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Received June 1, 1978

Metal-Ammonia Solutions. 11.

Au⁻, a Solvated Transition Metal Anion

Sir:

Historically, the chemistry of metals in solution is characterized by their ability to form positive ions. However, stable negative metal ions are well known in the gas phase,¹ liquid CsAu behaves much like other molten ionic salts,² and ammonia solutions of numerous anions of the main group elements are known, e.g., anions such as Pb₉⁴⁻.^{3,4} Recently, the existence of alkali metal anions in amine and ether solvents was proven,⁵ although the existence of such species in liquid ammonia is still questionable. Finally, Zintl et al. observed in the potentiometric titration of a sodium-ammonia solution by an AuI-ammonia solution an end point corresponding to 1 equiv of Au⁺ added to 2 equiv of Na⁰.⁴ The authors interpreted their data as showing the formation of an "intermetallic phase", although the data could also imply the existence of Au⁻. We report here spectroscopic and electrochemical evidence for the first transition metal anion in any solvent, and the first metal anion in ammonia, viz., Au⁻.

Solutions of auride ions can be prepared in a number of ways, the simplest of which is the dissolution of metallic gold in ammonia solutions of cesium, rubidium, or potassium. Since dissolution is considerably faster at ambient temperature, much of the spectroscopic work described here was carried out in a cell capable of withstanding the 10-atm vapor pressure of ammonia at that temperature. The apparatus consists of a 1-mm quartz optical cell connected by a graded seal to a Pyrex solution make-up bulb and a pressure stopcock. Portions of solutions in the make-up bulb can be tipped into the optical cell and diluted as required for spectroscopic analysis by distilling ammonia from the solution left in the make-up bulb. By using ratios of absorbances on the broad tail of the solvated electron band before and after dilution, and the weight of gold used, estimates were obtained for the extinction coefficient of Au⁻ at ambient temperature.

The inability of sodium, lithium, strontium,⁶ or barium⁶ solutions to dissolve gold probably arises from surface effects because a sodium-[2.2.2]-cryptand solution will dissolve gold⁶ and because Au⁻ can be prepared by using lithium and a method which eliminates surface problems, specifically, cocondensation.

The cocondensation technique as used in this investigation involves the simultaneous vacuum vaporization of lithium and gold and their subsequent cocondensation along with gaseous ammonia onto a liquid nitrogen cooled surface. Warming the

resultant matrix to the melting point of ammonia produces solutions of Au⁻. The present apparatus is similar to one described elsewhere,⁷ except that this one is constructed completely of quartz and has two optical windows spaced 0.3 and 10 mm apart attached to the bottom. This cell was also used for the spectroscopic experiments conducted below the boiling point of ammonia, even if cocondensation was not required.

The spectroscopic evidence for the existence of Au⁻ in liquid ammonia is illustrated by the results of a typical experiment conducted at ambient temperature. A 2 × 10⁻² M cesium-ammonia solution dissolved sufficient gold to make a 3 × 10⁻³ M cesium auride solution. Absorption bands at 289 and 356 nm increased in intensity as the gold dissolved. After complete dissolution, the solvated electrons continued to decompose (by reaction with the solvent to form amide), the 356-nm band continued to increase, but the intensity of the 289-nm band remained constant. A partially decomposed cesium-ammonia solution also showed the 356-nm band; furthermore, rubidium and potassium solutions each have a similar band, the positions of which are in agreement with those for the respective amides published elsewhere.⁸ When the broad solvated electron band at 1850 nm had virtually disappeared, concentration of the solution by evaporation of the solvent caused pure metallic gold to precipitate, as did freezing the solution. The intensity of the 289-nm band decreased during these processes.

Similar experiments show an absence of other bands in gold-containing solutions; bands with extinction coefficients >25 could have been detected. The cocondensation of gold with ammonia produces a solution which contains only a black precipitate of gold. Yet the triple cocondensation of lithium and an excess of gold with ammonia still produces the Au⁻ band, but no solvated electrons, demonstrating that Au⁻ is stable even in the absence of solvated electrons.

Solutions of gold with cesium, rubidium, and potassium at ambient temperature all exhibit the Au⁻ band at 289 nm. At -65 °C this band occurs at 277.1 nm in the case of a Cs-CsAu solution and at 278.4 nm for a LiAu solution. Yet the temperature coefficients for the two solutions (determined from data at temperatures less than the boiling point of ammonia) are identical, -18 cm⁻¹/deg. This difference in peak position is small (cf. CsNH₂ and LiNH₂ at 327.5 and 298.0 nm, respectively⁸) but real.

