystal fixed by a little wax on a diamond was adjusted using a telescope. After centering the crystal, an Inconel 750X (International Nickel Company, Inc.) gasket 250 μm thick was placed on the diamond so that the crystal was located in the center of the gasket hole with a diameter of 600–400 μm. Methanol–ethanol (4:1) was used as hydrostatic pressure fluid. Pressure was calibrated using the shift of the R<sub>1</sub> ruby fluorescence line (Piermarini, Block, Barnett & Forman, 1975). The deviation of the position of the crystal at high pressures was negligibly small. Unit-cell dimensions at eight different pressures were refined by a least-squares

Table 1. Crystal data of Pt(dmg)<sub>2</sub> at atmospheric pressure

[Pt(C<sub>4</sub>H<sub>7</sub>N<sub>2</sub>O<sub>2</sub>)<sub>2</sub>], *M<sub>r</sub>* = 425.30, orthorhombic, space group *Ibam*, *Z* = 4.

#### (a) Temperature dependence of the lattice constants

<i>T</i> (K)	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å <sup>3</sup> )	No. of reflections used
300	16.7735 (14)	10.5790 (15)	6.5175 (5)	1156.5 (2)	23
250	16.6548 (11)	10.6015 (7)	6.4762 (3)	1143.5 (1)	20
200	16.5631 (25)	10.6222 (20)	6.4448 (10)	1133.9 (3)	23
150	16.4701 (14)	10.6523 (13)	6.4177 (5)	1126.0 (2)	18

#### (b) Experimental conditions

<i>T</i> (K)	300	150
<i>D<sub>z</sub></i> (Mg m <sup>-3</sup> )	2.443	2.509
Scan method	2θ-ω	ω
μ(Ag Kα) (mm <sup>-1</sup> )	69.5	71.3
2θ <sub>max</sub> (°)	45	50
Range of <i>h</i> , <i>k</i> and <i>l</i>	0 ≤ <i>h</i> ≤ 22 0 < <i>k</i> ≤ 14 0 < <i>l</i> ≤ 8	0 ≤ <i>h</i> ≤ 24 0 ≤ <i>k</i> ≤ 15 0 < <i>l</i> ≤ 8
No. of reflections measured [  <i>F</i>   > 3σ( <i>F</i> )]	839	1133
No. of independent reflections	531	716
No. of parameters refined	70	79
( <i>d</i> / <i>σ</i> ) <sub>max</sub>	0.4	0.6
<i>R</i>	0.033	0.029
<i>wR</i>	0.048	0.042
<i>S</i>	1.27	1.75

procedure using an adequate number of reflections with 10 < θ < 21° (Mo Kα). The (110) faces of two crystals, which were cut to less than 0.1 mm along *c*, were attached to the faces of diamonds. Intensity data at 2.39 and 3.14 GPa were collected on a Rigaku automated four-circle diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). Four angular parameters for each reflection were calculated to check the path of the X-ray beam and the shadowing of the cones. Stronger intensities were used at 3.14 GPa, if two equivalent reflections *hkl* (0 ≤ *h* ≤ 15, 0 ≤ *k* ≤ 7, 0 ≤ *l* ≤ 6) and  $\bar{h}\bar{k}\bar{l}$  (-17 ≤ *h* ≤ 0, -7 ≤ *k* ≤ 0, -6 ≤ *l* ≤ 0) showed large intensity differences. Corrections for Lorentz and polarization factors were made but not for absorption and extinction. Crystal data and experimental conditions at high pressures are given in Table 2.

### Structure determination

#### Structures at 300 and 150 K at atmospheric pressure

The positions of Pt, N and C atoms in the chelate five-membered ring were determined from three-dimensional sharpened Patterson maps. The electron density maps using the phases calculated with these five atoms revealed other heavy atoms. Difference Fourier maps at 150 K indicated that H atoms of one methyl group, C(3)H<sub>3</sub>, are disordered with two orientations. While a diffuse peak between the O atoms was assigned as an H atom linked to O(1) at 300 K, a sharp peak was found *ca* 0.7 Å from O(2) between the two O atoms at 150 K. The structures were refined by the

Table 2. *Crystal data at high pressures at 300 K*Orthorhombic, space group *Ibam*,  $Z = 4$ .

