Three-Dimensional Determinations of the Crystal Structures of Bis(dimethylglyoximato)palladium(II) and Bis(dimethylglyoximato)platinum(II)

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Abstract

Bis(dimethylglyoximato)palladium(II), $Pd(C_4H_7N_2O_2)_2$, $C_8H_{14}N_4O_4Pd$, crystallizes in the orthorhombic space group *Ibam*, with $a = 16.762$ (5), $b = 10.496$ (2), $c = 6.501$ (1) Å, $V = 1144$ Å^3, $Z = 4$ and $D_c = 1.98$ Mg m^{-3}. The corresponding platinum complex, bis(dimethylglyoximato)platinum(II), $Pt(C_4H_7N_2O_2)_2$, $C_8H_{14}N_4O_4Pt$, is isomorphous, with $a = 16.821$ (1), $b = 10.558$ (1), $c = 6.513$ (1) Å, $V = 1157$ Å^3, $Z = 4$, $D_m = 2.40$, and $D_c = 2.464$ Mg m^{-3}. Because of the reported discrepancies in angles and distances for the Pd and Pt dimethylglyoximato complexes the structures of both complexes were redetermined using three-dimensional counter X-ray data. Refinement by full-matrix least squares led to final $R(F^2)$ values of 0.047 (764 reflections above 2σ) and 0.066 (588 reflections above 2σ) for Pd(DMG)$_2$ and Pt(DMG)$_2$ respectively. Refinement of Pd(DMG)$_2$ in the centrosymmetric space group *Iba*2 showed no significant change or improvement. Contrary to the reported value of 3.03 (6) Å for the O···O distance in the Pt^{II} complex, a distance of 2.62 (2) Å was observed in both complexes, which is in the usual range for hydrogen-bonded O···O. Similarly, the M–N–O angles in both complexes were around 120° instead of the 135° reported in the earlier Pt^{II} study. The central metal atoms in both complexes have identical coordination geometries. The structures are isomorphous with that of the corresponding Ni^{II} complex and no significant difference in molecular parameters was observed in going from Pd^{II} to Pt^{II}, probably as a consequence of the lanthanide contraction in the latter complex. The earlier angles and distances, particularly for the Pt complex, were erroneous, probably because the structure determinations were done only on projections. The average bond distances involving the metal atoms are Pd–N 1.965 (4) Å, and Pt–N 1.96 (2) Å. The hydrogen-bond (O···O) distance is 2.626 (4) Å in Pd(DMG)$_2$ and 2.62 (2) Å in Pt(DMG)$_2$. The structures are compared with those of other metal-glyoxime complexes.

Introduction

The intramolecular O···O distance reported for Cu^{II} (Frasson, Bardi & Bezzi, 1959), Ni^{II} (Godycki & Rundle, 1953; Williams, Wohlauer & Rundle, 1959) and Pd^{II} (Williams *et al.*, 1959) complexes of dimethylglyoxime ranges from 2.40 (4) to 2.70 (4) Å, whereas a considerably longer distance [3.03 (6) Å] was reported for bis(dimethylglyoximato)platinum(II) (Frasson, Panattoni & Zannetti, 1959). On the basis of this exceptional length a significant difference in hydrogen-bond strength was suggested for the Pt^{II} complex compared with the other glyoxime complexes. The difference in length was attributed to a large Pt–N–O angle (135°) compared with the M–N–O angles in the other complexes of this type where this angle was never observed to deviate from 120° by more than 5°. Unless there is something very unusual about the Pt dimethylglyoxime complex, the discrepancy in the reported angles and O···O distances for the Pd and Pt complexes does not seem realistic and may be the result of insufficient data (*hk*0 and *h*0*l* reflections only) used in the reported structure determinations.

Since the results of these studies are often cited in various investigations of these and related compounds (*e.g.* Hara, Shirotani & Onodera, 1976; Hartley, 1973), it appeared that greater accuracy would be desirable. As part of a comprehensive study of short intramolecular hydrogen bonds, three-dimensional structure determinations of the Pd^{II} and Pt^{II} dimethylglyoxime complexes were carried out. The results are reported in this paper and the structures are compared with those of other metal glyoxime complexes.

