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Terminal and New Bridging Coordination of Methylguanidine, Arginine, and Canavanine to Platinum(II). The First Crystallographic Study of Bonding between a Transition Metal and a Guanidine Ligand

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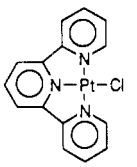
The compound [Pt(trpy)Cl]Cl reacts with the guanidine-containing compounds methylguanidine, arginine, and canavanine to form the yellow monometallic complexes $[Pt(trpy)MeGua]^{2+}$, $[Pt(trpy)ArgH]^{2+}$, and $[Pt(trpy)CanH]^{2+}$ and the red bimetallic complexes $[\{Pt(trpy)\}_2MeGua]^{4+}$, $[\{Pt(trpy)\}_2Arg]^{3+}$, and $[\{Pt(trpy)\}_2Can]^{3+}$. The yellow and the red complexes containing each of the three ligands are separated by cation-exchange chromatography, and the corresponding PF_6^-, ClO_4^-, and BPh_4^- salts are isolated by precipitation. The stability of the complexes upon heating and acidification and the relative difficulties of displacement of the guanidine ligands are studied semiquantitatively. The compositions of the new complexes are determined by mass, UV-vis, IR, and ^1H, ^{13}C, and ^{195}Pt NMR spectroscopy. In the yellow complexes, each guanidine ligand probably binds to a $Pt(trpy)^{2+}$ group through a trigonal (imino-type) nitrogen atom. In the red complexes, each guanidine ligand bridges two $Pt(trpy)^{2+}$ groups, probably through a tetrahedral (amino-type) and a trigonal nitrogen atom. This unprecedented bridging coordination of a guanidine ligand to transition-metal atoms is confirmed by the crystallographic study of $[\{Pt(trpy)\}_2Can](ClO_4)_3 \cdot 5.5H_2O$. It crystallizes in the space group $P2_1$ (No. 4) with the following lattice properties: a = 12.733 (3) Å, b = 27.039 (4) Å, c = 14.813 (3) Å, β = 115.219 (8)°, V = 4614 (2) Å^3, and Z = 4. The structure was refined to a R_w value of 0.0572. In both types of the complex, which coexist in the solid state, the two $Pt(trpy)^{2+}$ groups are nearly parallel and nearly eclipsed; the Pt-Pt distances of 2.9884 (7) and 2.9872 (8) Å are virtually identical, but the bond distances involving the Pt atoms and the guanidine group are different. This and a previous report (Ratilla, E. M. A.; Kostić, N. M. *J. Am. Chem. Soc.* **1988**, *110*, 4427) show that the arginine side chain is a potential ligand in metalloproteins and in metal-dependent enzymes.

I. Introduction

The known functions of arginyl residues in enzymes and in other proteins depend on the positive charge of its side chain. The guanidinium cation, whose normal pK_a value is ca. 12.5, exists throughout the usual pH range of protein stability. It participates in recognition of anionic substrates, binds cofactors, forms internal hydrogen bonds and salt bridges, and enhances protein hydrophilicity.[1-4] Although transition metals are common in metalloproteins and in metal-activated enzymes, coordination of such a metal to the arginyl site chain in a protein has only recently been achieved.[5] The complex chloro(2,2′:6′,2″-terpyridine)-platinum(II), $[Pt(trpy)Cl]^+$ is shown below.



It reacts with Arg 91 in cytochromes *c* from horse heart and from tuna heart; the guanidine group in the side chain displaces the Cl^- ligand from the labeling reagent, and the $Pt(trpy)^{2+}$ chromophore becomes attached covalently to the side chain. This displacement reactioin, which occurs even at pH 7.0, is possible because the hydrophobic environment and the macrodipole of the proximate α-helical backbone diminish the basicity of the guanidine group in Arg 91.[5] In this research, the usual sequence of discoveries is reversed: evidence of the labeling of Arg 91 in the cytochromes *c* prompted us to prepare the corresponding model complexes of platinum(II) with free arginine and with its analogues.

This is a report on the reactions between $[Pt(trpy)Cl]^+$ and the following guanidine-containing ligands, which are listed in Table I: arginine, *N*-acetylarginine, canavanine (the δ-oxa analogue of arginine), methylguanidine, and guanidine itself. Few conclusive studies of transition-metal complexes with guanidine ligands have been made.[6-8] With this work, we begin our systematic research into the formation and properties of these unexplored complexes.

II. Experimental Procedures

Chemicals. The guanidine compounds (L-enantiomers of the amino acids) and the chromatographic materials were obtained from Sigma Chemical Co., the deuteriated solvents and KPF_6 were obtained from Aldrich Chemical Co., $NaBPh_4$ was obtained from J. T. Baker Chemical Co., and $[Pt(trpy)Cl]Cl_2 \cdot 2H_2O$ was obtained from Strem Chemicals. This last compound, which can easily be prepared,[9] now is available from Aldrich Chemical Co.[10] Distilled water was demineralized to the point of a resistance greater than 16 MΩ cm. The common solvents and other chemicals were of the reagent grade.

Absorption Spectroscopy. The UV-visible spectra were recorded with an IBM 9430 spectrophotometer, whose monochromator contains two gratings. The IR spectra between 4000 and 200 cm^{-1} were recorded with an IBM IR98 Fourier-transform instrument, whose sample chamber was flushed with dry air. The mulls of the dried samples in Nujol were smeared on CsI plates; the pellets of the dried samples in KBr (for the middle IR region) were prepared as usual.

NMR Spectroscopy. The ^1H spectra of solutions in D_2O, $(CD_3)_2CO$, and $(CD_3)_2SO$ were recorded at 300 MHz with Nicolet NT300 and Bruker WM300 spectrometers, using residual protons or dioxane as internal references. Complexes prepared in H_2O were dissolved in D_2O by successive cycles of lyophilization and dissolution in D_2O. The ^{13}C spectra of solutions in D_2O—H_2O, if present, did not need to be removed completely—were recorded with the same spectrometers, using acetone or dioxane as internal standards. The ^{195}Pt spectra of solutions were recorded at 64.4 and 42.9 MHz with the Bruker WM300 and WM200 instruments, respectively. A solution 0.20 M both in $K_2[PtCl_4]$ and in NaCl was an external reference (0 ppm). The resonances were sought between +1450 and −2000 ppm. Two-dimensional NOESY spectra of a degassed 10 mM solution of $[\{Pt(trpy)\}_2Can]Cl_3$ in D_2O were recorded with the Nicolet NT 300 instrument; the mixing time was 300 ms.

Mass Spectrometry. The FAB spectra were obtained with a Kratos MS50 instrument. The samples were dissolved as follows: $[\{Pt(trpy)\}_2Arg](BPh_4)_3$ in CH_3CN, $[\{Pt(trpy)\}_2MeGua](BPh_4)_4$ in CH_2Cl_2, and $[\{Pt(trpy)\}_2Can](ClO_4)_3$ in 3-nitrobenzyl alcohol. In the first two cases, 3-nitrobenzyl alcohol was added as a liquid matrix.

Other Procedures. The pH values were measured with a Fisher Accumet 805 MP instrument; the results were not corrected when D_2O was the solvent. Elemental microanalyses of the solids, done repeatedly by

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Table I. Guanidine Ligands[a]

name	formula[b]	guanidinium pK_a	charge	symbol
arginine	$H_2NC(=NH)NH(CH_2)_3CH(NH_3^+)COO^-$	12.5	0	ArgH
	$H_2NC(=NH)NH(CH_2)_3CH(NH_2)COO^-$	12.5	−1	Arg
N^{α}-acetylarginine	$H_2NC(=NH)NH(CH_2)_3CH(NHCOCH_3)COO^-$	12.5	−1	AcArg
canavanine	$H_2NC(=NH)NH(O)(CH_2)_2CH(NH_3^+)COO^-$	7.0	0	CanH
	$H_2NC(=NH)NH(O)(CH_2)_2CH(NH_2)COO^-$	7.0	−1	Can
guanidine	$H_2NC(=NH)NH_2$	13.5	0	Gua
methylguanidine	$H_2NC(=NH)NHCH_3$	13.5	0	MeGua

[a] With neutral guanidine group, as in the platinum(II) complexes. [b] The part set in boldface corresponds to group R in the structural formulas in the text.

Galbraith Laboratories, Inc., are barely satisfactory even though the samples for them were purified. On the one hand, it may be difficult to precipitate a homogeneous salt of a complex cation and a desired anion when the solution contains buffer anions in much higher concentrations. On the other hand, the standard microanalytical methods demonstrably are imperfect—there were discrepancies even in the analysis of $[\{Pt(trpy)\}_2Can](ClO_4)_3 \cdot 5.5H_2O$, whose composition was determined by a complete crystallographic analysis (see below).

Stability of [Pt(trpy)Cl]Cl in Basic Solution. Aqueous solutions that were 50 mM in [Pt(trpy)Cl]Cl and 25, 50, or 100 mM in NaOH showed no irreversible change in their UV–vis spectra over 10 days at room temperature. A 10 mM solution of this complex, kept at 70 °C for 16 days with occasional adjustment of pH to ca. 9.0, also did not show any significant spectral changes. A 15 mM solution of the complex in 30 mM phosphate buffer of pH 8.0, kept at 80 °C for 5 days, yielded a single band of $[Pt(trpy)Cl]^+$ upon chromatography on CM 52, with an 85 mM phosphate buffer of pH 7.0 as eluent.

