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# Tetrakis(imidazole)platinum(II) Bis(triiodides). The Crystal and Molecular Structure of Tetrakis(1,2-dimethylimidazole)platinum(II) Bis(triiodide)

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*The synthesis, characterisation and structure of compounds with formula* $Pt(ligand)_4I_6$ *is described, in which the ligands are 1-methylimidazole, 2-methylimidazole and 1,2-dimethylimidazole (DMIz). Upon treatment of acidic solutions containing the* $Pt(ligand)_4^{2+}$ *cations, with a large excess of aqueous KI, invariably precipitates of the above formula result. Infrared and NMR spectra of the compounds in organic solvents agree with the presence of* $Pt(ligand)_4^{2+}$ *cations, whereas polyiodide anions are suggested from far-IR spectra (solid state) and visible spectra* ($CH_3CN$ *solution). To understand the poor solubility in aqueous solution (other* $Pt(ligand)_4^{2+}$ *compounds, with Cl, Br, I,* $ClO_4$ *anions, are very soluble) the structure of one of these mutually similar compounds was solved with the aid of single-crystal X-ray diffraction.* $Pt(DMIz)_4I_6$ *crystallizes in the monoclinic space group* $P2_1/c$ *with two formula units in a unit cell of dimensions* a = 9.376(3), b = 19.849(6) *and* c = 10.387(3) Å, $\beta$ = 113.25(3)°. *The structure has been determined by the heavy-atom method, using both Pt and I in the starting model, and refined by least-squares techniques to* $R = 0.035$ *and* $R_w = 0.040$ *for 3615 reflections. It consists of discrete* $Pt(1,2\text{-}DMIz)_4^{2+}$ *and* $I_3^-$ *ions. The Pt(II) is square planar coordinated by the four 1,2-DMIz ligands, with Pt–N distances of 2.009(8) and 2.014(5) Å and a N–Pt–N angle of 88.6(3)°. Two of the four DMIz ligands occur in two unequally-occupied disordered positions (72% and 28%), which do not influence the crystal packing. The I–I distances in the* $I_3^-$ *ion are 2.856(1) and 3.005(1) Å, whereas the I–I–I angle is 177.71(3)°. There are no unusual, short intermolecular contacts between the cations and the anions, and between the anions and I atoms from other anions.*

## Introduction

Coordination of Platinum by imidazole type ligands has recently obtained increased interest, due to the fact that Platinum anti-tumour compounds, such as *cis*-$Pt(NH_3)_2Cl_2$, are known to react in a specific manner with the imidazole N(7)-atom in guanosine [1–5]. Recent research from this laboratory has determined that many well-defined coordination compounds of Platinum salts and substituted imidazoles exist [6–8]. During these investigations very insoluble products were obtained, analysing as $Pt(ligand)_4(I)_6$, with the ligands 1-methylimidazole (NMIz), 2-methylimidazole (2MIz) and 1,2-dimethylimidazole (DMIz). Because the details of the structure of the $Pt(ligand)_4^{2+}$ with $I_3^-$, were not *a priori* clear, a detailed investigation, including vibrational spectra, electronic spectra, conductivities, NMR-spectra and X-ray diffraction was undertaken. The results are described in this paper with special attention to the three-dimensional structure of $Pt(1,2\text{-}DMIz)_4(I_3)_2$.

## Experimental

### Starting Products

N-methylimidazole (NMIz), 2-methylimidazole (2-MIz) and 1,2-dimethylimidazole (DMIz) were obtained commercially and were used without further purification. $K_2PtCl_4$ was used as commercially obtained and converted to the iodide compounds as described previously [6, 7].