Experimental

Synthesis and crystal growth

Bis(*dimethylglyoximato*)*platinum*(II). Potassium tetrachloroplatinate was first obtained by the reaction of PtCl$_2$ in HCl with a stoichiometric amount of KCl

(Johnson, 1966). The dark-gray Pt dimethylglyoxime complex was then prepared by refluxing an ethanolic solution of dimethylglyoxime with potassium tetrachloroplatinate in a minimum amount of water for about 2 h. The precipitate was filtered, washed with ethanol, and dried. Attempts to obtain crystals from solvents other than nitrobenzene were not successful. Very small crystals were obtained when a fairly concentrated solution of the complex in nitrobenzene was cooled from about 383 K to room temperature over a period of 8–10 h.

Bis(*dimethylglyoximato*)*palladium*(II). The complex was prepared by the reaction of the Pd(8-hydroxyquinoline)$_2$ complex with dimethylglyoxime in molten naphthalene in a special three-necked cell. The two reactants were allowed to mix by diffusion over a period of 2–3 d in an oven at 363 K. Most of the excess naphthalene was decanted off and the rest was allowed to solidify in the bottom of the cell. The crystals of Pd(DMG)$_2$ were separated by dissolving the remaining naphthalene in acetone.

Crystal data

On the basis of precession photographs, both crystals were found to belong to the orthorhombic system and the systematic extinctions hkl with $h + k + l$ odd, $0kl$ with k odd and $h0l$ with h odd indicated that the space group was *Ibam* or *Iba*2. Subsequent successful refinement was consistent with the previously reported space group *Ibam*. The needle axis in the crystals corresponds to the c axis. For each of the compounds accurate values of the unit-cell parameters were determined from a least-squares refinement of the angular settings of 14 carefully centered reflections on a Picker programmed diffractometer using Mo $K\alpha_1$ radiation with a narrow vertical slit in front of the detector and a low take-off angle.

Pt(DMG)$_2$: orthorhombic, space group *Ibam*, $a = 16\cdot821$ (1), $b = 10\cdot558$ (1), $c = 6\cdot513$ (1)°, $Z = 4$, $D_c = 2\cdot464$, D_m (flotation) $= 2\cdot40$ Mg m^{-3}, $M_r = 425\cdot1, \mu$(Mo $K\alpha_1$) $= 12\cdot78$ mm^{-1}.

Pd(DMG)$_2$: orthorhombic, space group *Ibam*, $a = 16\cdot762$ (5), $b = 10\cdot496$ (2), $c = 6\cdot501$ (1) Å, $Z = 4$, $D_c = 1\cdot98$ Mg m^{-3}, $M_r = 336\cdot4, \mu$(Mo $K\alpha_1$) $= 1\cdot61$ mm^{-1}.

Collection and reduction of intensity data

For each complex an extensive set of three-dimensional intensity data was collected on the diffractometer using Zr-filtered Mo $K\alpha$ radiation. The approximate dimensions of the Pd(DMG)$_2$ crystal were $0\cdot13 \times 0\cdot15 \times 0\cdot37$ mm, and for the Pt(DMG)$_2$ crystal $0\cdot03 \times 0\cdot03 \times 0\cdot22$ mm. For the Pd(DMG)$_2$ complex, a scan rate of 1° min^{-1} and background counts for 20 s at both ends of each scan were recorded. The variable θ–

2θ scan was taken from $0\cdot45°$ below to $0\cdot45°$ above the 2θ settings for $K\alpha_1$ ($\lambda = 0\cdot70926$ Å) and $K\alpha_2$ ($\lambda = 0\cdot71354$ Å) respectively. For Pt(DMG)$_2$, a scan rate of $0\cdot25°$ min^{-1} was used and stationary-counter backgrounds were taken for 40 s at both ends of each scan. The variable 2θ range for this complex was $0\cdot45°$ below to $0\cdot50°$ above the $K\alpha_1$ and $K\alpha_2$ settings respectively. The intensities of 2701 and 1823 reflections were measured for the Pd and Pt complexes respectively. These intensities included at least two equivalent forms out to $2\theta = 60°$ and three standard reflections measured after every 50 to 100 reflections as a check on the crystal and instrument stability. The total change in intensity for Pd(DMG)$_2$ was less than 2% and the data were not corrected for this change. In the case of Pt(DMG)$_2$ the intensity change was about 21% and the data were corrected for this straight-line decrease. Background and Lorentz–polarization corrections were made using the usual equations. The seven bounding faces for Pd(DMG)$_2$ were identified by an optical method and absorption corrections were applied with a transmission factor ranging from $0\cdot78$ to $0\cdot83$. In the case of Pt(DMG)$_2$, the crystal was bounded by eight faces which were used to define the crystal shape and dimensions. The transmission factor in the absorption correction for this complex ranged from $0\cdot70$ to $0\cdot84$. Equivalent and duplicate reflections were averaged, reducing the number of reflections to 915 for the Pd complex and 917 for the Pt complex. The Friedel pairs were assumed to be equivalent for the refinement in *Ibam*.

