We have found similar hydroxylations in the voltammetry of dimethoxybenzenes, methoxyphenols, and catechols. Sivaramaih and Krishnan have recently postulated a follow-up hydroxylation in the prolonged coulometric oxidation of catechol in sulfuric acid.[3]

Most of the hydroxylations of biological significance appear to involve molecular oxygen and hydroxyl or perhydroxyl radicals,[4] but nucleophilic reactions are not excluded and have been definitely established in some cases.[5] The exact pathways of hydroxylation in the biosynthesis of plant phenolics are particularly not well understood,[6] and the electrochemical studies may have particular relevance here. We are currently investigating the full range of these anodic hydroxylations including the kinetics and pH dependence.

**Acknowledgment.** The support of this work by the National Institutes of Health through Grant GM-13791 is gratefully acknowledged.

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## Amide Tautomerism. Evidence for the Iminol Form of Trimethylacetamide in a Platinum Complex

*Sir:*

Several claims for amide tautomerism have been made in the past, based on solvent effects on the ORD spectra of optically active N-substituted benzamides,[1] the uv spectra of amides of trichloroacetic and benzoic acids,[2] and the infrared spectrum of urea.[3] The evidence which has been presented is far from conclusive and the nmr studies of Skulski, Palmer, and Calvin[4] have shown that, in at least the first case, the results are better explained in terms other than amide–iminol equilibrium. In the course of a study of the constitution of platinum blue[5] and its analogs, we have isolated a material which we believe does contain an amide in its tautomeric, iminol form.

Solid dichlorobis(acetonitrile)platinum(II) and trimethylacetamide were ground together, and the dry mixture was gently heated until its pale yellow color had turned to deep green. After extracting the reaction mixture with ether and evaporating the blue ether solution to dryness, the unreacted amide was sublimed from the mixture. Solution of the remaining solid in ether and slow evaporation of this solution yielded several crops of blue-green, spear-shaped needles (I), mp 157–159° dec. *Anal.* Calcd for $PtCl_2[(CH_3)_3CCONH_2]_2$: Pt, 41.66; O, 6.83; N, 5.98; C, 25.65; H, 4.74. Found: Pt, 41.92; O, 6.85; N, 6.15; C, 25.72; H, 4.58.

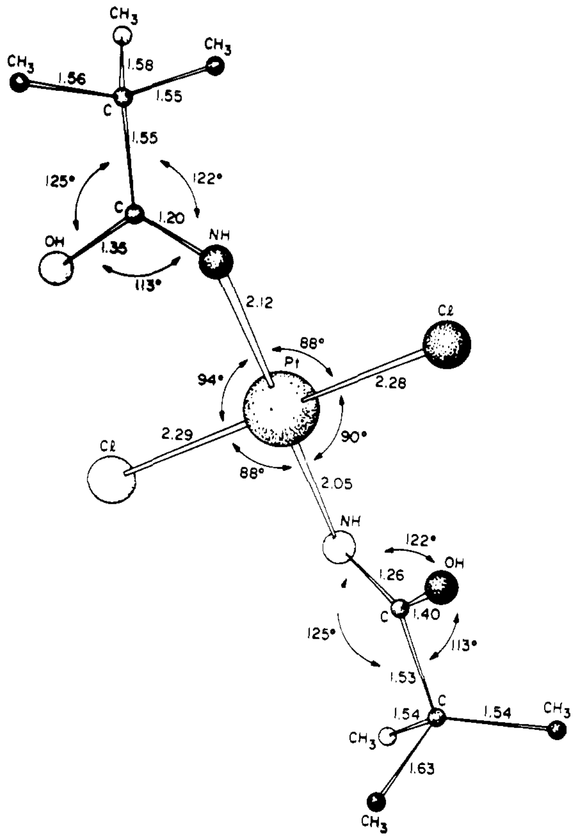

Figure 1. The molecular structure of dichlorobis(trimethylacetamide)platinum(II).

