

- (19) W. F. Edgell and J. Lyford, *Inorg. Chem.*, **9**, 1932 (1970).
 (20) Standard deviations on intensities were computed as $\sigma(I) = [P + 0.25(T_p/T_b)^2(B_1 + B_2) + (0.04I)^2]^{1/2}$, where P is the total peak count in a scan of time T_p , B_1 and B_2 are the background counts each in time T_b , and I is the intensity equal to $P - 0.5(T_p/T_b)(B_1 + B_2)$.
 (21) G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr., Sect. A*, **27**, 368 (1971).
 (22) S. Raman, *Acta Crystallogr.*, **14**, 148 (1961).
 (23) "International Tables for X-Ray Crystallography", Vol. III, Kynoch Press, Birmingham, England, 1962, p 202.
 (24) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).
 (25) Not identified.
 (26) M. Calligaris, G. Nardin, and L. Randaccio, *Coord. Chem. Rev.*, **7**, 385 (1972), and references therein.
 (27) C. Floriani and G. Fachinetti, *J. Chem. Soc., Chem. Commun.*, 615 (1974).
 (28) C. Floriani, unpublished results.
 (29) M. Y. Darensbourg, D. J. Darensbourg, D. Burns, and D. A. Drew, *J. Am. Chem. Soc.*, **98**, 3127 (1976); M. Darensbourg, H. Barros, and C. Borman, *J. Am. Chem. Soc.*, **99**, 1647 (1977), and references therein.
 (30) C. D. Pribula and T. L. Brown, *J. Organomet. Chem.*, **71**, 415 (1974).
 (31) S. W. Ulmer, P. M. Skarstad, J. M. Burlitch, and R. E. Hughes, *J. Am. Chem. Soc.*, **95**, 4469 (1973).
 (32) Data taken from ref 3.
 (33) D. P. Schlusser, W. R. Robinson, and W. F. Edgell, *Inorg. Chem.*, **13**, 153 (1974).
 (34) W. C. Hamilton, *Acta Crystallogr.*, **12**, 609 (1959).
 (35) C. K. Johnson, "ORTEP", Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

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Synthesis and Structural Characterization of cis-Dichlorobis(*N*-methylimidazole)platinum(II) and cis-Dibromobis(*N*-methylimidazole)platinum(II)

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The synthesis and spectroscopic properties of *cis*-dichloro- and *cis*-dibromobis(*N*-methylimidazole)platinum(II), Pt(C₄H₆N₂)₂Cl₂ and Pt(C₄H₆N₂)₂Br₂, are described. The dichloro complex crystallizes in four distinct crystal modifications, all containing the *cis*-Pt(C₄H₆N₂)₂Cl₂ unit as deduced from far-IR spectra, conductivity measurements, and (high-temperature) X-ray powder patterns. The dibromo complex crystallizes in two forms, each of which is isomorphous with one of the forms of the dichloro complex. The crystal structure of one of the forms of the dichloro complex has been determined from three-dimensional single-crystal X-ray data obtained by counter methods. The complex crystallizes in space group *Fddd* of the orthorhombic system with 16 formula units in a cell of dimensions $a = 12.586$ (6), $b = 30.431$ (16), and $c = 12.920$ (5) Å. The observed and calculated densities are 2.29 (2) and 2.309 g cm⁻³, respectively. The structure has been refined by full-matrix least-squares methods to a value of the conventional *R* factor (on *F*) of 0.046 using 1701 independent data. The platinum(II) center lies on a crystallographic twofold axis and is coordinated to two *cis* chloride ions at 2.296 (2) Å and to two imine nitrogen atoms at 2.015 (6) Å. The geometry at platinum is approximately square planar, with *cis* bond angles in the range 89.2–91.6°. There is no evidence for hydrogen bonding or strong intermolecular interactions in the crystal. This apparent absence of strong intermolecular forces may be the reason for the existence of multiple crystalline forms.

Introduction

As a part of a study on the structure–activity relationships of platinum complexes with antitumor activity² we are currently investigating a number of platinum complexes with imidazoles and pyrazoles as ligands. A preliminary report about the synthesis of Pt(II) and Pd(II) complexes with imidazole has appeared.³ It has been found that the complex *cis*-Pt(Iz)₂Cl₂ (Iz = imidazole) shows cytostatic activity in mice bearing the tumour L1210 leukemia.⁴ There is good evidence in the literature that hydrogen bonding is an important factor in determining the activity of the complex.⁵ In order to study the possible influence of the hydrogen bonding capacity of the complex on the activity we have synthesized the *cis*-dichloro complex of Pt(II) with *N*-methylimidazole as the ligand. The synthesis and characterization of a number of other compounds with this ligand like the *trans* compounds and compounds containing four *N*-methylimidazole ligands coordinated to Pt(II) are described elsewhere.⁶ The complex *cis*-Pt-(NMIz)₂Cl₂ (NMIz = *N*-methylimidazole), however, was found to exist in four different crystal forms with slightly different spectroscopic properties. The *cis*-dibromo analogue exists in at least two different crystal forms which are isomorphous with two of the four crystal forms of the *cis*-dichloro complex. In order to understand these properties we determined the crystal and molecular structure of one of the crystal

forms of *cis*-Pt(NMIz)₂Cl₂. The present paper reports the synthesis and spectroscopic properties of all four crystal forms and the X-ray structure of one crystal form.