Determination of the structure and refinement

The structure solutions for both compounds proceeded in a similar manner. In both cases there are four M(DMG)$_2$ molecules per unit cell. The space group *Ibam* has 16 general positions, which requires that the four metal atoms per unit cell be constrained at special positions with $2/m$ symmetry. There is, therefore, only one dimethylglyoxime group in the asymmetric unit in each structure with heavy atoms located at the centers of symmetry. All light atoms apart from the H atoms lie in the mirror plane at $z = 0$. Because of this symmetry restriction, the z coordinates, and B_{13} and B_{23} of all nonhydrogen atoms were not allowed to vary in subsequent least-squares refinements.

In all calculations, the scattering factors used for the Pt, Pd and Cl atoms were those of Cromer & Waber (1965) while the anomalous-scattering factors for these atoms were taken from Cromer (1965) and included in F_c in the refinements (Ibers & Hamilton, 1964). The scattering factors for the remaining atoms were taken from Ibers (1962).

As an independent check on the reported coordinates (Williams *et al.*, 1959), the coordinates for all non-hydrogen atoms in Pd(DMG)$_2$ were determined from a

Patterson map. Since the Pd atoms were located at the origin, the Patterson synthesis was essentially equivalent to a Fourier synthesis. From the large Patterson vectors, eight could be selected which satisfied known structural features of the complex. Without refinement, the R factor with these atoms included was 0·296. Full-matrix least-squares refinement was performed with the 764 reflections having $F_o^2 > 2\sigma(F_o^2)$ where $\sigma(F_o^2) = [\sigma_{counting}^2 + (0·05F_o^2)^2]^{1/2}$. Least-squares refinement in which the scale factor and the positional and anisotropic temperature factors for all non-hydrogen atoms were varied converged with $R = \sum [(|F_o|^2 - |kF_c|^2)/\sum |F_o|^2] = 0·061$ and $r = [\sum w(|F_o|^2 - |kF_c|^2)/\sum w|F_o|^4]^{1/2} = 0·092$. The least-squares program minimized the function $\sum w(|F_o|^2 - |kF_c|^2)^2$. At this stage chemically reasonable positions for H atoms were determined which were consistent with a difference Fourier synthesis. Four more cycles of refinement were carried out in which all positional and thermal parameters of nonhydrogen atoms and positional parameters of H atoms (B fixed at 8 Å^2) were allowed to vary. This reduced R to 0·047 and r to 0·067.

Although about 520 measured Friedel pairs showed no discrepancies, the statistical distribution of normalized scattering factors for Pd(DMG)$_2$ was in much better agreement with the theoretical values for a noncentrosymmetric structure than those for a centrosymmetric structure. Therefore, efforts were also made to refine the structure in the noncentrosymmetric space group Iba2. The Friedel pairs were averaged assuming $hkl \equiv h\bar{k}l$ and $hk\bar{l} \equiv h\bar{k}\bar{l}$ to obtain 1691 reflections out of which 1330 having $I > 2\sigma(I)$ were used in the refinement. The x and y coordinates for all non-hydrogen atoms were obtained from a difference Fourier map with the Pd atom at the origin. Since all of the Fourier peaks were at z = 0, the z coordinates were taken to be slightly greater or less than zero based upon a chemically reasonable puckering scheme of the chelate ring. Six cycles of refinement on positional and anisotropic thermal parameters of nonhydrogen atoms led to $R = 0·061$ and $r = 0·104$. After inclusion of H atoms at chemically reasonable positions, a few more cycles of refinement reduced the agreement factors to $R = 0·048$ and $r = 0·075$ for 1330 reflections and 78 variables in Iba2, compared with $R = 0·047$ and $r = 0·067$ for 917 reflections and 54 variables in Ibam. Thus there is no significant improvement based on the 'r' factor ratio test (Hamilton, 1964). The z parameters of the atoms (Pd fixed at z = 0) were still very close to zero, and the bond distances and angles were virtually the same as with Ibam parameters. The choice of Ibam appears, therefore, to be well established.

