complexes is more carefully defined, it will be interesting to compare with results with those found for model compounds such as those discussed here.

Acknowledgment. We are grateful to the NIH for support for this research through Grant GM29222 to L.G.M. A grant from the NSF to Emory University facilitated the purchase of the NMR equipment and the Nova/Eclipse computer. L.G.M. thanks the Alexander von Humboldt Foundation for a Senior Scientist Award. We thank Johnson-Matthey, Inc., for a loan of K_2PtCl_4.

Supplementary Material Available: Tables of least-squares planes and deviations of individual atoms from these planes, atom coordinates, bond lengths, bond angles, anisotropic temperature factors, hydrogen coordinates and temperature factors, and observed and calculated structure factors (36 pages). Ordering information is given on any current masthead page.

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Platinum Complexes with Iminodiacetate and (Methylimino)diacetate, Including Genuine Meridional Complexes

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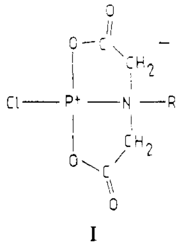
Reactions of $PtCl_4^{2-}$ with LH_2 (iminodiacetic acid, $idaH_2$, or (methylimino)diacetic acid, $midaH_2$) have been reported in the literature to yield platinum(II) complexes with the ligand meridional, $K[Pt(ida)Cl]\cdot 2HCl$ and $H[Pt(mida)Cl]\cdot 2HCl$. These compounds are platinum(IV) complexes, $Pt(L)Cl_3^-$, with the ligand facial, which may be prepared directly from K_2PtCl_6 and LH_2. Reaction of K_2PtCl_4 with LH_2 at ambient temperature gives $K[Pt(LH)Cl_2]$, in which the ligand is bidentate, coordinating through the N atom and one O atom. Genuine *mer*-$Pt(L)Cl^-$ may be obtained (more readily for L = mida) by careful addition of alkali to a solution of $Pt(LH)Cl_2^-$. Heating a solution of K_2PtCl_4 with excess LH_2 gives sparingly soluble $Pt(LH)_2$ (previously reported for L = ida), which, with alkali, gives soluble $Pt(L)_2^{2-}$. These compounds contain bidentate ligand. For $Pt(ida)_2^{2-}$, slow cis-trans isomerization occurs in solution. At high pH, inversion about coordinated nitrogen becomes rapid. In alkaline D_2O solutions, the methylene group of the coordinated arm is specifically deuterated. The compound described in the literature as $H_{2n}[Pt(mida)_2]_n$ is the platinum(IV) compound $Pt(mida)_2$. This complex, and $Pt(ida)_2$, may be prepared by reaction of the corresponding platinum(II) complex, $Pt(LH)_2$, with hydrogen peroxide.

Introduction

Iminodiacetic acid, $HN(CH_2CO_2H)_2$ ($idaH_2$), and its *N*-methyl analogue, $CH_3N(CH_2CO_2H)_2$ ($midaH_2$), coordinate to most metal ions. In the vast majority of these complexes, the ligand coordinates facially through the N atom and two deprotonated carboxylate groups (e.g., *trans*-$Ni(ida)_2^{2-}$,[1] *cis*- and *trans*-$M(ida)_2^-$ (M = Co, Rh)[2,3]). This preference for facial coordination is thought to be due to significant angle strain at nitrogen in the alternative meridional configuration.[2] *mer* coordination has been claimed, however, for two types of complexes: (i) octahedral complexes where this configuration has been forced by the disposition of the other ligands (e.g., *trans-mer*-$Co(dien)(ida)^+$,[4] dien = $NH_2CH_2CH_2NHCH_2CH_2NH_2$); (ii) complexes with metal ions with a strong preference for square-planar coordination, for which *fac* coordination is not possible (e.g., $Pd(L)(H_2O)$[5] and $Pt(L)Cl^-$ (I)[6] (LH_2 = $idaH_2$ or $midaH_2$)).



I

Close reading of the report by Smith and Sawyer on the platinum compounds[6] indicated that a reexamination of this system was warranted. The proposed *mer* compounds were isolated only with "hydrochloric acid of crystallization", as $K[Pt(ida)Cl]\cdot 2HCl$ and $H[Pt(mida)Cl]\cdot 2HCl$, with no report of acid-free material. Also, bis(ligand) complexes were reported—$Pt(idaH)_2$, with the ligand bidentate (through N and one O atom), soluble, as expected, in dilute alkali, and "$H_{2n}[Pt(mida)_2]_n$", quite insoluble in water or alkali. It was difficult to see why two ligands, so similar, would behave so differently.

When we commenced this work, the only platinum(IV) compounds known involving these ligands were *fac*-$Na[Pt(CH_3)_3(L)]$, where facial coordination of the tridentate ligand is forced by the *fac* disposition of the three methyl groups.[7]

We describe here the preparation of platinum(IV) complexes with these ligands, the results of our attempts to reproduce the preparations reported by Smith and Swayer,[6] and the characterization by NMR of the platinum(II) complexes that are actually formed in reactions between K_2PtCl_4 and these ligands.

Results

^1H NMR data are given in Table I and ^{13}C data in Table II . Satisfactory analytical data were obtained for all compounds isolated (Table III).

Platinum(IV) Complexes, $K[Pt(L)Cl_3]$. Heating K_2PtCl_6 with K(midaH) in aqueous solution at pH 5–6 gave a yellow microcrystalline solid that was analyzed as $K[Pt(mida)Cl_3]$. Its IR spectrum shows $\nu_{C=O}$ at 1660 cm^{-1}. Since uncoordinated –COOH groups usually absorb above 1700 cm^{-1},[8] both ligand carboxyl groups are coordinated. A band assignable to ν_{Pt-Cl} occurs at 334 cm^{-1}. Molar conductance of a 10^{-3} M aqueous soluton was 136 Ω^{-1} cm^2 mol^{-1} (cf. 147 Ω^{-1} cm^2 mol^{-1} for 10^{-3} M $[N(CH_3)_4]Cl$).

The ^1H NMR spectrum in D_2O (Table I) shows a singlet for the *N*-methyl group, with "satellites" from coupling to ^{195}Pt (I = $^1/_2$, 34% abundance). The methylene protons give an AB pattern, superimposed on an ABX pattern (half the total intensity of the AB pattern, X = ^{195}Pt).

