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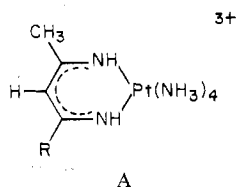
Synthesis of β -Diimine Chelates by Condensation of 2,4-Pentanedione with $\text{Pt}(\text{NH}_3)_6\text{Cl}_4$, $\text{Pt}(\text{en})_3\text{Cl}_4$, and $\text{Au}(\text{en})_2\text{Cl}_3$. Crystal and Molecular Structure of *trans*- $[\text{Pt}(\text{NH}_3)_2(2,4\text{-pentanediiiminate})_2](\text{ClO}_4)_2$

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$\text{Pt}(\text{NH}_3)_6\text{Cl}_4$, $\text{Pt}(\text{en})_3\text{Cl}_4$, and $\text{Au}(\text{en})_2\text{Cl}_3$ react with β -diketones in aqueous base to form species having one or two β -diimine chelate rings, depending upon reaction conditions. The complexes formed using 2,4-pentanedione have been characterized by elemental analyses and ^1H and ^{13}C NMR. One of the Au(III) complexes contains a 14-membered macrocyclic ring. Cis and trans isomers of $[\text{Pt}(\text{NH}_3)_2(2,4\text{-pentanediiiminate})_2](\text{ClO}_4)_2$ have been isolated, and an x-ray crystallographic study of the trans isomer has been completed. The complex crystallizes in the monoclinic space group $P2_1/c$ with $Z = 2$. Unit cell parameters are $a = 8.504(3) \text{ \AA}$, $b = 9.369(2) \text{ \AA}$, $c = 12.601(2) \text{ \AA}$, $\beta = 96.14(2)^\circ$, and $V = 998.2(4) \text{ \AA}^3$. The structure was solved by standard Patterson and Fourier techniques to a conventional R of 0.044 and a weighted R of 0.052. The cation has planar, π -delocalized β -diimine chelate rings, and a crystallographic center of symmetry is located at the Pt atom.

It was shown recently that β -diketones undergo condensation reactions with $\text{Pt}(\text{NH}_3)_6\text{Cl}_4$ in aqueous base.^{2,3} The products were assigned structure A ($R = \text{CH}_3, \text{CF}_3$) based on proton



NMR spectra and elemental analyses. Under the reaction conditions employed, the $\text{Pt}(\text{NH}_3)_6^{4+}$ cation is deprotonated, and it is believed that carbonyls of the β -diketone are attacked by the nucleophilic coordinated amides. Condensation occurs accompanied by loss of a proton to form a β -diimine chelate ring.

In the initial work there was evidence of additional reaction products, but these were not isolated and characterized. We have now investigated the reaction of 2,4-pentanedione with $\text{Pt}(\text{NH}_3)_6\text{Cl}_4$ more fully and have isolated and characterized additional reaction products containing two β -diimine rings. The structure of one of these products has been determined by x-ray methods. $\text{Pt}(\text{en})_3\text{Cl}_4$ also condenses readily with 2,4-pentanedione, and a structure for the predominant product is proposed.

Similar condensation reactions occur for $\text{Au}(\text{en})_2\text{Cl}_3$ with β -diketones in aqueous base. This paper describes the preparation and characterization of two Au(III) condensation products, one of which contains a 14-membered macrocyclic ring.

Experimental Section

Starting Materials. $\text{Pt}(\text{NH}_3)_6\text{Cl}_4$ was prepared from reaction of K_2PtCl_6 with liquid ammonia as described in detail previously.³ K_2PtCl_4 is used as a catalyst in this reaction, and yields of up to 80% have been obtained. $\text{Pt}(\text{en})_3\text{Cl}_4$ was prepared according to an established procedure.⁴ $\text{Au}(\text{en})_2\text{Cl}_3$ was prepared by the method of Block and Bailar.⁵

$[\text{Pt}(\text{NH}_3)_4(2,4\text{-pentanediiiminate})](\text{ClO}_4)_3$, Complex I. This complex is readily prepared using the previously reported procedure of Evans, Everett, and Sargeson.³ Proton NMR in $\text{Me}_2\text{SO}-d_6$ provides a facile means of identification: CH_3 , 2.08; CH , 4.67 ppm relative to sodium 3-(trimethylsilyl)-1-propanesulfonate (DSS).

***trans*- $[\text{Pt}(\text{NH}_3)_2(2,4\text{-pentanediiiminate})_2](\text{ClO}_4)_2$, Complex II.** In a typical reaction 500 mg of $\text{Pt}(\text{NH}_3)_6\text{Cl}_4$ and 600 mg of 2,4-pentanedione are stirred in 10 mL of H_2O for 2 h at 60°C . The pH is maintained around 11 by addition of NaOH solution. Then solid NaClO_4 is added to the reaction mixture at 30°C until a light yellow precipitate forms. This product is nearly pure II. After one or two