The structure of Pt(DMG)$_2$ was refined beginning with the reported coordinates of Frasson, Panattoni & Zannetti (1959). Two least-squares cycles on the positional and isotropic thermal parameters of the non-hydrogen atoms yielded $R = 0·163$ and $r = 0·251$. Of

917 independent and standard reflections measured, 588 having $F_o^2 > 2\sigma(F_o^2)$ were used in the refinement. Three subsequent cycles after the introduction of anisotropic vibrational parameters for all nonhydrogen atoms reduced R to 0·070 and r to 0·109. A difference Fourier synthesis at this stage revealed the approximate location of the H atom in the hydrogen bond and positions for some methyl H atoms could be located. Therefore, chemically reasonable positions consistent with the difference Fourier synthesis were calculated for the remaining H atoms and were included in the final refinement. Three cycles holding methyl H atoms at fixed positions, refining the hydrogen-bonded H isotropically and allowing all other atoms to vary anisotropically, gave the final $R = 0·066$ and $r = 0·101$. Since further refinement with nonhydrogen atoms anisotropic and all H atoms isotropic showed no significant reduction in the R factors, the parameters from the previous refinement are reported. A final difference Fourier synthesis revealed no residual electron density maxima greater than 2·38 e Å^{-3}, and these peaks occurred in the vicinity of the Pt atom. All other residuals were less than 1·3 e Å^{-3}. The maximum shift in any positional parameter after the final least-squares cycle was less than one-tenth the estimated standard deviation of that parameter. The final positional parameters are given in Tables 1 and 2. Unobserved reflections $[F_o^2 < 2\sigma(F_o^2)]$ were not included in the calculations but are listed in the structre factor tables.*

* Lists of structure factors and anisotropic thermal parameters for both compounds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34127 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional parameters for* Pd(DMG)$_2$

Here and elsewhere in this paper the e.s.d.'s from the least-squares refinement are given in parentheses.

	x	y	
Pd	0	0	
O(1)	0·1617 (1)	0·0927 (2)	
O(2)	−0·0491 (2)	−0·2667 (2)	
N(1)	0·1169 (2)	−0·0109 (2)	
N(2)	0·0139 (2)	−0·1861 (3)	
C(1)	0·1464 (2)	−0·1253 (3)	
C(2)	0·0859 (2)	−0·2269 (3)	
C(3)	0·2340 (2)	−0·1473 (4)	
C(4)	0·1059 (3)	−0·3651 (4)	

	x	y	z
H(1)	0·251 (3)	−0·236 (5)	0
H(2)	0·164 (4)	−0·376 (6)	0
H(3)	0·259 (2)	−0·107 (4)	0·096 (4)
H(4)	0·086 (2)	−0·398 (4)	0·096 (4)
H(5)	−0·086 (4)	−0·226 (6)	0

Table 2. *Positional parameters for* Pt(DMG)$_2$

H-atom parameters were not refined.

	x	y	
Pt	0	0	
O(1)	0·1607 (9)	0·0894 (14)	
O(2)	−0·0499 (9)	−0·2634 (14)	
N(1)	0·1166 (9)	−0·0157 (16)	
N(2)	0·0141 (9)	−0·1831 (15)	
C(1)	0·1477 (12)	−0·1285 (19)	
C(2)	0·0868 (11)	−0·2264 (17)	
C(3)	0·2361 (11)	−0·1490 (23)	
C(4)	0·1060 (13)	−0·3659 (19)	

	x	y	z
H(1)	0·2499	−0·2318	0
H(2)	0·1613	−0·3833	0
H(3)	0·2609	−0·0954	0·1019
H(4)	0·0832	−0·4014	−0·1188
H(5)	0·1168	0·1592	0