Experimental Section

Starting Materials. Commercially available *N*-methylimidazole (abbreviated as NMIz) (Merck) was used without further purification. Platinum was commercially available as the tetrachloroplatinate, K₂PtCl₄ (Drijfhout, Amsterdam).

Synthesis of the Compounds. The compound *cis*-Pt(NMIz)₂I₂ was used as a starting material. This compound was synthesized by an improved procedure according to the method of Dhara.⁷ A total of 415 mg (1 mmol) of K₂PtCl₄ was dissolved in 20 mL of water, and 4 g (about 24 mmol) of KI was added to yield a solution of 0.05 M PtI₄²⁻ and 1 M I⁻. To this solution 164 mg (2 mmol) of the ligand was added. The *cis* compound precipitated immediately and was filtered, washed with ethanol and dry diethyl ether, and dried in vacuo at room temperature. A total of 613 mg (1 mmol) of the *cis*-diiodo compound was suspended in water, and a solution of 340 mg (2 mmol) of AgNO₃ in water was added. The suspension was stirred for 1 h and the precipitate of AgI was filtered. The filtrate presumably contains the *cis*-diaquo species. After addition of a 20-fold excess of NaCl or NaBr respectively, the *cis*-dichloro or the *cis*-dibromo compound precipitated. The product was filtered, washed with ethanol and dry diethyl ether, and dried in vacuo at room temperature. The *cis*-dichloro compound could be recrystallized from 2 N HCl or by dissolving the compound in DMF (minimum amount) and adding a fivefold excess (by volume) of 2 N HCl. The *cis*-dibromo compound

could be recrystallized by dissolving the compound in the minimum volume of DMF and adding water in a 1:1 volume ratio.

Analyses. C, H, and N analyses were carried out by standard procedures at the Organisch Chemisch Instituut, TNO, Utrecht, The Netherlands.

Anal. Calcd for *cis*-Pt(NMIZ)₂Cl₂: C, 22.3; H, 2.8; N, 13.0. Found: C, 22.4; H, 2.9; N, 13.0.

Anal. Calcd for *cis*-Pt(NMIZ)₂Br₂: C, 18.5; H, 2.3; N, 10.8. Found: C, 18.6; H, 2.4; N, 10.8.

Physical Methods. Infrared spectra of the compounds pressed in KBr disks and as Nujol mulls were recorded on a Beckman Acculab instrument (4000–250 cm⁻¹). No decomposition of the compounds occurs in KBr as can be seen from the spectra recorded in Nujol mull, which are identical with those recorded in KBr. Far-infrared spectra of the compounds pressed in polyethylene disks were recorded on a Beckman IR720 interferometer (500–20 cm⁻¹). X-ray powder diffraction photographs were obtained with a Guinier-de Wolff camera using Cu K α radiation. Proton NMR spectra were recorded on a Varian T-60 instrument. The spectrum of *cis*-Pt(NMIZ)₂Cl₂ was recorded in Me₂SO and the spectrum of *cis*-Pt(NMIZ)₂Br₂ recorded in DMF. The conductivity of 0.001 M solutions of the compounds in DMF was measured with a Philips PR 9501 conductivity bridge.

Collection and Reduction of the X-ray Data. Examination of a crystal of β -*cis*-Pt(NMIZ)₂Cl₂ by precession photography revealed that the material crystallized in the orthorhombic system. The observed systematic absences of $(h + k)$, $(k + l)$, and $(h + l)$ odd, $(h + 1) \neq 4n$ for $h0l$, $(k + 1) \neq 4n$ for $0kl$, and $(h + k) \neq 4n$ for hkl indicated the space group *Fddd* (No. 70). The cell constants and their estimated standard deviations as determined by least-squares procedures are $a = 12.586$ (6), $b = 30.431$ (16), and $c = 12.920$ (5) Å. The measured density of the crystals by flotation in bromoform/carbon tetrachloride mixtures is 2.29 (2) g cm⁻³, which is in good agreement with the value of 2.309 g cm⁻³ calculated for 16 molecules per unit cell. Hence, in space group *Fddd*, the platinum atoms are constrained to lie on either a crystallographic twofold axis or an inversion center. In view of the known *cis* geometry, the former is the only reasonable choice.

