

Table I. Chlorine-35 Line Broadening for Mercury Species in the Presence of Various Proteins

protein	line width increase, ^a Hz		
	Hg ²⁺	CH ₃ Hg ⁺	PMB
insulin ^b	42 (8:1) ^d	10 (ND) ^e	32 (6:1) ^d
papain ^c	47 (4:1) ^d	5 (ND)	36 (6:1) ^d
α-chymotrypsin ^c	21 (6:1) ^d	9 (ND)	41 (ND)
alkaline phosphatase ^b	59 (5:1) ^d	6 (ND)	27 (ND)

^a6:1 metal:protein ratio. ^bpH 8.0. ^cpH 5.0. ^dApparent stoichiometry of Hg-protein complex. ^eND = not possible to determine stoichiometry of complex.

Also shown on Figure 1 is the curve for *p*-(chloromercuri)-benzoic acid (PMB). This organomercurial exhibits significantly greater line broadening than methylmercury. However, in PMB, as in CH₃Hg⁺, one mercury coordination site is occupied by the protein and the second is occupied by the organic moiety. Therefore, for line broadening to occur, chloride must occupy a third coordination site. The greater line broadening for PMB vs. CH₃Hg⁺ could be due to one or more of the following: (1) stronger binding to the protein, (2) stronger association of chloride ion, (3) a faster chloride-exchange rate, or (4) a longer correlation time. It is certain that (4) must be a factor due to the larger mass of organic moiety as well as the fact that the ionized carboxylate group could be weakly attracted to other parts of the protein. The 6:1 stoichiometry seen for PMB may be due to weaker binding of PMB to insulin than to Hg²⁺ or perhaps to the steric obstruction of the benzoic acid moiety, which might cause a significantly slower halide exchange at two binding sites.

Table I is a summary of the observed chlorine-35 line broadening for mercury, methylmercury, and PMB in the presence of several proteins. In all cases, binding of the organomercurial to the protein is confirmed by fluorescence measurements. For all proteins with equivalent amounts of organomercurial, line broadening is greater for PMB than for methylmercury. Again it seems probable that (4) is at least partly responsible for this effect. Reinforcing the assumption are the results for α-chymotrypsin with PMB, producing significantly greater line broadening than Hg²⁺. Additional studies are under way to determine if similar bromide complexes exist as well as to measure the correlation times and the halide ion exchange rates for these species.

Registry No. Hg²⁺, 14302-87-5; CH₃Hg⁺, 22967-92-6; PMB, 59-85-8; insulin, 9004-10-8; papain, 9001-73-4; chymotrypsin, 9004-07-3; alkaline phosphatase, 9001-78-9.

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Synthesis of Monoamine Platinum(II) Complexes and Crystal Structure of Potassium Trichloro(isopropylamine)platinate(II) Hemihydrate

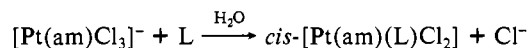
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Although K[Pt(NH₃)Cl₃]^{1,2} and K[Pt(py)Cl₃]^{3,4} (py = pyridine derivative) have been known for many years, the methods used to synthesize these complexes are not suitable for monoamine platinum(II) compounds. Kukushkin et al.^{5,6} prepared some

complexes [Pt(NH₃)₄][Pt(am)Cl₃]₂ (am = amine) from [Pt-(Me₂SO)(am)Cl₂] through a very long procedure of oxidation, replacement, and reduction. A method for the preparation of mononucleoside platinum complexes by the direct reaction of K₂PtCl₄ and the nucleoside in DMF has been reported,⁷ but the method is not applicable to amine complexes. We have recently reported the synthesis of such compounds from the reaction of K₂PtCl₄ with the amine in aqueous solution in the presence of KCl.⁸ But the method is strictly limited to bulky amines like *tert*-butylamine and isopropylamine because of the rapid formation of the disubstituted compound [P(am)₂Cl₂].