Chromatography of I on a silica gel column yielded three fractions. The first, eluted with $CHCl_3$, gave yellow crystals (II) in 70% yield, mp 173–176° dec. *Anal.* Calcd for $PtCl_2[(CH_3)_3CCONH_2]_2$: mol wt, 468. Found: Pt, 41.44; O, 6.58; N, 5.88; C, 25.77; H, 4.59; mol wt (in $CHCl_3$), 440. Continued elution with $CHCl_3$ led to the collection of a second yellow material (III) in 20% yield, and, finally, elution with ether gave a deep blue, amorphous powder (IV). Compounds III and IV had analyses identical with those of I and II, and, moreover, the yellow needles II and III appear to be isostructural with the original blue-green needles I, as demonstrated by X-ray powder patterns. Thus was it demonstrated that the apparently homogeneous needles I are really mixed crystals of the three components, II, III, and IV.

The crystal structure of I has been solved in large part[6] and showed that its major component, II, has the molecular structure pictured in Figure 1. The analysis, however, was not nearly good enough to allow us to locate the hydrogens in the amide group or to distinguish the oxygen and nitrogen atoms, though it is usually assumed that the amide has its normal form and is bonded to the metal through its oxygen atom. Nonetheless, the proton nmr spectra of I and II in $CDCl_3$ suggest that the proton configurations within their amide groups is not that usually assumed for this ligand.

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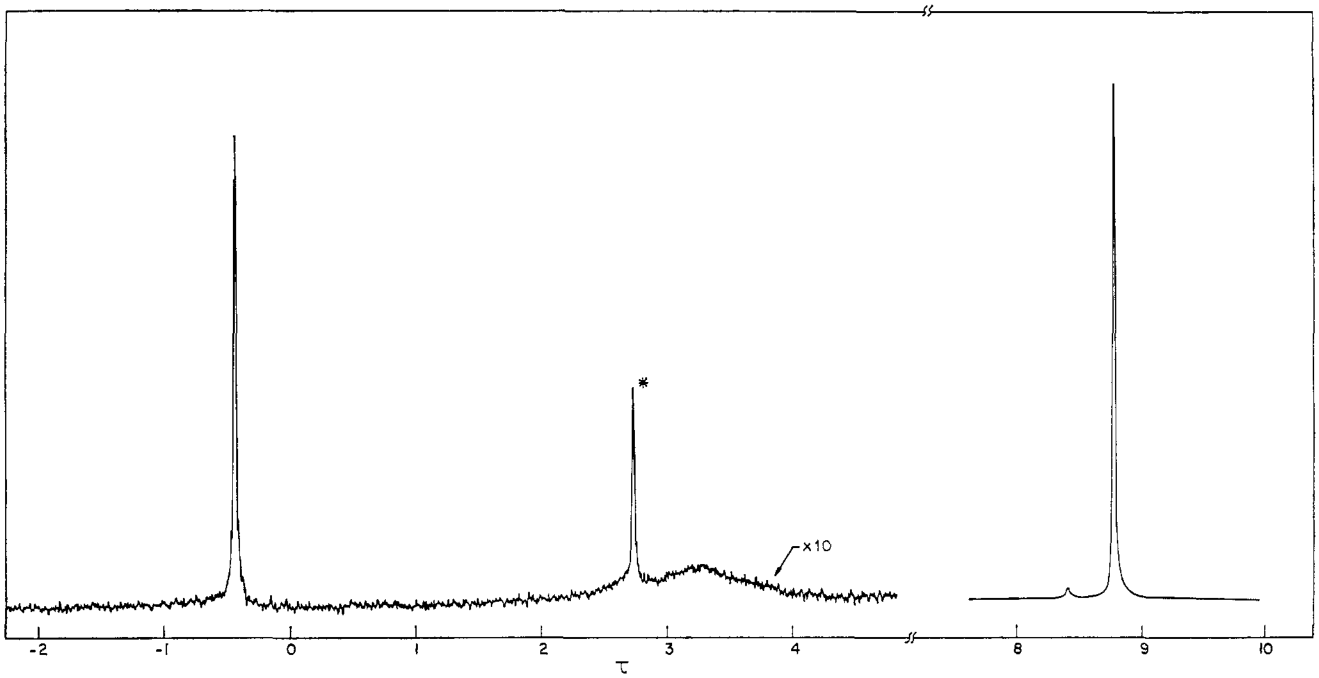