recrystallizations in H_2O , carried out by addition of solid NaClO_4 , the following analysis was obtained. Anal. Calcd for $\text{PtN}_6\text{C}_{10}\text{H}_{24}\text{O}_8\text{Cl}_2$: C, 19.30; H, 3.86; N, 13.50. Found: C, 19.29; H, 3.88; N, 13.60. Proton NMR in $\text{Me}_2\text{SO}-d_6$: CH_3 , 2.00 ppm; CH , 4.43 ppm; NH , 7.33 ppm relative to DSS. Carbon-13 NMR in $\text{Me}_2\text{SO}-d_6$ (Figure 1A): CH_3 , 24.9 ($J_{195\text{Pt}} = 14.4 \text{ Hz}$); CH , 91.5 ($J_{195\text{Pt}} = 19.2 \text{ Hz}$); CN , 159.0 ($J_{195\text{Pt}} = 3.0 \text{ Hz}$) ppm relative to Me_4Si . Mass spectra show a complex fragmentation pattern, beginning with the peak of the cation $-2 \times \text{NH}_3$ (m/e 389).

***cis*- $[\text{Pt}(\text{NH}_3)_2(2,4\text{-pentanediiiminate})_2](\text{ClO}_4)_2$, Complex III.** This product is obtained as the perchlorate salt when excess NaClO_4 is added to the filtrate from the preparation of II and the solution is allowed to stand at room temperature for several hours. After several recrystallizations from H_2O using NaClO_4 , the golden-yellow product was free of complex II (by NMR) and the following analysis was obtained. Anal. Calcd for $\text{PtN}_6\text{C}_{10}\text{H}_{24}\text{O}_8\text{Cl}_2$: C, 19.30; H, 3.86; N, 13.50; Cl, 11.39. Found: C, 19.22; H, 3.78; N, 13.68; Cl, 11.06. Complex III is readily distinguished from II by its proton NMR spectrum in $\text{Me}_2\text{SO}-d_6$: CH_3 , 1.97 and 2.05; CH , 4.50; NH , 7.00 and 7.58 ppm relative to DSS. Carbon-13 NMR in $\text{Me}_2\text{SO}-d_6$ (Figure 1B): CH_3 , 23.7 ($J_{195\text{Pt}} = 17.3 \text{ Hz}$) and 24.7 ($J_{195\text{Pt}} = 14.0 \text{ Hz}$); CH , 91.5 ($J_{195\text{Pt}} = 21.5 \text{ Hz}$); CN , 157.7 ($J_{195\text{Pt}} = 4.3 \text{ Hz}$) and 159.0 ($J_{195\text{Pt}} = 3.7 \text{ Hz}$) ppm relative to Me_4Si .

$[\text{Pt}(\text{en})(N,N'\text{-bis}(2\text{-aminoethyl)-2,4\text{-pentanediiiminate})]_3$, Complex IV. In a typical preparation 500 mg of $[\text{Pt}(\text{en})_3]\text{Cl}_4$ in 4 mL of H_2O at pH 11 (NaOH) is treated dropwise with 600 mg of 2,4-pentanedione. The solution is stirred at room temperature for 2 h during which time a yellow-orange color develops. The solution is then cooled to 0°C and treated with solid NaI to precipitate the products as iodide salts. This precipitate contains two products which may be separated by ion-exchange chromatography on a column of SP Sephadex (SP-C25-120). An orange minor product, eluted from the column with 0.2 M NaCl , has not been obtained in sufficient amounts for characterization. The predominant orange product, IV, is eluted with 0.5 M NaCl . The eluted liquid is evaporated to a solid, and IV is separated from NaCl by extraction with ethanol. The filtered ethanol solution is evaporated, and IV is recrystallized from an aqueous solution by addition of solid NaI . The product melts at 178°C (uncorrected). Anal. Calcd for $\text{PtN}_6\text{C}_{11}\text{H}_{27}\text{I}_3 \cdot 1/3\text{H}_2\text{O}$: C, 15.95; H, 3.41; N, 10.15; I, 45.97; Pt, 23.6. Found: C, 15.51; H, 3.34; N, 9.83; I, 46.68; Pt, 23.4. Proton NMR in D_2O : CH_3 , 2.30 and 2.33; CH_2 , 3.03 (multiplet) and 3.80 (multiplet); CH , 5.18 ppm relative to DSS. Carbon-13 NMR in D_2O (Figure 2): CH_3 , 22.6 (poorly resolved doublet, $J_{195\text{Pt}} \approx 10 \text{ Hz}$); CH_2 , 48.2 (multiplet) and 57.7 ($J_{195\text{Pt}} = 14.3 \text{ Hz}$) and 60.4 ($J_{195\text{Pt}} = 17.4 \text{ Hz}$); CH , 103.8 ($J_{195\text{Pt}} = 19.1 \text{ Hz}$); CN , 165.2 and 168.3 ppm relative to Me_4Si .

The chloride salt of this complex was prepared in the following manner. The ethanol extract of the chromatographed product (above) was allowed to stand for several days during which time crystals of NaCl and the orange product formed. These were separated by hand picking, and the orange product was recrystallized by slow evaporation of a solution in a 1:1 water-ethanol solvent mixture. Anal. Calcd for $\text{PtN}_6\text{C}_{11}\text{H}_{27}\text{Cl}_3 \cdot 3\text{H}_2\text{O}$: C, 22.06; H, 5.56; N, 14.03. Found: C, 22.05; H, 4.91; N, 14.10.