Monoamine platinum(II) compounds are important since they can be the starting material for the synthesis of the mixed-ligands complexes [Pt(am)(L)Cl₂]. If the reaction is done in water and the conditions strictly controlled, only the *cis* isomer will be formed since the *trans* effect follows the order Cl > amine.



Cis mixed-ligand complexes are important especially in view of the potent antitumor activity of *cis* Pt(II) complexes. If compounds with two different neutral ligands could be systematically synthesized, the screening range of platinum complexes would be largely extended and antitumor activity, toxicity, and solubility could be significantly modified.

We have now developed a new method for the synthesis of ionic complexes [Pt(am)Cl₃]⁻ that should be applicable to almost all amines or other nitrogen ligands. This method is described below. The compound with isopropylamine gave crystals suitable for X-ray diffraction. Its crystalline structure was studied, and the results are now reported.

Experimental Section

K₂PtCl₄ was bought from Johnson Matthey and Co., Limited, and was recrystallized in water before use. The elemental analyses were performed by Galbraith Laboratories. The IR spectra were measured on a Perkin-Elmer 783 or Digilab FT50 instrument (CsI beam splitter). The ¹H NMR spectra were recorded on a Varian EM-360L instrument (concentration about 0.05 M).

[Pt(am)I₂]₂. These compounds were synthesized as already reported.⁹

Synthesis of K[Pt(am)Cl₃]. One millimole of the iodo-bridged dimer [Pt(am)I₂]₂ was suspended in ~15 mL of water to which 6 mmol of AgNO₃ was added. The mixture was stirred at room temperature in the dark for 2 days. The precipitate (AgI) was filtered out, and 8 mmol of KCl were added to the filtrate. The mixture was stirred for 24 h, and the precipitate (AgCl) was removed by filtration. The filtrate was evaporated to dryness and the residue was dried under vacuum for 24 h. The yellow product was dissolved in acetone, and the precipitate (KCl and KNO₃) was filtered out. The filtrate was evaporated to dryness and the residue dissolved in water. The mixture was again filtered and the filtrate evaporated to dryness. The residue was dried under vacuum.

K[Pt(CH₃NH₂)Cl₃]¹·1/2H₂O: Yield 80%; dec pt 164–177 °C. Anal. Calcd: C, 3.15; H, 1.58; N, 3.67; Cl, 27.97. Found: C, 3.59; H, 1.39; N, 4.00; Cl, 27.99.

K[Pt(C₂H₅NH₂)Cl₃]¹·1/2H₂O: Yield 80%; dec pt 170–183 °C. Anal. Calcd: C, 6.08; H, 2.04; N, 3.55; Cl, 26.94. Found: C, 6.56; H, 2.06; N, 3.86; Cl, 26.72.

K[Pt(*i*-C₃H₇NH₂)Cl₃]¹·1/2H₂O: Yield 65%; dec pt 185–209 °C. Anal. Calcd: C, 8.81; H, 2.47; N, 3.43; Cl, 26.03. Found: C, 9.03; H, 2.64; N, 3.32; Cl, 25.91.

K[Pt(*c*-C₄H₉NH₂)Cl₃]¹·1/2H₂O: Yield 45%; dec pt 158–198 °C. Anal. Calcd: C, 11.46; H, 2.63; N, 3.32; Cl, 25.27. Found: C, 11.46; H, 2.77; N, 3.44; Cl, 24.32.

K[Pt(*c*-C₆H₅NH₂)Cl₃]¹·1/2H₂O: Yield 65%, dec pt 172–190 °C. Anal. Calcd: C, 13.81; H, 3.01; N, 3.22; Cl, 24.46. Found: C, 14.25; H, 3.15; N, 3.49; Cl, 23.67.