## (a) Pressure dependence of lattice constants

<i>P</i> (GPa)	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å <sup>3</sup> )	No. of reflections used
0.59	16.614 (5)	10.407 (7)	6.3792 (4)	1103.0 (8)	16
1.17	16.459 (9)	10.283 (13)	6.2511 (8)	1058.0 (15)	17
1.55	16.360 (8)	10.245 (9)	6.1926 (8)	1037.9 (10)	13
1.81	16.297 (6)	10.223 (7)	6.1557 (5)	1025.5 (8)	14
2.39	16.163 (2)	10.183 (3)	6.0781 (5)	1000.6 (4)	11
2.72	16.102 (6)	10.179 (8)	6.0452 (4)	990.8 (9)	14
3.14	16.047 (6)	10.153 (7)	6.0089 (5)	979.0 (8)	18
3.84	15.938 (4)	10.129 (6)	5.9491 (4)	960.4 (6)	21

## (b) Experimental conditions

<i>P</i> (GPa)	2.39	3.14
<i>D<sub>x</sub></i> (Mg m <sup>-3</sup> )	2.823	2.983
Scan method	$\omega$	$\omega$
$2\theta_{\max}$ (°) (Mg <i>K</i> $\alpha$ )	50	50
Range of <i>h</i> , <i>k</i> and <i>l</i>	$0 \leq h \leq 17$ $0 \leq k \leq 6$ $0 \leq l \leq 6$	$0 \leq h \leq 17$ $0 \leq k \leq 7$ $0 \leq l \leq 6$
No. of independent reflections [ $ F  > 3\sigma(F)$ ]	115	115
$(\Delta/\sigma)_{\max}$	0.3	0.5
<i>R</i>	0.044	0.038
<i>S</i>	4.9	4.5

full-matrix least-squares program *RADIEL* (Coppens, Guru-Row, Leung, Stevens, Becker & Yang, 1979) on the basis of *F* magnitudes with equal weights. The populations of disordered H atoms of the C(3)H<sub>3</sub> group at 150 K were also refined. Anisotropic thermal parameters are used for heavy atoms and isotropic thermal parameters for H. Atomic scattering factors for Pt, O, N and C atoms were taken from *International Tables for X-ray Crystallography* (1974). Scattering factors given by Stewart, Davidson & Simpson (1965) were used for H. Maximum heights in the final difference Fourier maps were  $1.0 \text{ e } \text{Å}^{-3}$  at 300 K and  $1.0 \text{ e } \text{Å}^{-3}$  at 150 K. The final positional parameters are listed in Table 3.\*

*Structures at high pressures (2.39 and 3.14 GPa)*

The coordinates of heavy atoms at atmospheric pressure were used as initial parameters at high pressures. The structures were refined using the block-diagonal least-squares method with equal weights and isotropic thermal parameters.

**Description of the structure**

Bis(dimethylglyoximato)platinum(II) molecules are stacked along *c* with an equivalent Pt–Pt distance of 3.2587 Å (300 K), *c*/2, rotating about the chain axis by

\* Lists of structure factors and anisotropic thermal parameters at 300 and 150 K and fractional coordinates and thermal parameters at 2.39 and 3.14 GPa have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51401 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Positional parameters ( $\times 10^4$ , for H  $\times 10^3$ ) and equivalent isotropic thermal parameters with e.s.d.'s in parentheses for Pt(dm<sub>g</sub>)<sub>2</sub> at atmospheric pressure*For non-H atoms,  $B_{\text{eq}} = \frac{1}{3} \pi^2 \sum_i U_{ij} a_i^* a_j^* a_i a_j$ .