Synthesis of [Pt(trpy)ArgH]Cl$_2$, [{Pt(trpy)}$_2$Arg]Cl$_3$, [{Pt(trpy)}$_2$Arg](PF$_6$)$_3$, and [{Pt(trpy)}$_2$Arg](BPh$_4$)$_3$. A solution containing 96.4 mg (0.18 mmol) of $[Pt(trpy)Cl]Cl \cdot 2H_2O$ and 31.4 mg (0.18 mmol) of L-arginine in 4 mL of water was kept at 70 °C for 7 days. At the beginning, and occasionally during the reaction, the pH was adjusted to ca. 9.0 by addition of a 1.0 M NaOH solution. The color turned from orange to dark red. The reaction mixture was filtered, evaporated to the minimum volume, and chromatographed on a column of CM 52 cation exchanger; both the equilibration and elution were done with a 85 mM potassium phosphate buffer of pH 7.0. A minor yellow band (ca. 10%) and a major red band (ca. 90%) were eluted in this order. (Since the yellow fraction gradually converts into the red one at room temperature, the chromatographic separation is best carried out at 4 °C at least until the first band is eluted off the column. Since the red fraction is stable upon heating, the rest of the separation can be done either at 4 °C or at room temperature.) Addition of a concentrated solution of KPF_6, followed by standing or evaporation, caused copious precipitation of the red compound. The precipitates were filtered off by centrifugation, washed with cold water and cold methanol, and dried in vacuo. Recrystallization of the red solid from a mixture of acetone and water (1:1) yielded tiny needles that were dried in vacuo. Anal. Calcd (found) for $C_{36}H_{35}N_{10}O_2F_{18}P_3Pt_2$: C, 29.52 (28.47); H, 2.41 (3.01); N, 9.56 (9.11); F, 23.34 (20.75). The red fraction from another similar synthesis was evaporated to ca. 10 mL, and a saturated solution of $NaBPh_4$ was added dropwise to it. The brownish red precipitate was filtered off by centrifugation, washed with cold water in the same way, and dried in vacuo. The yield was 34 mg or 34% with respect to [Pt(trpy)Cl]Cl. Anal. Calcd (found) for $C_{108}H_{95}N_{10}O_2B_3Pt_2$: C, 65.24 (60.91); H, 4.83 (4.67); N, 7.05 (6.80); B, 1.61 (1.66); Pt, 19.64 (19.62). Principal fragments, m/z values, and relative abundancies: $[\{Pt(trpy)\}_2Arg]BPh_4^+$, 1348, 1.2; $[\{Pt(trpy)\}_2Arg]BPh_3^+$, 1270, 1.7; $[\{Pt(trpy)\}_2Arg]BPh_2^+$; 1192, 1.8; $[\{Pt(trpy)\}_2Ag]^+$, 1029, 6.0; $[\{Pt(trpy)\}_2(ArgH - CO_2)]^+$, 984, 1.4; $Pt(trpy)^+$, 428, 100.

Synthesis of [{Pt(trpy)}$_2$Arg](PF$_6$)$_3$. A solution containing 267.5 mg (0.50 mmol) of $[Pt(trpy)Cl]Cl \cdot 2H_2O$ and 43.6 mg (0.25 mmol) of arginine in 10 mL of water was kept at 70 °C for 7 days, and the pH was adjusted to ca. 9.0 as before. Because the chromatography yielded only the red product, this step can be omitted from the procedure. The PF_6^- salt was prepared as before.

Reaction of [Pt(trpy)Cl]Cl with N^{α}-Acetyl-L-arginine. A solution containing 60.0 mg (0.030 mmol) of $[Pt(trpy)Cl]Cl \cdot 2H_2O$ and 6.5 mg (0.030 mmol) of the arginine derivative in 1 mL of water was treated like the corresponding mixture containing arginine; see above. The color changed, and the pH decreased, as in this other reaction.

Synthesis of [Pt(trpy)CanH]Cl$_2$, [{Pt(trpy)}$_2$Can]Cl$_3$, and [{Pt(trpy)}$_2$Can](PF$_6$)$_3$. A solution containing 100.0 mg (0.187 mmol) of $[Pt(trpy)Cl]Cl \cdot 2H_2O$ and 32.9 mg (0.187 mmol) of canavanine in 7 mL of an 85 mM potassium phosphate buffer of pH 8.5 was kept at 40 °C for 9 h. The color turned from orange to deep red. The reaction mixture was filtered and evaporated to the minimum volume. Cation-exchange chromatography on CM 52, with the same buffer as an eluent, yielded two bands. The yellow fraction, whose yield with respect to [Pt(trpy)Cl]Cl was 65%, was eluted at 4 °C with the 85 mM buffer flowing at a rate of ca. 15 mL h^{-1}. The red fraction, whose yield was 35%, was eluted at room temperature with the 125 mM buffer flowing at a rate of ca. 30 mL h^{-1}. Both buffers were of pH 8.5. The same products were obtained when 51.2 mg (0.187 mmol) of canavaninium sulfate were used instead of the equimolar amount of the free base. The treatment with KPF_6, as in the case of arginine complexes, yielded very little yellow precipitate and much red precipitate.

Table II. Crystallographic Data for $[\{Pt(trpy)\}_2Can](ClO_4)_3 \cdot 5.5H_2O$

chem formula: $C_{35}H_{44}N_{10}O_{20.5}Cl_3Pt_2$	space group: $P2_1$ (No. 4)
a = 12.733 (3) Å	T = −50 ± 1 °C
b = 27.039 (4) Å	λ = 0.71073 Å
c = 14.813 (3) Å	ρ_{calcd} = 2.058 g cm^{-3}
β = 115.219 (8)°	μ = 63.83 cm^{-1}
V = 4614 Å^3	transm coeff: 0.9954–0.7086
Z = 4	$R(F_o$ or $F_o^2)$ = 0.0418
fw = 1429.3	$R_w(F_o$ or $F_o^2)$ = 0.0572

Synthesis of [{Pt(trpy)}$_2$Can](PF$_6$)$_3$. A mixture containing 225 mg (0.42 mmol) of $[Pt(trpy)Cl]Cl \cdot 2H_2O$ and 57.5 mg (0.21 mmol) of canavaninium sulfate in 10 mL of water was kept at 40 °C for 4 days, and the pH was occasionally adjusted to ca. 9.0 with a 1.0 M NaOH solution. The reaction mixture yielded a single red band on the CM 52 column; this band was eluted as before. The red solution was evaporated in vacuo to a concentration of ca. 120 mM. To 0.20 mL of this solution was added 0.60 mL of a saturated aqueous solution of KPF_6, and the mixture was left at 4 °C. The red precipitate was filtered and washed with cold methanol and cold diethyl ether. Yield: 34 mg or 92%; decomposes at 187 °C. Anal. Calcd (found) for $C_{35}H_{33}N_{10}O_3F_{18}P_3Pt_2$: C, 28.66 (27.99); H, 2.27 (2.67); N, 9.55 (8.83); Pt, 26.60 (24.80).

Synthesis of [{Pt(trpy)}$_2$Can](ClO$_4$)$_3$·5.5H$_2$O. A mixture containing 112.5 mg (0.210 mmol) of $[Pt(trpy)Cl]Cl \cdot 2H_2O$ and 18.5 mg (0.105 mmol) of free-base canavanine in 5.0 mL of water was heated and adjusted with NaOH as in the previous procedure, but was not chromatographed. To this solution was added a saturated solution of 551 mg (4.5 mmol) of $NaClO_4$ in water. The first precipitate was filtered, washed with water, and dried in vacuo. The filtrate was concentrated to ca. 1.0 mL, and the second precipitate was similarly obtained. Total yield: 90 mg or 66%. Anal. Calcd (found) for $C_{35}H_{44}N_{10}O_{20.5}Cl_3Pt_2$: C, 29.40 (29.82); H, 3.08 (3.39); N, 9.80 (9.77); Cl, 7.46 (6.95); Pt, 27.30 (26.22). Principal fragments, m/z values, and relative abundancies: $[\{Pt(trpy)\}_2CanH](ClO_4)_2^+$, 1231, 22.5; $[\{Pt(trpy)\}_2Can]ClO_4^+$, 1130, 28.2; $[\{Pt(trpy)\}_2Can]^+$, 1031, 8.4; $Pt(trpy - H)^+$, 427, 100.

X-ray Crystallographic Analysis of [{Pt(trpy)}$_2$Can](ClO$_4$)$_3$·5.5H$_2$O. A solution of 60 mg of this compound in ca. 1.0 mL of hot water was left to cool to the room temperature and to evaporate slowly through pinholes for 1 week. Large, well-formed pinacoidal crystals grew. One of them was cleaved to the approximate dimensions 0.51 × 0.52 × 0.54 mm. Although a C-centered orthorombic cell with all angles of 90.00 ± 0.05° was a possibility, axial photographs ruled out mmm symmetry. The technical details are summarized in Table II. The structure was solved by direct methods, with an Enraf-Nonius CAD4 diffractometer and the standard programs. Only the four independent Pt atoms were located from the E map; the other non-hydrogen atoms were found by repeated least-squares refinements and difference-Fourier syntheses. Hydrogen atoms bonded to carbon atoms were placed in calculated positions and used only for the calculation of structure factors. Only the platinum and oxygen atoms in the cations and the chlorine atoms in the anions were refined with anisotropic thermal parameters.

Analysis of [{Pt(trpy)}$_2$Can]Cl$_3$ by Job's Method.[11] Solutions containing various mole fractions of [Pt(trpy)Cl]Cl and of canavanine or canavaninium sulfate were prepared in an 85 mM phosphate buffer of pH 8.5–8.9 and were kept in sealed tubes, at 40 °C, for up to 22 days. The total concentration of the reactants was 1.00 mM. In the preliminary experiments, aliquots were examined spectrophotometrically throughout the reaction. In definitive experiments, the absorbances were measured only at the end in order to avoid evaporation. Formation of the complex was accompanied by the growth of a new band at 480 nm. For mole fractions of [Pt(trpy)Cl]Cl above 0.67, the absorbance at 480 nm was corrected by subtracting the small contribution of this compound. In order to minimize deviations from the Beer law, the solutions were diluted to 100 μM and their spectra recorded in a 10-cm cell. After the spectrophotometric measurements, the solutions were combined and their mixture, after evaporation to a small volume and centrifugation, was chromatographed on a CM 52 column, as before. A single red band was obtained.