K[Pt(NH₃)Cl₃]¹·H₂O: Yield 50%. X-ray diffraction methods have shown that this compound was identical with the one reported earlier.²

Crystal Data: [Pt(*i*-C₃H₇NH₂)Cl₃]¹·1/2H₂O, fw = 408.67, monoclinic, C2/c, *a* = 29.153 (24) Å, *b* = 5.928 (3) Å, *c* = 12.178 (7) Å, β = 96.95 (6)°, *V* = 2089 (2) Å³, *F*(000) = 1496, *D*_c = 2.598 Mg m⁻³, *Z* = 8, λ(Mo Kα) = 0.71069 Å, μ(Mo Kα) = 146.9 cm⁻¹, and *T* = 293 K.

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Table I. Refined Coordinates ($\times 10^4$) and Equivalent Isotropic Temperature Factors ($\times 10^3$)

	x	y	z	$U_{eq}, \text{\AA}^2$
Pt	1024.4 (2)	2726.9 (8)	1675.2 (4)	38.5
K	421 (1)	3438 (5)	4051 (2)	49
Cl(1)	605 (1)	1573 (6)	52 (2)	54
Cl(2)	566 (1)	5926 (5)	1678 (2)	47
Cl(3)	1441 (1)	3798 (9)	3313 (3)	74
N	1417 (5)	-106 (2)	1680 (10)	63
O	0	419 (20)	2500	51
C(1)	1840 (9)	-233 (41)	1199 (20)	124
C(2)	2100 (7)	-2418 (35)	1400 (16)	99
C(3)	1947 (7)	1096 (31)	376 (16)	92

Crystallographic Measurements and Structure Resolution. The crystals were obtained by recrystallization from a mixture of acetone and ethanol. An hexagonal brownish plate was chosen after examination under a polarizing microscope for homogeneity. The crystal mounted roughly along the *b* axis had the following distances (mm) between the indicated pairs of faces: $0.038 (100\bar{1}00) \times 0.254 (001\bar{0}01) \times 0.340 (011\bar{0}\bar{1}\bar{1}) \times 0.340 (01\bar{1}\bar{0}\bar{1}\bar{1})$. The cell parameters were obtained from the refined angles of 15 well-centered reflections on a Syntex PI diffractometer using graphite-monochromatized $\text{Mo K}\alpha$ radiation.

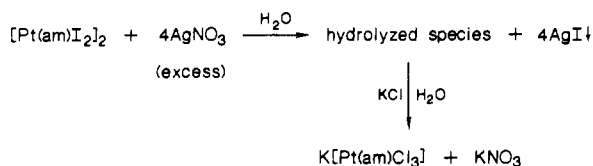
A set of 3058 independent reflections ($h, k, \pm l$) were measured as described previously¹⁰ ($2\theta_{\max} = 60^\circ$). On the basis of the criterion $I > 2.5\sigma(I)$, 1765 reflections were used for the structure resolution. The intensity data were corrected for absorption from the equations of the crystal faces (transmission factors from 0.063 to 0.568) and for Lorentz and polarization effects.

The coordinates of the Pt atom were located from the three-dimensional Patterson map. The position of all the other non-hydrogen atoms were obtained by structure factor and difference-Fourier calculations. The refinement was done by using full-matrix least-squares calculations minimizing $\sum w(F_o - F_c)^2$. Isotropic secondary extinction corrections¹¹ were included in the calculations. A residual peak located on the 2-fold axis was assigned to a water molecule. The H atoms (except those in CH_3 and H_2O) were fixed at the calculated positions with isotropic $B = 6.0 \text{\AA}^2$ ($\text{C-H} = 0.95 \text{\AA}$, $\text{N-H} = 0.85 \text{\AA}$). Individual weights $w = 1/\sigma^2(F)$ were applied. The refinement of the scale factor, coordinates, and anisotropic temperature factors of all atoms converged to $R = \sum |F_o| - |F_c| / \sum |F_o| = 0.055$ and $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} = 0.044$. The refined coordinates are listed in Table I.