Results and discussion

Nature of the structures

A stereoscopic view of the unit cell showing the complete packing is given in Fig. 1. The bond distances, angles, and orientations of the ellipsoids are shown in Figs. 2 and 3. The structures are isomorphous with each other and with the corresponding Ni complex (Godycki & Rundle, 1953). The central metal atom in each compound is coordinated to four N atoms having the expected square-planar geometry. The planar molecules are stacked with metal atoms directly above each other separated by $\frac{1}{2}c$ = 3·250 (3) Å in Pd(DMG)$_2$ and 3·256 (3) Å in Pt(DMG)$_2$. The packing pattern in the two structures is the same as that in Ni(DMG)$_2$ but differs from the packing in Cu(DMG)$_2$ and other glyoximato complexes (Ferraris & Viterbo, 1969). The observed distances for the two independent N−C and C−CH$_3$ bonds in the same molecule are equal within experimental errors, suggesting higher D_{2h} molecular symmetry rather than the C_{2h} symmetry required by the space group. A comparison of the bond angles in the coordination plane (Table 3) indicates

some twisting of the dimethylglyoxime molecules to allow for the intermolecular hydrogen bonds. The thermal-vibration amplitudes appear to be generally slightly smaller for Pd(DMG)$_2$ than for Pt(DMG)$_2$. The orientations of the ellipsoids (Figs. 2 and 3), particularly for the more precisely defined ellipsoids in the Pd complex, suggest that most of the anisotropic motion is due to hindered rotation about the axis perpendicular to the molecule (see, for example, the long axes of the methyl carbon ellipsoids). The mean value of U_{33} is slightly lower than the mean of all U_{11} and U_{22} values, providing additional support for the choice of space group *Ibam*.

Bond distances and angles

Because of the overwhelming contribution to the structure factors from Pt[II] and because of the very small size of the crystal used for the measurement of intensities for this complex, the standard deviations of the light-atom parameters are higher in Pt(DMG)$_2$ than in Pd(DMG)$_2$ and than those which might be expected
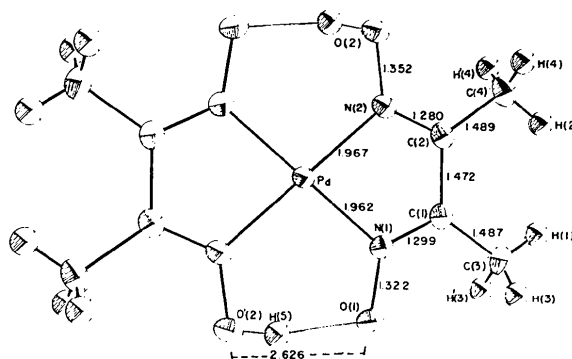
Fig. 2. The structure of the Pd(DMG)$_2$ molecule indicating the atom-labeling scheme, important bond distances (Å) and thermal ellipsoids. The standard deviations are: Pd−N and O−N, 0·003–0·004 Å; N−C, C−C and O···O, 0·004–0·005 Å.

Fig. 3. The structure of the Pt(DMG)$_2$ molecule showing the atom-labeling scheme, bond distances (Å) and vibrations of the thermal ellipsoids. The standard deviations are Pt−N, O−N, N−C and O···O, 0·02 Å; and C−C, 0·03 Å.
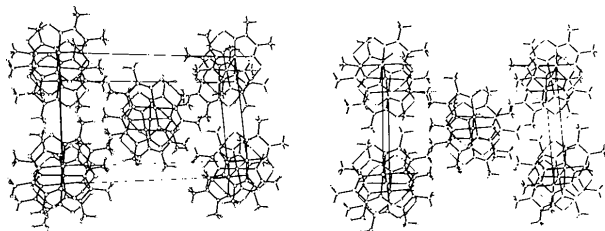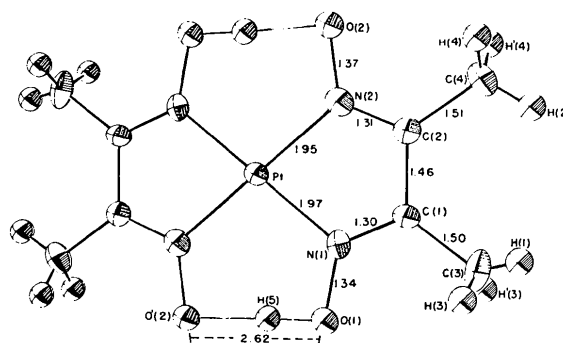

Fig. 1. A stereoscopic view of a unit cell showing the packing of the molecules. The crystallographic a axis lies along the horizontal direction, the b axis is vertical and the c axis completes a right-handed coordinate system.

for the value of R. The bond distances and angles are given in the figures and Table 3. None of the observed differences in distances and angles, expected to be chemically equivalent, can be regarded as significant. The average M—N distance in both complexes is 1·96 (2) Å which is in good agreement with the Pd(Pt)—N(oxime) distances observed for glyoximato complexes and other similar complexes having intermolecular hydrogen bonds (*e.g.* Pfluger, Harlow & Simonsen, 1970). A comparison of various distances and angles with those of some related compounds is given in Table 4.