Synthesis of [Pt(trpy)MeGua]Cl$_2$, [{Pt(trpy)}$_2$MeGua]Cl$_4$, and [{Pt(trpy)}$_2$MeGua](PF$_6$)$_4$. A solution containing 32 mg (0.060 mmol) of [Pt(trpy)Cl]Cl·2H$_2$O and 13 mg (0.12 mmol) of methylguanidine hydrochloride in 4 mL of water was kept at 80 °C for 5 days, and the pH was occasionally adjusted to ca. 8.0 with NaOH. The minor yellow (ca. 10%) and the major red (ca. 90%) products were separated, and the corresponding PF_6^- salts were obtained, as in the previous synthesis involving arginine. The yield of the red salt was 27 mg or 60% with respect to [Pt(trpy)Cl]Cl. Anal. Calcd (found) for $C_{32}H_{29}N_9F_{24}P_4Pt_2$: C, 25.45 (27.52); H, 1.93 (2.40); N, 8.35 (8.64); Pt, 25.84 (24.41).

Synthesis of [{Pt(trpy)}$_2$MeGua](BPh$_4$)$_4$. A mixture containing 128.6 mg (0.24 mmol) of [Pt(trpy)Cl]Cl·2H$_2$O and 13.3 mg (0.12 mmol) of methylguanidine hydrochloride in 5 mL of water was kept at 70 °C for 10 days and the pH was occasionally adjusted to ca. 9.0 with NaOH. Since an aliquot of the reaction mixture gave a single band on a CM 52 column, the bulk of it was not chromatographed. The precipitate, obtained by adding to the reaction mixture an excess of a saturated solution of NaBPh$_4$ in water, was filtered, washed with water, and dried. Yield: 140 mg or 53%. Principal fragments, m/z values, and relative abundancies: [{Pt(trpy)}$_2$(MeGua − H)](BPh$_4$)$_2^+$, 1566, 1.4; [{Pt(trpy)}$_2$(MeGua − H)]BPh$_4^+$, 1247, 10.4; [{Pt(trpy)}$_2$(MeGua − H)]$^+$, 928, 100; Pt(trpy)$^+$, 428, 33.3.

Reactions of [Pt(trpy)Cl]Cl with Guanidine. A solution containing 16.0 mg (0.030 mmol) of [Pt(trpy)Cl]Cl·2H$_2$O and 5.8 mg (0.060 mmol) of guanidine hydrochloride in 1 mL of water was treated like the corresponding mixture containing methylguanidine hydrochloride. The color changed, and the pH decreased, as in this other reaction. The minor yellow (ca. 10%) and the major red (ca. 90%) products were separated on the CM 52 column, as before.

Stability of the Complexes. Effects of acids and of added nucleophiles on the complexes in aqueous solutions were examined by UV–vis spectrophotometry. All the red complexes proved stable indefinitely at 7 < pH < 9 and upon heating. The yellow complexes, however, converted into their red counterparts upon concentration and heating and therefore had to be cooled. The reverse conversion occurred, albeit slowly, upon addition of an excess of the guanidine ligands to the mildly acidic solutions of the corresponding red complexes. The following experiments were done at room temperature. At pH <5, the red complex [{Pt(trpy)}$_2$Arg]$^{3+}$ decomposed slowly in the presence of an excess of Cl^- anions; at pH < 2, it decomposed immediately even when the noncoordinating H_3PO_4 and H_2SO_4 were used for acidification. The yellow complex [Pt(trpy)CanH]$^{2+}$ remained stable as the pH was lowered to 2 with H_2SO_4. Separate additions of the 100-fold, 10000-fold, and 20000-fold excesses, respectively, of the KI, KBr, and KCl caused no apparent decomposition of [Pt(trpy)CanH]$^{2+}$ after 2 h; decomposition became evident after 1 day and pronounced after 2 days. The red complex [{Pt(trpy)}$_2$Can]$^{3+}$ proved stable at pH 8.5 even in the presence of a 70000-fold excess of KBr. The complex decomposed, however, as the pH was lowered to 4.5 with H_2SO_4.

Conversion of the yellow [Pt(trpy)CanH]$^{2+}$ into the red [{Pt(trpy)}$_2$Can]$^{3+}$ in aqueous solution was followed by the growth of absorption at 480 nm. The solutions of the yellow complex were thermostated in closed containers, and aliquots were examined spectrophotometrically. The reaction was considered complete when the absorbance quotient A_{480}/A_{244} ceased increasing. At 40 °C for 48 h, a 77 μM solution remained stable, a 0.31 mM solution reacted slightly, and a 1.5 mM solution reacted noticeably. At 80 °C, the full conversion of the yellow complex into the red complex took the following times: 40, 18, and 6 h for the 77 μM, 0.31 mM, and 1.5 mM solutions, respectively. A solution that was 50 μM in the yellow [Pt(trpy)CanH]$^{2+}$ and a solution that was 50 μM both in this complex and in [Pt(trpy)Cl]$^+$ underwent the conversion into the red [{Pt(trpy)}$_2$Can]$^{3+}$ at approximately the same rate.

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III. Formation of the Guanidine Complexes

The complex [Pt(trpy)Cl]$^+$ is stable under the reaction conditions, and it is unreactive toward amino and carboxylate groups of amino acids.[12–14] As the ligands in Table I react with this complex, all of them release protons; when the pH becomes constant, the substitution is completed. The three ligands whose reactions were studied in more detail—the amino acids arginine and canavanine and the simple ligand methylguanidine—all yield similar products. Evidently, it is the guanidine group that displaces the Cl^- ligand and coordinates to the Pt(trpy)$^{2+}$ fragment.

In our previous study, concerning cytochrome *c*, reactivity of Arg 91 toward [Pt(trpy)Cl]$^+$ was attributed to the position of this amino acid residue in the protein. The basicity of its guanidine group is diminished—and consequently the pK_a value is lowered from the typical value of 12.5—by the hydrophobic environment and by the macrodipole of the adjacent α-helical segment of the polypeptide chain.[5] The hypothesis of diminished basicity was confirmed by showing that canavanine, whose guanidinium group has a pK_a of 7.0,[15] reacts with [Pt(trpy)Cl]$^+$ readily under the mild conditions of protein labeling. In the present study, this and other similar reactions are investigated more fully.

The reactivity of [Pt(trpy)Cl]$^+$ toward the guanidine ligands depends on their intrinsic basicity and on the reaction conditions, as established in systematic examination (by cation-exchange chromatography and UV–vis spectrophotometry) of the reaction mixtures held for various times, at different temperatures, and in solutions of different basicity. Other conditions being equal, canavanine (pK_a = 7.0) is more reactive than other ligands (pK_a $\approx$ 13); it reacts already at room temperature and in neutral solutions, whereas the other ligands require heating, mildly basic medium, or both. The substitution reaction is accelerated, and the preponderance of the red product over the yellow product is enhanced, at higher pH values. The pH of the reaction mixture was kept below ca. 9.5 lest the hydroxide ions attack the complexes irreversibly.

Since [Pt(trpy)Cl]$^+$ reacts with the very basic ligands in mildly basic solution, where only a minuscule fraction of the guanidine group (pK_a $\approx$ 13) is deprotonated, the chloride ligand must be labile. This lability probably is caused by the aromatic terpyridine ligand; indeed, the chloride ion is displaced from [Pt(trpy)Cl]$^+$ approximately 10^3–10^4 times faster than from the analogous aliphatic complex, [Pt(dien)Cl]$^+$.[16] This facile reactivity, together with its other advantages, makes [Pt(trpy)Cl]Cl useful as a selective and noninvasive reagent for labeling of proteins.[5,12–14]

The ^{195}Pt NMR spectra recorded during the reaction between [Pt(trpy)Cl]$^+$ and canavanine show the decline of the signal at −1206 ppm and the growth of the pair of signals at −959 and −974 ppm. The corresponding conversion of the yellow [Pt(trpy)CanH]$^{2+}$ to the red [{Pt(trpy)}$_2$Can]$^{3+}$ may amount simply to addition of the second Pt(trpy)$^{2+}$ group to the yellow complex.

IV. Properties and Composition of the Guanidine Complexes

The spectroscopic properties of the new complexes are summarized in Table III. In approximately neutral aqueous solutions, the yellow complexes have the net charge +2 because arginine and canavanine ligands exist as zwitterions. The red complexes of these ligands have the net charge +3 because two Pt(trpy)$^{2+}$ groups diminish the basicity of the α-amino group so that the amino acids exist as carboxylate anions. The red complex of methylguanidine, which cannot be deprotonated in this way, has a charge of +4. The relative mobilities on the CM 52 cation exchanger are consistent with these charges. The yellow products are eluted faster than the corresponding red ones, and the red complex of methylguanidine is eluted slower than the red complex

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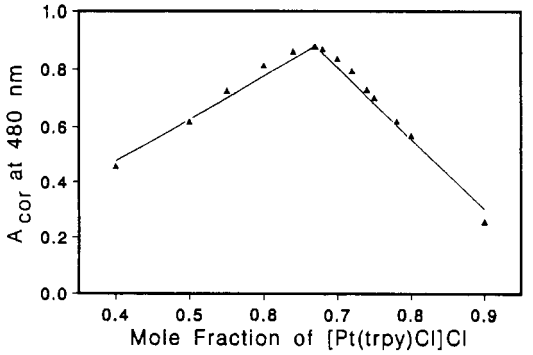

Figure 1. Job's plot for $[\{Pt(trpy)\}_2Can]Cl_3$.

of arginine under identical chromatographic conditions. The various spectroscopic methods of characterization yield consistent descriptions of the new compounds in solution.