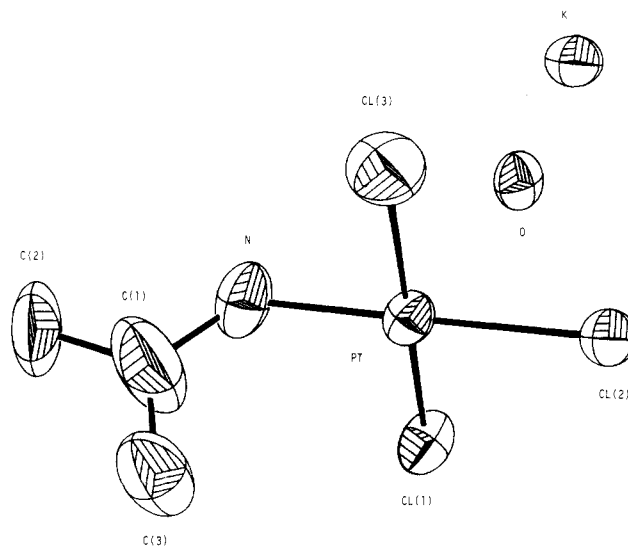
The scattering curves of Cromer and Waber¹² were used except for hydrogen.¹³ The anomalous dispersion terms¹⁴ of Pt, Cl, and K were included in the calculations, which were done on a Cyber 830 computer with programs already described.¹⁰

Results and Discussion

We have developed a new method for the synthesis of monoamine Pt(II) complexes from the cleavage of the iodo-bridged dimers with a silver salt. The dimers can be synthesized from the reaction of $[\text{Pt}(\text{am})_2\text{I}_2]$ in perchloric acid.⁹ The new method involves the following reactions:



In the presence of a silver salt, the dimers are cleaved, producing hydrolyzed species, which will react with KCl to form $\text{K}[\text{Pt}(\text{am})\text{Cl}_3]$. The yields vary from 45 to 80%. Compound with NH_3 , methylamine, ethylamine, isopropylamine, cyclobutylamine and cyclopentylamine have been synthesized. X-ray diffraction methods have shown that the ammine complex was identical with the compound $\text{K}[\text{Pt}(\text{NH}_3)\text{Cl}_3] \cdot \text{H}_2\text{O}$ reported earlier.² The other compounds were characterized by proton NMR, and IR spectroscopy, and the isopropylamine and cyclopentylamine complexes

**Figure 1.** Labeled diagram of $\text{K}[\text{Pt}(i\text{-C}_3\text{H}_7\text{NH}_2)\text{Cl}_3] \cdot \frac{1}{2}\text{H}_2\text{O}$.**Table II.** Bond Distances (\AA) and Angles (deg) in $[\text{Pt}(i\text{-C}_3\text{H}_7\text{NH}_2)\text{Cl}_3]^-$

Distances			
Pt-Cl(1)	2.299 (3)	N-C(1)	1.43 (3)
Pt-Cl(2)	2.320 (3)	C(1)-C(2)	1.51 (3)
Pt-Cl(3)	2.296 (4)	C(1)-C(3)	1.34 (3)
Pt-N	2.03 (1)		
Angles			
Cl(1)-Pt-Cl(2)	89.9 (1)	Cl(3)-Pt-N	89.3 (4)
Cl(1)-Pt-Cl(3)	178.7 (1)	Pt-N-C(1)	123 (1)
Cl(1)-Pt-N	89.9 (4)	N-C(1)-C(2)	115 (2)
Cl(2)-Pt-Cl(3)	91.0 (1)	N-C(1)-C(3)	124 (2)
Cl(2)-Pt-N	179.1 (4)	C(2)-C(1)-C(3)	117 (2)

were studied X-ray diffraction. The crystal structure of the cyclopentylamine is very disordered and should be published later.

Infrared spectroscopy has shown that the compounds crystallize with water of hydration. The two crystal structure determinations have confirmed the presence of a half-molecule of water per Pt atom. This water of hydration is held quite strongly since the crystals used in crystallography were recrystallized in a mixture of acetone and ethanol.