## (a) At 300 K

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B<sub>eq</sub></i> (Å <sup>2</sup> × 10) <sup>†</sup>
Pt	0 (0)	0 (0)	0 (0)	325 (2)
O(1)	1633 (8)	−908 (14)	0 (0)	45 (4)
O(2)	−495 (8)	2630 (12)	0 (0)	49 (4)
N(1)	1175 (7)	146 (20)	0 (0)	37 (3)
N(2)	152 (8)	1870 (13)	0 (0)	37 (4)
C(1)	1464 (12)	1267 (20)	0 (0)	42 (5)
C(2)	892 (12)	2262 (19)	0 (0)	44 (5)
C(3)	2355 (13)	1473 (26)	0 (0)	56 (7)
C(4)	1059 (18)	3623 (22)	0 (0)	75 (9)
<i>B</i> (Å <sup>2</sup> × 10)				
H(O1)	128 (9)	−174 (14)	0 (0)	26 (37)
H(C3a)	257 (11)	89 (15)	0 (0)	47 (46)
H(C3b)	254 (6)	185 (8)	158 (13)	36 (21)
H(C4a)	62 (8)	397 (13)	0 (0)	13 (30)
H(C4b)	136 (5)	402 (9)	163 (15)	43 (23)

## (b) At 150 K

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B<sub>eq</sub></i> (Å <sup>2</sup> × 10) <sup>‡</sup>
Pt	0 (0)	0 (0)	0 (0)	161 (1)
O(1)	1648 (5)	−874 (8)	0 (0)	202 (18)
O(2)	−512 (6)	2627 (8)	0 (0)	238 (19)
N(1)	1191 (5)	146 (11)	0 (0)	180 (19)
N(2)	138 (4)	1825 (8)	0 (0)	160 (17)
C(1)	1494 (7)	1278 (10)	0 (0)	176 (22)
C(2)	880 (7)	2251 (11)	0 (0)	210 (23)
C(3)	2385 (7)	1476 (13)	0 (0)	270 (27)
C(4)	1051 (9)	3637 (12)	0 (0)	297 (30)
<i>B</i> (Å <sup>2</sup> × 10)				
H(O2)	−83 (12)	216 (21)	0 (0)	82 (75)
H(C3a)‡	274 (13)	67 (21)	0 (0)	18 (61)
H(C3b)‡	250 (11)	200 (14)	116 (28)	28 (39)
H(C3c)‡	265 (11)	229 (19)	0 (0)	20
H(C3d)‡	265 (9)	111 (14)	162 (28)	20
H(C4a)	163 (8)	392 (12)	0 (0)	25 (30)
H(C4b)	81 (6)	406 (9)	124 (16)	45 (24)

† Å<sup>2</sup> × 10<sup>2</sup> for Pt.

‡ The populations for disordered H atoms are H(C3a), H(C3b) 0.55 (30); H(C3c), H(C3d) 0.45.

*ca* 90° as shown in Fig. 1. All the atoms except H lie in mirror planes at  $z = 0$  and  $z = \frac{1}{2}$ .

*Structural changes with variation of temperature*

(a) O–H...O. Bond distances and angles at 300 and 150 K are listed in Tables 4 and 5 respectively. Frasson *et al.* (1959) reported a large value of 3.03 Å at room temperature for the O...O distance. In the present measurement, however, the short O...O distances of 2.638 Å at 300 K and 2.643 Å at 150 K show the existence of a strong intramolecular hydrogen bond between the O atoms. A strong hydrogen bond was also observed in Ni(dm<sub>g</sub>)<sub>2</sub> (2.654 Å) (Godycki & Rundle, 1953), NiG<sub>2</sub> (2.453 Å) (Calleri, Ferraris & Viterbo, 1967), PtG<sub>2</sub> (2.655 Å) (Ferraris & Viterbo, 1969) and Ni(BQD)<sub>2</sub> (2.480, 2.43 Å) (Leichert & Weiss, 1975*b*; Endres, Keller, Moroni & Weiss, 1975) (G = glyoximato, BQD = 1,2-benzoquinone dioximato). In three-dimensional difference Fourier maps based on the final atomic parameters, a broadened peak corresponding to a proton is found at a distance of 1.06 Å from O(1)

between the O atoms at 300 K, whereas a well defined proton peak is located at 0.73 Å from O(2) at 150 K. This implies that the proton attached to O(1) at 300 K moves to O(2) at 150 K. The O(1)—H...O(2) angle is 159° at 300 K and O(1)...H—O(2) is 178° at 150 K. The intramolecular unsymmetrical hydrogen bond is compatible with the results of infrared spectra (Blinč & Hadzi, 1958).