### Synthesis

Three different synthetic pathways appeared possible for the preparation of the compounds $PtL_4$-

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$I_6$. The synthesis in case of L = NMIz will be given as an example. Originally, $Pt(NMIz)_4I_2$ (prepared according to ref. 6) was dissolved in water and treated with an excess of KI, followed by acidification to pH = 1 using 2 *M* HCl. After a few days standing in the open air, dark brown needles were formed, which after washing with water and drying *in vacuo,* analysed as $Pt(NMIz)_4I_6$. The same compounds could be obtained when $Pt(NMIz)_4I_2$ in water was treated with KI to which 2 equivalents of $I_2$ were added. Then immediately brown precipitates were formed. Because it was initially assumed that a Pt(IV) compound was present, a synthetic attempt starting from *cis*-$Pt(NMIz)_2I_4$ was undertaken. A hot solution of this compound in DMF in the presence of an excess of NMIz was treated with cold water, upon which a brown precipitate analysing as $Pt(NMIz)_4I_6$ was formed. The first two methods yield similar products in case of DMIz and 2MIz as ligands. The third method could only be applied in case of NMIz. Recrystallisation from a mixture of acetone and toluene proved to be useful in obtaining crystalline precipitates in case of DMIz and NMIz.

### *Crystal Structure and Molecular Geometry*

*Crystal data.* $C_{20}H_{32}N_8I_6Pt$, $M$ = 1340.99, Monoclinic $a$ = 9.376(3), $b$ = 19.849(6), $c$ = 10.387(3) Å, $\alpha$ = 113.25(3)°. $U$ = 1776.1 Å$^3$, $Z$ = 2, $D_c$ = 2.507 g cm$^{-3}$, $D_m$ = 2.49(2) g cm$^{-3}$, $F_{000}$ = 1208, $\lambda$(Mo-K$\alpha$) = 0.71069 Å, $\mu$ (Mo-K$\alpha$) = 94.5 cm$^{-1}$, space group $P2_1/c$.

### *Intensity Data Collection*

A suitable specimen, a needle-shaped crystal measuring approximately 0.54 X 0.24 X 0.15 mm, was mounted on a SYNTEX $P2_1$ Four-Circle Diffractometer with a scintillation counter and a graphite monochromator (parallel). X-ray intensity data of 3888 unique reflections were measured in the $\theta-2\theta$ scan mode, up to $(\sin\theta)/\lambda$ = 0.64 Å$^{-1}$, 3615 of which with $I \geqq 1.96\sigma(I)$ were used for the structure determination. Accurate cell parameters and the orientation matrix were determined from a least-squares treatment of the angular settings of 15 high-order reflections.

The scan speed depended upon the intensity, *i.e.* 4° min$^{-1}$ below 150 cps to 30° min$^{-1}$ above 1500 cps. Stationary background measurements were taken at each side of the scan range, with a ratio of 0.5 for each background time to the scan time. After every 100 reflections a standard reflection was measured to check for misorientation and radiation damage. No radiation damage was observed. The intensity data were empirically corrected for absorption, using $\psi$ scans around the diffraction vectors of 12 selected reflections.

### *Structure Determination and Refinement*

The intensity data were corrected for Lorentz and polarisation effects. The structure was solved by means of a three-dimensional Patterson synthesis, using Pt and the $I_3^-$ ion as a heavy-atom starting model. During the location of the light atoms from difference Fourier maps it became apparent that one of the two independent DMIz ligands in the asymmetric unit is disordered over two orientations which are related to each other by an approximate mirror plane roughly in the ab plane. The site occupancy factors for both orientations were refined to be 0.72(1) and 0.28(1). Whereas for the ordered ligand 1, as for Pt and the I atoms, all C and N atoms could be refined with anisotropic temperature factors, stable refinement for the split atoms in the partially occupied ligands 2 and 3 was only possible with an isotropic model. The positions of hydrogen atoms bonded to the aromatic C atoms were fixed at coordinates calculated from the carbon coordinates to which they are attached. The conformations of the methyl groups in ligand 1 were derived from information about the H-atom positions from difference-Fourier syntheses. The methyl hydrogens in the disordered ligands 2 and 3 could not be located. All H-atoms were included in the structure factor calculations (assuming C–H distances of 0.95 Å and U values of 0.05 Å$^2$), but were not refined. The standard deviation in the structure factor F is defined as $\sigma(F) = \sigma(I)/2|F_o|\ Lp)$ with the weighting scheme: $1/w = [\sigma(F)]^2 + (0.012|F_o|)^2$. Full-matrix least-squares refinements resulted in final R-factors of R = 0.035 and $R_w$ = 0.040*. A final difference-Fourier map only showed residual densities up to 0.6 e Å$^3$. Programmes used during the refinements are those of the SYNTEX XTL and SHELTXTL systems, used with a Data General Eclipse Computer. Final positional parameters are listed in Table I. Atomic scattering factors for Pt, I, N, C and H were taken from ref. 9. Observed and calculated structure factors, as well as final anisotropic thermal parameters and coordinates for the H atoms are listed in Supplementary Material, deposited with the Editor.