The large temperature coefficient is one distinguishing characteristic of a charge-transfer-to-solvent transition; another is a large extinction coefficient.⁹ For the slightly asymmetric auride band, the extinction coefficient is estimated at 5 × 10⁴ L/(mol cm) at -65 °C and 7 × 10⁴ L/(mol cm) at ambient temperature. For comparison, other anions which exhibit charge-transfer-to-solvent transitions in ammonia, i.e., e⁻_{am}, I⁻, and NH₂⁻, exhibit extinction coefficients of 4.5 × 10⁴ L/(mol cm) at -65 °C,¹⁰ 1.8 × 10⁴ L/(mol cm) at -78 °C,¹¹ and 3.48 × 10³ L/(mol cm) at -49 °C,¹² respectively, and temperature coefficients of -10 cm⁻¹/deg,^{10,13} -22 cm⁻¹/deg,¹¹ and -17 cm⁻¹/deg.¹²

The chemical behavior of the gold solutions and the large extinction and temperature coefficients of the gold-related band indicate the presence of a solvated gold anion. To further confirm our assignment, preliminary electrochemical experiments were undertaken.

The electrochemical cell used was a standard three-compartment cell described elsewhere.^{14,15} A silver wire was used as a pseudoreference electrode and a platinum disk as the working electrode. Solvated electrons were generated coulometrically,¹⁵ using 0.1 M CsI as a supporting electrolyte. Metallic gold was then introduced into the solution and allowed to dissolve. A potential scan starting at -2.6 V showed an anodic wave at -2.1 V and upon reversal a cathodic wave at -2.5 V, demonstrating that the species in solution is oxidized at a potential nearly that of the solvated electron's.

To confirm that the spectroscopic and electrochemical experiments involve the same species, cyclic voltammetry was performed on a Cs-CsAu solution. The same waves described above were observed, but quantitative results were not possible owing to the large uncompensated resistance.

These experiments prove the existence of a solvated gold anionic species, Au_y^{x-} . An alkali metal species is probably not part of this anion because the various alkali cations have so little effect on its spectroscopic properties. Au^- seems the most likely species because the electron configuration would be $5d^{10}6s^2$, the extinction coefficient is approximately the same as the solvated electron's, and the Zintl potentiometric titration indicates a stoichiometry of Au_x^{x-} .⁴

More detailed electrochemical experiments on the gold species in liquid ammonia are currently in progress, as is work to extend these ideas to other metals and solvents. For example, ethylenediamine stabilizes alkali metal anions better than ammonia and, indeed, a cesium-ethylenediamine solution has been observed to dissolve gold.

Acknowledgments. We acknowledge the support of the National Science Foundation and the Robert A. Welch Foundation for generous support; the University of Texas Graduate School provided funds (to W.J.P.) for specialized equipment. We extend our appreciation to Mr. Towfik Teherani and Professor A. J. Bard for their assistance in the electrochemical experiments and to Professor J. C. Thompson, whose seminar stimulated our initial thoughts on this subject.

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Received June 7, 1978

^{13}C - ^{13}C and ^{13}C -H Coupling Constants in 2,2,4,4-Tetramethylbicyclo[1.1.0]butane

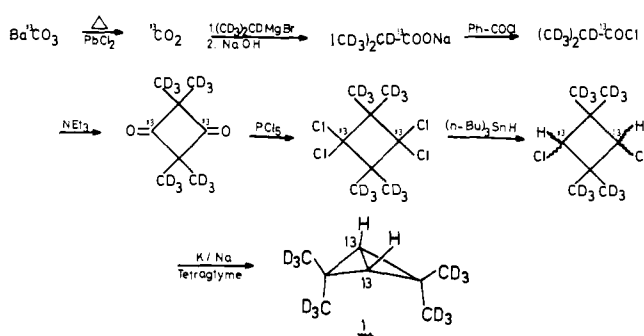
Sir:

The orbitals forming the central bond of bicyclo[1.1.0]butane are characterized by an extremely small s character,¹ which is related to the ^{13}C - ^{13}C coupling constant $^1J_{\text{CC}}$ by eq 1:²

$$^1J_{\text{CC}} = 621s_{\text{A}}s_{\text{B}} - 10.2 \quad (1)$$

The extraordinarily low s character and the theoretical prediction of $^1J_{\text{C}(1)-\text{C}(3)}$ in bicyclobutane being negative^{2,3} have given rise to several investigations on ^{13}C - ^{13}C coupling constants in bicyclobutane derivatives.²⁻⁷