Diffraction data were collected on a Picker four-circle automatic diffractometer equipped with molybdenum radiation and a graphite monochromator. The wavelength was assumed to be $\lambda(\text{Mo K}\alpha_1)$ 0.70926 Å. A prismatic crystal bounded by the faces (010), (101), (101), and (001) was mounted on a glass fiber roughly perpendicular to the (101) face. The crystal fragment is best described as a cube of side 0.404 mm cut along a face diagonal (001) to yield a trigonal prism. The data were collected at a takeoff angle of 1.2°. A total of 3004 intensities (including standard reflections) was collected by the θ - 2θ scan technique in the range $2\theta(\text{Mo K}\alpha) \leq 68^\circ$ at a scan rate of 1° (2 θ) min⁻¹. There were very few intensities above background at values of $2\theta > 68^\circ$. To allow for the presence of both K α_1 and K α_2 radiations, the reflections were scanned from 0.85° in 2θ below the calculated K α_1 peak position to 0.85° in 2θ above the calculated K α_2 peak position. Stationary-counter, stationary-crystal background counts of 20 s were taken at each end of the scans. Throughout the data collection the intensities of three standard reflections were monitored after every 100 reflections. These three reference reflections showed no appreciable variation in intensity.

Data reduction was carried out using the method of Ibers and co-workers.⁸ After correction for background radiation, the intensities I were assigned standard deviations according to the formula

$$\sigma(I) = [C + 0.25(t_s/t_b)^2(B_H + B_L) + (pI)^2]^{1/2}$$

where the quantities have their usual meanings⁸ and the value of p was selected as 0.04. The values of I and $\sigma(I)$ were corrected for Lorentz-polarization effects and for absorption. The absorption coefficient for this compound with Mo K α radiation is 118.6 cm⁻¹, and for the sample used the transmission coefficients were found to range from 4.59 to 9.99. Of the 2892 independent data, the 1701 with $I > 3\sigma(I)$ were considered to be observed; only these data were used in the subsequent calculations.

Solution and Refinement of the Structure. In space group *Fddd* the platinum atom is constrained to lie on one of the three twofold axes. The position of the platinum atom was located from a three-dimensional Patterson function;⁹ it was found to lie on the twofold axis which is parallel to the crystallographic b axis. The positions of the remaining nonhydrogen atoms were determined from subsequent difference Fourier maps. Isotropic least-squares refinement of these

Table I. Positional Parameters for Pt(NMIZ)₂Cl₂

atoms	x	y	z
Pt	0.12500 (1)	0.26668 (1)	0.12500 (1)
Cl	0.24372 (16)	0.32000 (5)	0.17447 (20)
N1	0.2296 (5)	0.2205 (2)	0.1710 (6)
C2	0.3319 (7)	0.2224 (3)	0.1572 (8)
N3	0.3799 (5)	0.1881 (2)	0.2030 (6)
C4	0.3015 (7)	0.1628 (2)	0.2461 (8)
C5	0.2093 (7)	0.1830 (2)	0.2259 (8)
C3	0.4946 (8)	0.1807 (3)	0.2066 (10)
H2	0.3681	0.2451	0.1205
H31	0.4954	0.1982	0.2862
H32	0.5169	0.1515	0.2064
H33	0.5334	0.1969	0.1538
H4	0.3117	0.1356	0.2802
H5	0.1406	0.1737	0.2483

positions gave values of the usual agreement factors $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ of 0.077 and 0.088, respectively. All least-squares calculations in this structural analysis were carried out on F , the function minimized being $\sum w(|F_o| - |F_c|)^2$ and the weights w being assigned as $4F_o^2/\sigma^2(F_o^2)$. In the calculation of F_o , the neutral atom scattering factors for Pt, Cl, N, and C were taken from ref 10a, while those for H were from Stewart, Davidson, and Simpson.¹¹ The effects of the anomalous dispersion of Pt and Cl were included, the values of $\Delta f'$ and $\Delta f''$ being taken from ref 10b. Anisotropic refinement of these atomic positions gave $R_1 = 0.047$ and $R_2 = 0.056$. Attempts to locate the hydrogen atoms at this stage were only partially successful. Of the three ring hydrogen atoms, only two [H(2) and H(4)] were located; of the three methyl hydrogen atoms, only one could be located. The positions of the other two methyl hydrogen atoms were calculated on the basis of tetrahedral geometry at C(3) and a C-H bond length¹² of 0.95 Å. Attempts to refine the positions of the hydrogen atoms failed, so all three ring hydrogen atoms were also placed in calculated positions, and no hydrogen positional parameter was refined. The isotropic thermal parameters of the hydrogen atoms [except for H(2)] showed a marked tendency to oscillate wildly, and so all hydrogen thermal parameters except that of H(2) were fixed at 7.0 Å². In the final cycle of least-squares refinement there were 1701 observations and 71 variables for a parameter:variable ratio of approximately 24:1. In this final cycle, no parameter shifted by more than 0.05 σ , which is taken as evidence that refinement had converged. The final values of R_1 and R_2 were found to be 0.046 and 0.055, respectively. Examination of the values of $|F_o|$ and $|F_c|$ in the later stages of refinement had suggested that the data may be suffering from the effects of secondary extinction, and a correction of the type suggested by Zachariasen^{13,14} was employed. The final value of the extinction coefficient was 4.1 (7) $\times 10^{-6}$.

