PREPARATION, PROPERTIES AND STRUCTURE OF DIHALOGENOBIS(N,N-DI-\textit{n}-BUTYLDITHIOCARBAMATO) COMPLEXES OF PALLADIUM AND PLATINUM

BY

J. WILLEMSE, J. A. CRAS, J. G. WIJNHOVEN and P. T. BEURSKENS

(Laboratory for Inorganic Chemistry and Crystallography, University of Nijmegen, Toernooiveld, Nijmegen, The Netherlands)

The preparation and properties of $M(Bu_2dtc)_2X_2$ ($M = \text{Pd, Pt}$ and $X = \text{Br, I}$) are reported. From the platinum complexes two isomers were isolated. The crystal structure of the cis-isomer of $Pt(Bu_2dtc)_2I_2$ is determined by a three-dimensional X-ray analysis. The orthorhombic cell, space group Fddd, with $a = 33.37(3)$, $b = 34.16(3)$, $c = 20.19(2)$ Å and $V = 23010(40)$ Å$^3$ contains 32 formula units. Atomic parameters were refined to a conventional $R$ value of 0.073 for 1417 independent non-zero reflections. The platinum atom is distorted octahedrally coordinated by two iodine and four sulfur atoms with average distances of $\text{Pt} - \text{I} = 2.66$ and $\text{Pt} - \text{S} = 2.35$ Å. The intra- and one of the intermolecular I-I distances (resp. 3.79 and 3.37 Å) are short compared with an I-I Van der Waals contact.

ESCA spectra show the other isomer to be a Pt(IV) complex too. NMR data suggest a trans-structure for this isomer.

With $Bu_4tds$ these complexes yield $M(Bu_2dtc)_3X$ ($M = \text{Pt, Pd}$ and $X = \text{Br, I}$) of which some properties are given.

Introduction

During our investigations on the oxidation of $Ni(Bu_2dtc)_2$ with halogens we found the reactions:

[1] $2 \text{Ni}(Bu_2dtc)_2 + I_2 \longrightarrow 2 \text{Ni}(Bu_2dtc)_2I$ (at $-30^\circ C$)$^1$.

[2] $3 \text{Ni}(Bu_2dtc)_2 + 2 X_2 \longrightarrow 2 \text{Ni}(Bu_2dtc)_3X + \text{NiX}_2$ ($X = \text{Cl, Br}$) (at $20^\circ C$)$^2$.

[3] $3 \text{Ni}(Bu_2dtc)_2 + 5 I_2 \longrightarrow 2 \text{Ni}(Bu_2dtc)_3I_4 + \text{NiI}_2$ (at $20^\circ C$)$^3$.

---


Nigo et al.\textsuperscript{4} described a product Ni(Et\textsubscript{2}dtc)\textsubscript{2}Br\textsubscript{2} resulting from the reaction of Ni(Et\textsubscript{2}dtc)\textsubscript{2} and Br\textsubscript{2}. However, reproducing their experiments we always found Ni(R\textsubscript{2}dtc)\textsubscript{3}Br for R = Et as well as for R = Bu. Furthermore, in addition to reaction [1] we neither succeeded in preparing the iodine compound Ni(Bu\textsubscript{2}dtc)\textsubscript{2}I\textsubscript{2}.

To extend the information about the redox behaviour of the dithiocarbamates of the nickel group metals we now report the direct halogenation of Pd(Bu\textsubscript{2}dtc)\textsubscript{2} and Pt(Bu\textsubscript{2}dtc)\textsubscript{2}. The investigations revealed the products to have the stoichiometry M(Bu\textsubscript{2}dtc)\textsubscript{2}X\textsubscript{2} (M = Pd, Pt; X = Br, I). Attempts to prepare compounds of the type M(Bu\textsubscript{2}dtc)\textsubscript{2}X failed. Neither did we succeed in obtaining M(Bu\textsubscript{2}dtc)\textsubscript{3}X by direct halogenation. The latter compounds, however, can be prepared by the reaction of M(Bu\textsubscript{2}dtc)\textsubscript{2}X\textsubscript{2} with Bu\textsubscript{4}tds.