(b) *H atoms of the two methyl groups.* Packing views in the (001) plane at 300 and 150 K are given in Figs. 2(a) and 2(b) respectively. The orientation of the H atoms in the methyl groups changes between 300 and 150 K. At room temperature, the two methyl groups are related by mirror symmetry; the mirror plane is through the Pt atom and the midpoint of C(1)—C(2) bond, and is perpendicular to the chelate plane. An intramolecular interaction with a distance of 2.34 Å is found between one H atom of the methyl group C(4)H<sub>3</sub> on the chelate plane and the negatively charged O(2) atom. The contact distance between adjacent chains, C(3)...O(1), is 3.249 Å. Two H atoms in the C(3)H<sub>3</sub> group deviate by ±60° from the chelate plane to decrease the intermolecular repulsion with O(1)—H in the adjacent chain. At 150 K, the C(4)H<sub>3</sub> group rotates by 60° so that the H atom on the chelate plane is in close contact with O(1) of the adjacent chain. The other methyl group, C(3)H<sub>3</sub>, is disordered with two orientations, that is, 50% of the C(3)H<sub>3</sub> group rotates by 60° around C(1)—C(3). An H atom of the rotated methyl group has an intermolecular interaction with the O(1) atom of the adjacent chain and an H atom of the original orientation has an intramolecular interaction with O(1). The negative charge on O(1) attracts H atoms of two methyl groups causing O...H—C interactions since the proton moves to O(2) at 150 K.

(c) *Molecular geometry.* The unsymmetrical O—H...O hydrogen bond should affect the bond distances in two independent O—N—C moieties. It is found that a

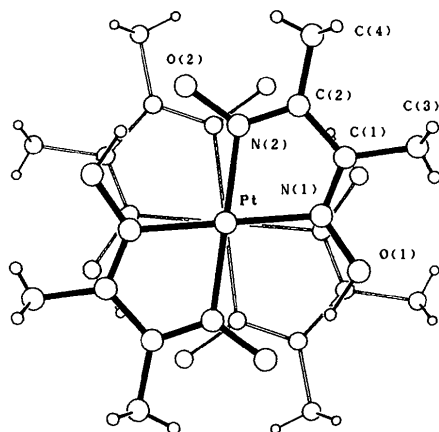


Fig. 1. The stacking mode between the adjacent Pt(dmga)<sub>2</sub> complexes in the chain showing atomic numbering.

Table 4. *Interatomic distances* (Å)