A final difference Fourier map showed peaks of up to 2.1 e Å⁻³ in the vicinity of the platinum atom. This residual density is presumably due to the approximate nature of our absorption correction, which was necessitated by our use of a crystal fragment, and is not wholly unexpected for a system with such a large value of μ . The positional and thermal parameters derived from the last cycle of least squares, along with their standard deviations as estimated from the inverse matrix, are presented in Tables I and II. A table of observed and calculated structure amplitudes is available.¹⁵

Results and Discussion

Repeated synthesis, as well as subsequent recrystallization, of the *cis*-dichloro compound resulted in different species having different infrared spectra and different X-ray powder diffraction patterns. All these species analyzed as Pt-(NMIZ)₂Cl₂ and proved to be nonelectrolytes in DMF solution. The far-infrared spectra of all species showed the presence of two Pt-Cl stretching vibrations, as expected for *cis* compounds. It is not possible that these different species are other isomers like the trans complex or the Magnus salt analogue Pt-(NMIZ)₄PtCl₄. These isomers have been synthesized and characterized and show completely different spectroscopic properties and different X-ray powder diffraction patterns, as described elsewhere.⁶

Comparison of the X-ray powder diffraction patterns of all the species obtained showed that in many cases mixtures of

Table II. Thermal Parameters (U_{ij} , Å²) for Pt(NMiz)₂Cl₂

atom	U_{11}^a	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt	0.0293 (2)	0.0358 (2)	0.0321 (2)	0.0 ^b	0.0015 (2)	0.0 ^b
Cl	0.0387 (8)	0.0424 (7)	0.0632 (13)	−0.0035 (6)	−0.0071 (9)	−0.0040 (8)
N1	0.031 (3)	0.041 (2)	0.040 (3)	0.002 (2)	0.000 (3)	0.002 (2)
C2	0.038 (4)	0.045 (3)	0.047 (4)	0.002 (3)	0.004 (3)	0.005 (3)
N3	0.032 (3)	0.048 (3)	0.048 (4)	0.005 (2)	0.000 (3)	0.006 (3)
C4	0.056 (5)	0.043 (3)	0.051 (5)	−0.002 (3)	0.004 (4)	0.007 (3)
C5	0.042 (4)	0.046 (3)	0.049 (5)	−0.003 (3)	−0.002 (4)	0.011 (3)
C3	0.042 (4)	0.067 (4)	0.064 (6)	0.009 (4)	−0.007 (5)	−0.005 (4)
atom	$U, \text{\AA}^2$		atom	$U, \text{\AA}^2$		
H2	0.08 (5)		H32 ^c	0.089		
H31 ^c	0.089		H33 ^c	0.089		
			H4 ^c	0.089		
			H5 ^c	0.089		

^a The form of the anisotropic thermal ellipsoid is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. ^b U_{12} and U_{23} for Pt are constrained to zero by the twofold site symmetry. ^c Thermal parameters for this atom were not varied.

Table III. Differences in the Infrared Spectra of the Different Modifications of the *cis*-Dichloro and *cis*-Dibromo Compounds

assignment ^a	<i>cis</i> -Pt(NMiz) ₂ Cl ₂				<i>cis</i> -Pt(NMiz) ₂ Br ₂	
	α	β	γ	δ	α	γ
C-H str	3140	3140			3140	3120
	3120	3115	3125	3120	3120	
CH ₃ bend	1420	1420	1430 sh	1425	1420	1425
	1410		1420		1410	1415
out of plane	840		845 sh	850	835	845 sh
C-H bend	820	815	835	825	820	830
	760	760	765	760	755	755
	735		740	735 sh	730	735

^a According to J. Reedijk, *Inorg. Chim. Acta*, 3, 517 (1969).

species were present. By careful examination of the X-ray powder photographs in combination with the infrared spectra it was possible to distinguish four different crystal forms defined as α , β , γ , and δ (see description of spectroscopic properties for the use of the symbols distinguishing these different crystal forms). In several samples mixtures of two or more of the crystal forms occurred. Fortunately, a number of samples consisted of only one of the different crystal forms and all of the four isomers could be obtained in a pure form.

Despite careful investigation, no special conditions could be found favoring the formation of one of the isomers. The synthesis of the compound as described in the experimental part may give all isomers, and often mixtures occur, although a slight preference seems to exist for the formation of the β isomer. Recrystallization of this β form from 2 N HCl gives the β form again. Recrystallization of the β form from a mixture of DMF and 2 N HCl gives either the α form or a mixture of the α and β forms.