### *Spectroscopic and Analytical Measurements*

Infrared spectra were recorded in pressed KBr discs and also as Nujoll mulls between KBr-plates on a Beckman Acculab Instrument (4000–250 cm$^{-1}$), Far-IR spectra were obtained on a Beckman IR 720 interferometer (500–20 cm$^{-1}$) as pressed discs in polythene. X-ray powder diagrams were

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*The function minimised was $\Sigma w(|F_o| - |F_c|)^2$. The unweighted and weighted residuals are defined as follows: $R = \Sigma(||F_o| - |F_c||)|\Sigma|F_o|$, $R_w = [\Sigma w(|F_o| - |F_c|)^2 \text{-} |\Sigma w F_o^2]^{1/2}$.

TABLE I. Final Refined Coordinates for the Non-hydrogen Atoms in $Pt(DMIz)_4(I_3)_2$ with Estimated Standard Deviations in Parentheses.

| Atom | x/a | y/b | z/c | U |
|---|---|---|---|---|
| Pt | 0 | 0 | 0 | |
| I(1) | 0.23992(6) | 0.10546(3) | 0.46676(5) | |
| I(2) | 0.48208(6) | 0.18365(3) | 0.40806(5) | |
| I(3) | 0.70319(7) | 0.26204(3) | 0.34708(6) | |
| N(11) | −0.0535(6) | −0.0912(3) | 0.0537(5) | |
| C(12) | −0.0152(7) | −0.1166(3) | 0.1800(7) | |
| N(13) | −0.0740(7) | −0.1801(3) | 0.1688(6) | |
| C(14) | −0.1487(8) | −0.1947(3) | 0.0276(7) | |
| C(15) | −0.1355(8) | −0.1400(3) | −0.0417(7) | |
| C(16) | 0.0740(10) | −0.0834(4) | 0.3157(8) | |
| C(17) | −0.0574(10) | −0.2254(4) | 0.2820(8) | |
| N(21)[a] | −0.1857(8) | 0.0419(4) | 0.0190(8) | 156(14) |
| C(22) | −0.3318(11) | 0.0453(5) | −0.0780(10) | 199(18) |
| N(23) | −0.4204(10) | 0.0777(5) | −0.0275(10) | 170(19) |
| C(24) | −0.3310(12) | 0.0994(6) | 0.1066(12) | 304(23) |
| C(25) | −0.1856(20) | 0.0735(9) | 0.1385(19) | 334(47) |
| C(26) | −0.3926(18) | 0.0148(7) | −0.2249(17) | 346(38) |
| C(27) | −0.5849(13) | 0.0958(6) | −0.1066(13) | 291(23) |
| N(31) | −0.2215(27) | 0.0246(13) | −0.0551(26) | 296(48) |
| C(32) | −0.2868(41) | 0.0672(18) | 0.0092(38) | 460(79) |
| N(33) | −0.4414(36) | 0.0711(15) | −0.0698(34) | 365(77) |
| C(34) | −0.4865(36) | 0.0405(16) | −0.1952(33) | 383(67) |
| C(35) | −0.3538(41) | 0.0107(16) | −0.1935(37) | 246(76) |
| C(36) | −0.1891(49) | 0.0883(22) | 0.1386(45) | 293(110) |
| C(37) | −0.5631(44) | 0.1092(19) | −0.0411(43) | 477(82) |

[a] For the disordered atoms N(21) through C(27) (site occupation factor 0.72) and N(31) through C(37) (s.o.f. 0.28) the isotropic temperature factors ($Å^2 \times 10^4$) are given.