Crystal Structure. A labeled diagram of the complex $\text{K}[\text{Pt}(i\text{-C}_3\text{H}_7\text{NH}_2)\text{Cl}_3] \cdot \frac{1}{2}\text{H}_2\text{O}$ is shown in Figure 1. The bond distances and angles are listed in Table II. The coordination around the Pt atom is square planar. The deviations from the weighted best plane are as follows (\AA): Pt, 0.0007 (5); Cl(1), -0.002 (3); Cl(2), -0.015 (3); Cl(3), -0.023 (4); N, -0.030 (13). The angles around the Pt atom are close to the expected 90 and 180° .

The Pt-Cl bonds (2.299 (3), 2.320 (3), and 2.296 (4) \AA) and Pt-N bond (2.03 (1) \AA) are normal and agree well with published values found in aminochloroplatinum(II) compounds.^{15,16} The three carbon atoms in the organic ligand are disordered as shown by the high thermal factors resulting in low precision of the C-C distances and angles around C(1).

The O atom of the water molecule is located on a 2-fold axis. Its close environment was examined for possible hydrogen bonds. There is no short N...O contact. There might be an interaction with two trans Cl atoms, the two distances $\text{O}\cdots\text{Cl}(2) = 3.35$ (1) \AA , but the angle $\text{Cl}(2)\text{-O-Cl}(2')$ is only 74.7 (2) $^\circ$. Therefore, the water molecule is probably not involved in hydrogen bonding. But the oxygen atom is fairly close to the potassium ion ($\text{O}\cdots\text{K} = 2.778$ (8) \AA). Furthermore, there are six chlorine atoms at distances of 3.199 (4)-3.316 (4) \AA from the K ion, suggesting that the packing energy around the K ion is an important sta-

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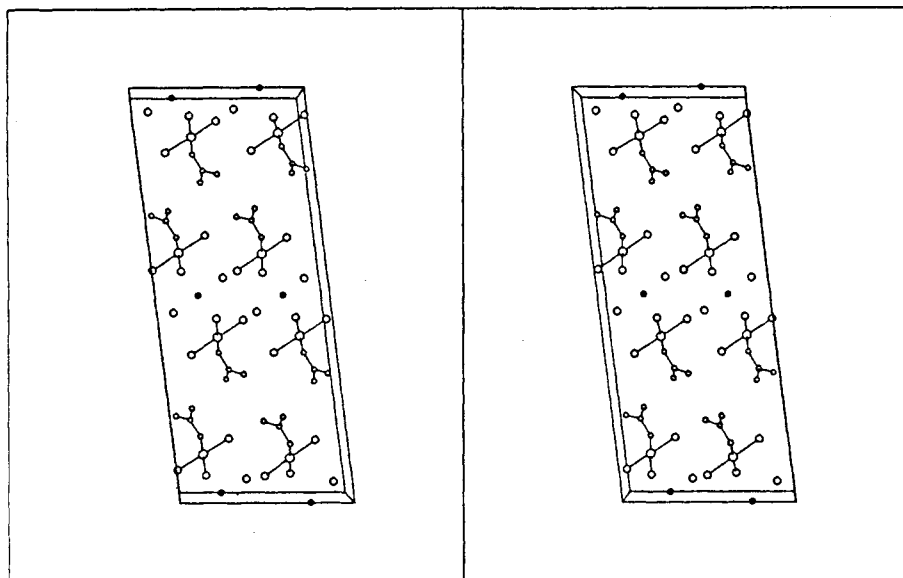


Figure 2. Packing of the molecules in the crystal $K[\text{Pt}(i\text{-C}_3\text{H}_7\text{NH}_2)\text{Cl}_3]\cdot\frac{1}{2}\text{H}_2\text{O}$ (the dark circles represent the O atoms, with the c axis horizontal and the b axis down).