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Table I. ^1H NMR Data[a]

			methylene protons			
compd	structure	pH or pD	H_A	H_B	J_{AB}	$N-CH_3$[b]
fac-$K[Pt(ida)Cl_3]$	II	7	4.53 (6.2)	3.78 (36.9)	17.9	
fac-$K[Pt(mida)Cl_3]$	II	7	4.58 (5.6)	4.11 (33.9)	16.8	3.19 (27.5)
mer-K[Pt(mida)Cl]	I	7	3.83 (71)	4.34 ($\leq$4)	15.7	2.99 (34)
$K[Pt(idaH)Cl_2]$	IV	~0	4.21	3.59	17.6	
			4.15	3.65	18.0	
$K_2[Pt(ida)Cl_2]$		7	3.82	3.33	16.6	
			3.70	3.39	17.0	
$K[Pt(midaH)Cl_2]$	IV	1.5	4.20	3.66	16.9	3.11 (32.0)
			4.03[c]	3.62[c]	16.9	
$K_2[Pt(mida)Cl_2]$		7	4.22	3.55	16.9	3.07 (32.2)
			3.88[c]	3.47[c]	16.9	
trans-$Pt(ida)_2^{2-}$[d] anti or syn	V or VI	5.7	3.82[c,e]	3.49[c,e]	17.0	
			3.60	3.44	16.6	
trans-$Pt(ida)_2^{2-}$[d] syn or anti	VI or V	5.7	3.80[c,e]	3.47[c,e]	16.9	
			3.59	3.43	16.7	
trans-anti-$Pt(mida)_2^{2-}$	V	5.5	4.13[c,e]	3.57[c,e]	15.4	2.99 (26.1)
			3.66	3.43	16.1	
trans-syn-$Pt(mida)_2^{2-}$	VI	5.5	4.16[c,e]	3.67[c,e]	15.5	3.03 (26.7)
			3.77	3.49	16.5	

[a] Chemical shifts in D_2O (in ppm) to lower shielding from TSS. Where available, coupling to ^{195}Pt is given in parentheses (in Hz). [b] For mida complexes. [c] Assigned to chelate ring protons. [d] Values from 300-MHz spectra. [e] These protons exchange with deuterium at high pD in D_2O.

Table II. ^{13}C NMR Data[a]

			methylene		carboxyl		*N*-methyl[b]	
compd	structure	pH or pD	δ	J_{Pt-C}	δ	J_{Pt-C}	δ	J_{Pt-C}
fac-$K[Pt(ida)Cl_3]$	II	7	59.74	17.6	184.66	20.4		
fac-$K[Pt(mida)Cl_3]$	II	7	70.03	14.6	182.43	8.8	53.84	<6
mer-K[Pt(ida)Cl]	I	4	57.57	23.4	189.14	29.3		
mer-K[Pt(mida)Cl]	I	4	68.28	23.4	187.23	32.3	52.60	25.3
$K[Pt(idaH)Cl_2]$	IV	1.5	57.28	24.4	188.95[c]	29.3		
			56.31	10.0	172.61	44.9		
$K[Pt(midaH)Cl_2]$	IV	1	66.37	19.5	188.01[c]	16.6	55.29	24.4
			63.52	10.7	171.71	18.5		
trans-$Pt(ida)_2^{2-}$ syn and anti	V and VI	5.5	56.18,[c,d] 56.23[c,d]	21.3	188.06[c,e]	14.7		
			58.39	13.9	175.23	34.5		
cis-$Pt(ida)_2^{2-}$ syn and anti	VII and VIII	5.5	57.36	~33[f]	186.92[c]	29.2		
			60.28	21.4	175.08	37.1		
trans-anti-$Pt(mida)_2^{2-}$	V	5.5	66.33	<12	188.01[c]	<8	53.46	25.4
			64.96	19.5	174.44	12		
trans-syn-$Pt(mida)_2^{2-}$	VI	5.5	66.21	<12	187.82[c]	<8	52.76	27.3
			64.96	19.5	174.21	12		

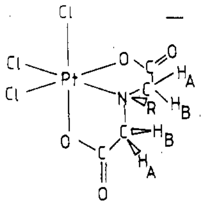
[a] Chemical shifts in ppm from external Me_4Si, with internal dioxane taken as 67.73 ppm; spectra in D_2O or H_2O. Coupling constants in Hz. [b] For mida complexes. [c] Assigned to C atom in chelate ring. [d] Peak disappears at high pD in D_2O. [e] Peak reduced in intensity at high pD in D_2O. [f] Peaks partly obscured.

Table III. Analytical Data[a]

compd	structure	% C	% H	% N	% Cl
fac-$K[Pt(ida)Cl_3]$	II	10.2 (10.2)	1.3 (1.1)	3.1 (3.0)	22.7 (22.6)
fac-$K[Pt(mida)Cl_3]$	II	12.2 (12.4)	1.7 (1.5)	2.8 (2.9)	21.4 (21.9)
mer-$K[Pt(mida)Cl]\cdot 2H_2O$	I	13.3 (13.3)	2.6 (2.5)	3.2 (3.1)	8.0 (7.9)
$K[Pt(idaH)Cl_2]$	IV	10.4 (10.5)	1.8 (1.8)	3.0 (3.1)	
$Pt(idaH)_2$	V and VI	20.9 (20.9)	2.6 (2.7)	6.1 (6.3)	
$Pt(midaH)_2$	V and VI	24.6 (24.6)	3.3 (3.4)	5.7 (5.7)	
$Pt(ida)_2$	IX	20.8 (21.0)	2.4 (2.2)	6.1 (6.1)	
$Pt(mida)_2$	IX	24.7 (24.8)	2.9 (3.0)	5.8 (5.7)	

[a] Calculated figures in parentheses.

From these data, it is clear that only one isomer is present of an ion, $Pt(mida)Cl_3^-$, in which the ligand is tridentate. *fac* (II, R = CH_3) and *mer* configurations are possible. As mentioned above, the *fac* structure would be expected to be more stable thermodynamically, because of lower angle strain at nitrogen.[2] Also, it would be expected to be kinetically preferred, if the reaction proceeds via the (undetected) intermediate III. Since the trans effect of chloride is greater than that of an O donor,[9] one of the mutually trans chloride ligands in III will be displaced in preference to chloride trans to O, to give the *fac* isomer, II.