(a) Bond distances	300 K	150 K	2.39 GPa	3.14 GPa
Pt—N(1)	1.976 (12)	1.968 (8)	2.01 (3)	1.97 (4)
Pt—N(2)	1.995 (13)	1.957 (8)	1.88 (7)	1.73 (5)
N(1)—O(1)	1.354 (24)	1.321 (13)	1.13 (9)	1.19 (10)
N(2)—O(2)	1.351 (18)	1.370 (12)	1.36 (7)	1.55 (6)
N(1)—C(1)	1.282 (29)	1.305 (15)	1.52 (12)	1.33 (13)
N(2)—C(2)	1.308 (24)	1.302 (14)	1.30 (7)	1.43 (6)
C(1)—C(2)	1.425 (29)	1.449 (16)	1.48 (8)	1.58 (9)
C(1)—C(3)	1.510 (30)	1.482 (17)	1.65 (7)	1.60 (8)
C(2)—C(4)	1.467 (31)	1.503 (18)	1.32 (11)	1.33 (9)
O(1)—H(O)	1.06 (15)			
O(1)...H(O)		1.92 (22)		
O(2)—H(O)		0.73 (22)		
O(2)...H(O)	1.63 (15)			
O(1)...O(2)	2.638 (19)	2.643 (12)	2.69 (6)	2.64 (6)
N(1)...N(2)	2.503 (22)	2.491 (12)	2.60 (9)	2.32 (9)
(b) Intermolecular short contacts				
Within a chain				
	300 K	150 K	2.39 GPa	3.14 GPa
O(2)...N(2)	3.405 (5)	3.377 (4)	3.20 (3)	3.22 (3)
O(2)...C(2)	3.349 (14)	3.290 (3)	3.12 (1)	3.09 (1)
N(2)...N(2)	3.299 (4)	3.241 (2)	3.09 (1)	3.08 (1)
O(1)...N(1 <sup>ii</sup> )	3.444 (7)	3.386 (4)	3.29 (4)	3.19 (3)
O(1)...C(1 <sup>ii</sup> )	3.293 (4)	3.247 (2)	3.09 (1)	3.04 (1)
N(1)...N(1 <sup>ii</sup> )	3.273 (4)	3.224 (2)	3.04 (1)	3.01 (1)
Between chains				
C(3)...O(1 <sup>iii</sup> )	3.249 (30)	3.241 (16)	2.93 (10)	2.95 (9)
C(4)...O(1 <sup>iii</sup> )	3.904 (32)	3.824 (16)	3.53 (7)	3.69 (6)
C(3)...O(2 <sup>iv</sup> )	3.730 (26)	3.593 (15)	3.46 (7)	3.28 (7)

Symmetry code: none *x, y, z*; (i)  $-x, y, 0.5-z$ ; (ii)  $x, -y, 0.5-z$ ; (iii)  $0.5-x, 0.5+y, -z$ ; (iv)  $0.5+x, 0.5-y, -z$ .

Table 5. *Bond angles* (°) at 300 and 150 K at atmospheric pressure

	300 K	150 K
N(1)—Pt—N(2)	78.2 (5)	78.8 (3)
Pt—N(1)—O(1)	120.1 (13)	120.2 (7)
Pt—N(2)—O(2)	119.2 (10)	121.9 (6)
Pt—N(1)—C(1)	116.8 (14)	117.0 (8)
Pt—N(2)—C(2)	115.9 (12)	117.1 (7)
O(1)—N(1)—C(1)	123.2 (15)	122.8 (9)
O(2)—N(2)—C(2)	125.0 (14)	121.1 (9)
N(1)—C(1)—C(2)	115.3 (19)	113.2 (11)
N(2)—C(2)—C(1)	113.9 (18)	113.9 (10)
N(1)—C(1)—C(3)	120.6 (19)	120.7 (10)
N(2)—C(2)—C(4)	119.6 (18)	121.2 (10)
C(2)—C(1)—C(3)	124.1 (19)	126.1 (10)
C(1)—C(2)—C(4)	126.6 (19)	124.9 (11)
N(1)—O(1)—H(O)	111.9 (80)	
N(2)—O(2)—H(O)		98 (17)
O(1)—H(O)...O(2)	159 (13)	
O(2)—H(O)...O(1)		178 (24)
N(1)—O(1)...O(2)	99.1 (11)	
N(2)—O(2)...O(1)		96.6 (5)

proton transfer from O(1) to O(2) at 150 K causes the shortening of N(1)—O(1) and the lengthening of N(2)—O(2). Moreover, the N(1)—C(1) distance is shorter by 0.26 Å than N(2)—C(2) at 300 K, whereas the former is a little longer than the latter at 150 K. For Ni(dmga)<sub>2</sub>, NiG<sub>2</sub>, Ni(BQD)<sub>2</sub>, PtG<sub>2</sub> and Pd(BQD)<sub>2</sub> (Leichert & Weiss, 1975a), the difference Fourier maps give no well-defined electron density peak corresponding to H between O...O, but the same trends observed in the O—N—C moieties may indicate that these compounds have an unsymmetrical O—H...O arrangement in which an H atom links to an O atom in the

O—N—C moiety with longer N—O and shorter N—C bonds than the counterpart.