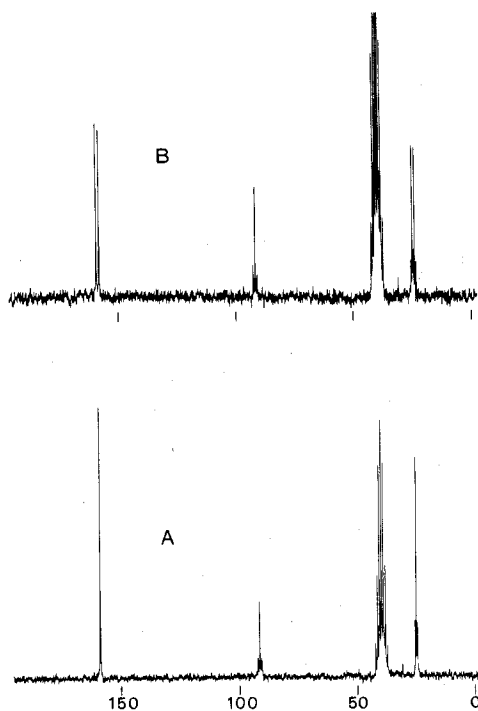


Figure 1. Carbon-13 NMR spectra in $\text{Me}_2\text{SO}-d_6$ solution: A, complex II; B, complex III. The scale is in ppm relative to Me_4Si (not shown). See Experimental Section for signal assignments.

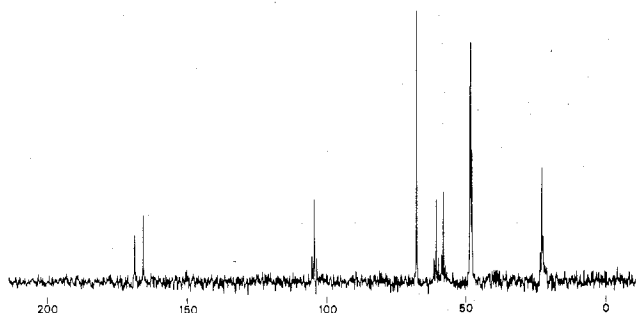


Figure 2. Carbon-13 NMR spectrum of IV in D_2O solution; scale is in ppm relative to Me_4Si (not shown). The strong signal at 67.4 ppm is the dioxane reference. See Experimental Section for signal assignments.

[Au(*N,N'*-bis(2-aminoethyl)-2,4-pentanediiimine)]₂, Complex V. A solution containing 1 g of $[\text{Au}(\text{en})_2]\text{Cl}_3$ in 40 mL of H_2O at pH 8.5 was treated dropwise with 0.6 g of 2,4-pentanedione. A red-orange color developed almost immediately. The solution was stirred at room temperature for about 7 min and then filtered. Addition of excess solid KI to the filtrate caused formation of a brownish precipitate. This was collected by filtration and extracted with several portions of water to form orange solutions. The dark brown, insoluble residue remaining was not identified. The combined orange solutions were treated with KI to precipitate the orange product which was collected by filtration, washed with cold ethanol, and dried in vacuo; yield 0.8 g or 54%. After one additional recrystallization in the same manner, the following data were obtained: mp 221–223 °C (uncor). Anal. Calcd for $\text{AuN}_4\text{C}_9\text{H}_{19}\text{I}_2$: C, 17.05; H, 3.03; N, 8.83. Found: C, 16.98; H, 3.06; N, 8.70. Proton NMR in $\text{Me}_2\text{SO}-d_6$: CH_3 , 2.30 ppm; CH_2 , 3.13 ppm (multiplet) and 3.87 ppm (multiplet); CH, 5.23 ppm; NH_2 , 7.17 ppm relative to DSS. Carbon-13 NMR in $\text{Me}_2\text{SO}-d_6$: CH_3 , 20.9 ppm; CH_2 , 48.3 and 59.4 ppm; CH, 99.4 ppm; CN, 158.2 ppm relative to Me_4Si .

[Au(5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraene)]PF₆, Complex VI. In a typical preparation, 1.0 g of $[\text{Au}(\text{en})_2]\text{Cl}_3$ was dissolved in 40 mL of H_2O , and the pH was adjusted to 9.0–9.5 with 2 N NaOH solution. Then 1.0 g of 2,4-pentanedione was added dropwise while maintaining the pH at 9.0–9.5 with NaOH. A red-orange color, characteristic of complex V, developed rapidly and was gradually replaced by a yellow-green color

as the reaction mixture was stirred at room temperature for 2 h. During this period, some of the gold was reduced as evidenced by a gold mirror on the inside of the reaction vessel. Also a small amount of unidentified green material precipitated.