The synthesis of the *cis*-dibromo complex always results in a compound which is isomorphous (X-ray and IR) with the γ form of *cis*-Pt(NMiz)₂Cl₂. Recrystallization of this compound results in a species which is isomorphous with the α form of the *cis*-dichloro complex or sometimes in a mixture of the α and γ forms.

High-temperature Guinier-de Wolff photographs of all crystal forms show that interconversion of one crystal form into another does not occur upon heating. The only transformation appears to be the isomerization of the *cis* compounds into the corresponding trans compounds in the 160–170 °C temperature region.

Description of Spectroscopic Data. The frequencies of the ligand absorption bands (in the regions of the infrared spectra where the difference between the crystal forms occur) are listed in Table III. The absorption bands are assigned analogously to that used for other *N*-methylimidazole complexes.¹⁶ The different crystal forms are denoted as α , β , γ , and δ , respectively. From these data it is concluded that the differences

Table IV. Far-Infrared Spectra of the Compounds (450–100 cm⁻¹)^a

Compounds	Pt-halogen str	ligand abs	other vibrations, Pt-halogen bending and Pt-ligand
<i>cis</i> -Pt(NMiz) ₂ Cl ₂ α	333 s, 320 s	386 w	288 w, 265 w, 208 w, 163 w, 110 m, br
β	333 s, 323 s	386 w	281 w, 258 w, 217 w, 193 w, 173 w, 106 m, br
γ	331 s, 324 s	388 w	287 w, 166 w, 100 w, br
δ	336 s, 324 s	386 w	285 w, 268 w, 222 w, 194 w, 167 w, 110 m, br
<i>cis</i> -Pt(NMiz) ₂ Br ₂ α	217 s, 205 s	384 w	264 m, 244 m, 226 w, 110 w
γ	223 s, 210 s	385 w	269 m, 247 m

^a Key: s = strong, m = medium, w = weak, br = broad.

Table V. d Values in Å Derived from the X-ray Powder Diffraction Patterns of the Different Crystal Forms (Only Values Higher Than 3.5 Å Have Been Tabulated)^a

<i>cis</i> -Pt(NMiz) ₂ Cl ₂				<i>cis</i> -Pt(NMiz) ₂ Br ₂	
α	β	γ	δ	α	γ
8.15 vs	8.58 s	9.20 w	7.93 vs	8.38 s	9.30 w
7.22 vs	7.53 m	7.89 m	7.65 vs	7.28 s	7.96 m
6.63 vw	6.68 s	7.72 m	6.37 vw	6.04 w	7.79 m
5.94 m	5.77 s	5.86 w	6.02 vw	4.58 s	5.90 m
5.64 w	4.48 w	4.48 s	5.50 m	4.55 m	4.55 s
5.27 vw	4.31 vw	4.03 w	5.23 vw	4.09 w	4.08 w
5.05 vw	4.02 m	3.99 w	4.63 s	3.98 vw	4.05 w
4.50 s	3.93 w	3.88 m	4.51 s	3.69 w	3.95 m
4.47 w	3.86 m	3.86 vw	4.44 w		3.93 w
4.41 s	3.77 m		4.35 w		
4.13 vw	3.69 m		4.25 s		
4.01 s			4.20 vw		
3.91 vw			4.07 w		
3.87 vw			3.99 s		
3.72 w			3.95 w		
3.65 w			3.81 s		
3.63 vw			3.70 s		
3.59 vw			3.63 vw		
3.56 s			3.60 w		
3.50 w					

^a Key: vs = very strong, s = strong, m = medium, w = weak, vw = very weak.

in the infrared spectra are caused by different orientations of the NMiz ligands in the crystal structures; this may be due to either different conformations of the complex unit or crystal packing effects.

The wavenumbers of the absorption bands in the far-infrared region (450–100 cm⁻¹) are listed in Table IV, together with the assignment of the platinum-halogen stretching vibrations and a ligand vibration. The spectra of the different crystal

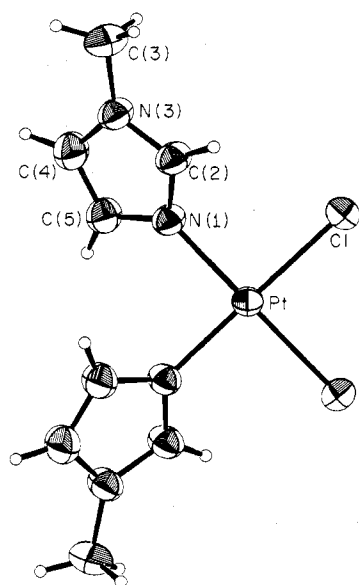


Figure 1. View of the coordination around platinum in *cis*-[Pt(NMIz)₂Cl₂]. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are represented as open spheres of arbitrary size.

