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The Proton Configuration in Mercuric Acetamide

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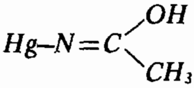
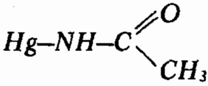
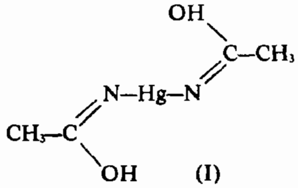
A recent crystal structure analysis of mercuric acetamide was claimed to show that the acetamide ligand was monodentate, and of the tautomeric form  $Hg{-}N{=}C(OH)(CH_3)$. *NMR spectra of this substance clearly demonstrate that the correct arrangement is*  $Hg{-}NH{-}C({=}O)(CH_3)$. *It is further shown that the supposed difference between the N–C and C–O bond lengths leading to the tautomeric iminol structure is statistically without significance. Mercuric acetamide on standing, and its methanol solution upon the addition of acetone, both disproportionate into acetamide and a polymer of the composition* $(HgNCOCH_3)_n$.

Introduction

Since its first preparation in 1852, by the dissolution of HgO in molten acetamide,[2] mercuric acetamide, $Hg(CH_3CONH)_2$, has been used frequently as a starting material for the preparation of other organo-mercury compounds,[3,4] and its molecular structure has been probed repeatedly using both Raman[5] and infrared[6-8] spectroscopy, and reactivity studies.[9] Most recently, a single crystal X-ray structure determination of mercuric acetamide has been reported.[10] The results showed clearly that contrary to conclusion based on Raman and infrared data, the acetamido anion was not functioning here as a bidentate ligand. However, because the hydrogen atoms were not located in the crystal structure, and because oxygen and nitrogen atoms could not be differentiated, it was not directly evident which atom of the ligand was bound to the metal. Based on the observed bond lengths in the acetamide group, the following molecular structure was proposed:



(I)

Structure I is unusual, in that it contains the acetamido anion in a tautomeric form. There has been only one thoroughly documented case of neutral amide tautomerism,[11] and only one case where an amido anion similar to that in structure I has been proposed.[12] Since several other plausible arrangements of protons in the mercury complex are readily imaginable, this investigation was initiated to determine, principally by NMR, which one is correct.

Experimental Section

Mercuric acetamide was prepared as described in the literature.[5,9,13] Red HgO was added to molten acetamide until no more would dissolve. After cooling, the product was recrystallized from either methanol, ethanol, or water, and finally from methanol. Products obtained from the various solvents were not noticeably different. The product recrystallized three times from methanol was used for the NMR measurements, and had the following analysis: Calcd. for $Hg(CH_3CONH)_2$: Hg, 63.34; C, 15.17; N, 8.84; O, 10.10; H, 2.54. Found: Hg, 63.50 (by difference); C, 15.19; N, 8.75; O, 10.09; H, 2.47; m.p. 201-203° (Lit. 195°).

Mercuric acetamide polymer was prepared by twice dissolving the monomer in methanol and precipitating with acetone. After the remaining monomer and acetamide were extracted with methanol using a Soxhlet apparatus, the powdery white polymer had the analysis: Calcd. for $(HgCH_3CON)_n$: Hg, 77.86; C, 9.32; N, 5.44; O, 6.21; H, 1.17. Found: Hg, 80.24 (by difference); C, 8.16; N, 4.07; O, 6.59; H, 0.94. The sample decomposed at *ca.* 270° without melting.

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[10] B. Kamenar and D. Grdenic, *Inorg. Chim. Acta*, *3*, 25 (1969).

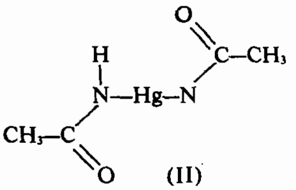
[11] D. B. Brown, M. B. Robin, and R. D. Burbank, *J. Amer. Chem. Soc.*, *90*, 5621 (1968).

[12] D. B. Brown, R. D. Burbank, and M. B. Robin, *J. Amer. Chem. Soc.*, *91*, 2895 (1969).

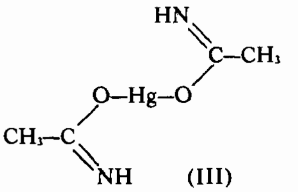
[13] J. W. Williams, W. T. Rainey, Jr., and R. S. Leopold, *J. Amer. Chem. Soc.*, *64*, 1738 (1942).

Results and Discussion

With acetamide acting as a monodentate ligand, structures II and III, as well as I, are likely candidates for the structure of mercuric acetamide.