The filtered reaction mixture was treated with excess solid NH_4PF_6 which precipitated the yellow macrocyclic complex VI. This was collected by filtration and washed first with a small amount of cold water to remove traces of the orange PF_6^- salt of complex V and then washed with cold methanol. Recrystallization was accomplished by dissolving the yellow product in a minimum amount of hot acetone, filtering the solution, and adding ethyl ether. The precipitate was collected by filtration, washed with ethyl ether, and dried in vacuo. The yield was 0.8 g (58%). The product decomposes over the temperature range 315–350 °C. Anal. Calcd for $\text{AuN}_4\text{C}_{14}\text{H}_{22}\text{PF}_6$: C, 28.58; H, 3.78; N, 9.52. Found: C, 28.80; H, 3.80; N, 9.38. Proton NMR in $\text{Me}_2\text{SO}-d_6$: CH_3 , 2.23 ppm; CH_2 , 3.83 ppm; CH, 5.05 ppm relative to DSS. Carbon-13 NMR in $\text{Me}_2\text{SO}-d_6$: CH_3 , 20.9 ppm; CH_2 , 57.8 ppm; CH, 99.3 ppm; CN, 159.2 ppm relative to Me_4Si . Mass spectra of the complex show prominent peaks at m/e of 443–441 which are assigned to the parent cation, cation – H, and cation – 2H, respectively. Also peaks at m/e 248 and 246 correspond to the macrocyclic ligand and its dianion, respectively.

Characterization of the Reaction Products. Proton NMR spectra were recorded on Varian A-60 or HA-100 instruments. Carbon-13 NMR spectra were run on Bruker HX-90-E or Varian XL-100 spectrometers located at the University of Iowa and Kansas State University, respectively. Mass spectra were run on a Varian-MAT CH-5 instrument, and infrared spectra in KBr pellets were taken using a Perkin-Elmer 421 grating spectrophotometer.

Elemental analyses were carried out using an F & M 185 C, H, N analyzer or were done by Chemalytics, Inc., Tempe, Ariz. Gravimetric analyses for Pt were carried out by firing samples in a muffle furnace.

Collection and Reduction of the X-Ray Data. Single crystals of *trans*-[Pt(NH_3)₂(2,4-pentanediiimine)₂](ClO_4)₂, II, suitable for x-ray study were grown in a slightly basic water–ethanol (1:1 by volume) mixture by slow evaporation at 0 °C. An air-stable, yellow crystal approximately 0.1 × 0.2 × 0.18 mm was mounted on a glass fiber with epoxy glue and aligned on a precession camera. Zero and upper layer photographs showed the crystal to belong to the monoclinic system and the observed systematic absences ($h0l$, l odd; $0k0$, k odd) uniquely defined space group $P2_1/c$ (C_{2h}^5 ; No. 14, second setting⁶). This was verified later by diffractometer data. A somewhat larger crystal was ground to a sphere of 0.17-mm radius and mounted on a Syntex $P2_1$ autodiffractometer with graphite-monochromated $\text{Mo K}\alpha$ radiation.

The unit cell dimensions and crystal orientation matrix were obtained by least-squares refinement of 2θ , χ , and ω for 15 centered reflections using standard Syntex programs. The cell constants obtained are $a = 8.504$ (3) Å, $b = 9.369$ (2) Å, $c = 12.601$ (2) Å, $\beta = 96.14$ (2)°, and $V = 998.2$ (4) Å³. Scans (ω) through several reflections showed no evidence of twinning. The crystal density, measured by flotation using a $\text{CH}_2\text{Br}/\text{CCl}_4$ mixture, was found to be 2.074 g/cm³. Assuming two formula units per unit cell, the calculated density is 2.070 g/cm³.

The intensity data were collected at 22 ± 2 °C by the θ - 2θ technique at variable scan rates from 1.0 to 29.3° min⁻¹ over the range $4^\circ < 2\theta < 60^\circ$ ($h, k, \pm l$). The background was measured for a time equal to half the total scan time at points 1° to each side of the $\text{K}\alpha_1$ and $\text{K}\alpha_2$ peaks. Three standard reflections, measured after every 97 reflections, showed an approximately linear decrease in intensity by an average of ~17% over the period of crystal exposure (217 h), and the crystal visibly darkened. Of a total of 2926 independent reflections measured, 2202 have $I \geq 3\sigma(I)$ and are considered observed and were used in refinement. The data were scaled to compensate for crystal decay, using intensities of the standard reflections. Corrections were made for Lorentz and polarization effects and for spherical absorption⁷ ($\mu = 77.1$ cm⁻¹). The initial scale and overall temperature factors were determined from a Wilson plot.