Table 3. *Interatomic angles* (°) *for* Pd(DMG)$_2$ *and* Pt(DMG)$_2$

	Pd(DMG)$_2$	Pt(DMG)$_2$
M—N(1)—O(1)	121·3 (2)	119 (1)
M—N(2)—O(2)	121·9 (2)	121 (1)
M—N(1)—C(1)	115·7 (2)	119 (1)
M—N(2)—C(2)	116·3 (2)	118 (1)
O(1)—N(1)—C(1)	123·0 (3)	123 (2)
O(2)—N(2)—C(2)	121·8 (3)	121 (2)
N(1)—C(1)—C(3)	121·3 (3)	122 (2)
N(2)—C(2)—C(4)	122·5 (3)	123 (2)
N(1)—C(1)—C(2)	114·0 (3)	112 (2)
N(2)—C(2)—C(1)	114·1 (3)	114 (2)
C(2)—C(1)—C(3)	124·7 (3)	127 (2)
C(1)—C(2)—C(4)	123·5 (3)	123 (2)
N(1)—O(1)—O(2)*	99·4 (2)	101 (1)
N(2)—O(2)—O(1)*	97·3 (2)	97 (1)
N(1)—M—N(2)	79·9 (1)	78·2 (7)
N(1)—M—N(2)*	100·2 (1)	101·8 (7)

* Related by an inversion center.

Table 4. *Comparison of average intermolecular distances* (Å) *and angles* (°) *with those of related compounds*

Compound*	M—N	O···O	N—M—N	M—N—O	Reference
Cu(DMG)$_2$	1·91 (4)	2·53 (4)	81 (1)	121	(a)
	1·96 (4)	2·70 (4)		125	
Ni(DMG)$_2$	1·85 (2)	2·40 (2)	80	118	(b)
	1·85 (2)		100	122	(c)
Pd(DMG)$_2$	1·99 (2)	2·59 (3)	–	–	(c)
	1·93 (2)				
Pt(DMG)$_2$	1·93 (4)	3·03 (6)	83	135	(d)
	1·95 (4)		97		
Ni(G)$_2$	1·868 (4)	2·45 (6)	82·2 (3)	122·8 (3)	(e)
	1·880 (4)				
Pd(G)$_2$	1·958 (7)	2·659 (12)	80·3 (4)	–	(f)
	1·991 (8)		99·7 (4)		
Pt(G)$_2$	1·968 (14)	2·655 (2)	78·0 (7)	118·7 (1·1)	(g)
	2·013 (14)		102·0 (7)	120·4 (1·2)	
Pt(DMG)$_2$	1·97 (2)	2·62 (2)	78·2 (7)	118·9 (1·3)	(h)
	1·95 (2)		101·8 (7)	121·2 (1·2)	
Pd(DMG)$_2$	1·962 (4)	2·626 (4)	79·9 (1)	121·3 (2)	(h)
	1·967 (3)		100·2 (1)	121·9 (2)	

References: (a) Frasson, Bardi & Bezzi (1959); (b) Godycki & Rundle (1953); (c) Williams *et al.* (1959); (d) Frasson, Panattoni & Zannetti (1959); (e) Calleri *et al.* (1967b); (f) Calleri, Ferraris & Viterbo (1967a); (g) Ferraris & Viterbo (1969); (h) this work.

* DMG = dimethylglyoxime; G = glyoxime.