(II)



(III)

If the atom adjacent to Hg (N or O) is represented as A, and the other non-carbon atom as B, then structure I requires a short A = C bond and a long B–C bond, whereas structures II and III require long A–C bonds and short B=C bonds. Kamenar and Grdenic[10] observed A–C and B–C bond distances of 1.23 and 1.33 Å, respectively, and on the basis of these, assigned structure I to mercuric acetamide. On statistical grounds, however, it appears that the data on this point is ambiguous. The estimated standard deviations given for the A–C and B–C bonds are $\sigma_{A-C} = \pm 0.09$ and $\sigma_{B-C} = \pm 0.08$ Å, respectively. The general criterion[14] used for distinguishing two bond distances is that for the difference ($\delta\ell$) to be real, it must exceed three times the standard deviation of the difference. In this case, in order for the difference in bond lenths to be statistically significant, $\delta\ell$ must exceed 0.36 Å, whereas the measured difference is only 0.10 Å. Thus the only meaningful statement about the A–C and B–C bond lengths which can be made from the X-ray data, is that they are approximately the same, in the vicinity of 1.2–1.4 Å. If this is accepted, then it is impossible to decide among the various structures I, II, and III on the basis of the X-ray data alone. The solution to this problem rests in the NMR spectrum.

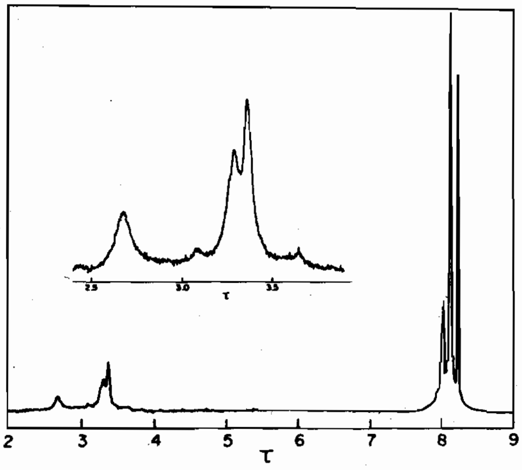


Figure 1. 220 MHz NMR spectrum of mercuric acetamide recrystallized three times from methanol (solvent is d_6–DMSO). Inset shows the low field region amplified ten-fold.

The NMR spectrum of mercuric acetamide at 220 MHz is presented in Figure 1. Obviously, the spectrum is much more complex than is possible for any of the postulated structures. This spectrum, however, can be attributed to a combination of three distinct species in solution. Comparison of Figure 1 with an authentic sample of acetamide shows that the absorption at $\tau = 8.25$ is due to the acetamide methyl protons, whereas the absorptions at $\tau = 2.73$ and $\tau = 3.35$ (strongly overlapped by the absorption at $\tau = 3.42$) are due to the two N–H protons of acetamide, separated because of the hindered rotation about the C–N bond.

Our attempts to eliminate acetamide from the sample led to some unexpected results. Dissolution of the crude complex in methanol followed by precipitation with acetone led to virtual elimination of acetamide in the solid, but also produced noticeable differences in the product. After two precipitations with acetone, the solubility of the product in methanol decreased by a factor of about 50, the melting point had increased to *ca.* 250°, and the NMR spectrum, although indicating that free acetamide had been eliminated, showed a large intensity increase in the $\tau = 8.03$ peak relative to that at $\tau = 8.15$. Apparently, addition of either acetone or ether to methanol solutions of mercuric acetamide yields a polymeric form of the complex. The effect of polymerization upon the NMR spectrum indicates that the broad peak at $\tau = 8.03$ is due to this polymer, whereas the monomer absorption falls at $\tau = 8.15$. Although never studied in detail, polymeric mercuric acetamide has been observed in the past,[4] and was assigned the structure $(HgCH_3CON)_n$.

Polymerization occurs not only in the presence of acetone in solution, but in the solid state at room temperature as well. Recrystallization of monomeric mercuric acetamide from methanol would be likely to isolate polymer with the sample if any were present, but acetamide should be eliminated. The existence of acetamide absorptions in the NMR spectrum of the recrystallized sample implies that polymerization had taken place after isolation of the product. This is also confirmed by integration of the CH_3 peak areas which shows acetamide and polymer in a 1:1 ratio, as required by reaction (1).

$$nHg(CH_3CONH)_2 \longrightarrow (HgCH_3CON)_n + nCH_3CONH_2 \qquad (1)$$

The near-identity of the NMR spectra of a given sample in dimethylsulfoxide, methanol, and water indicates that polymerization probably is not taking place upon dissolution or in solution, since such a process would be expected to be solvent dependent. That polymerization does occur in the solid state is confirmed by the NMR spectrum of the soluble portions of a sample of mercuric acetamide which had been prepared two years previously. Acetamide was by far the major soluble component of this material, with only small amounts of the monomer remaining.

The NMR absorption at $\tau = 8.15$ is clearly due to the methyl protons of the monomer, and that at $\tau = 3.42$ is attributable to the remaining NH or OH

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(14) D. W. J. Cruickshank, *Acta Cryst.*, 2, 65 (1949).