Solution and Refinement of the Structure. The structure was solved by the heavy-atom method.⁸ A three-dimensional Patterson map revealed the relative positions of the Pt and Cl atoms and that the Pt atom is at the inversion center. The remaining nonhydrogen atoms were located after two Fourier syntheses. Atomic scattering factors from Cromer and Waber⁹ were used. After several cycles of full-matrix least-squares refinement in which temperature factors were varied

Table I. Atomic Positional and Thermal Parameters

Atom	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pt	0	0	0	0.01266 (5)	0.00873 (4)	0.00431 (2)	0.00233 (3)	-0.00139 (2)	-0.00050 (2)
N(1)	0.1805 (7)	-0.1130 (6)	-0.0462 (4)	0.0157 (8)	0.0122 (6)	0.0055 (3)	0.0030 (6)	-0.0010 (4)	-0.0014 (4)
N(2)	0.1288 (6)	0.0465 (7)	0.1389 (4)	0.0158 (8)	0.0119 (5)	0.0045 (3)	0.0023 (6)	-0.0032 (4)	-0.0013 (4)
N(3)	0.0805 (8)	0.1823 (6)	-0.0668 (5)	0.0210 (10)	0.0098 (6)	0.0065 (4)	0.0003 (6)	0.0001 (5)	0.0002 (4)
C(1)	0.4281 (10)	-0.2384 (9)	-0.0396 (8)	0.0184 (13)	0.0141 (10)	0.0120 (8)	0.0045 (9)	0.0004 (9)	-0.0026 (7)
C(2)	0.3158 (7)	-0.1413 (6)	0.0106 (5)	0.0133 (8)	0.0084 (6)	0.0079 (5)	0.0019 (5)	-0.0005 (5)	-0.0003 (4)
C(3)	0.3566 (7)	-0.0893 (7)	0.1129 (6)	0.0146 (9)	0.0119 (7)	0.0079 (5)	0.0041 (7)	-0.0029 (6)	-0.0012 (5)
C(4)	0.2717 (9)	0.0003 (5)	0.1717 (6)	0.0149 (9)	0.0088 (6)	0.0058 (4)	-0.0003 (5)	-0.0021 (4)	0.0008 (3)
C(5)	0.3410 (10)	0.0507 (10)	0.2785 (6)	0.0201 (12)	0.0135 (8)	0.0064 (5)	0.0000 (9)	-0.0041 (6)	-0.0000 (6)
Cl	0.1588 (2)	0.4578 (2)	0.1632 (1)	0.0169 (2)	0.0094 (1)	0.0063 (1)	0.0013 (2)	-0.0004 (1)	-0.0001 (1)
O(1)	0.2299 (9)	0.4410 (9)	0.0687 (5)	0.0393 (17)	0.0230 (10)	0.0088 (5)	-0.0039 (12)	0.0062 (7)	-0.0023 (6)
O(2)	0.2638 (7)	0.4059 (6)	0.2516 (4)	0.0274 (11)	0.0212 (10)	0.0097 (4)	0.0051 (8)	-0.0033 (6)	0.0034 (5)
O(3)	0.0181 (8)	0.3713 (7)	0.1591 (6)	0.0234 (11)	0.0193 (9)	0.0177 (7)	-0.0052 (8)	0.0006 (6)	-0.0053 (7)
O(4)	0.1227 (9)	0.6027 (6)	0.1867 (5)	0.0342 (14)	0.0092 (6)	0.0111 (5)	0.0028 (7)	-0.0010 (7)	0.0004 (4)

^a Numbers in parentheses are estimated standard deviations in the least significant digits. ^b The form of the anisotropic temperature factor is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

isotropically for Pt and isotropically for all other atoms and anomalous scattering factors were used for Pt and Cl, convergence was attained with $R_1 = 0.060$ and $R_2 = 0.081$, where $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, $R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2]^{1/2}$, and $w = 1/\sigma^2(F_o)$. During refinement the quantity minimized was $\sum w(|F_o| - |F_c|)^2$.

Three additional cycles of least-squares refinement in which temperature factors for all (nonhydrogen) atoms were allowed to vary anisotropically gave convergence at $R_1 = 0.046$ and $R_2 = 0.058$, and the largest shift of any parameter was 8% of σ . A difference Fourier map was generated at this point in order to locate hydrogen atoms. Eleven of the twelve hydrogen atoms in the asymmetric unit were found. The one not located (H(12)) is within 2.5 Å of platinum, and idealized coordinates were used for this atom in subsequent refinements. Isotropic temperature factors for hydrogen atoms were taken as 1.3 times the isotropic temperature factors of the atoms to which the hydrogens are bound. Several additional cycles of full-matrix least-squares refinement in which coordinates and anisotropic temperature factors were varied for all nonhydrogen atoms and coordinates were varied for hydrogen atoms (except H(12)) resulted in final values for R_1 and R_2 of 0.044 and 0.052, respectively. A final difference Fourier map showed residual electron density around platinum and also near O(1), O(3), and H(5) (0.6–1.0 e/Å³ for the latter three).

Final positional and thermal parameters for all nonhydrogen atoms are listed in Table I. Selected bond lengths and angles are given in Table II. Table III, containing the observed and calculated structure factors, and Table IV, containing positional and thermal parameters for hydrogens, are included in the supplementary material.

Results and Discussion

Condensation of 2,4-Pentanedione with Pt(NH₃)₆Cl₄. Platinum(IV) ammine complexes have long been known for their acidic properties.¹⁰ Values of pK_{a1} and pK_{a2} for Pt(NH₃)₆⁴⁺ have been reported to be around 7.0 and 10.1–10.5, respectively,^{11–13} and salts of the cations Pt(NH₃)₅(NH₂)³⁺, Pt(NH₃)₄(NH₂)₂²⁺, and Pt(NH₃)₃(NH₂)₃⁺ have been isolated from aqueous base.^{11,14} Experiments in this laboratory have shown that in aqueous base, Pt(NH₃)₆⁴⁺ reacts with a variety of β -diketones to form yellow or orange products containing one or more β -diimine chelate rings such as in A. These reactions are believed to involve nucleophilic attack of a coordinated amide at a carbonyl and condensation to an imine followed by similar formation of a second imine at the other carbonyl and loss of a proton, forming the β -diimine ring.