Mass Spectra. The FAB spectra show that the red complexes each contain two $Pt(trpy)^{2+}$ groups per guanidine-containing ligand. Only the singly charged fragments occurred in significant amounts; multiply charged ones were evident just in the first few scans. The same phenomenon was observed in similar studies of other transition-metal complexes with polypyridyl ligands.[17-20]

Absorption Spectra. The electronic spectra permit both qualitative comparisons among the complexes and their quantitative determination in solution. The charge-transfer bands in the region 300–350 nm depend on the identity of the ligand L in $[Pt(trpy)L]^{n+}$, whereas the aromatic bands in the region 200–300 nm are characteristic of the $Pt(trpy)^{2+}$ fragment itself. Displacement of the chloride ligand from $[Pt(trpy)Cl]^+$ by the guanidine ligands causes changes in the former region, but does not affect the latter one markedly. The spectra of all the yellow complexes containing guanidine, arginine, canavanine, and methylguanidine are similar to one another. So are the spectra of the red complexes; evident in all of them is an additional band at ca. 480 nm. Because all of the guanidine-containing compounds react similarly with $[Pt(trpy)Cl]^+$, all of them probably coordinate to platinum(II) in the same way—through the guanidine group.

The yellow and the red products always occur together. The former cannot be obtained by itself, but since it converts into the latter, the latter can be obtained alone if the mixture of [Pt(trpy)Cl]Cl and the guanidine ligand in the correct ratio is heated for several days. Therefore, the composition of the yellow complex could not, but that of the red complex could, be determined by Job's method. This method was applied to the red complex of canavanine, which is representative of the red complexes with the other guanidine ligands as well. As Figure 1 shows, the complex contains exactly two $Pt(trpy)^{2+}$ groups per canavanine ligand.

IR Spectra. The strong band at 344 cm^{-1} in the spectrum of [Pt(trpy)Cl]Cl, corresponding to the Pt–Cl vibration, disappears upon formation of the complexes. The bands at 1663 and 1684 cm^{-1} in the spectra of the guanidine-containing compounds, corresponding to the C–N vibrations, shift upon complexation by 18–59 cm^{-1} to lower frequencies.

^{1}H NMR Spectra. They proved particularly informative because the resonances of the aromatic $Pt(trpy)^{2+}$ group and of the aliphatic guanidine-containing ligands occur in separate regions of the spectra. (The guanidine protons are undetectable in D_2O solutions because of exchange, but are evident when the spectra are recorded in $(CD_3)_2SO$ and $(CD_3)_2CO$ solutions.) The relative intensities of the signals confirmed that the ratio of $Pt(trpy)^{2+}$ to the ligand is 1:1 in the yellow complexes and 2:1 in the red complexes. As expected, the protons whose chemical shifts are most affected by coordination are those in the guanidine group and those that sit nearest to the guanidine group in the organic ligand (namely, H^6 in arginine and CH_3 in methylguanidine) and to the platinum atom in the $Pt(trpy)^{2+}$ fragment (namely, H^6 and H^5).

^{13}C NMR Spectra. Listed below are the downfield movements of the ^{13}C resonances in the guanidine-containing ligands as they form the respective red complexes. The carbon atoms in the amino acids are ordered as follows: COO^-, α, β, γ, δ (absent in canavanine), and ζ. For arginine: 0.2, 0.3, 0.5, 1.1, 1.5, and 9.3 ppm. For canavanine: 2.2, –0.2, 0.8, 2.4, none, and 6.8 ppm. The carbon atoms in methylguanidine, CH_3 and C, correspond to the δ and ζ atoms in arginine; their respective movements are 1.7 and 8.5 ppm. The great perturbations of the C^ζ atoms confirm that all three ligands coordinate through the guanidine group. In the arginine complex, the perturbation increases monotonically along the amino acid chain toward the guanidine group. In the canavanine complex, however, even the carboxylate carbon atom is significantly affected by coordination. Perhaps the arginine chain in solution extends away from the $Pt(trpy)^{2+}$ groups, whereas the canavanine chain in solution adopts a conformation in which the carboxylate anion is attracted to these positively charged groups. On the one hand, noncovalent interactions among ligands commonly manifest themselves in the perturbed chemical shifts.[21,22] On the other hand, the two-dimensional ^{1}H NMR spectra (NOESY) of $[\{Pt(trpy)\}_2Can]^{3+}$ do not contain off-diagonal peaks attributable to an interaction between the terpyridine and α-CH protons. Because, in molecules of this size, NOE effects may be absent for other reasons,[23] these ^{1}H NMR spectra do not rule out noncovalent interactions as the cause of the unusual ^{13}C chemical shifts.

The arginine and methylguanidine complexes each show a single set of ^{13}C terpyridine resonances—evidence that the two $Pt(trpy)^{2+}$ groups in each complex are equivalent. The canavanine complex, however, shows doubling of the terpyridine resonances—evidence that the two $Pt(trpy)^{2+}$ groups in it are inequivalent. It is uncertain whether this inequivalence stems from the putative noncovalent interactions discussed above.

^{195}Pt NMR Spectra. Since the ^{195}Pt chemical shift of platinum(II) complexes depends greatly on the ligands,[24,25] ^{195}Pt NMR spectroscopy is well-suited to the study of the new guanidine complexes. The chemical shifts, versus $[PtCl_4]^{2-}$, of the yellow complexes $[Pt(trpy)L]^{2+}$ fall in the narrow range from –1166 to –1177 ppm (when L is MeGua or ArgH) and at –1206 ppm (when L is CanH), near the chemical shifts of $[Pt(trpy)Im]^{2+}$ (–1150 ppm)[12] and of $[Pt(trpy)HisH]^{2+}$ (–1146 ppm).[12] Since in the last two complexes imidazole and histidine are coordinated through the trigonal nitrogen atom,[12] the guanidine ligands probably are also coordinated through such an atom. The canavanine complex differs from the methylguanidine and arginine complexes because it has an oxygen atom, whereas the other two have an organic substituent, attached to the guanidine group; see Table I. The methylguanidine and canavanine complexes show one signal each, whereas the arginine complex shows a major and a minor signal close to each other. These properties are related to structures of the complexes in section V.

The ^{195}Pt NMR spectra of the red complexes $[\{Pt(trpy)\}_2L]^{n+}$ containing three guanidine ligands L differ from those of the yellow complexes and among themselves. Their chemical shifts, in the narrow range from –957 to –994 ppm, are by more than 200 ppm lower than the shifts of the yellow complexes, presumably because guanidine coordinates weaker as a bridging ligand than as a terminal ligand. The spectra of the methylguanidine and arginine complexes at ambient temperature, in aqueous solution, contain one signal each, whereas the spectrum of the canavanine complex contains two equal signals 15 ppm apart. This doubling probably is caused by the slightly different environments of two $Pt(trpy)^{2+}$

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Table III. Spectroscopic Properties of Guanidine Complexes and of Their Precursors