II

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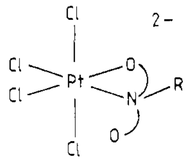


III

In related ring-closure reactions for platinum(IV) complexes with ethylenediaminetetraacetate, the trans effect has been shown to operate in this way to produce a kinetically favored isomer, even when this is not the product most stable thermodynamically.[10]

Coupling to ^{195}Pt is markedly different for the two methylene protons. Since

$$^3J_{\text{Pt-N-C-H}} \approx K \cos^2 \phi \tag{1}$$

where K is a constant and ϕ is the dihedral angle between the planes PtNC and NCH,[11,12] the proton with the larger coupling to ^{195}Pt is that labeled H_B in II ($\phi_B \approx 142°$) rather than that labeled H_A ($\phi_A \approx 79°$).[7] Consequently, H_A is labeled as the less shielded proton. This chemical shift order is similar to that for *fac*-Pt(CH$_3$)$_3$(mida)$^-$ [7] and *fac* complexes of Co(III)[2] and Rh(III).[3]

The ^{1}H-decoupled ^{13}C NMR spectrum in D$_2$O shows three singlets (two flanked by satellites) corresponding to carboxyl, methylene, and *N*-methyl groups. The assignments in Table II have been confirmed with use of multiplicities in the ^{1}H-coupled spectrum. The carboxyl carbon nucleus is significantly less shielded than in the free ligand, as expected if carboxylate is coordinated.[13] Coupling between ^{195}Pt and the C atoms in the chelate ring would be expected to be relatively small, since contributions from two- and three-bond coupling pathways are expected to be opposite in sign and will therefore partially cancel.[14] The observed coupling constants, 8.8 and 14.6 Hz for the carboxyl and methylene C atoms, respectively, fulfill this expectation. It is, however, surprising that the *N*-methyl C atom has no detectable coupling to ^{195}Pt, in view of the relatively large $^3J_{\text{Pt-N-CH}_3}$ coupling, 27.5 Hz (although other examples are known where $^2J_{\text{Pt-X-C}} << {}^3J_{\text{Pt-X-CH}_3}$ e.g., couplings to the *S*-methyl group in [Pt(CH$_3$)$_3$(μ_3-SCH$_3$)][15]).

An analogous compound, K[Pt(ida)Cl$_3$] (II, R = H), was obtained from the corresponding reaction using K(idaH). Its IR spectrum shows bands at 3160 ($\nu_{\text{N-H}}$), 1675 ($\nu_{\text{C=O}}$), and 330 ($\nu_{\text{Pt-Cl}}$) cm^{-1}. The molar conductance for a 10^{-3} M solution was 155 Ω^{-1} cm^2 mol^{-1}. Since we commenced our work, the same compound has been reported by Zheligovskaya and Al Ansari.[16] Their statement that the compound is a nonelectrolyte, with conductance 10 Ω^{-1} cm^2 mol^{-1} is, however, certainly in error! No NMR data were reported there.

The ^{1}H NMR spectrum shows the expected {AB + $^1/_2$(ABX)} pattern (X = ^{195}Pt; Table I). As with other systems,[2,3,7] the chemical shift difference between the methylene protons (0.75 ppm) is greater than in the mida complex. The ^{1}H-decoupled ^{13}C spectrum shows the expected two singlets with satellites, the methylene carbon nucleus is more shielded by 10 ppm than in the mida complex, and its coupling to ^{195}Pt is sightly greater. The carboxyl carbon nucleus is only slightly less shielded than in the mida analogue, but its coupling to platinum (20.4 Hz) is very much greater, illustrating the susceptibility of couplings to ring carbon atoms to the effects of an apparently minor substituent charge. A ^{195}Pt NMR spectrum could not be obtained for either of these compounds, probably because of partial decoupling of the Pt nucleus from ^{14}N.

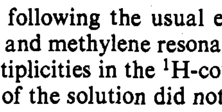
The bis(ligand) platinum(IV) complexes, Pt(L)$_2$, may be obtained from the reaction of K$_2$PtCl$_6$ with excess ligand, but they are best prepared by peroxide oxidation of the platinum(II) compounds, Pt(LH)$_2$ (see below).

Mono(ligand) Complexes of Platinum(II), Pt(LH)Cl$_2^-$ and Pt(L)Cl$^-$. Smith and Sawyer[6] claimed that the yellow compounds "K[Pt(L)Cl]·2HCl" were obtained by heatng aqueous solutions of K$_2$PtCl$_4$ with 2 molar equiv of LH$_2$ for 5 h and then concentratng and cooling. Their mida complex was contaminated with midaH$_2$ and so was converted to "H[Pt(mida)Cl]·2HCl" by cation exchange. These compounds were assigned structure I, with ligand coordination *mer*.

In our hands, no more than traces of yellow products were obtained by this procedure, even if heating was prolonged for several days. However on one occasion, a preparation with midaH$_2$ gave yellow crystals after 14 days' heating in a stream of air, followed by 2 weeks' standing in a refrigerator. Its ^{1}H NMR spectrum in D$_2$O was identical with that reported for "Pt(mida)Cl$^-$" by Smith and Sawyer but it was also identical with that previously obtained for the platinum(IV) complex K[Pt(mida)Cl$_3$] (II, R = CH$_3$), prepared, as described above, from K$_2$PtCl$_6$ and K(midaH). Its solution was not acidic. None of this product was obtained from a similar reaction under nitrogen.

A sample of K[Pt(mida)Cl$_3$] was converted to H[Pt(mida)Cl$_3$] by cation exchange. Its ^{1}H NMR spectrum was similar to that of the potassium salt and to that reported by Smith and Sawyer[6] for "H[Pt(mida)Cl]·2HCl". Its aqueous solutions are, of course, acidic. The ^{1}H NMR and IR spectra reported by Smith and Sawyer for "K[Pt(ida)Cl]·2HCl" are also identical with those we obtained for K[Pt(ida)Cl$_3$]. There is no doubt that our compound is a platinum(IV) complex, rather than a platinum(II) compound solvated with HCl. Its molar conductance corresponds to a 1:1 electrolyte (see above), and its solutions are not acidic. Smith and Sawyer presumably obtained these platinum(IV) compounds under conditions (prolonged reaction times?) where aerial oxidation occurred.

Reactions between K$_2$PtCl$_4$ and the ligands were then monitored by NMR. Equimolar amounts of K$_2$PtCl$_4$ and midaH$_2$ were dissolved in D$_2$O. With gentle warming, the solution slowly changed from red to yellow and ^{1}H NMR peaks due to midaH$_2$ decreased as new peaks grew—an *N*-methyl resonance with satellites and two AB quartets with additional minor peaks from platinum coupling. The new species is assigned as Pt(midaH)Cl$_2^-$ (IV, R = CH$_3$) in which the ligand is bidentate, with methylene resonances from chelated and free arms of the ligand.



IV

The ^{1}H-decoupled ^{13}C NMR spectrum showed, in addition to peaks due to midaH$_2$, one signal corresponding to an *N*-methyl group, two methylene signals, and two carboxyl signals (each peak flanked by satellites). The carboxyl resonance at 188.01 ppm is assigned to the coordinated arm and that at 171.71 ppm to the uncoordinated arm, following the usual empirical rule.[13] Assignments of methyl and methylene resonances in Table II were confirmed from multiplicities in the ^{1}H-coupled spectrum. The ^{1}H NMR spectrum of the solution did not change on standing, but heating the yellow solution on a steam bath caused it to revert to a red color (PtCl$_4^{2-}$), and peaks due to Pt(midaH)$_2$ (see below) grew.