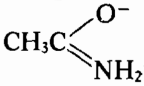
protons. Although this latter band is strongly overlapped by one of the acetamide NH absorptions, the ratio of CH_3 to NH or OH protons in the monomer may be obtained by subtracting from this combined band an area equal to that of the acetamide NH absorption at $\tau = 2.73$. Experimentally, the value found for this ratio is 2.84, in good agreement with the expected value of 3.0.

Other important features of the NMR spectrum of the monomer (Figure 1) are the satellite bands centered about the proton absorption at $\tau = 3.42$. The satellites result from the spin-spin coupling with ^{199}Hg, a nucleus having $S = 1/2$ and a natural abundance of 16.86%. A large number of alkyl mercury compounds have been examined by NMR,[15] and it has been found that the coupling of ^{199}Hg to protons which are on carbons α and β to the mercury are in the range $J = 100$-200 c.p.s. However, couplings to protons which are on carbon atoms γ to the mercury have $J = 0$-30 c.p.s. Clearly the observed value of $J = 125$ c.p.s. rules out structures I and III, both of which contain three intervening atoms between hydrogen and mercury. On the other hand, for a compound such as that shown by structure II. the observed coupling constant is most appropriate.

In further support of structure II, we note that the absorption band at $\tau = 3.42$ is in just that region expected for an amide proton. If, on the other hand, the proton were on oxygen, the ligand becomes structurally similar to the carboxylate anion, for which the absorption is expected at much lower fileds. For the cases where amide tautomerism has been substantiated,[11,12] the oxygen-bound proton gave rise to signals at $\tau = -0.44$ for the neutral species and $\tau = -1.10$ for the anionic species.

Another factor in favor of the proton being on the nitrogen atom in mercuric acetamide is the width of the $\tau = 3.42$ absorption. Although the band width cannot be readily measured in the overlapped absorptions, it is possible to measure it in spectra of the partially polymerized material which has been freed of acetamide. The observed halfwidth of 15 c.p.s. in these samples is clearly indicative of quadrupolar relaxation, as expected for an N–H bond.

Additional evidence against structure III rests in the apparent preference for Hg–N over Hg–O bonds in this type of compound. Studies of the reactivity of mercuric acetamide,[9] observed structures for mercuric diacetylhydrazide[4] and related compounds, and the apparent formation of Hg–N bonds in the dibenzamido complex of Hg^{II} [16] all lead to the expectation of Hg–N bonding in mercuric acetamide.

Considering the wide range of C–O and C–N bond lengths admitted by the X-ray analysis, it is not difficult to reconcile the crystallographic data with structure II. Acetamide itself contains C = O and C–N bond lengths of 1.260 and 1.334 Å, respectively.[17] The differences between these bond lengths and the 1.20 and 1.47 Å lengths characteristic of the « pure » C = O and C–N bonds is ascribable to the importance of the charge-separated resonance form  $CH_3C\begin{smallmatrix}\nearrow O^-\\ \searrow NH_2^+\end{smallmatrix}$ in the ground state. Since charge separation is not required in any of the principal resonance structures of the acetamido anion, an even closer equality of the C–O and C–N bond lengths (approximately 1.3 Å) is to be expected. This is the result obtained in the crystallographic study after account is taken of the errors involved, and demonstrates that structure II is consistent with the data.

It should be pointed out that structure II was considered by Kamenar and Grdenic[10] as a resonance form of I, for the purpose of explaining the infrared spectrum of mercuric acetamide. This spectrum has remained a puzzle, because it displays two N–H vibrational frequencies where only one is expected. In light of what has been found in this investigation, the infrared spectrum is understandably complex, since the system most likely contains three components-monomeric mercuric acetamide, acetamide, and polymeric mercuric acetamide.

As regards the polymeric mercuric acetamide, Brodersen and Kunkel[4] observed that heating the monomer to 240° resulted in the sublimation of acetamide, and the formation of the product expected from the mercuration of mercury acetamide. Russian workers[18,19] have investigated the effect of ions upon solutions of mercuric acetamide and suggested that the gels so formed are the products of the hydrolysis and polymerization of the monomer. The basic unit of this polymer was assigned the formula CH_3-CONH–Hg–OH. While we cannot comment further on the composition of the polymeric gel, it is apparent that the polymer prepared in our work has the formula $(HgCH_3CON)_n$, as first reported for the product of the thermal synthesis by Brodersen and Kunkel.[4] This can be seen from the analytical data on a carefully dried sample of the hygroscopic material. Moreover, infrared spectra show no absorptions in either the N–H or O–H regions, and the NMR spectrum of the polymer has only a CH_3 absorption. Samples which have not been scrupulously protected from moisture do exhibit a broad absorption near 3400 cm^{-1} in the infrared due to adsorbed water.

One other point should be mentioned. The investigations reported in this paper concern the structure of mercuric acetamide in solution, and there is no proof that the same arrangement of atoms obtains in the solid. However, the crystallographic data are consistent with the solution structure, and there is no reason to believe that the structures in the two phases are not the same.

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