compd[a]	λ_{max}, nm[b] (ϵ, M^{-1} cm^{-1})	NMR chem shifts, ppm: ^1H[c] Pt(trpy)	^1H[c] ligand	^{13}C[d] Pt(trpy)	^{13}C[d] ligand	^{195}Pt[e]	IR bands, cm^{-1}[f]
[Pt(trpy)Cl]Cl[g]	342 (13 300), 270 (24 300), 242 (27 800)	8.08 m (4,4'), 7.88 d (3,3'), 7.82 m (6), 7.37 m (5)		157.0 (3), 153.5 (3'), 150.4 (6), 142.7 (4), 142.4 (4'), 129.1 (5), 125.4 (2), 124.1 (2')		−1080	3425 (br, m), 3117 (sh, m), 2986 (sh, s), 2934 (s), 1736 (vs), 1605 (sh, s), 1468 (s), 1447 (s), 1383 (sh, vs), 1259 (br, s), 1173 (sh, m), 1101 (sh, vs), 1022 (s), 937 (s), 795 (sh, s), 717 (m), 702 (sh, m), 585 (br, m), 517 (m), 476 (w), 457 (s), 394 (br, m), 368 (m), 344 (s), 294 (br, s)
arginine[h]			3.73 t (α), 3.22 t (δ), 1.87 m (β), 1.67 m (γ)		177.7 (COO^-), 155.9 (ζ), 54.9 (α), 40.8 (δ), 29.5 (β), 24.3 (γ)		3489 (vs), 3346 (sp, vs), 3288 (br, vs), 3105 (br, vs), 2953 (sp, vs), 2937 (vs), 2981 (vs), 2868 (vs), 2351 (m), 2324 (m), 1705 (vs), 1684 (vs), 1645 (vs), 1607 (vs), 1564 (vs), 1474 (sp, s), 1452 (s), 1441 (s), 1423 (sp, vs), 1379 (sp, s), 1362 (s), 1331 (sp, vs), 1302 (s), 1188 (s), 1136 (sp, vs), 1121 (s), 1080 (sp, s), 1011 (vs), 928 (m), 854 (s), 811 (s), 797 (vs), 752 (vs), 631 (vs), 662 (vs), 607 (sp, m), 552 (sp, m), 495 (w), 303 (w)
[Pt(trpy)ArgH]Cl_2[i]	332 (10 600), 273 (22 900), 244 (29 100)					−1168, −1177 (1.0:1.4)	
[{Pt(trpy)}$_2$Arg]Cl_3[j]	488 (3700), 309 (24 000), 270 (54 800), 244 (66 000)	8.33 m (6,4'), 8.19 t (4), 7.96 m (3,3'), 7.58 t (5)	3.75 t (α), 3.51 t (δ), 2.09 m (β), 1.85 m (γ)	156.8 (3), 153.4 (3'), 151.2 (6), 142.9 (4'), 142.8 (4), 129.7 (5), 125.5 (2), 124.0 (2')	177.9 (COO^-), 165.2 (ζ), 55.2 (α), 42.3 (δ), 30.0 (β), 25.4 (γ)	−982 [−957]	3744 (m), 3406 (br, vs), 3302 (br, s), 3096 (br, s), 3028 (br, m), 2930 (m), 2860 (m), 2361 (m), 2336 (m), 1628 (vs), 1603 (sp, vs), 1558 (sp, vs), 1502 (m), 1477 (sp, s), 1452 (sp, s), 1446 (s), 1400 (sp, s), 1346 (m), 1315 (sp, s), 1292 (m), 1252 (br, s), 1188 (m), 1171 (m), 1140 (m), 1109 (m), 1094 (m), 1075 (m), 1032 (sp, s), 839 (vs), 773 (sp, s), 741 (m), 723 (m), 660 (m), 648 (m), 559 (sp, vs), 517 (m), 461 (m), 434 (br, w)
canavanine[k]			3.93 m (γ), 3.82 m (α), 2.20 m (β)		174.0 (COO^-), 157.6 (ζ), 68.7 (γ), 52.2 (α), 29.0 (β)		3489 (vs), 3346 (sp, vs), 3288 (br, vs), 3105 (br, vs), 2953 (sp, vs), 2937 (vs), 2881 (vs), 2868 (vs), 2361 (m), 2324 (m), 1705 (vs), 1684 (vs), 1645 (vs), 1607 (vs), 1564 (vs), 1474 (sp, s), 1452 (s), 1441 (s), 1423 (sp, vs), 1379 (sp, s), 1362 (s), 1331 (sp, vs), 1302 (s), 1236 (sp, s), 1188 (s), 1178 (sp, s), 1157 (m), 1144 (m), 1136 (sp, vs), 1096 (sp, s), 1068 (sp, s), 1026 (sp, vs), 941 (sp, s), 918 (sp, s), 878 (sp, s), 789 (sp, s), 766 (sp, m), 708 (sp, s), 696 (br, s), 536 (s), 503 (s), 455 (s), 411 (sp, m), 354 (sp, m)
[Pt(trpy)CanH]Cl_2[k]	336 (10 400), 274 (19 300), 244 (27 500)	8.20 m (4,4'), 8.12 t (3,3'), 8.40 t (6), 7.64 m (5)	4.19 t (γ), 3.63 t (α), 2.10 m (β)	156.7 (3), 153.9 (3'), 151.1 (6), 142.5 (4), 142.0 (4'), 128.3 (5), 124.5 (2), 122.8 (2')	173.3 (COO^-), 158.7 (ζ), 70.5 (γ), 51.3 (α), 28.2 (β)	−1206	3246 (br, m), 1730 (sp, s), 1640 (sh, s), 1607 (sp, s), 1290 (m), 1169 (w), 1074 (w), 841 (s), 771 (sp, s), 558 (s), 519 (m), 447 (br, m), 394 (m), 308 (m)
[[Pt(trpy)]$_2$Can]Cl_3[l]	480 (4000), 310 (23 000), 270 (48 000), 244 (60 000)	8.12 m (4,4'), 7.86 m (3,3'), 8.25 m (6), 7.49 (m) (5)	4.27 t (γ), 3.63 t (α), 2.11 m (β)	154.3, 155.1 (3); 152.0 152.6 (3'); 150.5, 150.7 (6); 142.1, 142.4 (4); 141.8 (4'); 128.7, 129.1 (5); 124.6, 124.8 (2); 122.9, 123.2 (2')	176.2 (COO^-), 164.4 (ζ), 71.1 (γ), 52.0 (α), 29.8 (β)	−959, −974 (1.0:1.0) [−970]	3662 (br, m), 3391 (br, s), 2975 (m), 2926 (sp, s), 2875 (m), 2375 (w), 2362 (w), 1625 (sh, s), 1607 (s), 1562 (m), 1516 (m), 1479 (sp, s), 1402 (sp, s), 1317 (sp, s), 1288 (m), 1250 (s), 1188 (w), 1169 (s), 1144 (m), 1112 (m), 1094 (sp, m), 1034 (sp, s), 843 (vs), 750 (sp, s), 775 (sp, s), 731 (sp, s), 656 (m), 644 (sp, m), 557 (sp, s), 518 (m), 459 (m), 436 (w), 352 (w)
methylguanidine[m]			in D_2O: 2.81 s (CH_3)		27.3 (CH_3), 157.5 (gua)		3354 (br, vs), 3180 (vs), 2926 (sp, s), 2854 (sp, m), 2349 (sp, w), 1663 (vs), 1460 (sp, s), 1427 (sp, s), 1377 (sp, m), 1173 (s), 1067 (br, m), 912 (sp, m), 563 (br, s)
			in DMSO: 2.70 d (CH_3), 7.32 s (gua), 7.79 s ($NHCH_3$)				

[Pt(trpy)MeGua]$^{2+}$ [a]	332 (9800), 273 (21 700), 244 (27 900)				–1166		3447 (vs), 3000 (m), 2925 (s), 2975 (s), 2363 (sp, s), 2338 (s), 1641 (s), 1609 (sp, s), 1479 (sp, s), 1456 (sp, s), 1400 (sp, s), 1317 (sp, m), 1261 (m), 1034 (m), 843 (vs), 768 (sp, s), 744 (sp, s), 714 (sp, s), 662 (w), 602 (sp, m), 559 (sp, s), 518 (w), 460 (w)
[[Pt(trpy)]$_2$MeGua](PF$_6$)$_4$ [c]		8.72 d (6), 7.80 t (5), 8.30 m (3,3'), 8.40 t (4), 8.53 t (4')	6.53 br, s (NH_2), 5.12 s (NH), 3.31 d (CH_3)		–994		3433 (br, s), 2955 (sp, vs), 2926 (sp, vs), 2850 (sp, s), 2361 (sp, m), 2325 (m), 1645 (br, s), 1612 (s), 1572 (s), 1538 (w), 1456 (sp, s), 1400 (sp, s), 1377 (sp, s), 1261 (sp, s), 1096 (br, s), 1032 (s), 845 (s), 804 (sp, s), 775 (sp, m), 557 (s), 516 (sp, m), 458 (m), 434 (m)
[[Pt(trpy)]$_2$MeGua]Cl$_4$ [f]	490 (3600), 309 (26 100), 270 (59 700), 244 (73 000)	8.29 m (6,4'), 8.17 t (4), 7.92 m (3,3'), 7.53 t (5)	3.08 s	155.3 (3), 152.8 (3'), 151.1 (6), 143.0 (4'), 142.8 (4), 129.8 (5), 125.5 (2), 123.9 (2')	–960 [–969]	29.0 (CH_3), 166.0 (gua)	

[a] In aqueous solutions of the complexes, Cl^- is presumed to be the counterion even in the presence of sulfate or phosphate ions. [b] For 8 to 15 μM solutions in an 85 mM potassium phosphate buffer of pH 7.0. [c] For solutions in D_2O at pH* 9.0, chemical shifts were recorded vs DSS with residual water as an internal reference; for solutions in $(CD_3)_2CO$ or DMSO-d_6, chemical shifts were recorded vs TMS with residual solvent or TMS as an internal reference; multiplicities and assignments are included. [d] For 100 mM solutions in D_2O at pH* 9.0, unless otherwise stated; assignments are included. [e] For 5 to 30 mM solutions at pH* 9.0 containing at least 30% D_2O, unless otherwise stated; the chemical shifts were recorded vs $[PtCl_4]^{2-}$ as an external reference and standard; the relative intensities of the signals are in parentheses. [f] PF_6^- salts of the complexes were used except [Pt(trpy)Cl]Cl; middle-IR spectra were run on KBr pellets, unless otherwise stated; far-IR spectra were run on Nujol mulls on CsI; Nujol absorptions are not reported. Abbreviations: vs, very strong; s, strong; m, medium; w, weak; sp, sharp; br, broad; sh, shoulder. [g] ^{13}C NMR and IR spectral data were taken from this work; the rest were taken from ref 12. [h] Free base. [i] ^{195}Pt NMR spectral data for the complex dissolved in a ca. 3 M potassium phosphate buffer of pH* 7.0. [k] NMR spectral data for the complex in D_2O dissolved in a ca. 3 M potassium phosphate buffer of pH* 7.0. [l] In brackets, ^{195}Pt NMR shift of a saturated solution of the PF_6^- salt in $(CD_3)_2CO$. [m] Hydrochloride. [n] ^{195}Pt NMR spectral data were obtained for a reaction mixture containing equimolar amounts of [Pt(trpy)Cl]Cl and MeGua·HCl in water, which was kept at 50 °C and pH 9.5 for 18 h and brought to pH* 7.0; additional signals at –1073 and –957 ppm correspond respectively to [Pt(trpy)Cl]Cl and to [[Pt(trpy)]$_2$MeGua]Cl$_4$. [o] For saturated solutions in $(CD_3)_2CO$. [p] NMR spectral data were obtained for the compound fully formed in a reaction between equimolar amounts of [Pt(trpy)Cl]Cl and MeGua·HCl in D_2O at pH* 9.0; additional ^1H signal at 2.81 ppm and ^{13}C signals at 27.3 and 157.5 ppm correspond to free methylguanidine. See footnote *j*.

groups in the same complex or by the coexistence of slightly different complexes. Since the difference is small, the two platinum atoms must have similar or identical ligands in the fourth coordination place. In aqueous solution at 325 K and in acetone solution, the two signals coalesce into one. Evidently, the two platinum atoms in the complex are easily made equivalent, or the two isomers of the complex are easily converted into each other. The doubling of signals in the ^{13}C and ^{195}Pt NMR spectra of $[\{Pt(trpy)\}_2Can]^{3+}$ probably has structural causes, which will be discussed in section V. The ^{195}Pt chemical shifts of the cationic complexes depend slightly on the anions in solution and somewhat more on the solvent, as Table III shows. The shift of the methylguanidine complex is independent of pH, whereas the shift of the arginine complex, which contains ionizable groups, changes in the pH range 7.0–9.0.