\section*{Experimental section}

As starting materials for the preparation of the compounds K\textsubscript{2}PdCl\textsubscript{4} and K\textsubscript{2}PtCl\textsubscript{4} (Drijfhout) were used. M(Bu\textsubscript{2}dtc)\textsubscript{2} was synthesized following the general procedure described by Thorn and Ludwig\textsuperscript{5}, using commercial CS\textsubscript{2} (Brocades) and Bu\textsubscript{2}NH(BDH). Bu\textsubscript{4}tds was commercially available (Fluka).

\textit{Analyses.} The C, H and N analyses were carried out in the micro analytical department of this university. Pd and Pt were analysed by atomic absorption spectrophotometry using aqua regia solutions of the metals as standards.

\textit{Spectra.} Infrared spectra in the 4000–625 cm\textsuperscript{-1} region were measured on a Perkin-Elmer 257 infrared spectrophotometer in KBr pellets. The spectra in the 700–200 cm\textsuperscript{-1} region were measured on a Hitachi – EPI – L instrument in CsI disks.

\textit{Magnetic susceptibility} was measured with a standard Gouy type balance.

\textit{Electrical conductivity} measurements were performed with a Metrohm Konduktoskop E 365 and a Philips PR 9510/00 conductivity cell at 25°C. The nitrobenzene was purified by freezing and vacuum distillation.

\section*{Preparation of the complexes}

\textit{Pd(Bu\textsubscript{2}dtc)\textsubscript{2}I\textsubscript{2}}

To a solution of 1 Mole of Pd(Bu\textsubscript{2}dtc)\textsubscript{2} in diethyl ether, cooled to \textdegree 10°C, 1 Mole of iodine in the same solvent, equally cooled to \textdegree 10°C, was added slowly with stirring. After 15 minutes, the reddish black precipitate was filtered off, washed with diethyl ether and dried.

cis-\(\text{Pt}(\text{Bu}_2\text{dtc})_2\text{I}_2\)

Equimolar amounts of \(\text{Pt}(\text{Bu}_2\text{dtc})_2\) and iodine, dissolved in diethyl ether were dropped slowly together at room temperature with stirring. A dark red product was obtained after evaporation of part of the solvent.

trans-\(\text{Pt}(\text{Bu}_2\text{dtc})_2\text{I}_2\)

Upon addition of a solution of iodine in diethyl ether all at once to an equimolar etheral solution of \(\text{Pt}(\text{Bu}_2\text{dtc})_2\), a brown precipitate was obtained immediately.

trans-\(\text{Pt}(\text{Bu}_2\text{dtc})_2\text{Br}_2\), trans-\(\text{Pt}(\text{Bu}_2\text{dtc})_2\text{IBr}\)

Using bromine or iodobromine\(^6\) instead of iodine, the same procedure as for the preparation of trans-\(\text{Pt}(\text{Bu}_2\text{dtc})_2\text{I}_2\) was followed. Yellow orange trans-\(\text{Pt}(\text{Bu}_2\text{dtc})_2\text{Br}_2\) and brown trans-\(\text{Pt}(\text{Bu}_2\text{dtc})_2\text{IBr}\) were obtained, respectively.

cis-\(\text{Pt}(\text{Bu}_2\text{dtc})_2\text{Br}_2\), cis-\(\text{Pt}(\text{Bu}_2\text{dtc})_2\text{IBr}\)

By recrystallisation of the trans-isomers from a chloroform-ether mixture, cis-\(\text{Pt}(\text{Bu}_2\text{dtc})_2\text{Br}_2\) and cis-\(\text{Pt}(\text{Bu}_2\text{dtc})_2\text{IBr}\) were obtained respectively.

\(\text{Pd}(\text{Bu}_2\text{dtc})_2\text{I}_3\)

To a saturated solution of 1 Mole of \(\text{Pd}(\text{Bu}_2\text{dtc})_2\text{I}_2\) in diethyl ether a solution of 1.3 Moles of \(\text{Bu}_4\text{tds}\) in the same solvent was added. After stirring, the reaction mixture was left standing to crystallize. Partial evaporation might be necessary. Brown crystals were obtained.