When the reaction mixture resulting from treating Pt(NH₃)₆⁴⁺ with 2,4-pentanedione is introduced onto a Sephadex cation-exchange column and eluted with NaCl solutions of increasing concentration, several yellow bands are observed. Some of these bands contain only small amounts of material and the corresponding reaction products have not been characterized. Use of the procedures described in the Experimental Section proved to be more practical than ion-exchange chromatography for isolation of the predominant complexes I–III.

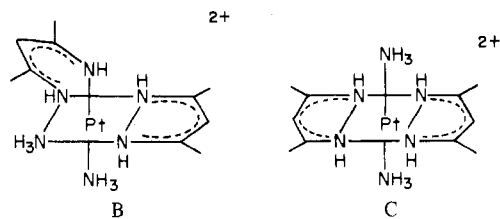
Table II. Bond Lengths and Selected Bond Angles for *trans*-[Pt(NH₃)₂(2,4-pentanedionate)₂](ClO₄)₂^a

Bond Lengths, Å			
Pt–N(1)	2.002 (5)	C(4)–C(5)	1.487 (10)
Pt–N(2)	2.011 (4)	C(2)–C(1)	1.506 (8)
Pt–N(3)	2.053 (5)	Cl–O(1)	1.401 (6)
N(1)–C(2)	1.316 (7)	Cl–O(2)	1.436 (6)
N(2)–C(4)	1.314 (8)	Cl–O(3)	1.441 (6)
C(2)–C(3)	1.388 (9)	Cl–O(4)	1.430 (5)
C(3)–C(4)	1.375 (9)		
Bond Angles, Deg			
N(1)–Pt–N(2)	90.3 (2)	N(1)–C(2)–C(3)	123.5 (5)
N(1)–Pt–N(3)	91.2 (2)	C(4)–C(3)–C(2)	128.5 (6)
N(2)–Pt–N(3)	90.1 (2)	C(3)–C(4)–C(5)	120.1 (6)
Pt–N(1)–C(2)	127.0 (4)	C(3)–C(2)–C(1)	119.7 (6)
Pt–N(2)–C(4)	127.0 (5)	N(1)–C(2)–C(1)	116.8 (6)
N(2)–C(4)–C(3)	123.6 (6)	N(2)–C(4)–C(5)	116.3 (6)

^a Estimated standard deviations in the least significant digits are given in parentheses.

Both proton and carbon-13 NMR spectra indicate that the cation of III has the cis geometry B. B has only C₂ symmetry, and two NMR signals are expected for the methyl carbons, the methyl protons, the imine carbons, and the NH's. These are observed as shown in Figure 1B and in the chemical shift data given in the Experimental Section. Satellites due to coupling with ¹⁹⁵Pt ($I = 1/2$; 33% abundance) may be seen in the carbon-13 spectrum.

NMR spectra of II are consistent with the high symmetry (D_{2h}) of the *trans* geometry C. Single resonances are observed for all chelate ring carbons and protons (see Figure 1A and Experimental Section). The *trans* structure for the cation of II has been confirmed by x-ray crystallography (*vide infra*), and the delocalized nature of the chelate rings as indicated in A–C has been verified.



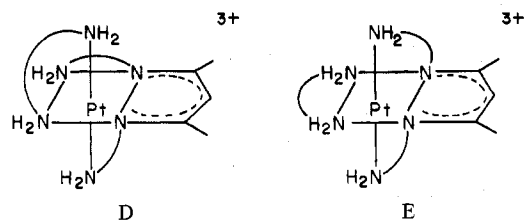
Infrared spectra (KBr pellets) of II and III are very similar except for (1) a 28-cm⁻¹ difference in a peak in the 1350-cm⁻¹ region and (2) a peak occurring at 1545 cm⁻¹ for III which is absent for II.

The nature of the minor products of condensation of 2,4-pentanedione with Pt(NH₃)₆⁴⁺, detected chromatographically, are as yet unknown. Large-scale reactions must be carried out to obtain practical amounts of these, or experimental conditions which increase their relative yields must be found.

One of these products may be the tris(β -diimine) complex. Some products may contain "dangling" ligands where only one carbonyl has undergone condensation; others may have new ligands formed through reactions at the γ carbon of 2,4-pentanedione.