V. Structures of the Complexes

A neutral monosubstituted guanidine group can exist as two tautomers; with reference to the character of an unsubstituted nitrogen atom (designated N^2), they are termed imino and amino forms.[15] (With reference to the substituted nitrogen atom, N^1,

these designations of the tautomers would be reversed. This revised nomenclature may be more logical because of the uniqueness of the atom N^1, but we will adhere to the existing convention.) Little is known about this tautomerism, and the neutral monosubstituted guanidine group is generally assumed, by textbook authors and even by Chemical Abstracts Service, to exist in the imino form. Both forms, however, seem to exist in the aqueous solution of arginine; the imino form is slightly favored.[26] Guanidine compounds containing aromatic[27] and electron-withdrawing[15] substituents seem to greatly favor the amino form. Indeed, the neutral guanidine group of canavanine exists exclusively as the amino tautomer in the solid state.[15] To our knowledge, tautomerism of canavanine in solution and of methylguanidine in either solid or solution has not been studied. In the absence of such knowledge, the structures of the new complexes will be discussed tentatively.

Yellow Complexes, [Pt(trpy)L]$^{2+}$. The ^{195}Pt chemical shifts indicate that the guanidine group is coordinated through a trigonal nitrogen atom. It could be either N^2 (in the imino tautomer) or N^1 (in the amino tautomer). Therefore both of the following structures are possible:

The methylguanidine and canavanine complexes show one ^{195}Pt signal each, whereas the arginine complex shows two unequal signals only 9 ppm apart. If the ^{195}Pt chemical shift is sensitive to the slight difference between N^1 and N^2 atoms as donors, the first two complexes perhaps exist in solution as a single tautomer each, whereas the third complex in solution may be a mixture of two tautomers. Alternatively, the two signals in the last case may be due to noncovalent interactions between the flexible arginine chain and the Pt(trpy)$^{2+}$ group.[21,22]

Red Complex [{Pt(trpy)}$_2$Can]$^{3+}$. To our knowledge, this is the first transition-metal complex containing a coordinated guanidine to be analyzed crystallographically. The two independent complex

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Table IV. Coordinates of the Non-Hydrogen Atoms in the Complex Cation of the Salt $[\{Pt(trpy)\}_2Can](ClO_4)_3 \cdot 5.5H_2O$