The N—Pt—N bite angles of  $78.8(3)^\circ$  at 150 K and  $78.2(5)^\circ$  at 300 K correspond to the  $78.0^\circ$  observed in  $\text{PtG}_2$ . N—Ni—N bite angles in  $\text{Ni}(\text{dmg})_2$ ,  $\text{NiG}_2$  and  $\text{Ni}(\text{BQD})_2$  are  $80$ ,  $82.1$  and  $83.6^\circ$  respectively, which are larger than N—Pt—N although the N...N distances remain constant in Ni and Pt complexes.

(d) *Temperature dependences of lattice constants.* The lattice constants at four different temperatures are given in Table 1. The lengths of  $a$  and  $c$  decrease monotonically by 1.8 and 1.5% respectively as the temperature is lowered from 300 to 150 K, whereas an elongation of 0.7% in  $b$  occurs. At 150 K, an H atom of the C(4)H<sub>3</sub> group has a short contact of 2.14 Å along  $b$  with an H atom in the chelate plane of the unrotated C(3)H<sub>3</sub> group in the adjacent chain; the repulsion between these H atoms results in the increase of  $b$ .

#### Structural changes at high pressures (2.39 and 3.14 GPa)

Lattice constants at eight different high pressures up to 3.84 GPa were obtained using two single crystals (Table 2). The ratios of lattice constants at high pressures to those at atmospheric pressure (Fig. 3) show the largest shrinkage along  $c$ . The metal—metal

separation within the chain, half of  $c$ , decreases continuously from  $3.2587(3)$  Å at atmospheric pressure to  $2.9745(2)$  Å at 3.84 GPa. This initial large shrinkage of Pt—Pt results in a considerable decrease in the electrical resistance from  $ca\ 10^{15}\ \Omega\ \text{cm}$  at atmospheric pressure to  $ca\ 10^3\ \Omega\ \text{cm}$  at 4.0 GPa. Metal—metal distances corresponding to the minimum electrical resistance are 2.86 Å at 6.7 GPa in  $\text{Pt}(\text{dmg})_2$  (Shirotani & Suzuki, 1986), 2.95 Å at 12.5 GPa in Magnus' green salt,  $\text{Pt}(\text{NH})_3\text{PtCl}_4$ , 2.91 Å at 16.0 GPa in dicarbonyl(acetylacetonato)iridium(I) (Interrante & Bundy, 1971), and 2.95 Å at 7.0 GPa in  $\text{MgPt}(\text{CN})_4 \cdot 7\text{H}_2\text{O}$  (Hara, Shirotani, Ohashi, Asami & Minomura, 1980). These distances are a little longer than the interatomic distances of 2.775 and 2.714 Å reported for the structures of metal crystals of Pt and Ir respectively (Pauling, 1960). The  $b$  lattice constant shows an initial large decrease and a slow decrease over  $ca\ 1.2$  GPa. This behavior corresponds to the elongation in  $b$  with lowering of temperature. Bond distances and short contacts between the chains at 2.39 and 3.14 GPa are given in Table 4. The N(2)—O(2) bond is 0.23 and 0.36 Å longer than N(1)—O(1) at 2.39 and 3.14 GPa respectively. This implies that a proton attaches to O(2), although the N—C distances do not support this definitively. The short contact of about 2.94 Å between C(3) and O(1) in the adjacent chains at high pressures indicates the existence of a strong C—H...O interaction. These facts show that the H atom moves from O(1) to O(2) and two methyl groups rotate by  $60^\circ$  at high pressures as observed at 150 K. The increase of frequencies of C=N and N—O

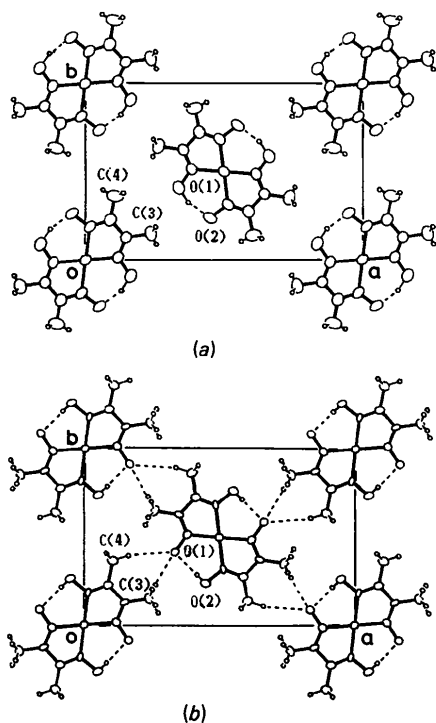


Fig. 2. Packing views in the (001) plane: (a) at 300 K and (b) at 150 K.