\(\text{Pt}(\text{Bu}_2\text{dtc})_3\text{Br}\)

1.2 Moles of \(\text{Bu}_4\text{tds}\) in chloroform were added to a solution of 1 Mole of \(\text{Pt}(\text{Bu}_2\text{dtc})_2\text{Br}_2\) (cis- or trans-isomer) in chloroform. After 10 hours of refluxing the mixture was cooled to room temperature and diethyl ether was added in such a quantity that precipitation just starts. The mixture was left standing to crystallize. A yellow precipitate was obtained.

\(\text{Pt}(\text{Bu}_2\text{dtc})_3\text{I}_3\)

When cis- or trans-\(\text{Pt}(\text{Bu}_2\text{dtc})_2\text{I}_2\) was used instead of \(\text{Pt}(\text{Bu}_2\text{dtc})_2\text{Br}_2\) the light brown triiodide compound was obtained analogous to the bromine compound.

\(\text{Pt}(\text{Bu}_2\text{dtc})_3\text{Cl}\)

To a solution of 2 Moles of \(\text{Bu}_4\text{tds}\) in hot acetone a solution of 1 Mole of \(\text{K}_2\text{PtCl}_4\) in water was added. The clear red solution was evaporated until precipitation occurred. After filtering and washing with water and diethyl ether, recrystallisation from an alcohol-diethyl ether mixture yielded a pure yellow coloured product.

¡ mMole of Pt(Bu$_2$dtc)$_3$I$_3$ (solid) was refluxed for 3 hours with 120 ml of 35% ammonia solution. The colour changed from brown to yellow. The precipitate was filtered and dried.$^7$

**Results and discussion**

As the complexes Pd(Bu$_2$dtc)$_2$X$_2$ (X = Br, I) are less stable in solution than the platinum analogues, most of the investigations were carried out on the latter compounds.

The reaction ofPt(Bu$_2$dtc)$_2$ with I$_2$ yields two products: a brown complex immediately precipitated when both reagents in diethyl ether were added together all at once with stirring, and a red product after evaporation of the solvent when the iodine solution was added dropwise to the Pt(Bu$_2$dtc)$_2$ solution. The brown complex was converted into the red compound when dissolved in chloroform and reprecipitated with diethyl ether. Both products were diamagnetic, their composition is the same, but they have different infrared spectra. The ESCA spectra of both compounds are identical and show only one absorption band to be present at the S(2$p^+$, 2$p^-$) binding energy of 165 eV, somewhat broadened due to the unresolved 2$p^+$ and 2$p^-$ absorption. In a thuram disulfide complex Bu$_4$tdsHgCl$_2$$^8$ two resolved peaks are present (164, 165 eV) due to the S atoms with two different environments. In Pt(Bu$_2$dtc)$_2$ one band is found at 164 eV.

In the region of S(2$s$) ejection energy the same pattern is found. From those spectra we can conclude that in our products dithiocarbamate is present as a ligand and not thuram disulfide. This is confirmed by the ESCA spectra recorded in the region of the Pt(4$f_{5/2}$, 4$f_{7/2}$) binding energy show absorptions at 79.3 and 76.0 eV compared with 77.0 and 73.6 eV for Pt(Bu$_2$dtc)$_2$, so oxidation of the metal has occurred.

Molecular weight measurement of Pt(Bu$_2$dtc)$_2$I$_2$ in chloroform solution at 37°C gives a value of 862, whilst 857 is the theoretical value for the monomer. In nitrobenzene a non-electrolyte character was found. Only the red product is stable in solution, so the latter measurements give merely information about this compound. X-ray crystallographic analysis of the red product showed this complex to be cis-Pt(Bu$_2$dtc)$_2$I$_2$.

---

$^7$ Tables of the elemental analyses of the compounds investigated, as well as the atomic parameters, structure factors and bond distances and angles within the two symmetry independent dithiocarbamato ligands of cis-Pt(Bu$_2$dtc)$_2$I$_2$ are available on request.