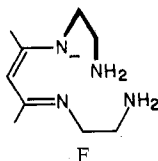
All efforts to effect condensation of 2,2,6,6-tetramethylheptane-3,5-dione with $\text{Pt}(\text{NH}_3)_6\text{Cl}_4$ in aqueous base have failed. Presumably this results either from steric interference to nucleophilic attack or from the relatively poor electrophilic character of the carbonyls in this β -diketone. Also no products from the reaction of the α -diketone biacetyl with $\text{Pt}(\text{NH}_3)_6\text{Cl}_4$ have been obtained thus far, although biacetyl reacts readily with $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$.^{2,3}

Condensation of 2,4-Pentanedione with $\text{Pt}(\text{en})_3\text{Cl}_4$. The $\text{Pt}(\text{en})_3^{4+}$ cation is even more acidic than the hexaammine cation,¹² and condensation with 2,4-pentanedione occurs readily under conditions similar to those used in preparing complexes I–III. Two yellow-orange bands are observed when the reaction mixture is eluted with NaCl on a Sephadex ion-exchange column as described in the Experimental Section. Elemental analyses of the predominant product, IV, are consistent with condensation of one β -diketone with $\text{Pt}(\text{en})_3^{4+}$ to form a β -diimine ring. Assuming the β -diimine chelate ring spans two coordinated ethylenediamine ligands, structures D (C_1 symmetry) and E (C_2 symmetry) are possible. Con-



denation of the β -diketone across a single en ligand is deemed sterically improbable.

Proton and ^{13}C NMR spectra (Experimental Section and Figure 2) are consistent with the low-symmetry isomer D, since two methyl ^1H and ^{13}C signals and two imine ^{13}C signals are observed. In D, one of the 2-aminoethyl groups must lie well out of the plane of the six-membered ring. This probably disrupts the conjugated β -diimine π system, and localized π bonds such as in F may best represent the tetradentate



ligand. In isomer E, both 2-aminoethyl groups must be out of the plane of the six-membered ring.

The minor product of this reaction has not been obtained in sufficient amounts for characterization. It could be isomer E, but it is believed more likely to be a species with two β -diimine rings. A hexadentate complex having only one 2-aminoethyl group out of the plane of each six-membered ring is possible and should have intraligand strain similar to that in structure D.

Condensation of 2,4-Pentanedione with $\text{Au}(\text{en})_2\text{Cl}_3$. In 1951 Block and Bailar⁵ showed that $\text{Au}(\text{en})_2\text{Br}_3$ acts as an acid, readily losing an amine proton to form $\text{Au}(\text{en})(\text{en-H})\text{Br}_2$. The $\text{p}K_a$ of $\text{Au}(\text{en})_2^{3+}$ is ~ 6.5 .⁵ Thus, at $\text{pH} \geq 8$, the nucleophilic $\text{Au}(\text{en})(\text{en-H})^{2+}$ cation is predominant. We have found $\text{Au}(\text{en})_2\text{Cl}_3$ reacts readily with β -diketones in aqueous base. The reaction products with 2,4-pentanedione have been fully characterized.

Complex V is formed within a few minutes by treating a basic aqueous solution of $\text{Au}(\text{en})_2\text{Cl}_3$ with a slight molar excess

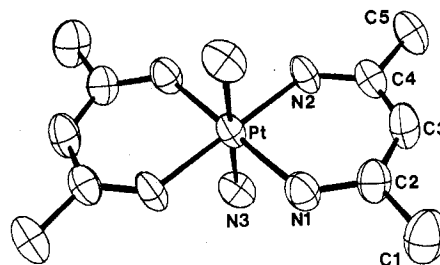
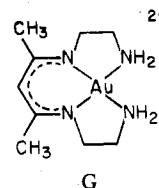


Figure 3. Cation of $\text{trans-}[\text{Pt}(\text{NH}_3)_2(2,4\text{-pentanediiimine})_2](\text{ClO}_4)_2$ showing the numbering scheme. Thermal ellipsoids are drawn at the 50% level.

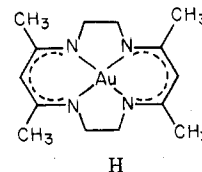
of 2,4-pentanedione under relatively mild conditions. Elemental analyses and NMR data are consistent with structure



G for the cation, and it is likely that condensation occurs by the same general mechanism as for the $\text{Pt}(\text{IV})$ complexes.

If the reaction is continued for a longer period and at higher pH, VI is the predominant product. All data obtained for VI support the symmetrical macrocyclic structure H for the cation. VI may also be obtained by treatment of V with 2,4-pentanedione for ~ 30 min at pH 12, and unsymmetrical macrocyclic complexes can be prepared in this manner from V and β -diketones with other substituents.¹⁵

The macrocyclic ligand shown in H was synthesized earlier

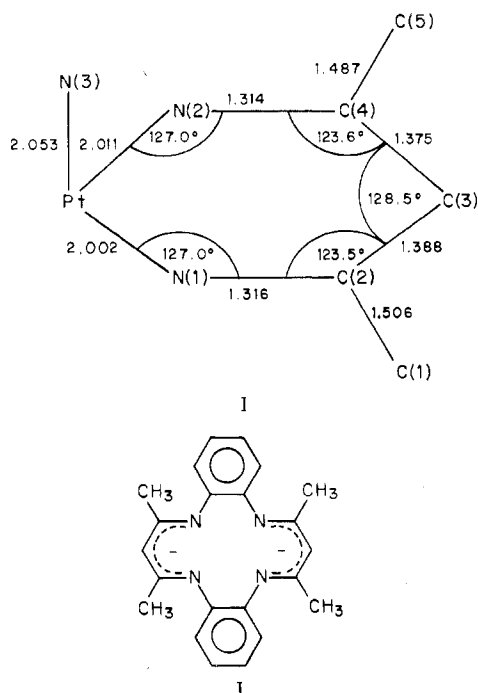


by Truex and Holm¹⁶ from a nontemplate procedure, and complexes of several divalent metal ions were prepared. The present template procedure appears more facile, however, and current efforts in this laboratory are directed toward determining the general utility of this reaction for preparing other related macrocyclic ligands.