TABLE II. Analytical Data, Far-IR Maxima ($cm^{-1}$) and Conductivities in Dimethylformamide of Compounds $Pt(ligand)_4I_6$.

| Compound | Analytical Data | | | Far-IR maxima[b] ($cm^{-1}$) | Conductivity (0.001 *M*) ($S\ cm\ mol^{-1}$) |
|---|---|---|---|---|---|
| | %C obs. calc. | %H obs. calc. | %N obs. calc. | | |
| $Pt(NMIz)_4(I_3)_2$ | 15.1(15.0)[a] | 1.9(1.9) | 8.7(8.7) | 140 vs 110 m | 150 |
| $Pt(2MIz)_4(I_3)_2$ | 14.9(15.0) | 1.9(1.9) | 8.7(8.7) | 140 vs 102 m | 137 |
| $Pt(DMIz)_4(I_3)_2$ | 17.9(18.0) | 2.4(2.4) | 8.4(8.1) | 139 vs 110 m | 144 |

[a] %Pt: 15.3(15.2); %I: 59.2(59.3). Calculated values in parentheses. [b] Only values assigned to $I_3^-$ are listed. Other bands occur at 279 m and 262 w (for NMIz), at 326 $cm^{-1}$ (for 2MIz) and at 326 m and 261 s (for DMIz).

obtained with a Guinier–de Wolff camera using Cu-Kα radiation. The samples were mounted with vaseline. NMR spectra were recorded in DMF-$d_7$ or $CD_3$-OD on a Varian T60 instrument, with TMS as an internal reference. Visible spectra were recorded on a Beckman DK-2A spectrometer (1000–300 nm) using acetonitrile as a solvent. The conductivity of 0.001 *M* solutions was measured with the aid of a Philips PR 9501 conductivity bridge. DMF was used as the solvent.

## Results and Discussion

### *General*

The three compounds are listed in Table II, together with their conductivities in DMF, analytical data and far-IR band maxima.

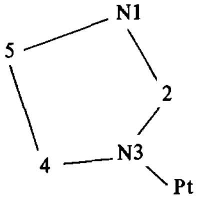
The synthesis of the compounds from $PtL_4I_2$ and KI in acidic medium, appears to occur by slow air oxidation of $I^-$. The generated $I_3^-$ is removed from the system by precipitation with the $PtL_4^{2+}$ ions.

TABLE III. $^1$H NMR Spectra[a] of Compounds Pt(ligand)$_4$(I$_3$)$_2$.

| Compound[b] | H5 | J(Pt–H5) | H4 | J(Pt–H4) | H2 | J(Pt–H2) | N–CH$_3$ |
|---|---|---|---|---|---|---|---|
| Pt(NMIz)$_4$(I$_3$)$_2$ | 7.40 | 7 | 7.03 | 23 | 8.19 | 20 | 3.84 |
| Pt(2MIz)$_4$(I$_3$)$_2$ | 7.10 | 7 | 7.00 | 21 | 2.43[c] | 5 | –[d] |
| Pt(DMIz)$_4$(I$_3$)$_2$ | 7.30 | 9 | 7.30 | 22 | 2.67[c] | 7 | 3.72 |

[a] Spectra are listed with chemical shifts in ppm relative to tetramethyl silane. Coupling constants are given in Hz. [b] Dimethylformamide-d$_7$ was used as the solvent, except for the compound with 2MIz, where CD$_3$OD was used. [c] This is the value for the CH$_3$-group at position 2. [d] No N–CH$_3$ group present.