Figure 2. The proton nmr spectrum of dichlorobis(trimethylacetamide)platinum(II) in $CDCl_3$. The peak marked with an asterisk is due to a solvent impurity.

The proton nmr spectrum of II, Figure 2, exhibits sharp absorptions at $\tau$ −0.44 and 8.77 and a broad band at *ca.* $\tau$ 3.25, with relative intensities of 1:9:1. The nmr spectrum of $(CH_3)_3CCONH_2$ itself in $CDCl_3$ contains a broad band at *ca.* $\tau$ 4.16 and a sharp band at $\tau$ 8.78, with relative intensities 2:9, as expected for the normal amide structure. Thus the comparison of the nmr spectra shows that the two protons are bonded to the nitrogen in the free amide, but that in the amide complex II there is only one proton on the nitrogen, the other presumably being on the oxygen. This last conclusion follows from the fact that the nmr of protons on amides almost invariably appear in the region $\tau$ 3–4 as very broad lines due to relaxation effects of the nitrogen quadrupole moment, whereas the low-field absorption in II ($\tau$ −0.44) is sharp and is found far outside the $\tau$ range quoted above. The hydroxyl proton of the iminol structure would be expected to exhibit a low-field shift, such as is observed in the isoelectronic pivalic acid ($\tau$ −2.08)[7] and protonated amides.[8] In addition, solution of I in an acetone–$D_2O$ mixture resulted in the deuteration of both the nitrogen and oxygen, as judged from the disappearance of the $\tau$ −0.44 and 3.25 bands following this treatment. The only interpretation compatible with all of the above facts is that the amide groups in II are in the -C(=NH)-OH iminol form. Since the C=N distance would be much shorter than the C–O distance, and it is the shorter of these that is bonded to the platinum in I (Figure 1), it appears that the iminol ligands bond through nitrogen rather than oxygen. Moreover, since the proton nmr of the needles I is simply the sum of those of the components separated by chromatography, there was no interconversion of compounds on the silica gel column.

The infrared spectrum of II is also consistent with the proposed iminol structure. Crystalline trimethylacetamide shows strong bands at 1655 and 1627 $cm^{-1}$, which can be assigned as the amide I [$\nu$(C=O)] and amide II [$\delta(NH_2)$] bands, respectively.[9] In the complex, however, there is only one absorption in this region, at 1639 $cm^{-1}$. For an iminol complex, only one band is expected in this region, a C=N stretching motion, and this we assign to the 1639-$cm^{-1}$ band. Moreover, the amide itself, having two N–H bonds, exhibits two N–H stretching vibrations at 3180 and 3370 $cm^{-1}$,[9] whereas the complex II has only one, at 3280 $cm^{-1}$, consistent again with the proposed iminol structure. The O–H stretching vibration of II in $CCl_4$ solutions can be located only with some difficulty (3020 $cm^{-1}$), for it is nearly coincident with the C–H stretching vibrations. However, on deuteration, the band shifts to 2280 $cm^{-1}$, where it is clearly visible.

Work is now in progress on the elucidation of the molecular and electronic structure of the amorphous blue material IV and the second yellow fraction III. Preliminary work shows that III has only one of its two amide groups in the iminol form, while IV does not contain the iminol configuration at all.

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## Facile N–O Bond Cleavages of Amine Oxides

*Sir:*

We wish to report a facile method of preparation of immonium salts, including the simplest member of this