Attempts to prepare solid samples of K[Pt(midaH)Cl$_2$] free from KCl, K$_2$PtCl$_4$, and midaH$_2$ were unsuccessful. Less soluble K[Pt(idaH)Cl$_2$] (IV, R = H) was obtained more readily from K$_2$PtCl$_4$ and idaH$_2$. Its IR spectrum shows $\nu_{\text{C=O}}$ at 1705 (free

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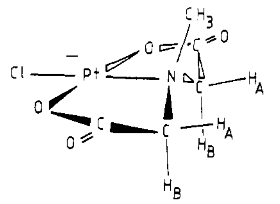

Figure 1. Preferred conformation for ligand in *mer*-Pt(mida)Cl$^-$ (I).

–COOH) and 1575 (coordinated –COO$^-$) cm^{-1} and ν_{N-H} at 3170 cm^{-1}. A solution in D_2O showed two AB quartets (with weaker peaks from coupling to ^{195}Pt). Its ^{1}H-decoupled ^{13}C spectrum showed four singlets with satellites, two from methylene groups and two from carboxyl. The carboxyl chemical shifts are similar to those in the mida analogue, but the Pt–C coupling constants are very much larger (Table II). As usual, the methylene C atoms are more shielded in the ida compound.

Because a proton is released from the ligand when Pt(LH)Cl_2^- forms, these solutions became quite acidic (pH 1–2). If the pD of a D_2O solution is raised to 7, the uncoordinated carboxyl group will deprotonate. If it is assumed that chemical shifts of the methylene protons adjacent to this carboxyl group will be affected more by this deprotonation than the methylene protons of the chelated arm, the more shielded of the AB quartets for Pt(midaH)Cl_2^- (Table I) may be assigned to the uncoordinated arm. A similar assignment could not be made for Pt(idaH)Cl_2^- because both sets of methylene proton shifts were affected significantly by increased pD. Attempts to measure changes in δ_C with increased pH were unsuccessful. As described below, Pt(L)Cl_2^{2-} is unstable at higher pH, and subsequent reaction reduces pH during the time required for a ^{13}C measurement.

When 1 M KOH solution was added cautiously to a solution of K[Pt(midaH)Cl_2] in equilibrium with K_2PtCl_4 and midaH_2 (pH 1.3) to increase the pH to 7.8, the pH subsequently fell again over 5 h, and the solution became paler. The ^{1}H-decoupled ^{13}C NMR spectrum of the solution showed a new set of peaks in addition to those from K[Pt(midaH)Cl_2] and free ligand—three singlets with satellites that may be assigned to coordinated carboxylate (187.23 ppm), methylene (68.28 ppm), and *N*-methyl (52.60 ppm). Since only three singlets were present, the compound does not contain bidentate ligand, and the spectrum is as expected for genuine *mer*-Pt(mida)Cl$^-$ (I, R = CH_3). Some pale yellow gelatinous material was also formed on the sides of the vessel. The IR spectrum of this material, after drying, indicated that it was predominantly a hydrated oxide, with a small amount of ligand incorporation.

After several cycles in which the pH was increased to 7–8 and then allowed to fall spontaneously to 4–5, *mer*-Pt(mida)Cl$^-$ became the predominant species in solution. When a solution at pH 7.5 was evaporated to dryness under a stream of nitrogen, an orange solid was obtained, containing the *mer* product mixed with KCl, K_2PtCl_4, and K_2(mida). Careful washing with small volumes of cold water removed these contaminants, leaving the less soluble K[Pt(mida)Cl]·$2H_2O$ as yellow needles. Analytical results confirmed that only one chloride ion was present per formula weight. The IR spectrum showed peaks due to water, $\nu_{C=O}$ at 1643 cm^{-1}, and ν_{Pt-Cl} at 320 cm^{-1}, consistent with the proposed structure, I.

The ^{1}H NMR spectrum of this product in D_2O, when run at low resolution, showed one singlet with satellites for the methyl protons and one AB quartet (with weaker peaks from coupling to platinum), as expected for a *mer* structure, in which the two methylene groups are related by symmetry. The more shielded methylene proton has a very large coupling with ^{195}Pt, 71 Hz, while coupling was not resolved for the less shielded proton. Figure 1 shows the preferred conformation (from models) of the *mer*-coordinated ligand, which is much more rigid than when the ligand is *fac*. The dihedral angle between the planes PtNC and NCH_A, ϕ_A, is close to 180°, while ϕ_B is close to 90°. From eq 1, we would expect $J_{Pt-N-C-H_A}$ to be large, and $J_{Pt-N-C-H_B}$ to be small, as observed, if H_A is more shield than H_B. This contrasts with the assignment for *fac*-Pt(mida)Cl_3^- above, where H_A is the proton with the smaller coupling to platinum and is less shielded.

At high resolution, the spectrum showed coupling between the *N*-methyl protons and the less shielded methylene protons (1 Hz), assigned as H_B. Such coupling was not observed for any other mida complex. From Figure 1, it will be seen that H_BCNC(Me) is almost coplanar, which allows each methyl proton to spend some time in the "planar W" configuration with H_B, which favors four-bond H–H couplng.[17]

It is also noticeable in the spectrum (100 MHz) that the platinum satellites are significantly broader than the central peaks. This has not been observed at 100 MHz for any of the other compounds described here and is probably attributable to relatively efficient relaxation of the ^{195}Pt nucleus by chemical shift anisotropy[18] enhanced by the presence of the relatively rigid tridentate ligand on one side of the complex.

Once formed, this complex is quite stable in solution, with no change in spectra over several weeks.

Analogous reactions between Pt(idaH)Cl_2^- and KOH produced *mer*-Pt(ida)Cl$^-$ in solution, identified by its ^{13}C NMR spectrum (Table II), but greater proportions of platinum metal and the gelatinous hydroxide were produced than with mida, and the product was not isolated.

Preparation of Bis(ligand) Platinum(II) Complexes, Pt(LH)$_2$. Smith and Sawyer[6] reported that Pt(idaH)$_2$ may be obtained by heating an aqueous solution of K_2PtCl_4 with 4 molar equiv of idaH_2 for at least 5 h on a steam bath. We have found that this procedure gives a good yield of Pt(idaH)$_2$ as a white microcrystalline precipitate (although a much shorter reaction time suffices). In agreement with these authors, its IR spectrum shows $\nu_{C=O}$ bands at 1596 (coordinated carboxylate) and 1730 (free carboxyl) cm^{-1}. This product is almost insoluble in water but dissolves readily on addition of dilute alkali. Reprecipitation occurs if acid is added to reduce the pH below 5.5.