Ring numbering scheme:



The rapid precipitation when some I$_2$ is added, confirms this mechanism. The synthesis from the Pt(IV) compound in the case of NMIz is quite surprising, and in fact initially suggested the presence of Pt(IV) compounds in the product. Apparently, the following reaction occurs in hot DMF after addition of water: 2 *cis*-Pt(NMIz)$_2$I$_4$ + 4 NMIz $\rightarrow$ Pt(NMIz)$_4$I$_2$ + Pt(NMIz)$_4$I$_6$.

The mechanism of the reaction was not further investigated.

### *Spectroscopic Data and Conductivity*

The conductivity data in DMF (Table II) are in agreement with a 1:2 electrolyte, suggesting the dissociation of the I$_3^-$ ions in this solvent. Infrared spectra show the presence of the ligand absorptions of NMIz, 2MIz and DMIz respectively. Compared to the free ligand absorptions, the shifts in some of the IR bands are similar as found for other Pt compounds with these ligands [6, 7]. Pt(DMIz)$_4$I$_6$ could be obtained in two different modifications, a red brown and a dark brown isomer, with slightly different IR-absorption intensities.

Far-infrared spectra (Table II) show the presence of some ligand bands between 250 and 450 cm$^{-1}$, as well as a very strong absorption around 140 cm$^{-1}$, which can be ascribed to the asymmetric I–I stretching frequency of I$_3^-$ ions [10]. A weaker band at 105–110 cm$^{-1}$ is tentatively assigned to the symmetric stretching of I$_3^-$, which would indicate the presence of asymmetric I$_3^-$ ions in the solid state, as this band is only allowed for unequal I–I bond lengths. No intense Pt–N vibrations could be detected in the far-IR region, which is known to be the case for many other Pt compounds [6, 7].

Proton NMR spectra of the compounds are summarised in Table III. All the signals expected for the respective ligands are found, with the appropriate Pt–H long range couplings. The positions of the resonance lines are almost equal to those of the previously reported Pt–imidazole compounds [6, 7]. The slight shift to lower magnetic field might be due to ion pairing between PtL$_4^{2+}$ and I$_3^-$ in these concentrated solutions, as the shifts are slightly solvent dependent.

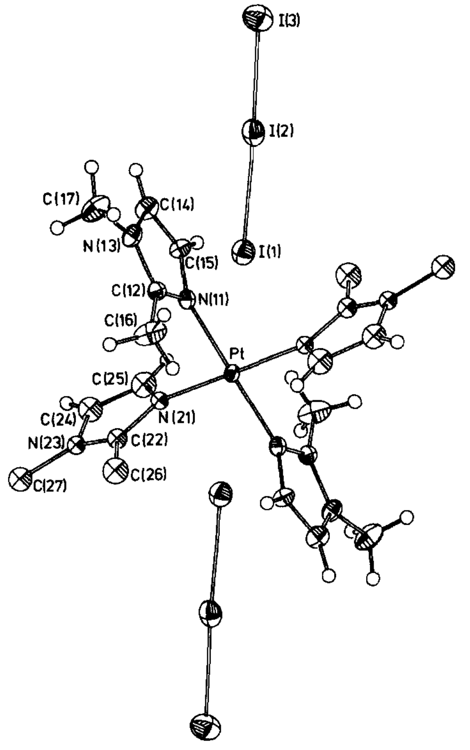


Fig. 1. ORTEP drawing scaled to include 50% probability and showing the labelling scheme for Pt(DMIz)$_4$(I$_3$)$_2$. Methyl hydrogen atoms at C(26) and C(27) are not drawn.