Table III. Main IR Bands (cm^{-1}) in $K[\text{Pt}(\text{am})\text{Cl}_3]\cdot\frac{1}{2}\text{H}_2\text{O}$ Complexes

am	$\nu(\text{O-H})$	$\nu(\text{N-H})$	$\delta(\text{O-H})$	$\delta(\text{N-H})$	$\nu(\text{P-Cl})$
CH_3NH_2	3545	3270	1597	1581	338
	3480	3242			319
		3145			297
CH_3ND_2 (deuteriated)	2649 (O-D)	2440 (N-D)	1180 (O-D)	1149 (N-D)	336
	2600 (O-D)	2385 (N-D)			315
					296
CH_3NH_2 (60°, 24 h)		3272		1581	338
		3244			318
		3142			297
					338
					319
$\text{C}_2\text{H}_5\text{NH}_2$	3698	3281	1591	1581	338
	3522	3210			319
		3133			298
$i\text{-C}_3\text{H}_7\text{NH}_2$	3598	3282	1591	1570	336
	3527	3275			318
		3237			297
		3213			
		3128			
$c\text{-C}_4\text{H}_9\text{NH}_2$	3600	3279	1590	1571	337
	3526	3237			319
		3206			298
		3135			
$c\text{-C}_3\text{H}_7\text{NH}_2$	3600	3270	1593	1568	336
	3522	3235			320
		3208			299
		3128			

bilizing factor in the crystal. The NH_2 group is probably involved in hydrogen bonds with one chloro ligand: $\text{N}\cdots\text{Cl}$ (2) = 3.42 (1) Å, and $\text{Pt-N}\cdots\text{Cl}$ (2) = 99.2 (4)° and $\text{C}(1)\text{-N}\cdots\text{Cl}$ (2) = 129 (1)°.

The packing of the molecules in the crystal is shown in Figure 2. It consists of layers parallel to the bc plane. Each two layers of complex anions are separated by layers of K^+ and water molecules. The latter are located at $x = 0$ and $\frac{1}{2}$ with the K ions on both sides. The chloride ligands of the complex anions are oriented toward the K^+ layers while the isopropylamine moieties are oriented toward each other.

Infrared Spectra. The IR spectra of the monoamine complexes were measured in the solid state. The O-H, N-H, and $\nu(\text{Pt-Cl})$ vibrations are shown in Table III. All of the spectra showed two sharp $\nu(\text{O-H})$ bands between 3480 and 3600 cm^{-1} . The crystal structure determinations of the isopropylamine and the cyclopentylamine complexes have shown the presence of a half-molecule of H_2O per Pt atom. Since the IR spectra of the five amine complexes were very similar, we suggest that all five compounds have similar structures. The water of hydration cannot be removed by drying under vacuum at room temperature. But anhydrous $\text{K}[\text{Pt}(\text{CH}_3\text{NH}_2)\text{Cl}_3]$ was prepared by drying under vacuum at 60

°C for 24 h. The IR spectrum of the deuteriated compound $\text{K}[\text{Pt}(\text{CH}_3\text{ND}_2)\text{Cl}_3]\cdot\frac{1}{2}\text{D}_2\text{O}$ was also recorded (Table III).

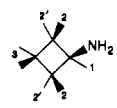
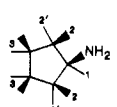
The N-H vibrations appear at lower frequency upon coordination, which weakens the N-H bonds. The NH_2 groups are also involved in hydrogen bonds with the chloride ligands as discussed earlier.

The symmetry of the complex ion is approximately C_{2v} . Three $\nu(\text{Pt-Cl})$ bands are expected; two are stretching vibrations of the cis bonds A_1 (sym) and B_1 (asym) while the third vibration of symmetry A_1 is the $\nu(\text{Pt-Cl})$ trans to am.¹⁷ We have observed three bands between 297 and 338 cm^{-1} .