According to Smith and Sawyer,[6] Pt(midaH)$_2$ could not be obtained by an analogous method. Instead, they obtained a white solid, insoluble in both acid and alkali, with only one $\nu_{C=O}$ band at 1702 cm^{-1}. They proposed a polymeric structure, "H_{2n}[Pt(mida)$_2$]$_n$", with all acetate arms coordinated (although it is difficult to see how this could be achieved if the N atoms remained bound and the platinum(II) atom retained its normal planar four-coordination). In fact, this product appears to be identical with the platinum(IV) complex Pt(mida)$_2$, which we have prepared either from K_2PtCl_6 and excess K(midaH) or by peroxide oxidation of a genuine sample of Pt(midaH)$_2$ (see below). We did, on one occasion, obtain a small yield of Pt(mida)$_2$ by evaporating to dryness on a steam bath a solution initially containing K_2PtCl_4 and midaH_2. Once again, it appears likely that Smith and Sawyer obtained their product under conditions where aerial oxidation occurred.

In our hands, reaction of K_2PtCl_4 and midaH_2 as described by Smith and Sawyer[6] gave only a pale yellow solution, with no solid product. If, however, this solution was concentrated to small volume and then cooled, a white microcrystalline solid deposited, which was analyzed as Pt(midaH)$_2$. Its IR spectrum shows $\nu_{C=O}$ bands at 1740 and 1600 cm^{-1}. Like Pt(idaH)$_2$, it is only very sparingly soluble in water but dissolves easily in alkaline solution, from which it may be reprecipitated with acid. These properties, and the NMR spectra discussed below, leave no doubt that our product is genuine Pt(midaH)$_2$.

NMR Spectra of Pt(L)$_2^{2-}$ Complexes. When Pt(LH)$_2$ dissolves in dilute alkali, the uncoordinated carboxyl groups deprotonate, giving Pt(L)$_2^{2-}$ in solution. There are four possible geometric isomers of Pt(LH)$_2$, V–VIII. The labels cis and trans refer to the configuration of N- and O-donor atoms about the metal, while syn and anti refer to configurations in which the uncoordinated acetate arms are on the same or opposite sides of the coordination plane, respectively.[19]

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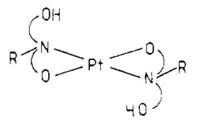
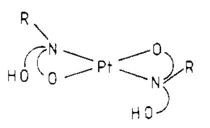
(19) We thank a reviewer for pointing out that the syn and anti isomers could alternatively be labeled racemic and meso.



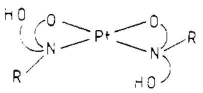
V

anti trans



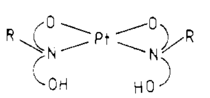
VI

syn trans



VII

anti cis



VIII

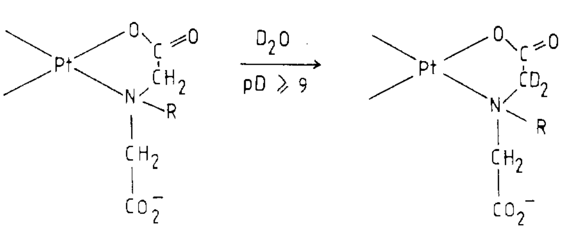
syn cis

For each isomer of $Pt(ida)_2^{2-}$ (ignoring platinum coupling) the ^1H-decoupled ^{13}C NMR spectrum would be expected to show two singlets in each of the methylene and carboxyl regions, corresponding to chelated and nonchelated acetate arms, and the ^1H NMR spectrum in D_2O would be expected to show two AB quartets.

To a first approximation, the ^1H-decoupled ^{13}C spectrum of a freshly prepared solution of $Pt(ida)_2^{2-}$ is as expected for one isomer only, showing two singlets with satellites in each of the methylene and carboxyl regions (Figure 2a). At pH 5.7, however, a 25-MHz spectrum run under optimum conditions showed a slight splitting in one of the methylene peaks, which was confirmed by a spectrum run at 75 MHz. It was therefore concluded that the solution contained two isomers whose ^{13}C peaks were almost coincident, assigned as anti and syn isomers for one geometric arrangement of donor atoms. At 25 MHz, the "satellite" peaks were noticeably broadened, and the 75-MHz spectrum showed no satellite peaks at all, presumably owing to fast relaxation of the platinum nucleus by chemical shift anisotropy at the higher field.[18] At higher pH, the splitting was no longer resolved, but there was no other change in the ^{13}C spectrum up to pH 14 in H_2O. There is therefore no rapid process interconverting coordinated and uncoordinated acetate arms at high pH.

The ^1H NMR spectrum in D_2O at pD 5.7 is consistent with this interpretation, showing four AB quartets. This pattern is evident at 100 MHz but is clearer at 300 MHz (Figure 3a). At 100 MHz, some weaker peaks due to platinum coupling are observed, but owing to the complexity of the spectrum, no attempt was made to determine the Pt–H coupling constants. At 300 MHz, no coupling was observed.

When the pD was increased to 9, two of the four AB quartets disappeared over several minutes, while the remaining peaks were unaffected (Figure 3b). At high pD, one pair of methylene protons in each coordinated ligand is selectively replaced by deuterium (eq 2). That it is the protons on the chelate ring that exchange is shown by the ^1H-decoupled ^{13}C spectrum of a solution at pD 13 in D_2O (Figure 2b) in which the more shielded methylene peak has effectively disappeared (due to loss of nuclear Overhauser enhancement, and the effect of C–D spin–spin coupling, on deuteration), and the less shielded carboxyl peak has been much reduced in intensity (loss of Overhauser enhancement). The other peaks are not affected. Since the carboxyl resonance to lower shielding may be confidently assigned to the coordinated carboxylate,[13] it is the methylene group of the chelate ring that is deuterated. That deuteration occurs exclusively on one arm is confirmed by the ^1H-coupled spectrum of the same solution (Figure 2c). The remaining methylene signal is split into a triplet by coupling to two protons ($^1J_{C-H}$ = 141.6 Hz), and the more shielded carboxyl resonance is also split into a triplet ($^2J_{CCH_2}$ = 4.9 Hz). The less shielded carboxyl resonance is a singlet. Deuteration of α-C atoms in amino acid chelate rings has been frequently observed, especially in cobalt(III) complexes.[20-22]



(2)

When the pD was further increased, the two remaining AB quartets in the ^1H spectrum collapsed to a singlet (with satellites at 100 MHz) (Figure 3c). Thus, the syn and anti isomers interconvert rapidly, and simultaneously, the methylene protons on the uncoordinated arm become equivalent. This process will