Table VI. Bond Distances (Å) and Angles (deg) for All Nonhydrogen Atoms in Pt(NMIz)₂Cl₂

Pt-Cl	2.296 (2)	N(3)-C(3)	1.462 (11)
Pt-N(1)	2.015 (6)	N(3)-C(4)	1.370 (10)
N(1)-C(2)	1.301 (10)	C(4)-C(5)	1.338 (11)
C(2)-N(3)	1.345 (10)	C(5)-N(1)	1.369 (10)
Cl-Pt-Cl'	90.1 (1)	N(1)-C(2)-N(3)	110.5 (7)
Cl-Pt-N(1)	89.2 (2)	C(2)-N(3)-C(4)	107.0 (7)
N(1)-Pt-N(1)'	91.6 (3)	C(2)-N(3)-C(3)	125.2 (7)
N(1)-Pt-Cl'	178.9 (6)	C(3)-N(3)-C(4)	127.8 (7)
Pt-N(1)-C(2)	125.1 (5)	N(3)-C(4)-C(5)	106.7 (7)
Pt-N(1)-C(5)	127.8 (5)	C(4)-C(5)-N(1)	108.9 (7)
C(2)-N(1)-C(5)	107.0 (6)		

forms appear to be slightly different. From the table, however, it is clear that all compounds have the *cis* geometry around platinum in view of the presence of two platinum-halogen stretching vibrations (A_1 and B_1 in C_{2v} symmetry).

Assignment of the platinum-ligand vibrations was not possible because of the low intensity of the other absorption bands in the spectra. The d values determined from the X-ray powder diffraction patterns of all crystal forms are listed in Table V. From these data it can be seen that all crystal forms are completely different. The X-ray powder photographs of the mixtures, which sometimes result from the synthesis, are composites of two or more of the X-ray powder diffraction patterns of the separate crystal forms.

From Table V, it can also be seen that the two crystal forms of the *cis*-dibromo compound are isomorphous with two of the four crystal forms of the *cis*-dichloro compound (the α and γ forms).

The ^1H NMR spectra of all compounds have shown that all compounds are identical in solution. Further details concerning the NMR spectra of these and related compounds have been published elsewhere.⁶

Description of the Structure of β -Pt(NMIz)₂Cl₂. In order to gain further insight into the structures of these complexes, we have undertaken a complete three-dimensional X-ray structure of one of the isomers (the β form); unfortunately, suitable crystals of the other isomers have not yet been obtained.

The complex consists of monomeric Pt(NMIz)₂Cl₂ units which are well separated from each other; a view of the molecule is given in Figure 1. The coordination around

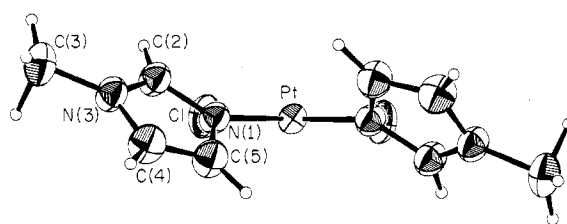


Figure 2. View of the complex along the C_2 axis, showing the relative orientations of the two imidazole rings.

Table VII. Least-Squares Planes in Pt(NMIz)₂Cl₂

atom	x	y	z	Δ , Å
Plane 1				
Atoms in the Plane Calculation				
N(1)	2.890	6.711	2.209	-0.006
C(2)	4.177	6.769	2.031	0.008
N(3)	4.782	5.723	2.623	-0.006
C(4)	3.794	4.953	3.179	0.002
C(5)	2.635	5.568	2.919	0.002
Atoms out of the Plane				
Pt	1.573	8.116	1.615	-0.118
C(3)	6.225	5.498	2.669	-0.049
Plane 2				
Atoms in the Plane Calculation				
Cl	3.068	9.738	2.254	0.014
Cl'	0.079	9.738	0.976	-0.014
N(1)	2.890	6.711	2.209	-0.016
N(1)'	0.257	6.711	1.021	0.016
Pt	1.573	8.116	1.615	0.000

platinum is *cis* square planar, with *cis* bond angles of 89.2 (2), 89.2 (2), 90.1 (1), and 91.6 (3)° and *trans* angles of 178.9 (6)°. The Pt-N(1) and Pt-Cl distances of 2.015 (6) and 2.296 (2) Å, respectively, are comparable with values found in related complexes.¹⁷⁻²³ The bond lengths and angles in the *N*-methylimidazole ligand are similar to those reported for a variety of metal complexes of imidazole and its derivatives.²³⁻²⁷ The distances and angles in the complex are listed in Table VI.