Molecular Structure of $\text{trans-}[\text{Pt}(\text{NH}_3)_2(2,4\text{-pentanediiimine})_2](\text{ClO}_4)_2$. The trans geometry (C) of II, initially suggested by the NMR data, was confirmed by preliminary film data and density measurements. In space group $P2_1/c$ with $Z = 2$, Pt must occupy the special position $\bar{1}$.

Final bond lengths and angles are given in Table II. The numbering scheme is shown in Figure 3. The Pt(IV) ion has nearly perfect octahedral coordination with all N–Pt–N angles around $90\text{--}91^\circ$. Bonds to the free NH_3 groups are slightly longer than those to the imine nitrogens. The chelate rings are planar and symmetrical; the maximum deviation from a least-squares plane including all five carbons, two imine nitrogens, and platinum is 0.05 \AA (N(1)). Angles surrounding C(2) and C(4) sum to 360.0° in each case, and corresponding angles on each side of chelate ring are identical within the limits of error; see structure I.

Bond distances around the chelate ring indicate substantial π delocalization as depicted in C, and it is reasonable to assume delocalization occurs also in complexes I, III, V, and VI. Crystal structures have been reported for complexes of several first-row transition metal ions having β -diimine chelate rings as part of the fully conjugated macrocyclic ligand J.^{17–20} In



these complexes, C-C and C-N bond lengths in the β -diamine rings are very close to those observed for C(2)-C(3), C(3)-C(4) and for N(1)-C(2), N(2)-C(4), respectively, in complex II. The C-CH₃ bond distances found for J range from 1.49 to 1.53 Å¹⁷⁻¹⁹ and are comparable to the average value of 1.50 Å found for II.

The perchlorate ions are ordered but show some distortion from rigorous tetrahedrality. The Cl-O(1) bond is somewhat shorter than the others, and O-Cl-O bond angles range from 106.3 to 113.9°.

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Registry No. I, 61158-28-9; II, 65732-06-1; III, 65681-99-4; IV, 65681-97-2; [Pt(en)(N,N'-bis(2-aminoethyl)-2,4-pentanediamine)]Cl₃, 65681-93-8; V, 65681-96-1; VI, 65681-95-0; [Pt(NH₃)₆]Cl₄, 16893-12-2; [Pt(en)₃]Cl₄, 12079-33-3; [Au(en)₂]Cl₃, 15278-22-5; 2,4-pentanedione, 123-54-6; ¹³C, 14762-74-4.

Supplementary Material Available: Table III, listing observed and calculated structure factor amplitudes for II, and Table IV, listing positional and thermal parameters for hydrogen atoms (11 pages). Ordering information is given on any current masthead page.

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A Critical Evaluation of the Location and Refinement of a Bridging Hydrogen Atom in a Transition-Metal Hydride, Mo₂(η^5 -C₅H₅)₂(CO)₄(μ -H)(μ -P(CH₃)₂), by X-Ray Diffraction¹

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A comparison of the structural parameters obtained by x-ray and neutron diffraction for the transition-metal hydride complex Mo₂(η^5 -C₅H₅)₂(CO)₄(μ -H)(μ -P(CH₃)₂) was performed to examine the discrepancies between the "x-ray-determined" and "neutron-determined" values for the structural parameters associated with the bridging hydride ligand. Within the experimental limitations of the x-ray analysis, the x-ray-determined hydrogen position reflects the covalent character of the bent Mo-H-Mo bond with the estimated region of maximum overlap displaced ca. 0.2 Å from the hydrogen nucleus along the Mo-H-Mo bisector toward the centroid of the Mo-H-Mo triangle. The consequences of this displacement are (1) an apparent shortening of 0.1 Å in the average x-ray-determined Mo-H distance of 1.79 (15) Å compared to the average neutron-determined Mo-H distance of 1.86 (1) Å and (2) a large increase in the Mo-H-Mo bond angle from the neutron-determined value of 122.9 (2)° to the x-ray-determined value of 133 (3)°. For closed-type, bent metal-hydrogen-metal bonds, one should then expect to find shorter average M-H bond distances and larger M-H-M bond angles by x-ray diffraction than by neutron diffraction.

In the past several years, a number of x-ray structural papers³ in which the authors have located and refined a position for the hydride ligand in a transition-metal hydride

complex have appeared in the literature. Due to the low x-ray scattering power of the hydrogen atom, the structural parameters calculated from the "refined" hydrogen position