The NMR spectra were consistent with this result. The cis-position of the dithiocarbamato ligands causes a magnetically different environment for the protons and hence a splitting of the NMR signals at sufficiently low temperatures. This effect is greatest in the multiplet of the proton group adjacent to the nitrogen atom. At a temperature of 37°C in CDCl₃ solutions the absorptions of this group show two partly overlapping triplets, which overlap is complete at high temperature. When a solution of the brown product in CDCl₃ is prepared at 0°C and the spectrum is recorded at once at the same temperature, only one triplet of the N-bonded methylene protons is observed. After some minutes, however, splitting of this triplet becomes visible and after some hours the spectrum is completely transformed into that of cis-Pt(Bu₂dtc)₂I₂. This leads to the conclusion that the brown product is a trans-isomer as the protons have the same magnetical environment. This isomer is unstable and in chloroform the more stable cis-isomer is formed. The transition rate is temperature-dependent. A more detailed NMR study is in progress and will be dealt with in a forthcoming publication.

No Raman spectra could be obtained due to the strong absorption of the complexes. The infra-red spectra differ especially in the 700–200 cm⁻¹ range. The cis-product shows two strong absorption bands in the C–S region (626 and 604 cm⁻¹) and two very strong absorptions in the Pt–S region (369 and 344 cm⁻¹), whereas the trans-isomer has one C–S frequency at 628 cm⁻¹ (very strong) and Pt–S frequencies at 366 cm⁻¹ (very strong) and 329 cm⁻¹ (medium). The C–N stretching frequencies of both isomers show no significant difference (1523 and 1520 cm⁻¹ for the cis- and trans-isomer, respectively).

The isolation of trans-Pt(Bu₂dtc)₂I₂ seems to be possible only due to the slight solubility of the compound in diethyl ether. This insolubility suggests a chain structure arising from insertion of iodine molecules between the planar Pt(Bu₂dtc)₂ units. Furthermore, it was possible to isolate the bromine analogues and Pt(Bu₂dtc)₂IBr. The trans-isomer of these complexes is more stable than trans-Pt(Bu₂dtc)₂I₂ and the cis-isomer could be best obtained by recrystallisation of the trans-modification. Pt-Br frequencies were observed at 237 cm⁻¹ for both cis- and trans-Pt(Bu₂dtc)₂Br₂ and at 217 cm⁻¹ for cis- as well as trans-Pt(Bu₂dtc)₂IBr.

\[ M(Bu₂dtc)₃X \quad (M = Pd, Pt \text{ and } X = Cl, Br, I, I₃) \]

With excess of Na(Et₂dtc) the complexes M(Bu₂dtc)₂I₂ give exchange and reduction reactions when refluxed in ethanol and M(Et₂dtc)₂ is obtained. Bu₄tds was detected in the reaction mixture. The same phenomenon was found with the complexes M(Bu₂dtc)₃I₃ (mentioned
which give also M(Et₂dtc)₂ and Bu₄tds upon refluxing with Na(Et₂dtc) in ethanol.

To obtain the trisdithiocarbamato complexes the dihalogenobisdithiocarbamato complexes have to be treated with thiuram disulfide. The reaction of K₂PtCl₄ with Bu₄tds resulting in Pt(Bu₂dtc)₃Cl could proceed via Pt(Bu₂dtc)₂Cl₂, although this intermediate was never detected.

From the reaction of Pt(Bu₂dtc)₃I₃ with ammonia solution Pt(Bu₂dtc)₃I was obtained, whereas the same reaction with Pd(Bu₂dtc)₃I₃ resulted in Pd(Bu₂dtc)₂.

The properties of the trisdithiocarbamato-complexes are the same as those prepared from M(Bu₂dtc)₂ (M = Pd, Pt) with CuBr₂(Bu₂dtc) or Bu₄bitt²⁺⁺Cu₂Br₂⁻⁻⁹, which were reported earlier¹⁰. Pd(Bu₂dtc)₃I₃ decomposed too fast in solution to perform measurements in solution. The platinum complexes are 1:1 electrolytes in nitrobenzene. The values of Λ₀ together with the experimental and calculated slopes A exp and A calc as given by the Onsager limiting law Λ = Λ₀ − Λ √c are given in Table I.

The values for λ⁺⁺ calculated from the known value of λ⁻⁻ (Cl⁻, Br⁻, I⁻) show good agreement with each other but are higher than those of Ni(Bu₂dtc)₃⁺⁺ (λ⁺⁺ = 3.5 Ω⁻¹ cm² ion⁻¹)¹. In view of the normal error in these measurements this discrepancy seems to be significant, no explanation, however, can be given.