The average intermetallic distance [3·253 (3) Å] observed in both complexes in the present study is of the same magnitude as that found in the corresponding Ni^{II} complex (3·245 Å) (Godycki & Rundle, 1953), suggesting more metal–metal interaction with the heavier metals. The metal–metal distance, however, differs considerably from the corresponding distances in bis(glyoximato)nickel(II) (4·196 Å; Calleri, Ferraris & Viterbo, 1967b), bis(glyoximato)palladium(II) (3·558 Å; Williams *et al.*, 1959), and bis(glyoximato)-platinum(II) (3·504 Å; Ferraris & Viterbo, 1969). Contrary to the reported results, no disagreement was observed in the two crystallographically different M—N and N—O bonds in either compound. The average N—O [1·34 (4) Å] and N—C distances [1·30 (3) Å] are within experimental errors of those observed in a number of similar complexes. The C—C distances are quite normal. There are only minor deviations from 120° for bond angles around N(1) and N(2) in either complex. The average M—N—O angle is 120 (1)° in the Pt complex and 121·6 (2)° in the Pd complex. The reported angle of 135° in the Pt dimethylglyoxime complex (Frasson, Panattoni & Zannetti, 1959) was erroneous probably because the structure determination was performed only on projections. The reported O···O distance [3·03 (6) Å] and the assumed hydrogen-bond strength for Pt(DMG)$_2$ are also misleading. An O···O distance of 2·62 (2) Å was found here for the Pt complex and 2·626 (4) Å for the Pd complex. As one would expect, no significant difference was observed in going from Pd^{II} to Pt^{II}, probably as a consequence of the lanthanide contraction in the latter complex. The corresponding O···O distances of 2·40 Å in bis(dimethylglyoximato)-nickel(II) and 2·445 Å in bis(glyoximato)nickel(II) are considerably shorter. The magnitude of the O···O distance observed in the present study is the same as that reported for the glyoximato complexes of Pd^{II} [2·659 (12) Å] and Pt^{II} [2·655 (21) Å]. The lengthening from Ni to Pd and Pt can be attributed to the steric effects imposed by the larger metal atoms.

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The Crystal and Molecular Structure of N-(2-Chlorophenyl)-3,6-dithiacyclohexene-1,2-dicarboximide

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Abstract

Crystals of N-(2-chlorophenyl)-3,6-dithiacyclohexene-1,2-dicarboximide are monoclinic, space group $P2_1$, with $a = 8.226$ (1), $b = 16.056$ (2), $c = 14.604$ (2) Å and $\beta = 91.97$ (2)°. The three-dimensional intensity data (2770 independent reflections) were obtained with a Syntex $P2_1$ automated four-circle diffractometer. The structure was solved by direct methods and refined to a conventional R value of 6.2%. The unit cell contains three symmetrically independent molecules which are different optical isomers and have different deformations of individual rings and somewhat different bond lengths. The conformations of the 3,6-dithiacyclohexene rings are half-chair in molecules (I) and (III) and midway between sofa and half-chair in molecule (II). The asymmetry parameters of these rings are $\Delta C_2(\mathrm{I}) = 0.7°$, $\Delta C_2(\mathrm{II}) = 15.1°$, $\Delta C_s(\mathrm{II}) = 14.1°$ and $\Delta C_2(\mathrm{III}) = 2.5°$. The chlorophenyl and imide rings are planar in molecule (I) and the angle between their planes is 76.7°. The imide ring is not planar in molecule (II) and the dihedral angle between its best plane and the phenyl-ring plane is 84.1°. The imide and phenyl rings in molecule (III) are nearly planar but are more corrugated than in molecule (I). Bond distances, angles

and conformations of the three independent molecules are compared with those of molecules of DTTHP (3,6-dithia-3,4,5,6-tetrahydrophthalimide) and N-(4-chlorophenyl)-3,6-dithiacyclohexene-1,2-dicarboximide.

Introduction

The present work is part of a study of N-substituted derivatives of 3,6-dithiacyclohexene-1,2-dicarboximide (Bukowska-Strzyżewska, Dobrowolska & Pniewska, 1978; Bukowska-Strzyżewska & Pniewska, 1979). These compounds, which are related to thalidomide, show pharmacological activity which can be related to their stereochemistry. The atom-numbering system of the title compound is shown below.
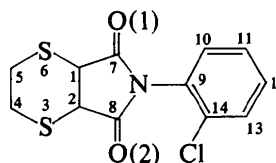
The aim of this work was to obtain new data concerning the conformation of the 3,6-dithiacyclohexene ring and to determine the influence of the 2-chlorophenyl substituent on the conformation of the imide ring and the spatial shape of the molecule.

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