atom	x	y	z	B_{eq},[a] Å^2	atom	x	y	z	B_{eq},[a] Å^2
Pt(1)	0.09206 (4)	0.000	−0.12651 (3)	1.86 (1)	C(42)	1.012 (1)	0.0556 (6)	0.550 (1)	3.2 (3)*
Pt(2)	0.11250 (4)	0.04220 (2)	0.06676 (3)	1.75 (1)	C(43)	0.922 (1)	0.0865 (7)	0.495 (1)	4.0 (3)*
Pt(3)	0.87029 (4)	−0.08060 (2)	0.59128 (3)	1.83 (1)	C(44)	0.805 (1)	0.0697 (7)	0.466 (1)	3.6 (3)*
Pt(4)	0.85714 (4)	−0.12790 (2)	0.40451 (3)	1.629 (9)	C(45)	0.789 (1)	0.0238 (6)	0.492 (1)	3.1 (3)*
O(1)	0.3061 (8)	0.1139 (4)	0.1039 (6)	2.3 (2)	C(46)	0.921 (1)	−0.2272 (5)	0.4934 (9)	2.1 (2)*
O(2)	0.5921 (8)	0.1294 (5)	0.1896 (8)	3.9 (3)	C(47)	1.005 (1)	−0.2629 (6)	0.545 (1)	3.1 (3)*
O(3)	0.6607 (9)	0.1711 (5)	0.3314 (8)	4.0 (3)	C(48)	1.120 (1)	−0.2561 (7)	0.572 (1)	3.5 (3)*
O(4)	0.6601 (7)	−0.1923 (3)	0.3595 (6)	2.0 (2)	C(49)	1.154 (1)	−0.2114 (6)	0.544 (1)	2.8 (3)*
O(5)	0.3220 (9)	−0.2270 (4)	0.1355 (8)	3.6 (3)	C(50)	1.072 (1)	−0.1760 (5)	0.4936 (9)	1.7 (2)*
O(6)	0.3946 (8)	−0.2168 (4)	0.3008 (7)	3.2 (2)	C(51)	1.100 (1)	−0.1267 (5)	0.4632 (9)	2.1 (2)*
N(1)	0.0779 (9)	−0.0660 (4)	−0.0857 (8)	2.2 (2)*	C(52)	1.205 (1)	−0.1083 (6)	0.480 (1)	2.7 (3)*
N(2)	−0.0783 (8)	−0.0025 (4)	−0.1934 (7)	1.8 (2)*	C(53)	1.212 (1)	−0.0608 (6)	0.446 (1)	3.0 (3)*
N(3)	0.0532 (9)	0.0714 (5)	−0.1933 (8)	2.5 (2)*	C(54)	1.112 (1)	−0.0331 (6)	0.3940 (9)	2.3 (2)*
N(4)	0.2679 (9)	0.0117 (5)	−0.0505 (8)	2.5 (2)*	C(55)	1.009 (1)	−0.0544 (5)	0.381 (1)	2.3 (2)*
N(5)	0.1624 (8)	−0.0197 (4)	0.1364 (7)	1.8 (2)*	C(56)	0.889 (1)	−0.0318 (5)	0.327 (1)	2.4 (2)*
N(6)	−0.0354 (9)	0.0242 (4)	0.0620 (8)	2.1 (2)*	C(57)	0.870 (1)	0.0139 (6)	0.285 (1)	2.5 (3)*
N(7)	0.0142 (9)	0.1064 (4)	0.0022 (8)	2.0 (2)*	C(58)	0.755 (1)	0.0297 (6)	0.236 (1)	3.2 (3)*
N(8)	0.2610 (9)	0.0684 (5)	0.0585 (8)	2.3 (2)*	C(59)	0.666 (1)	0.0029 (6)	0.239 (1)	3.1 (3)*
N(9)	0.9133 (8)	−0.1428 (4)	0.6616 (7)	1.8 (2)*	C(60)	0.693 (1)	−0.0441 (5)	0.286 (1)	2.4 (2)*
N(10)	1.0331 (9)	−0.0664 (4)	0.6526 (8)	2.1 (2)*	C(61)	0.315 (1)	0.0489 (5)	0.0135 (9)	2.0 (2)*
N(11)	0.8795 (9)	−0.0070 (5)	0.5487 (8)	2.4 (2)*	C(62)	0.356 (1)	0.1097 (6)	0.214 (1)	2.7 (3)*
N(12)	0.6971 (9)	−0.0880 (4)	0.5159 (8)	2.3 (2)*	C(63)	0.386 (1)	0.1632 (7)	0.253 (1)	3.5 (3)*
N(13)	0.9572 (8)	−0.1827 (4)	0.4727 (7)	1.8 (2)*	C(64)	0.464 (1)	0.1872 (7)	0.206 (1)	3.5 (3)*
N(14)	1.0026 (8)	−0.1000 (4)	0.4145 (7)	1.7 (2)*	C(65)	0.584 (1)	0.1611 (6)	0.248 (1)	3.1 (3)*
N(15)	0.8015 (9)	−0.0598 (4)	0.3317 (8)	2.1 (2)*	C(66)	0.648 (1)	−0.1256 (5)	0.4537 (9)	1.8 (2)*
N(16)	0.7079 (9)	−0.1458 (4)	0.4033 (8)	2.2 (2)*	C(67)	0.610 (1)	−0.1867 (6)	0.254 (1)	3.2 (3)*
N(17)	0.4252 (9)	0.0627 (5)	0.0346 (8)	2.7 (2)*	C(68)	0.583 (1)	−0.2389 (6)	0.209 (1)	3.2 (3)*
N(18)	0.482 (1)	0.2399 (5)	0.2437 (9)	3.3 (3)*	C(69)	0.499 (1)	−0.2659 (6)	0.236 (1)	2.4 (3)*
N(19)	0.5376 (9)	−0.1392 (5)	0.4314 (8)	2.5 (2)*	C(70)	0.397 (1)	−0.2359 (6)	0.226 (1)	3.2 (3)*
N(20)	0.552 (1)	−0.2857 (5)	0.3358 (9)	3.2 (3)*	Cl(1)	0.4932 (3)	−0.0952 (1)	0.0361 (3)	2.77 (8)
C(1)	0.163 (1)	−0.0970 (5)	−0.0317 (9)	2.1 (2)*	Cl(2)	0.0785 (3)	0.1320 (2)	0.2917 (3)	3.64 (9)
C(2)	0.138 (1)	−0.1457 (7)	−0.007 (1)	3.4 (3)*	Cl(3)	−0.5320 (3)	0.0236 (2)	−0.5735 (3)	3.16 (8)
C(3)	0.031 (1)	−0.1600 (7)	−0.036 (1)	3.5 (3)*	Cl(4)	0.5116 (3)	−0.1393 (2)	−0.3224 (3)	3.17 (8)
C(4)	−0.060 (1)	−0.1270 (6)	−0.092 (1)	2.9 (3)*	Cl(5)	0.4551 (3)	0.0783 (2)	−0.2141 (3)	4.3 (1)
C(5)	−0.037 (1)	−0.0814 (6)	−0.1199 (9)	2.4 (2)*	Cl(6)	0.0930 (4)	0.2926 (2)	−0.1901 (3)	4.4 (1)
C(6)	−0.126 (1)	−0.0445 (5)	−0.1784 (9)	2.2 (2)*	O(7)	0.4547 (9)	−0.0771 (5)	0.1083 (8)	3.9 (2)*
C(7)	−0.244 (1)	−0.0470 (6)	−0.214 (1)	2.8 (3)*	O(8)	0.616 (1)	−0.1057 (5)	0.0848 (9)	4.3 (3)*
C(8)	−0.311 (1)	−0.0059 (6)	−0.266 (1)	2.6 (3)*	O(9)	0.472 (1)	−0.0562 (5)	−0.0334 (9)	4.6 (3)*
C(9)	−0.258 (1)	0.0355 (7)	−0.276 (1)	3.6 (3)*	O(10)	0.424 (1)	−0.1350 (6)	−0.018 (1)	6.3 (4)*
C(10)	−0.135 (1)	0.0365 (6)	−0.239 (1)	2.5 (3)*	O(11)	0.109 (1)	0.0809 (6)	0.295 (1)	5.4 (3)*
C(11)	−0.065 (1)	0.0797 (5)	−0.2418 (9)	2.2 (2)*	O(12)	−0.019 (1)	0.1404 (6)	0.310 (1)	5.8 (3)*
C(12)	−0.106 (1)	0.1237 (6)	−0.288 (1)	3.1 (3)*	O(13)	0.059 (1)	0.1559 (7)	0.204 (1)	7.3 (4)*
C(13)	−0.034 (1)	0.1606 (7)	−0.294 (1)	4.2 (4)*	O(14)	0.174 (1)	0.1604 (8)	0.363 (1)	8.1 (5)*
C(14)	0.088 (1)	0.1483 (7)	−0.246 (1)	3.9 (3)*	O(15)	−0.494 (1)	−0.0097 (7)	−0.488 (1)	7.0 (4)*
C(15)	0.124 (1)	0.1052 (6)	−0.196 (1)	2.8 (3)*	O(16)	−0.6499 (9)	0.0280 (5)	−0.6188 (8)	4.1 (2)*
C(16)	0.273 (1)	−0.0368 (8)	0.183 (1)	2.7 (3)*	O(17)	−0.492 (1)	0.0073 (6)	−0.6414 (9)	5.1 (3)*
C(17)	0.298 (1)	−0.0820 (6)	0.230 (1)	3.2 (3)*	O(18)	−0.485 (1)	0.0713 (7)	−0.541 (1)	6.8 (4)*
C(18)	0.209 (1)	−0.1119 (7)	0.228 (1)	3.9 (4)*	O(19)	0.625 (1)	−0.1601 (5)	−0.2891 (9)	4.4 (3)*
C(19)	0.100 (1)	−0.0934 (6)	0.188 (1)	3.0 (3)*	O(20)	0.496 (1)	−0.1000 (5)	−0.3895 (8)	4.3 (3)*
C(20)	0.077 (1)	−0.0465 (5)	0.141 (1)	2.3 (2)*	O(21)	0.497 (11)	−0.1185 (7)	−0.241 (1)	7.7 (5)*
C(21)	−0.039 (1)	−0.0232 (5)	0.0940 (9)	2.2 (2)*	O(22)	0.423 (2)	−0.1749 (8)	−0.363 (1)	8.8 (5)*
C(22)	−0.148 (1)	−0.0425 (6)	0.076 (1)	2.9 (3)*	O(23)	0.477 (1)	0.0364 (6)	−0.152 (1)	6.0 (3)*
C(23)	−0.248 (1)	−0.0146 (6)	0.026 (1)	3.3 (3)*	O(24)	0.348 (1)	0.0982 (7)	−0.243 (1)	7.4 (4)*
C(24)	−0.239 (1)	0.0333 (6)	−0.005 (1)	3.1 (3)*	O(25)	0.526 (2)	0.112 (1)	−0.174 (2)	12.7 (8)*
C(25)	−0.129 (1)	0.0528 (5)	0.0145 (9)	2.3 (2)*	O(26)	0.470 (2)	0.0648 (9)	−0.299 (1)	9.7 (6)*
C(26)	−0.099 (1)	0.1000 (5)	−0.015 (1)	2.4 (3)*	O(27)	0.146 (1)	0.3415 (6)	−0.177 (1)	5.6 (3)*
C(27)	−0.179 (1)	0.1373 (7)	−0.059 (1)	3.8 (3)*	O(28)	0.173 (1)	0.2541 (8)	−0.105 (1)	8.4 (5)*
C(28)	−0.144 (1)	0.1798 (6)	−0.082 (1)	3.1 (3)*	O(29)	0.100 (2)	0.2702 (8)	−0.272 (1)	9.3 (5)*
C(29)	−0.025 (1)	0.1866 (7)	−0.062 (1)	3.8 (3)*	O(30)	−0.006 (1)	0.2923 (8)	−0.174 (1)	8.3 (5)*
C(30)	0.045 (1)	0.1472 (6)	−0.019 (1)	3.0 (3)*	O(W1)	0.413 (1)	0.6482 (5)	0.3905 (8)	4.3 (3)*
C(31)	0.842 (1)	−0.1788 (6)	0.667 (1)	2.6 (3)*	O(W2)	0.304 (1)	0.3606 (6)	0.059 (1)	5.4 (3)*
C(32)	0.889 (1)	−0.2222 (6)	0.720 (1)	3.0 (3)*	O(W3)	0.246 (1)	0.6463 (6)	0.879 (1)	5.5 (3)*
C(33)	1.003 (1)	−0.2279 (6)	0.767 (1)	2.9 (3)*	O(W4)	0.232 (1)	0.7690 (6)	0.367 (1)	5.9 (3)*
C(34)	1.079 (1)	−0.1918 (6)	0.766 (1)	3.0 (3)*	O(W5)	0.397 (1)	0.7846 (6)	0.848 (1)	6.2 (4)*
C(35)	1.036 (1)	−0.1485 (5)	0.715 (1)	2.3 (2)*	O(W6)	0.248 (1)	0.2690 (6)	0.105 (1)	5.9 (3)*
C(36)	1.103 (1)	−0.1069 (5)	0.7080 (9)	2.0 (2)*	O(W7)	0.384 (1)	0.7111 (6)	0.526 (1)	6.0 (3)*
C(37)	1.220 (1)	−0.1031 (6)	0.747 (1)	2.8 (3)*	O(W8)	0.280 (1)	0.7419 (7)	0.946 (1)	6.6 (4)*
C(38)	1.269 (1)	−0.0576 (6)	0.732 (1)	2.8 (3)*	O(W9)	0.234 (1)	0.1636 (6)	0.588 (1)	6.4 (4)*
C(39)	1.200 (1)	−0.0194 (6)	0.681 (1)	2.8 (3)*	O(W10)	0.264 (1)	0.0673 (7)	0.530 (1)	6.7 (4)*
C(40)	1.079 (1)	−0.0251 (5)	0.6386 (9)	1.9 (2)*	O(W11)	0.383 (2)	0.2427 (9)	0.454 (1)	9.2 (5)*
C(41)	0.991 (1)	0.0086 (5)	0.5796 (9)	2.1 (2)*					

[a] Starred values denote atoms refined isotropically. Values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

cations, designated types I and II, are shown in Figure 2. The numerical findings are listed in Tables IV–VI.

In both types, the two $Pt(trpy)^{2+}$ groups are attached to the unique nitrogen atom (N^1) and to one of the other two nitrogen

Table V. Important Bond Distances (Å) in the Complex Cation of $[\{Pt(trpy)\}_2Can](ClO_4)_3 \cdot 5.5H_2O$[a]

type I		type II	
Pt(1)–Pt(2)	2.9884 (7)	Pt(3)–Pt(4)	2.9872 (8)
Pt(1)–N(4)	2.06 (1)	Pt(3)–N(12)	2.01 (1)
Pt(2)–N(8)	2.07 (1)	Pt(4)–N(16)	1.95 (1)
Pt(1)–N(1)	1.92 (1)	Pt(3)–N(9)	1.93 (1)
Pt(1)–N(2)	1.965 (9)	Pt(3)–N(10)	1.91 (1)
Pt(1)–N(3)	2.13 (1)	Pt(3)–N(11)	2.11 (1)
Pt(2)–N(5)	1.93 (1)	Pt(4)–N(13)	1.93 (1)
Pt(2)–N(6)	1.92 (1)	Pt(4)–N(14)	1.95 (1)
Pt(2)–N(7)	2.12 (1)	Pt(4)–N(15)	2.10 (1)
C(61)–N(4)	1.34 (2)	C(66)–N(12)	1.33 (2)
C(61)–N(8)	1.26 (2)	C(66)–N(16)	1.38 (2)
C(61)–N(17)	1.36 (2)	C(66)–N(19)	1.35 (2)
N(8)–O(1)	1.40 (1)	N(16)–O(4)	1.43 (1)

[a] Two independent molecules (types I and II) coexist in the unit cell.