<table>
<thead>
<tr>
<th>X⁻</th>
<th>Λ₀</th>
<th>λ⁻⁻</th>
<th>λ⁺⁺</th>
<th>A exp</th>
<th>A calc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl⁻</td>
<td>29.4</td>
<td>22.7¹¹</td>
<td>6.7</td>
<td>66</td>
<td>68</td>
</tr>
<tr>
<td>Br⁻</td>
<td>28.8</td>
<td>21.9¹¹</td>
<td>6.9</td>
<td>66</td>
<td>67</td>
</tr>
<tr>
<td>I⁻</td>
<td>28.3</td>
<td>21.3¹¹</td>
<td>7.0</td>
<td>67</td>
<td>67</td>
</tr>
<tr>
<td>I₃⁻</td>
<td>27.3</td>
<td>20.4</td>
<td>6.9</td>
<td>71</td>
<td>66</td>
</tr>
</tbody>
</table>

¹ Bu₄bitt²⁺: 3,5-bis(N,N-di-n-butyliminimum)-1,2,4-trithiolane ion (see ref. 10).
Molar weight measurements of Pt(Bu₂dtc)₃Cl and Pt(Bu₂dtc)₃I₃ in chloroform at 37°C are in agreement with the 1:1 electrolyte character of these complexes, the value found is half of the calculated molecular weight Pt(Bu₂dtc)₃Cl: found 445, calc 844; Pt(Bu₂dtc)₃I₃: found 595, calc 1180.

The compounds were expected to be diamagnetic. Measurements however show the same features as the complexes with CuCl₂, CuBr₂ and AuBr₂. A temperature independent paramagnetism of which the value is rather high for a TIP term¹⁰. Values of χₘ₀ in cgs units are given in Table II.

Table II

<table>
<thead>
<tr>
<th>Compound</th>
<th>χₘ₀ in cgs units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd(Bu₂dtc)₃I₃</td>
<td>1209 × 10⁻⁶</td>
</tr>
<tr>
<td>Pt(Bu₂dtc)₃Cl</td>
<td>1847 × 10⁻⁶</td>
</tr>
<tr>
<td>Pt(Bu₂dtc)₃I</td>
<td>1191 × 10⁻⁶</td>
</tr>
<tr>
<td>Pt(Bu₂dtc)₃I₃</td>
<td>860 × 10⁻⁶</td>
</tr>
</tbody>
</table>

The NMR spectra are completely analogous to those of Pt(Bu₂dtc)₃CuCl₂¹⁰. The infrared spectra in the region 700–200 cm⁻¹ show the M—S stretching bands at the same place as the earlier reported M(Bu₂dtc)₃⁺ complexes. For a discussion about those frequencies we refer to this article¹⁰.

Table III

<table>
<thead>
<tr>
<th>Compound</th>
<th>C—N stretching frequencies in cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>M(Bu₂dtc)₃Cl</td>
<td>1538³</td>
</tr>
<tr>
<td>M(Bu₂dtc)₃Br</td>
<td>1538³</td>
</tr>
<tr>
<td>M(Bu₂dtc)₃I</td>
<td>1529³</td>
</tr>
<tr>
<td>M(Bu₂dtc)₃I₃</td>
<td>1525</td>
</tr>
<tr>
<td>[M(Bu₂dtc)₃]₂Cu₂Cl₆</td>
<td>1525¹⁰</td>
</tr>
<tr>
<td>M(Bu₂dtc)₃CuCl₂</td>
<td>1531¹⁰</td>
</tr>
<tr>
<td>[M(Bu₂dtc)₃]₂Cu₂Br₆</td>
<td>1525¹⁰</td>
</tr>
<tr>
<td>M(Bu₂dtc)₃CuBr₂</td>
<td>1537¹⁰</td>
</tr>
<tr>
<td>M(Bu₂dtc)₃AuBr₂</td>
<td>1531¹⁰</td>
</tr>
</tbody>
</table>
In Table III the C—N stretching frequencies of the \( M(\text{Bu}_2\text{dtc})_3^+ \) complexes, prepared so far, are given. There is a significant increase as compared with the C—N stretching frequencies of \( M(\text{Bu}_2\text{dtc})_2 \) (\( M = \text{Ni} \) 1515 cm\(^{-1}\) (solid), 1502 (soln.); \( M = \text{Pd} \) 1502 (solid), 1504 (soln.); \( M = \text{Pt} \) 1527 (solid), 1510 (soln.)). This can be explained in view of the greater participation of the lone pair on the nitrogen atom in the \( \pi \)-bonding of the C—N bond, and therefore a shortening of the C—N distance, caused by the increase of the formal oxidation state of the central metal from +2 to +4.