The *N*-methylimidazole ligands are planar, with no atom deviating from the least-squares plane through the five atoms by more than 0.008 Å. The platinum and methyl carbon atoms lie only 0.118 and 0.049 Å out of this plane, respectively. The dihedral angle between the plane of the imidazole ring and the square plane around platinum is 41.7°; this compares with the value of 49.2° reported²³ for the related complex *trans*-[Pt(NH₃)₂(NMIz)₂]²⁺. The closest intramolecular contact involving the nonhydrogen atoms of the NMIz ligands is 3.36 (2) Å. If the two ligands were coplanar with the PtN₂Cl₂ plane, this separation would be reduced to 2.56 Å. The dihedral angle between the planes of the two coordinated NMIz ligands is 62.4°. A view of the molecule showing this arrangement is given in Figure 2. The least-squares planes in the molecule are tabulated in Table VII.

As expected in the absence of any potential donor atom, there is no hydrogen bonding in the crystals. Consequently, the packing of the monomeric units is very loose; the closest Pt-Pt separation in the crystals is 4.622 (1) Å and the shortest intermolecular Cl...N contact is 4.589 (7) Å. This absence of any strong intermolecular forces may well be the origin of the observation of several crystal forms. These other forms may merely involve different packing arrangements of structurally similar units, but in view of the IR data (vide supra) it is more probable that they contain different relative orientations of the NMIz ligands.

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Registry No. *cis*-Pt(NMIz)₂Cl₂, 61617-01-4; *cis*-Pt(NMIz)₂Br₂, 67577-08-6; *cis*-Pt(NMIz)₂I₂, 67577-09-7.

Supplementary Material Available: A listing of observed and calculated structure amplitudes (10 pages). Ordering information is given on any current masthead page.

References and Notes

- (1) (a) The University of North Carolina. (b) Delft University of Technology.
- (2) M. J. Cleare, *Coord. Chem. Rev.*, **12**, 349 (1974); A. Khan, Ed., *J. Clin. Hematol. Oncol.*, **7** (1977).
- (3) J. Reedijk and J. K. de Ridder, *Inorg. Nucl. Chem. Lett.*, **12**, 585 (1976).
- (4) To be submitted for publication.
- (5) R. W. Gellert and R. Bau, *J. Am. Chem. Soc.*, **97**, 7379 (1975).
- (6) C. G. van Kralingen and J. Reedijk, *Inorg. Chim. Acta*, in press.
- (7) S. C. Dhara, *Indian J. Chem.*, **8**, 193 (1970).
- (8) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).
- (9) For a description of the programs used in this structural analysis, see D. L. Lewis and D. J. Hodgson, *Inorg. Chem.*, **13**, 143 (1974).
- (10) "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England: (a) Table 2.2A; (b) Table 2.3.1.
- (11) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
- (12) M. R. Churchill, *Inorg. Chem.*, **12**, 1213 (1973).
- (13) W. H. Zachariasen, *Acta Crystallogr., Sect. A*, **24**, 212 (1968).
- (14) D. J. Hodgson and J. A. Ibers, *Acta Crystallogr., Sect. B*, **25**, 469 (1969).
- (15) Supplementary material.
- (16) J. Reedijk, *Inorg. Chim. Acta*, **3**, 517 (1969).
- (17) E. O. Schlemper, *Inorg. Chem.*, **8**, 2740 (1969).
- (18) B. Morosin, paper presented at the American Crystallographic Association Meeting, Charlottesville, Va., March 1975.
- (19) K. W. Nordquest, D. W. Phelps, W. F. Little, and D. J. Hodgson, *J. Am. Chem. Soc.*, **98**, 1104 (1976).
- (20) D. W. Phelps, W. F. Little, and D. J. Hodgson, *Inorg. Chem.*, **15**, 2263 (1976).
- (21) G. G. Messmer and E. L. Amma, *Inorg. Chem.*, **5**, 1775 (1966).
- (22) L. G. Purnell and D. J. Hodgson, *J. Am. Chem. Soc.*, **98**, 4759 (1976).
- (23) J. W. Carmichael, N. Chan, A. W. Cordes, C. K. Fair, and D. A. Johnson, *Inorg. Chem.*, **11**, 1117 (1972).
- (24) F. L. Phillips, F. M. Shreeve, and A. C. Skapski, *Acta Crystallogr., Sect. B*, **32**, 687 (1976).
- (25) A. Santoro, A. D. Mighell, M. Zocchi, and C. W. Reimann, *Acta Crystallogr., Sect. B*, **25**, 842 (1969).
- (26) B. K. S. Lundberg, *Acta Crystallogr.*, **21**, 901 (1966).
- (27) J. F. Kirner, C. A. Reed, and W. R. Scheidt, *J. Am. Chem. Soc.*, **99**, 2557 (1977), and references therein.