^1H NMR Spectra. The low-field proton NMR spectra were measured in D_2O . All the peaks appear at lower field upon coordination (Table IV). The coupling constant $^3J(^{195}\text{Pt-H}_1)$ was calculated for the CH_3NH_2 (44 Hz) and $\text{C}_2\text{H}_5\text{NH}_2$ (48 Hz) complexes. For the other complexes, the proton in position 1 is a multiplet of low intensity and its coupling constant could not be calculated. When the spectrum of $\text{K}[\text{Pt}(\text{CH}_3\text{NH}_2)\text{Cl}_3]$ was

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Table IV. Chemical Shifts (ppm) and $\Delta\delta$ (Complex-Ligand) of the $K[\text{Pt}(\text{am})\text{Cl}_3]$ Complexes in D_2O

am	H_1	H_2	$\text{H}_{2'} + \text{H}_3$
$^1\text{CH}_3\text{-NH}_2$ (pH 7)	2.37 (s + d)		
$\Delta\delta$	0.07		
$^1\text{CH}_3\text{-NH}_2$ (pH 4)	2.37 (t + dt)		
$\Delta\delta$	0.07		
$^2\text{CH}_3\text{-}^1\text{CH}_2\text{-NH}_2$	2.67 (q + dq)	1.23 (t)	
$\Delta\delta$	0.12	0.20	
$(^2\text{CH}_3)_2\text{-}^1\text{CH-NH}_2$	3.11 (m)	1.27 (d)	
$\Delta\delta$	0.11	0.25	
	3.47 (m)	2.24 (m)	1.65 (m)
$\Delta\delta$	0.16	0.14	0.05
	3.35 (m)	2.05 (m)	1.59 (m)
$\Delta\delta$	0.15	0.12	0.07

measured in a slightly acid medium, coupling of the methyl protons with the amine protons were observed with $^3J(\text{CH}_3\text{-NH}_2) = 7$ Hz. At neutral pH or slightly basic pH, the coupling was absent. Proton exchange is rapid in free amines but is considerably slower when the amines are complexed to a metal. The coupling constant $^3J(\text{H}_1\text{-H}_2)$ in the ethylamine and isopropylamine complexes is 8 Hz. For the cyclic amines, the four protons in position 2 are not equivalent. The two protons (H_2) that are closer to the amino group are more deshielded upon coordination than the other two ($\text{H}_{2'}$).

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Registry No. $K[\text{Pt}(\text{CH}_3\text{NH}_2)\text{Cl}_3]$, 39729-73-2; $[\text{Pt}(\text{C}_2\text{H}_5\text{NH}_2)_2]_2$, 105691-65-4; $[\text{Pt}(i\text{-C}_3\text{H}_7\text{NH}_2)_2]_2$, 105691-66-5; $[\text{Pt}(c\text{-C}_4\text{H}_7\text{NH}_2)_2]_2$, 105691-70-1; $[\text{Pt}(c\text{-C}_5\text{H}_9\text{NH}_2)_2]_2$, 105709-78-2; $[\text{Pt}(\text{NH}_3)_2]_2$, 105691-63-2; $[\text{Pt}(\text{CH}_3\text{NH}_2)_2]_2$, 105691-64-3; $K[\text{Pt}(\text{C}_2\text{H}_5\text{NH}_2)\text{Cl}_3]$, 109282-42-0; $K[\text{Pt}(i\text{-C}_3\text{H}_7\text{NH}_2)\text{Cl}_3] \cdot 1/2\text{H}_2\text{O}$, 109282-43-1; $K[\text{Pt}(c\text{-C}_4\text{H}_7\text{NH}_2)\text{Cl}_3]$, 109282-44-2; $K[\text{Pt}(c\text{-C}_5\text{H}_9\text{NH}_2)\text{Cl}_3]$, 109282-45-3; $K(\text{Pt}(\text{NH}_3)\text{Cl}_3) \cdot \text{H}_2\text{O}$, 20574-25-8.