TABLE IV. Bond Distances (A) and Bond Angles (°) in $Pt(DMIz)_4(I_3)_2$ and Relevant Intermolecular Contact Distances (A) and Angles (°).

| Ligand 1 | | Disordered Ligands 2 and 3 | | | |
|---|---|---|---|---|---|
| Pt–N(11) | 2.014(5) | Pt–N(21) | 2.009(8) | Pt–N(31) | 1.99(3) |
| N(11)–C(12) | 1.317(8) | N(21)–C(22) | 1.344(13) | N(31)–C(32) | 1.36(5) |
| C(12)–N(13) | 1.361(9) | C(22)–N(23) | 1.313(14) | C(32)–N(33) | 1.36(5) |
| N(13)–C(14) | 1.384(9) | N(23)–C(24) | 1.380(15) | N(33)–C(34) | 1.35(5) |
| C(14)–C(15) | 1.337(10) | C(24)–C(25) | 1.369(23) | C(34)–C(35) | 1.37(5) |
| C(15)–N(11) | 1.382(8) | C(25)–N(21) | 1.391(20) | C(35)–N(31) | 1.51(4) |
| C(12)–C(16) | 1.480(10) | C(22)–C(26) | 1.527(18)[a] | C(32)–C(36) | 1.36(6)[a] |
| N(13)–C(17) | 1.439(10) | N(23)–C(27) | 1.476(16)[a] | N(33)–C(37) | 1.49(5)[a] |
| Pt–N(11)–C(12) | 128.4(5) | Pt–N(21)–C(22) | 127.8(7) | Pt–N(31)–C(32) | 129(2) |
| Pt–N(11)–C(15) | 124.1(4) | Pt–N(21)–C(25) | 125.4(9) | Pt–N(31)–C(35) | 127(2) |
| C(15)–N(11)–C(12) | 107.5(6) | N(11)–Pt–N(21) | 88.6(3) | N(11)–Pt–N(31) | 92.6(8) |
| N(11)–C(12)–N(13) | 109.2(6) | C(25)–N(21)–C(22) | 106.8(10) | C(35)–N(31)–C(32) | 103(3) |
| C(12)–N(13)–C(14) | 107.7(6) | N(21)–C(22)–N(23) | 110.1(9) | N(31)–C(32)–N(33) | 109(3) |
| N(13)–C(14)–C(15) | 106.5(6) | C(22)–N(23)–C(24) | 109.1(9) | C(32)–N(33)–C(34) | 114(3) |
| C(14)–C(15)–N(11) | 109.1(6) | N(23)–C(24)–C(25) | 106.2(12) | N(33)–C(34)–C(35) | 104(3) |
| N(11)–C(12)–C(16) | 127.4(6) | C(24)–C(25)–N(21) | 107.6(14) | C(34)–C(35)–N(31) | 110(3) |
| N(13)–C(12)–C(16) | 123.4(6) | N(21)–C(22)–C(26) | 126.7(10) | N(31)–C(32)–C(36) | 115(3) |
| C(12)–N(13)–C(17) | 126.8(6) | N(23)–C(22)–C(26) | 123.2(10) | N(33)–C(32)–C(36) | 136(4) |
| C(14)–N(13)–C(17) | 125.5(6) | C(22)–N(23)–C(27) | 125.7(10) | C(32)–N(33)–C(37) | 129(3) |
| | | C(24)–N(23)–C(27) | 124.8(10) | C(34)–N(33)–C(37) | 117(3) |
| I(1)–I(2) | 3.005(1) | | | | |
| I(2)–I(3) | 2.856(1) | I(1)–I(2)–I(3) | 177.71(3) | | |
| Pt···I(1) | 4.933(1) | I(2)···I(3′)–I(2′) | 106.33(2) | | |
| I(2)···I(3′) | 4.335(1) | I(3)–I(2)···I(3′) | 90.58(2) | | |
| I(1)···C(14) | 4.062(7) | I(3)···N(13′) | 3.727(7) | | |
| I(1)···C(26′) | 4.081(16) | I(3)···C(14′) | 3.948(8) | | |
| I(1)···C(27) | 4.078(12) | I(3)···C(22′) | 3.943(9) | | |
| I(1)···C(34) | 3.67(3) | I(3)···N(23′) | 3.788(10) | | |
| I(2)···C(15′) | 4.004(7) | I(3)···C(24′) | 3.951(11) | | |
| I(2)···C(17′) | 4.100(9) | I(3)···C(32′) | 3.77(4) | | |
| I(3)···C(12′) | 3.884(7) | I(3)···N(33′) | 3.81(3) | | |

[a] Methyl hydrogen atoms at C(26), C(27), C(36), C(37) not included in the calculations.