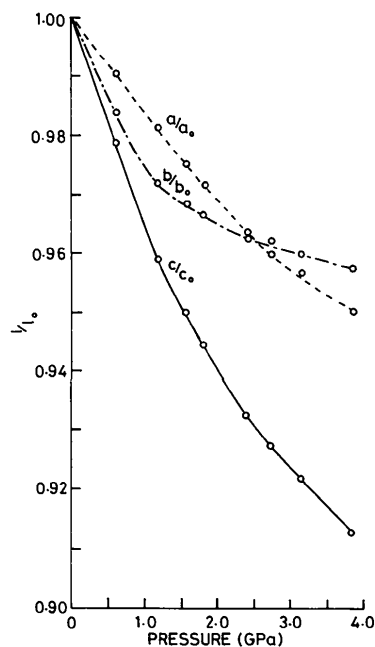


Fig. 3. The axial parameters vs pressure.

stretching modes with increasing of pressure observed for Pt(dmg)<sub>2</sub> (Hara & Nicol, 1978; Tkacz & Drickamer, 1986) indicates the shortening of these bond distances. Some bonds are unreasonably long at high pressures. This seems to be a result of the poor accuracy of the determinations at high pressures.

*Relationship between the molecular structure and physical properties*

The drastic decrease of the electrical resistance and the red shift in the absorption peak at 16 300 cm<sup>-1</sup> is interpreted in terms of the decrease of Pt—Pt separation within a chain as the pressure rises. A powder X-ray diffraction measurement (Shirotani & Suzuki, 1986) shows that the Pt—Pt distance decreases monotonically up to 13.0 GPa. The strong intermolecular metal—ligand  $d\pi-\pi^*$  or ligand—ligand  $\pi-\pi^*$  interactions within a chain and C—H...O interactions between chains may play an important role in the reverse behavior observed for the electrical resistance at high pressures.

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**Mixed-Valence Linear-Chain Complexes: X-ray Structural Characterization of a Pd<sup>II</sup>/Pd<sup>IV</sup>Br<sub>2</sub> Chain and of Three Mixed-Metal Chains, [NiPt(en)<sub>4</sub>Cl<sub>2</sub>]<sup>4+</sup>, [PdPt(pn)<sub>4</sub>Cl<sub>2</sub>]<sup>4+</sup> and [NiPt(pn)<sub>4</sub>Cl<sub>2</sub>]<sup>4+</sup>, all as Perchlorate Salts**

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**Abstract**

The X-ray crystal structures of the mixed-valence linear-chain complexes [Pd(en)<sub>2</sub>][Pd(en)<sub>2</sub>Br<sub>2</sub>]-

(ClO<sub>4</sub>)<sub>4</sub> (1), [Ni(en)<sub>2</sub>][Pt(en)<sub>2</sub>Cl<sub>2</sub>](ClO<sub>4</sub>)<sub>4</sub> (2), [Pd(pn)<sub>2</sub>]-[Pt(pn)<sub>2</sub>Cl<sub>2</sub>](ClO<sub>4</sub>)<sub>4</sub> (3) and [Ni(pn)<sub>2</sub>][Pt(pn)<sub>2</sub>Cl<sub>2</sub>](ClO<sub>4</sub>)<sub>4</sub> (4), where en = 1,2-ethanediamine and pn = 1,2-propanediamine, are reported. Crystal data are as follows: (1) bis(1,2-ethanediamine)palladium(II) dibromobis(1,2-ethanediamine)palladium(IV) tetra-

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