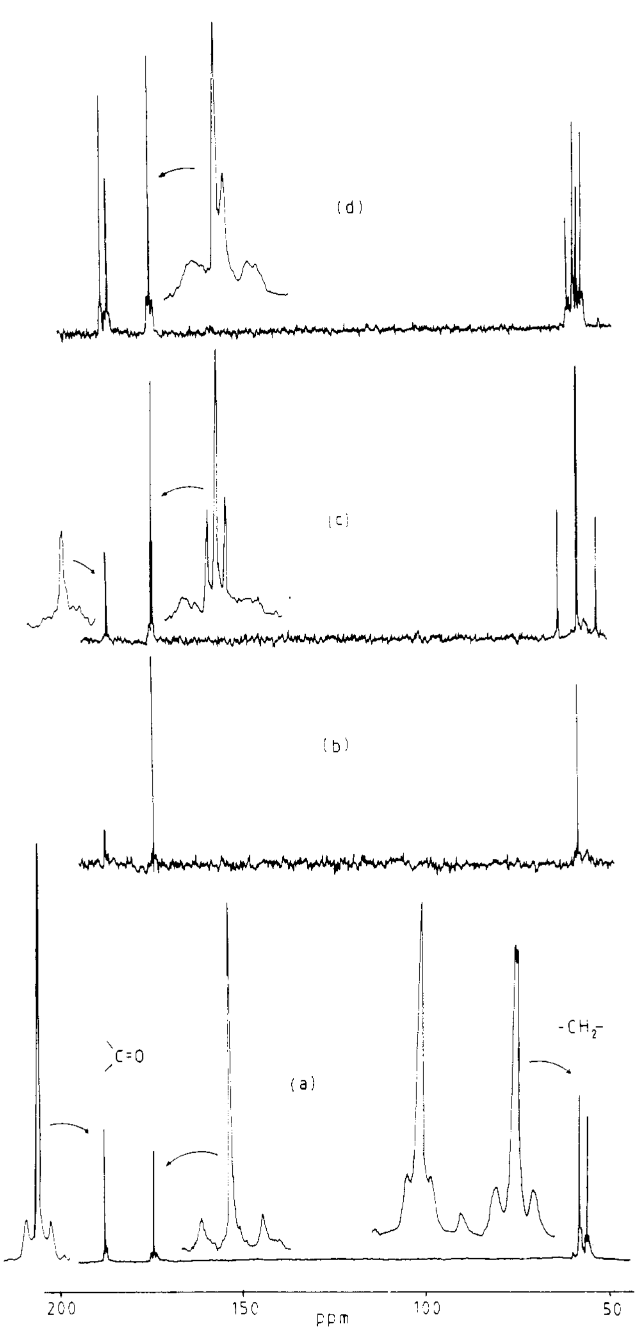


Figure 2. 25.05-MHz ^{13}C NMR spectra of $Pt(ida)_2^{2-}$: (a) freshly prepared solution at pH 5.7 in H_2O (trans isomers only) (^1H decoupled); (b) ^1H-decoupled solution in D_2O at pD 13; (c) solution as in (b), but ^1H coupled; (d) solution in H_2O at pH 5.7, after heating at 95 °C for 45 min. Inset sections are 12-fold expansions.

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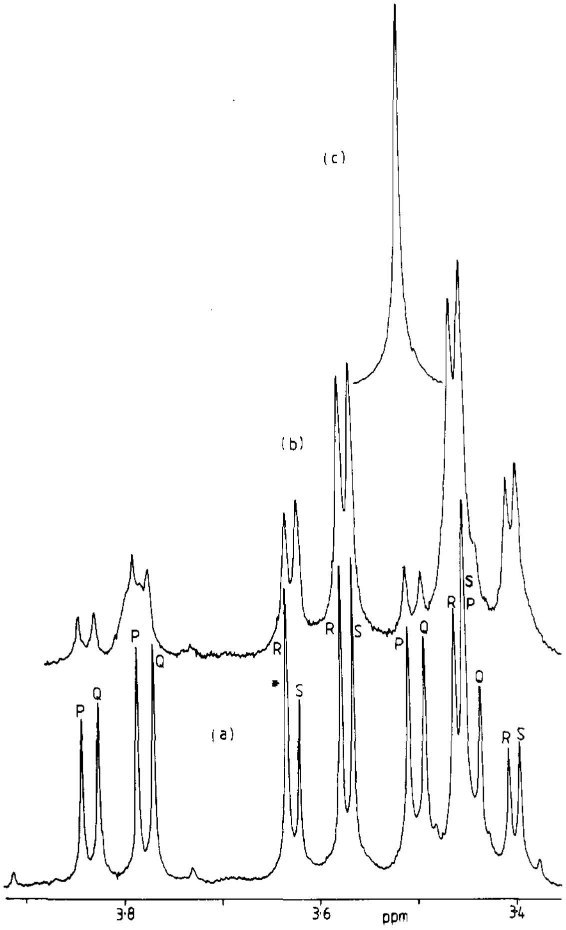
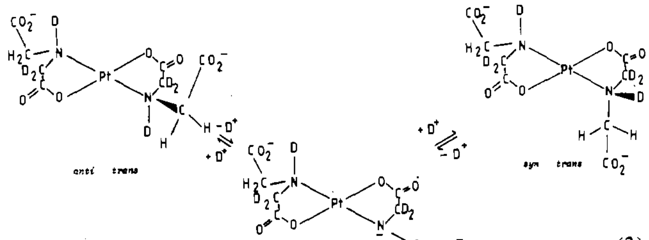


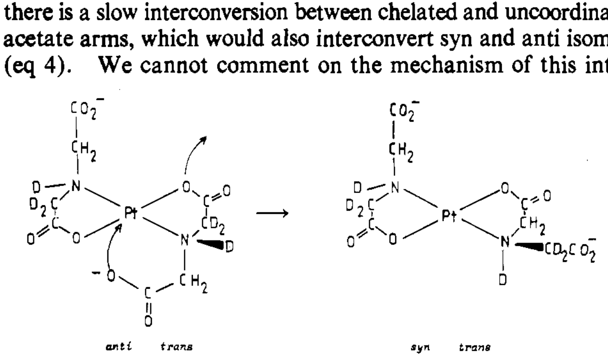
Figure 3. 300-MHz ^{1}H NMR spectra of Pt(ida)$_2^{2-}$ in D_2O: (a) freshly prepared solution at pD 5.7 (labels P, Q, R, S identify the four AB quartets; an asterisk marks the peak due to free ligand coincident (at high pH, this peak shifts out of the illustrated region)); (b) solution after 10 min at pD 9 (after longer standing, peaks due to quartets P and Q disappear entirely); (c) solution at pD 14.

involve deprotonation at nitrogen in the alkaline solution, with subsequent inversion (eq 3).



(3)

When D_2SO_4 was added to an alkaline D_2O solution to return the pD to 5.7, the spectrum initially showed two AB quartets (similar to Figure 3b). After several hours' standing, weak peaks of the other two quartets became visible and slowly grew. Thus, there is a slow interconversion between chelated and uncoordinated acetate arms, which would also interconvert syn and anti isomers (eq 4). We cannot comment on the mechanism of this interconversion, which may be compared with the much faster interchange between free and coordinated arms in Pd[N(CH_2CO_2)$_3$]$_2^{4-}$.[24]



(4)

In all of the above spectra, there was no evidence for the presence of more than one geometrical arrangement of the donor atoms (trans or cis) about the metal. However, if an alkaline solution of Pt(ida)$_2^{2-}$ in H_2O was allowed to stand for several days or, more rapidly, if a solution at pH 5.5 was heated, the ^{1}H-decoupled ^{13}C spectrum showed two new singlets with satellites in each of the carboxyl and methylene regions, which could only be due to a new isomer, cis or trans, with peaks due to syn and anti isomers again coincident (Figure 2d).