Electronic absorption spectra recorded in $CH_3CN$ solution show the two bands characteristic for the $I_3^-$ ion [11], with maxima at 360 and 290 nm and extinction coefficients of 40000 $dm^3$ $mol^{-1}$ $cm^{-1}$ and 80000 $dm^3$ $mol^{-1}$ $cm^{-1}$.

Finally, the X-ray powder diagrams of the new compounds were recorded and compared with the corresponding compounds $Pt(ligand)_4I_2$. No lines due to the latter compounds were found, and no isomorphism was found for any combination of compounds. Two different X-ray patterns were observed for the two, differently-coloured isomers of $Pt(DMIz)_4I_6$. To obtain more information about the solid state structure of the compounds, an X-ray structural investigation of the dark brown isomer of $Pt(DMIz)_4I_6$ was undertaken. The results of this investigation are described in the next section.

### *Description of the Structure of* $Pt(DMIz)_4(I_3)_2$

An ORTEP drawing of the structure containing the centrosymmetric $[Pt(DMIz)_4]^{2+}$ cation together with the two closest $I_3^-$ anions is depicted in Fig. 1, whereas the molecular packing is shown in Fig. 2. In both drawings only one of the two observed conformations of the complex cation is given, as ligand 2 with atoms N(21) through C(27) (and centrosymmetric equivalents) are statistically present in only 72% of all cases. In the rest of the cations this ligand site is occupied by ligand 3 (atoms N(31) through C(37)).

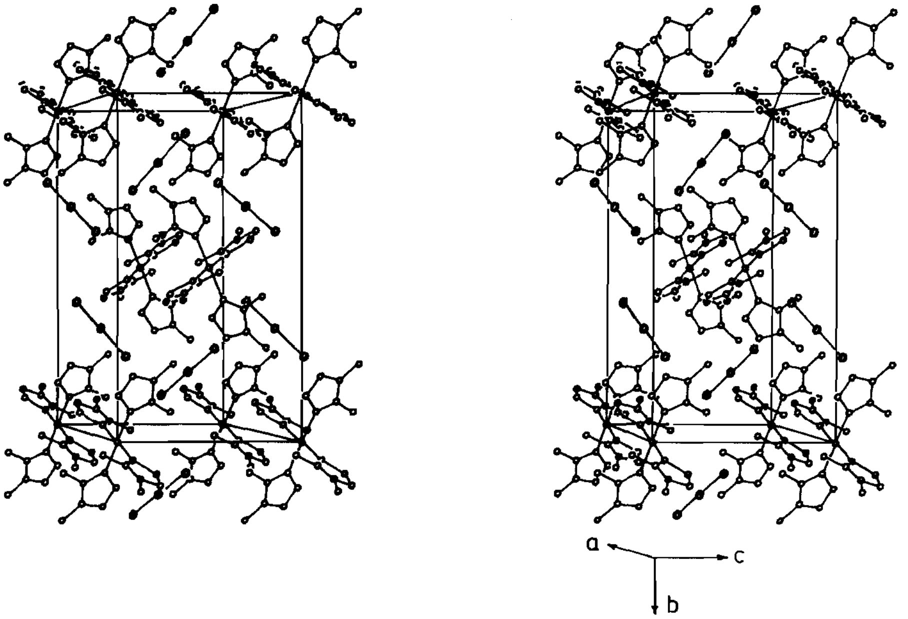


Fig. 2. Stereo projection of the unit cell content of $Pt(DMIz)_4(I_3)_2$.

As Fig. 3 shows, ligand 3 is related to ligand 2 by a 22° rotation around the Pt–N(11) bond followed by a 175° rotation around the Pt–N(31) vector. Both ligand planes almost coincide so that the molecular packing in the crystal remains essentially unaltered.