Effects of the counter ion are present in that the frequency decreases with a greater anion.

Crystal structure determination of \( \text{cis-Pt}(n-\text{Bu}_2\text{dtc})_2\text{I}_2 \)

Crystal data

\text{Bis(}N,N\text{-di-}n\text{-butyldithiocarbamato)platinum(IV) di-iodide, Pt-} \ \text{(Bu}_2\text{dtc})_2\text{I}_2, \ F.W. = 857.6, \text{ crystallizes as very thin, dark red needles elongated along } c. \text{ The crystals are orthorhombic, space group Fddd, with } \text{ } a = 33.37(3), \text{ } b = 34.16(3) \text{ and } c = 20.19(2) \, \text{Å, } V = 23010 \, \text{Å}^3. \text{ The calculated density (1.98 g cm}^{-3} \text{ with } Z = 32) \text{ is in agreement with the measured value (1.95 g cm}^{-3} \text{), determined by the flotation method.}

A crystal of approximate dimensions 0.04 x 0.1 x 0.5 mm\(^3\) was mounted with the needle axis along the \( \phi \)-axis of a Nonius automatic diffractometer. Intensity data were measured with Zr-filtered Mo-radiation using the moving-counter moving-crystal method with a scan speed of 10° min\(^{-1}\). After every 10 reflections a reference reflection was measured to allow corrections to be made for slow fluctuations in the measuring performance. Of the 2707 independent reflections theoretically attainable within the limit \( \Theta = 20^\circ \), 1417 reflections were used for the structure determination.

Absorption corrections (linear absorption coefficient \( \mu = 75.85 \, \text{cm}^{-1} \)) were calculated by the Busing and Levy\(^{12} \) procedure, using \( 6 \times 6 \times 12 \) volume components and 6 accurately located boundary planes. The minimum and maximum absorption factors in the intensities were 1.29 and 2.11, respectively. Lorentz and polarisation corrections were performed in the usual way.

---


**Structure Determination**

The positions of the platinum, iodine and sulfur atoms were determined from a sharpened three-dimensional Patterson function. A subsequent difference Fourier synthesis gave the positions of the remaining non-hydrogen atoms. The positional, isotropic and anisotropic (Pt and I) vibrational parameters and the scaling factor were refined by full-matrix least-squares methods. The function that was minimized was $w(|F_o| - |F_c|)^2$ with $w = (\sigma^2(F_o) + (0.05 |F_o|)^2)^{-1}$, $\sigma^2(F_o)$ being calculated from counting statistics\(^\text{13}\).

The atomic scattering factors were corrected for the anomalous scattering component ($\Delta f$) using data from the International Tables\(^\text{14}\).

Refinement of the positional and vibrational parameters of the butyl-carbon atoms led to improbable bond distances and angles. According to our experience with similar structures we presume the butyl chains to be disordered. The most probable positions of the last three carbon atoms of the butyl chains were found from a new difference Fourier synthesis. Two cycles of least-squares refinement, holding this atomic positions fixed with $B = 6.0 \, \text{Å}^2$, reduced the occupancy factors from 1.0 to 0.5 for the greater part of these atoms. This procedure reduced the conventional R-value to 0.073. Attempts to find other butyl chains from the final difference Fourier synthesis failed. We therefore presume that the positions of the butyl carbon atoms as listed\(^7\) give the most probable situation of the butyl chains in this structure. Parameter shifts in the last refinement cycle were less than 0.5 e.s.d. The final difference Fourier map showed some maxima of about 1.3 $\text{eÅ}^{-3}$ around the heavy atoms and 1.0 $\text{eÅ}^{-3}$ in the neighbourhood of the butyl chains.