Since Pt(idaH)$_2$ was isolated from hot solution, when cis and trans isomers would be in equilibrium, the isomer isolated would be the less soluble and is therefore assigned as the less polar trans isomer (V and VI). The "new" isomer would then be assigned as cis (VII and VIII). This assignment is consistent with the observation that all Pt–C coupling constants are larger in magnitude of the "new" isomer. For C atoms on the uncoordinated arm, this coupling must be transmitted through the Pt–N bond, and for C atoms of the chelate ring, this coupling path probably makes a larger contribution than the path through Pt–O, a weaker bond. In the cis isomer, the Pt–N bond is trans to carboxylate, of lower trans influence than N, so these coupling constants will be larger in magnitude than for the trans isomer, where the N atoms are mutually trans.

H_2SO_4 was added to an aqueous solution containing a mixture of *cis*- and *trans*-Pt(ida)$_2^{2-}$, to precipitate a sample of Pt(idaH)$_2$, which was filtered off. This solid was redissolved in D_2O at pD 5.7 and the ^{13}C spectrum run of the solution. It showed only peaks due to the "original" isomer, assigned above as trans. The cis isomer was apparently too soluble to be precipitated by the acid. No attempt was made to examine ^{1}H NMR spectra of cis–trans mixtures.

The ^{1}H-decoupled 21.4-MHz ^{195}Pt NMR spectrum of a freshly prepared aqueous soluton of Pt(ida)$_2^{2-}$ (mixture of trans isomers) at pH 6 showed a singlet at −1649 ppm from Na_2PtCl_6. This is in the chemical shift region expected for platinum coordinated to two N and two O atoms (cf. *cis*-Pt(NH_3)$_2$(H_2O)$_2^{2+}$, −1593 ppm[22]). The peak was broad (140 Hz wide at half-height), probably due mainly to partial decoupling of ^{14}N nuclei from platinum. Separate peaks due to syn and anti isomers were not observed. The spectrum did not change significantly up to pH 14.

A sample was heated at pH 9, to produce a mixture of cis and trans isomers. In addition to the peak at −1649 pm, a peak was observed at −1801 ppm, which was assigned to the cis isomer, which was significantly broader (230 Hz). Again, peaks due to syn and anti isomers were not resolved.

The ^{1}H NMR spectrum of a freshly prepared solution of Pt(mida)$_2^{2-}$ in D_2O at pD 5.5 showed two *N*-methyl singlets with satellites, with approximate intensity ratio 1:2. These are assigned to *syn-trans* and *anti-trans*-Pt(mida)$_2^{2-}$, since the two Pt–N–CH_3 coupling constants are almost identical (Table I). Because of the different trans influences of N and O, cis and trans isomers would be expected to give different coupling constants. Steric constraints might be expected to be more important here, with *N*-methyl replacing N–H in the ida analogue, and of the four possible isomers, anti-trans (V) would be most preferred sterically. The more abundant of the two isomers observed is therefore assigned as this isomer and the other as syn-trans (VI). The ^{1}H spectrum also showed two AB quartets, with weaker peaks due to platinum coupling (not analyzed) for the methylene protons of each isomer.

When a D_2O solution was allowed to stand at pD 14 for several minutes, one of the AB quartets for each isomer disappeared, as chelated acetate arms were selectively deuterated, as with Pt(ida)$_2^{2-}$. Since, of course, the *N*-methyl group is not affected by alkali, the spectrum did not indicate any rapid inverison at nitrogen, in contrast to that of Pt(ida)$_2^{2-}$

As expected, the ^{1}H-decoupled ^{13}C spectrum showed two

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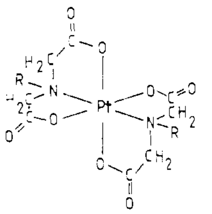
[24] Smith, B. B.; Sawyer, D. T. *Chem. Commun.* **1968**, *1454*.

N-methyl resonances, with satellites. The methylene resonances for the syn and anti isomers were almost coincident, but the carboxyl peaks for the two isomers were clearly resolved (Table II).

When a solution of $Pt(mida)_2^{2-}$ at pD 5.5 was heated for 30 min at 100 °C, spectra showed no new peaks assignable to cis isomers. Either cis isomers are much less stable thermodynamically than trans, due to steric interactions between the substituents on the adjacent N atoms, or the energy barrier for isomerization is much higher than for the ida complex.

The ^1H decoupled ^{195}Pt spectrum of a freshly prepared solution of $Pt(mida)_2^{2-}$ at pH 6 showed two broad peaks (each with width at half-height 140 Hz) with intensity ratio 2:1 at −1596 and −1619 ppm, respectively, assigned to anti-trans (V) and syn-trans (VI) isomers.

Peroxide Oxidations of $Pt(LH)_2$. When aqueous suspensions of $Pt(LH)_2$ were warmed with excess hydrogen peroxide, white solids that were analyzed as $Pt(L)_2$ were obtained. For both ida and mida compounds, only one strong $\nu_{C=O}$ band was observed, at 1710 cm^{-1}. This is only slightly above the "normal range" for coordinated carboxylate,[8] so the compounds are formulated as octahedral platinum(IV) complexes with all carboxylate groups coordinated. The compounds are quite insoluble in water, dilute acids and alkalis, and common organic solvents. No structural information from solution NMR is therefore available, but the ligands are presumably facially coordinated. If, as postulated above, the solid starting complexes $Pt(LH)_2$ have N atoms trans, it is also likely that they will be trans in the product, IX.



IX

Experimental Section

Starting Materials. K_2PtCl_4 was prepared by the literature method.[25] Iminodiacetic acid (BDH) and (methylimino)diacetic acid (Aldrich) were used as supplied.

Instruments and Methods. IR spectra were run as Nujol mulls on a Perkin-Elmer 283b spectrometer. ^1H NMR spectra were run on a JEOL PS-100 (CW) instrument, using internal lock (solvent HDO), with sodium 3-(trimethylsilyl)propanesulfonate (TSS) as internal reference. ^{13}C (25 MHz) and ^{195}Pt (21.4 MHz) spectra were run on a JEOL FX-100 spectrometer, with double-precision mode, using a 10-mm tunable probe. ^{13}C spectra were run on internal lock, with D_2O either as the solvent or, if the solvent was H_2O, in a coaxial capillary. Typically, 13 000 scans were required, with 3-s delay between 10-μs pulses (37° tilt), and with spectrum width 8000 Hz and 16K data points. Dioxane was used as internal reference. Its shift relative to external tetramethylsilane was taken as 67.73 ppm.[26] ^{195}Pt spectra were run with use of a ^7Li external lock. Typically, 5000 scans were used, with 0.3-s delay between 20-μs pulses (70° tilt), spectrum width 20 000 Hz, and 8K data points. Peaks were referenced to a separate sample of Na_2PtCl_6 in aqueous solution (0.5 g/mL).[27] In all cases, shifts to lower shielding are positive.