Table VI. Important Bond Angles (deg) in the Complex Cation of $[\{Pt(trpy)\}_2Can](ClO_4)_3 \cdot 5.5H_2O$[a]

type I		type II	
N(1)–Pt(1)–N(4)	101.3 (4)	N(9)–Pt(3)–N(12)	101.8 (4)
N(1)–Pt(1)–N(2)	84.0 (4)	N(9)–Pt(3)–N(10)	85.3 (5)
N(2)–Pt(1)–N(3)	79.0 (4)	N(10)–Pt(3)–N(11)	76.4 (4)
N(3)–Pt(1)–N(4)	95.7 (4)	N(11)–Pt(3)–N(12)	96.6 (5)
Pt(1)–N(4)–C(61)	124 (1)	Pt(3)–N(12)–C(66)	122 (1)
N(5)–Pt(2)–N(8)	103.1 (5)	N(13)–Pt(4)–N(16)	103.7 (5)
N(5)–Pt(2)–N(6)	83.9 (5)	N(13)–Pt(4)–N(14)	82.2 (4)
N(6)–Pt(2)–N(7)	79.0 (5)	N(14)–Pt(4)–N(15)	78.5 (4)
N(7)–Pt(2)–N(8)	94.1 (4)	N(15)–Pt(4)–N(16)	95.6 (5)
Pt(2)–N(8)–C(61)	127.3 (9)	Pt(4)–N(16)–C(66)	130.7 (8)
N(4)–C(61)–N(8)	121 (1)	N(12)–C(66)–N(16)	118 (1)
N(8)–C(61)–N(17)	121 (1)	N(16)–C(66)–N(19)	121 (1)
N(4)–C(61)–N(17)	118 (1)	N(12)–C(66)–N(19)	120 (1)

[a] See footnote *a* of Table V.

atoms (N^2 or N^3) in the canavanine side chain. (This local numbering within the guanidine group should not be confused with the numbering in the whole complexes; the latter system is used in Figure 2 and in Tables IV–VI.) The two types differ from each other noticeably in the torsion angle about the C^{α}–C^{β} (C(63)–C(64) in type I and C(68)–C(69) in type II) bond in the canavanine ligand, but this difference is insignificant. The canavanine COO^- group does not approach the $Pt(trpy)^{2+}$ groups in the crystalline state. Although this finding militates against the possibility of noncovalent interactions in solution, they cannot be ruled out (see above).

The four $Pt(trpy)^{2+}$ groups have very similar dimensions—they are somewhat puckered, the bond angles involving the platinum atoms deviate from the ideal values of 90 and 180°, and the Pt–N distances within each group vary. These distortions, evident also in terpyridyl complexes of platinum(II)[28-30] and palladium(II),[31,32] show the strain in this tridentate ligand.

In complexes of both types, the guanidine group is planar, and its bond angles are close to 120°. The two differ from each other in the bond distances involving the guanidine group and the platinum atoms. In type I, the C–N^1 (C(61)–N(8)) distance is shorter than the other two C–N distances, as in canavanine itself,[15] and the two Pt–N distances are equal and relatively long. In type II, the three C–N distances are approximately equal, as in most crystals containing arginine,[33-35] but the two Pt–N distances are

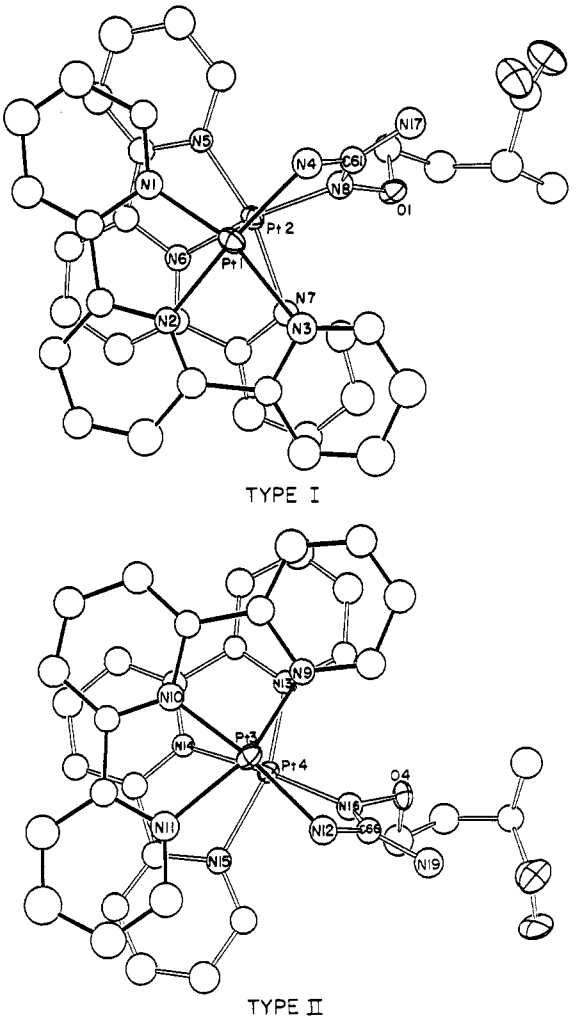

Figure 2. Molecular structures (ORTEP drawings with 50% ellipsoids) of the two types of complex cation that coexist in the crystal of $[\{Pt(trpy)\}_2Can](ClO_4)_3 \cdot 5.5H_2O$. The skeleton of the upper $Pt(trpy)^{2+}$ group is darkened for clarity.

unequal and relatively short. The complexes of types I and II may perhaps be considered derivatives, respectively, of the amino and imino tautomers of the guanidine group. Although canavanine itself in the crystalline state exists as the amino tautomer, the tautomeric equilibrium perhaps is affected by coordination to the platinum atoms.

The two $Pt(trpy)^{2+}$ groups are nearly parallel with each other—the dihedral angle between the average planes is ca. 9° in type I and ca. 7° in type II. Although the $Pt(trpy)^{2+}$ groups are oblique with respect to the guanidine plane—the corresponding dihedral angles in both types fall in the range 68–71°—this deviation from orthogonality probably is insufficient to allow significant overlap between the π orbitals of the $Pt(trpy)^{2+}$ and guanidine groups.

The $Pt(trpy)^{2+}$ groups in the crystal are nearly eclipsed with each other; they probably remain inequivalent in solution and give rise to two sets of ^{13}C NMR resonances. It is difficult to determine whether the two ^{195}Pt NMR signals, which are only 15 ppm apart, arise from the difference between the complexes of types I and II or from the inequivalence of the platinum atoms within each of these complexes. The average torsion angle about the Pt–Pt axis—because of the non-90° bond angles it depends somewhat on the choice of the other two defining atoms—in the complexes of both types I and II is ca. 21°. The distance between the average

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$Pt(trpy)^{2+}$ planes (ca. 2.8 Å in both types I and II) is shorter than the typical interlayer distances in columnar platinum(II) complexes (3.1–4.2 Å)[36–38] and shorter than these distances in the analogous complexes $[Pt(trpy)(SCH_2CH_2OH)]^+$[28] and $[Pd(trpy)Cl]^+$[31,32] (3.40–3.50 Å). The last two complexes associate by noncovalent forces in the head-to-tail arrangement, and the $M(trpy)^{2+}$ groups overlap only partially. The sole complex of the $[\{M(trpy)\}_2L]^{n+}$ type known before this report is $[\{Pt(trpy)\}_2Pt(SCH_2CH_2NH_2)_2]^{4+}$,[30] in which the torsion angle between the two $Pt(trpy)^{2+}$ units appears to be ca. 90°.

The Pt-Pt distance in $[\{Pt(trpy)\}_2Can]^{3+}$ (ca. 2.99 Å in both types I and II) is much shorter than the distances between the nonbonded platinum atoms in $[\{Pt(trpy)\}_2Pt(SCH_2CH_2NH_2)_2]^{4+}$ (ca. 4.42 Å)[30] and in stacked $[Pt(trpy)(SCH_2CH_2OH)]^+$ (ca. 3.57 Å)[28] and is comparable to the distances between the weakly bonded platinum atoms in the partially oxidized $[Pt(CN)_4]^{(2-\delta)-}$ anions (2.8–3.0 Å)[39] but is longer than the distances between the singly-bonded platinum atoms in the binuclear Pt(III)–Pt(III) and Pt(I)–Pt(I) compounds (2.5–2.8 Å).[40–43] The band at ca. 480 nm in the absorption spectra of the $[\{Pt(trpy)\}_2L]^{n+}$ complexes with MeGua, Arg, and Can as bridging ligands L probably is due to electronic interactions between the π systems and between the metal orbitals of the two proximate $Pt(trpy)^{2+}$ groups.

Red Complexes $[\{Pt(trpy)\}_2MeGua]^{4+}$ and $[\{Pt(trpy)\}_2Arg]^{3+}$. The structures of these complexes, in the main, probably are similar to the structure of their canavanine homologue. Since they show one ^{195}Pt signal each, the two platinum atoms in each complex probably are equivalent or nearly so, at least in solution. Attempts so far to obtain a suitable single crystal of either of these complexes have failed.

VI. Conclusions and Prospects

This study shows, for the first time, that guanidine group can act as a bridging ligand in bimetallic complexes. The N–N distance of ca. 2.3 Å is compatible with single bonds involving first-row and second-row transition metals. This study also corroborates our recent report that Arg 91 in two cytochromes *c* can be labeled with a $[Pt(trpy)Cl]^+$ complex.[5] Our findings may point the way toward a heavy-atom tag for arginine residues in proteins, a tool needed by protein crystallographers.[44] These findings also show that the arginine side chain is a potential ligand in metalloproteins and in metal-dependent enzymes. Arginine coordination should be facilitated by environmental effects, such as hydrophobicity and proximity to α-helical polypeptide segments, that diminish the basicity of the guanidine group. Although arginine certainly is not as common a bioligand as histidine, the similarity between the trigonal nitrogen atoms in the guanidine group and in the imidazole ring is worth noting.

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Supplementary Material Available: For the crystal and molecular structures of $[\{Pt(trpy)\}_2Can](ClO_4)_3 \cdot 5.5H_2O$, a table giving details of the crystallographic method, drawings showing the atom numbering, and tables of bond distances, bond angles, calculated coordinates of hydrogen atoms, expressions for displacement parameters *B* and *U*, least-squares planes, and torsion angles (23 pages); a table of observed and calculated structure factors (39 pages). Ordering information is given on any current masthead page.

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