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Dimeric (Pentamethylcyclopentadienyl)rhodium and -iridium Complexes. 4.¹⁻⁴ Crystal and Molecular Structure of [(η^5 -C₅Me₅)RhBr]₂(μ -Br)₂ and of the Partially Halide-Exchanged Species [(η^5 -C₅Me₅)RhX]₂(μ -X')₂ Obtained by Recrystallization of the Bromo Complex from 1,2-Dichloroethane

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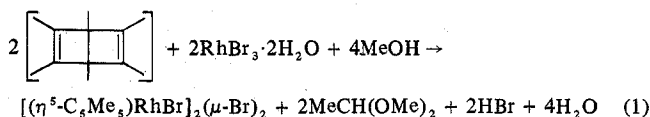
The complex di- μ -bromo-dibromobis(pentamethylcyclopentadienyl)dirhodium, [(η^5 -C₅Me₅)RhBr]₂(μ -Br)₂, has been investigated by means of single-crystal X-ray diffraction studies. The complex crystallizes from acetone in the centrosymmetric triclinic space group *P*1̄ with *a* = 8.755 (1) Å, *b* = 8.943 (2) Å, *c* = 16.137 (3) Å, α = 91.40 (2)°, β = 104.86 (1)°, γ = 93.58 (1)°, *V* = 1217.7 (4) Å³, ρ (obsd) = 2.26 (2) and ρ (calcd) = 2.17 g cm⁻³ for *Z* = 2 (dimers), and mol wt 795.88. Each molecule lies on a center of symmetry; the asymmetric unit consists of two independent half-molecules of the title compound. Diffraction data were collected with a Syntex P2₁ diffractometer and the structure was solved via Patterson, difference-Fourier, and least-squares refinement techniques yielding *R*_F = 5.1% and *R*_{wF} = 2.7% for all 3208 independent reflections with 4° < 2 θ < 45° (Mo K α radiation). All atoms, including hydrogens, were located and refined. Rhodium-rhodium distances in the two independent molecules are 3.854 (1) and 3.841 (1) Å as compared to 3.7191 (6) Å in the chloro complex [(η^5 -C₅Me₅)RhCl]₂(μ -Cl)₂. Rhodium-(terminal bromide) distances are 2.523 (1) and 2.532 (1) Å, while rhodium-(bridging bromide) linkages are 2.577 (1) and 2.587 (1) Å in molecule I and 2.566 (1) and 2.575 (1) Å in molecule II. The two Rh-Br-Rh bridge angles are 96.54 (3) and 96.70 (3)°. Recrystallization of [(η^5 -C₅Me₅)RhBr]₂(μ -Br)₂ from 1,2-dichloroethane was found to result in halogen exchange, the crystal actually studied having the approximate net composition (as determined by an X-ray diffraction study) [(η^5 -C₅Me₅)RhCl_{0.67}Br_{0.33}]₂(μ -Cl_{0.95}Br_{0.05})₂. This species crystallizes in the centrosymmetric monoclinic space group *P*2₁/c with *a* = 8.430 (1) Å, *b* = 9.253 (1) Å, *c* = 15.760 (2) Å, β = 106.83 (1)°, *V* = 1176.7 Å³, ρ (obsd) = 1.831 (12) g cm⁻³, and *Z* = 2. Diffraction data (two forms, complete to 2 θ = 45°, using Mo K α radiation) were collected with a Syntex P2₁ diffractometer, and the structure was refined to *R*_F = 4.4% and *R*_{wF} = 5.1% for those 1479 independent reflections with $|F_o| > 0$. The crystals are isomorphous with those of the pure complex [(η^5 -C₅Me₅)RhCl]₂(μ -Cl)₂, and the structure elucidated shows only small differences relative to the chloro complex.

Introduction

We have previously reported the results of X-ray structural analyses of the species [(η^5 -C₅Me₅)RhCl]₂(μ -H)(μ -Cl),² [(η^5 -C₅Me₅)RhCl]₂(μ -Cl)₂,³ [(η^5 -C₅Me₅)IrCl]₂(μ -H)(μ -Cl),⁴ and [(η^5 -C₅Me₅)IrCl]₂(μ -Cl)₂.⁴ We have now extended these studies to [(η^5 -C₅Me₅)RhBr]₂(μ -Br)₂, a complex previously reported by Gill and Maitlis.⁵

Experimental Section

Our first sample of [(η^5 -C₅Me₅)RhBr]₂(μ -Br)₂ was prepared directly from the reaction of rhodium(III) bromide dihydrate (Chemical Procurement Laboratories) and hexamethyl(Dewar benzene) (Aldrich) in methanol (eq 1). The complex was recrystallized from 1,2-



dichloroethane. [We note here that Gill and Maitlis recrystallized this species from chloroform/benzene⁵ and that the recrystallization of [(η^5 -C₅Me₅)RhI]₂(μ -I)₂ from chloroform/methanol appears in the literature.⁶] Unfortunately (but, perhaps, interestingly), this "recrystallization" step results in halide exchange between the bromide and the 1,2-dichloroethane. A crystal structure of the resulting "[(η^5 -C₅Me₅)RhX]₂(μ -X')₂" was performed and the details appear below.