^1H (300 MHz) and ^{13}C (75 MHz) spectra were run on a Bruker CXP-300 instrument at the Brisbane NMR Centre by L. Lambert.

Microanalyses were carried out by J. Kent and P. Nobbs of this department.

Routine pH measurements were made with use of Merck narrow-range indicator strips, checked against glass electrode measurements.

$K[Pt(ida)Cl_3]$ (II, R = H). A 0.59-g sample of K_2PtCl_6 (1 mmol) and 0.2 g of $idaH_2$ (1.5 mmol) were dissolved in 75 mL of hot water, and the pH was adjusted to 5–6 with 1 M KOH solution. The solution was heated on a steam bath for 2 days, with occasional additions of KOH to maintain the pH near 5.5. The solution was then concentrated to 5 mL under a stream of air on the steam bath, filtered while hot, and allowed to cool. The product crystallized as yellow needles, contaminated with K_2PtCl_6. Two recrystallizations from hot water were required to give a pure product, 0.38 g (66%).

$K[Pt(mida)Cl_3]$ (II, R = CH_3). A procedure similar to that above gave 70% yield.

$H[Pt(mida)Cl_3]$. A 0.157-g sample of $K[Pt(mida)Cl_3]$ was dissolved in 10 mL of water, and the solution was passed down a column of Amberlite IR-120(H) resin (BDH analytical grade). The eluted solution was concentrated on a steam bath and then evaporated to dryness in a stream of air, to give 0.132 g of yellow solid (91%), which was dried in a vacuum desiccator over silica gel. It is very soluble in water, acetone, and ethanol.

$K[Pt(mida)Cl_3]$ from K_2PtCl_4 and $midaH_2$. A 0.83-g sample of K_2PtCl_4 (2 mmol) and 0.59 g of $midaH_2$ (4 mmol) were dissolved in 100 mL of water and heated on a steam bath in a stream of filtered air for 14 days, with occasional additions of water to replace losses by evaporation. The mixture was then allowed to stand 14 days in a refrigerator. A small amount of $Pt(midaH)_2$ was removed by filtration, the filtrate was concentrated at 10 mL on a rotary evaporator, and the yellow solid was allowed to crystallize. It was filtered off, washed with a small volume of water, and air-dried. This product was identical in all respects with $K[Pt(mida)Cl_3]$ prepared from K_2PtCl_6, as described above. Approximately 0.1 g was obtained.

A similar procedure using $idaH_2$ gave $Pt(idaH)_2$ as the major product.

***mer*-$K[Pt(mida)Cl]\cdot 2H_2O$ (I, R = CH_3).** A 0.5532-g sample of K_2PtCl_4 (1.33 mmol) and 0.2057 g of $midaH_2$ (1.39 mmol) were dissolved in 5 mL of water. The solution was gently heated on a steam bath for 15 min and then allowed to stand overnight, during which time the pH fell to 1.3. KOH solution (1 M) was then added to increase the pH to 7.8. After 5 h, the pH had dropped to 4.4. More KOH solution was added to bring the pH to 6.9, and similar adjustments were made periodically over 2 days. Then with pH 7.5, the solution was evaporated to dryness in a stream of nitrogen, to give an orange solid consisting of the product mixed with K_2PtCl_4, K(midaH), and KCl. The solid was transferred to a small glass sinter and washed with small volumes of cold water, leaving the product as yellow needles on the sinter. The yield was 0.051 g (8.5%).

$K[Pt(idaH)Cl_2]\cdot H_2O$ (IV, R = H). A 0.41-g sample of K_2PtCl_4 (1.0 mmol) was dissolved in 75 mL of water and 0.133 g of $idaH_2$ (1 mmol) was added. The solution was heated on a steam bath until it turned yellow (30 min) and then cooled. The volume was then reduced to 5 mL on a rotary evaporator without further heating. A small amount of $Pt(idaH)_2$ was filtered off, and the filtrate was placed in a vacuum desiccator over silica gel until yellow crystals formed, which were filtered off, washed with a small volume of ice-cold water and then with ethanol, and air-dried. The yield was 0.65 g (45%).

$Pt(idaH)_2$ (V and VI, R = H).[6] A 0.415-g sample of K_2PtCl_4 (1.0 mmol) was dissolved in 75 mL of water, and 0.53 g of solid $idaH_2$ (4 mmol) was added. The mixture was heated on a steam bath for 2 h and then allowed to cool. A white microcrystalline product formed, which was crystallized form the colorless solution, washed with water and then ethanol, and air-dried. The yield was 0.35 g (76%).

$Pt(midaH)_2$ (V + VI, R = CH_3). A 0.415-g sample of K_2PtCl_4 (1.0 mmol) was dissolved in 75 mL of water, and 0.59 g of solid $midaH_2$ (4 mmol) was added. The solution was refluxed under nitrogen for 2 h, and then the volume was reduced to 10 mL with use of a rotary evaporator, with heating. A white solid began to crystallize. The stoppered flask was allowed to stand overnight in a refrigerator, and the solid was filtered off, washed with water and then ethanol, and air-dried. The yield was 0.156 g (32%).

$Pt(ida)_2$ (IX, R = H). A 0.1-g sample of $Pt(idaH)_2$ (0.22 mmol) was suspended in 5 mL of water, and 1 mL of 30% hydrogen peroxide solution was added. The suspension was warmed on a steam bath. Vigorous effervescence occurred. After 1 h, the mixture was cooled, and the white solid was filtered off, washed with water and then ethanol, and air-dried. The yield was 0.052 g (52%).

$Pt(mida)_2$ (IX, R = CH_3). A similar procedure using $Pt(midaH)_2$ gave 73% yield.

Acknowledgment. We thank the Australian Research Grants Committee for financial support.

Registry No. I·K (R = H), 94668-03-8; II·K (R = H), 94668-02-7; II·K (R = CH_3), 94570-92-0; II·H (R = CH_3), 94570-97-5; IV·K (R = H), 94570-93-1; IV·K (R = CH_3), 94570-98-6; IX (R = H), 94570-95-3; IX (R = CH_3), 94570-96-4; $Pt(idaH)_2$, 23124-67-6; $Pt(midaH)_2$, 94570-94-2; K_2PtCl_6, 16921-30-5; K_2PtCl_4, 10025-99-7.

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