**Description of the Structure**

The positional parameters of the most important atoms are given in Table IV. The coordination of the platinum is illustrated in Figure 1. Some bond angles and distances are given in Figure 2. The crystal structure analysis revealed the compound to be $\text{cis-Pt}($Bu$_2$dtc)$_2$I$_2$. The platinum atom is in distorted octahedral coordination with two iodine and four sulfur atoms.

---


Fig. 1. Projection of two molecules of cis-Pt(Bu₂dtc)₂I₂ along the c-axis (omitting the butyl chains). The positions of a twofold axis, a twofold screw axis and one iodine atom of a third molecule are shown.

Fig. 2. Bond angles (degrees) and distances (Å) with e.s.d.'s of the cis-Pt(Bu₂dtc)₂I₂ (omitting the butyl chains).

The following angles are not given in the figure:
I(1)-Pt-S(1) (90.9 ± 3°), I(1)-Pt-S(2) (94.4 ± 3°), I(2)-Pt-S(3) (95.3 ± 3°), I(2)-Pt-S(4) (90.1 ± 3°), S(1)-Pt-S(3) (96.2 ± 4°) and S(2)-Pt-S(4) (97.2 ± 4°).

The intramolecular I(1)-I(2) distance (3.787 ± 0.005 Å) is intermediate between the length of an I—I bond (2.68 Å) in I₂ and an I—I van der Waals contact (4.30 Å), suggesting a three center bond PtI₂.
One of the intermolecular I—I distances \([I(1)-I(1') = 3.729 \pm 0.004 \text{ Å}]\) also is very short compared with the normal van der Waals contact, indicating weak intermolecular binding. Such pairs of molecules are connected by normal van der Waals contacts \([I(2')-I(2'') = 4.394 \pm 0.005 \text{ Å}]\), forming a helix of iodine atoms as shown in Figure 1.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Pt</th>
<th>0.25399(5)</th>
<th>0.23179(4)</th>
<th>0.25643(7)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I(1)</td>
<td>0.2553(1)</td>
<td>0.1708(1)</td>
<td>0.1752(2)</td>
<td></td>
</tr>
<tr>
<td>I(2)</td>
<td>0.3178(1)</td>
<td>0.2044(1)</td>
<td>0.3211(2)</td>
<td></td>
</tr>
<tr>
<td>S(1)</td>
<td>0.2078(3)</td>
<td>0.2637(3)</td>
<td>0.1886(6)</td>
<td></td>
</tr>
<tr>
<td>S(2)</td>
<td>0.2911(3)</td>
<td>0.2724(3)</td>
<td>0.1853(5)</td>
<td></td>
</tr>
<tr>
<td>S(3)</td>
<td>0.2064(3)</td>
<td>0.2040(3)</td>
<td>0.3291(5)</td>
<td></td>
</tr>
<tr>
<td>S(4)</td>
<td>0.2433(3)</td>
<td>0.2780(3)</td>
<td>0.3406(5)</td>
<td></td>
</tr>
<tr>
<td>C(1)</td>
<td>0.246(1)</td>
<td>0.287(1)</td>
<td>0.158(2)</td>
<td></td>
</tr>
<tr>
<td>C(2)</td>
<td>0.210(1)</td>
<td>0.246(1)</td>
<td>0.375(2)</td>
<td></td>
</tr>
<tr>
<td>N(1)</td>
<td>0.242(1)</td>
<td>0.313(1)</td>
<td>0.111(2)</td>
<td></td>
</tr>
<tr>
<td>N(2)</td>
<td>0.189(1)</td>
<td>0.255(1)</td>
<td>0.425(2)</td>
<td></td>
</tr>
</tbody>
</table>

Acknowledgements

The authors are grateful to Dr. P. Biloen of the Koninklijke/Shell Laboratory for recording the ESCA spectra, to Dr. J. H. Noordik for measuring the X-ray intensity data and to Prof. J. J. Steggerda for his continuous interest.

(Received June 7th, 1973)