Supplementary Material Available: Tables SI–SIII, listing anisotropic temperature factors, fixed coordinates of the hydrogen atoms, and the weighted least-squares plane (2 pages); Table SIV, listing observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

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Pressure Enhancement of Substitution and Oxidative-Addition Reactions of Rhodium(I) Complexes

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Our interest in the intimate nature of substitution reactions of square-planar systems has led to a series of detailed studies on complexes of Pt(II) and Pd(II).^{2,3} The various reaction steps, viz. solvolysis, solvent substitution, and ligand substitution, were

studied as a function of steric hindrance and leaving- and entering-group effects. The reported activation parameters underline the associative nature of these reactions under all conditions. High-pressure kinetic measurements proved to be of significant help in the assignment of further mechanistic details.

Relatively few kinetic studies have been reported on the substitution reactions of Rh(I) complexes,^{4,5} and to our knowledge the effect of pressure on such reactions was not studied to date. These complexes are furthermore of particular interest because of their ability to produce octahedral Rh(III) complexes via oxidative-addition reactions, which play an important role in homogeneous catalysis.⁶ Earlier studies on oxidative-addition reactions of Ir(I) complexes resulted in volumes of activation as large as $-44 \text{ cm}^3 \text{ mol}^{-1}$, which means that the second-order rate constant will double on increasing the pressure by 400 bar (i.e. 40 MPa).⁷ The systems investigated in this study were studied at ambient pressure before,^{5,8,9} and the reported kinetic parameters suggested a promising pressure enhancement. This could be of significant importance in synthetic and homogeneous catalytic cycles involving these or related complexes of Rh(I).

Experimental Section

$\text{Rh}(\text{acac})(\text{P}(\text{O}Ph)_3)_2$, $\text{Rh}(\text{tfac})(\text{P}(\text{O}Ph)_3)_2$, $\text{Rh}(\text{acac})(\text{cod})$, and $\text{Rh}(\text{tfac})(\text{cod})$ were synthesized as described before^{5,10} (acac = acetylacetonate, tfac = trifluoroacetylacetonate, cod = cycloocta-1,5-diene). $\text{Rh}(\text{cup})(\text{CO})(\text{PPh}_3)$ was synthesized as described for $\text{Rh}(\text{acac})(\text{CO})(\text{PPh}_3)$ by using cupferron (ammonium salt of *N*-nitrosophenylhydroxylamine) instead of acetylacetonate.¹¹ Chemical analysis and UV-vis spectra were in good agreement with the theoretically expected values and those reported before, respectively. Rate constants for the substitution reactions were obtained by following the formation of $\text{Rh}(\text{phen})(\text{cod})^+$ at 482 nm on a thermostated (± 0.1 °C) high-pressure stopped-flow system.¹² The oxidative-addition reactions were followed at 340, 400, and 385 nm for the acac, tfac, and cup complexes, respectively, with a modified Zeiss PMQII spectrophotometer equipped with a thermostated high-pressure cell.¹³ All the reactions were studied under pseudo-first-order conditions. The observed first-order rate constants were calculated from plots of $\ln(A_t - A_\infty)$ vs. t , where A_t and A_∞ are the absorbances at time t and infinity, respectively. Such plots were linear for at least 2–3 half-lives of the reaction.

Results and Discussion

The investigated reactions are such that the observed first-order rate constant, k_{obsd} , depends linearly on the concentration of phen (1,10-phenanthroline) and methyl iodide for substitution and oxidative addition, respectively. This can be expressed as in (1),

$$k_{\text{obsd}} = k[\text{L}] \quad (1)$$

where L = phen or CH_3I . The experimental data confirm this expression, and no evidence could be found for a two-term rate law usually observed for substitution reactions of square-planar complexes.² Accordingly, the pressure dependence of k was estimated from the pressure dependence of k_{obsd} at constant [L],¹⁴

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