Relevant interatomic distances and bond angles are listed in Table IV, together with a few relatively short intermolecular contacts. The structure clearly confirms the presence of $I_3^-$ ions in the lattice, without appreciable Pt····I interaction. The coordination around the Pt(II) ion is square planar, with almost equal Pt–N bonds. These bond distances are similar to those observed in other Pt compounds [8, 12]. The intramolecular distances in the DMIz ligands are similar to those observed in other coordination compounds containing substituted imidazoles, [8, 12, 13].

As expected and as shown especially from the more precise data of ligand 1, the ring bond lengths N(11)–C(15) and N(13)–C(14) are significantly longer than the other three. The angles between the coordinated ligands and the $PtN_4$ coordination plane are both 85° for ligand 1 and 2 *vs.* the Pt–N(11)–N(21) plane and they are 73° for ligand 1 and 79° for ligand 3 *vs.* the Pt–N(11)–N(31) plane, indicating an almost perpendicular orientation. These deviations from 90° are smaller than in the previously reported structure of $Pt(NMIz)_4$-$PtCl_6$, where angles from 50 to 110° were found [8]. This might be related to the steric effect of the methyl group at the 2-position in the imidazole ring in case of DMIz.

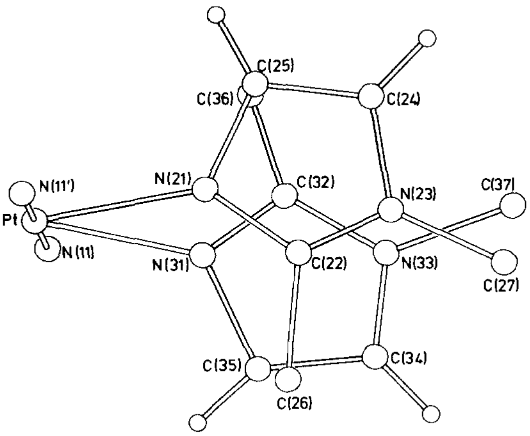


Fig. 3. Disordered arrangement of one of the ligand sites with site occupational factors of 0.72 and 0.28 for the two possibilities. Direction of view approximately along *b*.

The two I–I distances observed in each $I_3^-$ are significantly different.

This observation agrees with the occurrence of the symmetric I–I stretching frequency in the far-IR spectrum (*vide supra*). Such an asymmetry has been observed before in other compounds and has been shown to be caused mainly by the asymmetric crystal field on the $I_3^-$ bonding electron system (see *e.g.* [14], and references therein). In the present case there appears to be a characteristic intermolecular interaction between the central I(2) atom of one $I_3^-$ ion and the I(3′) end atom of a neighbouring unit (see Table IV and Fig. 2). This rather weak interaction (I(2)···I(3′) 4.335 Å) is, with an I(2)···I(3′)–I(2′) angle of 106.33(2)°, different from the T-shaped arrangement as observed in other triiodides ($Cs^+$ [15], $NH_4^+$ [16], $(C_2H_5)_4N^+$ [17]); in these cases I(2) is collinear with the $I_3^-$ ion containing I(3′). The shortest intermolecular I···C and I···N contacts (Table IV) and associated I···H distances are normal; they give no simple correlation to the asymmetry of the $I_3^-$ ion.

## Concluding Remarks

The present study has shown that $I_3^-$ ions can be easily precipitated with cations such as $Pt(ligand)_4^{2+}$, with substituted imidazoles as ligands. The insolubility of such compounds in aqueous solution must be the driving force for the precipitation of $Pt(NMIz)_4(I_3)_2$ from acid solutions containing $Pt(NMIz)_4^{2+}$ and $I^-$ in the presence of air. The poor solubility of these compounds in water, compared to organic solvents, might be due to the weak solvation of the $Pt(ligand)_4^{2+}$ cations and the $I_3^-$ ions, and is not related to a special Pt——I interaction.

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