Scheme I



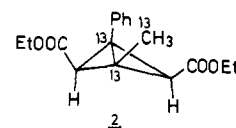
We intended to determine $^1J_{\text{C}(1)-\text{C}(3)}$ in an alkyl-substituted bicyclobutane to exclude possible influences of polar substituents. For this purpose the readily accessible 2,2,4,4-tetramethylbicyclobutane⁸ seemed to be the most suitable compound, since ^{13}C labeling of the two bridgehead carbons and deuteration of the methyl groups would lead to a hydrocarbon, the proton spectrum of which would allow a precise determination of $^1J_{\text{C}(1)-\text{C}(3)}$ in absolute value and sign.

Starting with 90% ^{13}C -labeled barium carbonate, we synthesized 2,2,4,4-tetra(trideuteriomethyl)bicyclo[1.1.0]butane-1,3- $^{13}\text{C}_2$ (**1**) as shown in Scheme I. The proton part of the AA'XX' spectrum of **1** showed the following four coupling constants: $^1J_{\text{C}(1)-\text{C}(3)} = -17.49 \pm 0.02$ Hz, $^1J_{\text{C}(1)-\text{H}} = +184.33 \pm 0.02$ Hz, $^2J_{\text{C}(1)-\text{H}} = -2.02 \pm 0.02$ Hz, $^3J_{\text{HH}} = +12.22 \pm 0.02$ Hz. The sign of $^1J_{\text{C}(1)-\text{C}(3)}$ was determined by heteronuclear double resonance.

We also synthesized compound **1** without deuterium in the methyl groups, to obtain all other coupling constants concerning the bridgehead carbons. The ^{13}C NMR spectrum exhibited 23.06 ± 0.12 Hz for $^1J_{\text{C}(1)-\text{C}(2)}$, 0.51 ± 0.12 Hz for $^2J_{\text{C}(1)-\text{C}(\text{exo})}$, and 2.88 ± 0.12 Hz for $^2J_{\text{C}(1)-\text{C}(\text{endo})}$. $^3J_{\text{C}(1)-\text{H}(\text{exo})} (= 4.60 \pm 0.10$ Hz) and $^3J_{\text{C}(1)-\text{H}(\text{endo})} (= 5.20 \pm 0.10$ Hz) were also determined. Moreover $^1J_{\text{C}(2)-\text{C}(\text{exo})} (= 40.3 \pm 0.2$ Hz) and $^1J_{\text{C}(2)-\text{C}(\text{endo})} (= 46.9 \pm 0.2$ Hz) were measured in natural ^{13}C abundance.

The value of -17.49 Hz for $^1J_{\text{C}(1)-\text{C}(3)}$ raises some remarkable aspects.

Considering the closely related carbon skeletons of **1** and **2**, the difference between $^1J_{\text{C}(1)-\text{C}(3)}$ in **1** and $^1J_{\text{C}(1)-\text{C}(3)}$ in **2** (-5.4 Hz) is extraordinarily large. This leads to the conclusion



that obviously substituents and/or steric influences exert a very strong effect of $^1J_{\text{C}(1)-\text{C}(3)}$ in bicyclobutane derivatives. On the other hand the value of -17.49 Hz is an absolute value rather close to $^1J_{\text{C}(1)-\text{C}(3)}$ in 1-cyanobicyclobutane (16 Hz, the sign being undeterminable).⁶ This coupling constant was measured in natural ^{13}C abundance and the absolute value of 16 Hz was regarded as rather uncertain.⁷ Our result, however, indicates that an absolute value of 16 Hz for the C(1)-C(3) bond in 1-cyanobicyclobutane would be quite a reasonable result. Recent investigations on other bicyclobutanes⁹ support this presumption. If 16 Hz is indeed the correct coupling constant, the sign will certainly have to be negative.

It should also be mentioned that the value of 184.33 Hz for $^1J_{\text{C}(1)-\text{H}}$ in **1** is ~ 20 Hz smaller than the corresponding value in the unsubstituted bicyclobutane.¹⁰ Using the Muller-Pritchard relationship between $^1J_{\text{CH}}$ and s character,¹¹ we obtain 36.9% s character in the C(1)-H bond of **1**, compared with 41.0% s character in the C(1)-H bond of bicyclobutane itself. This reduced s character, however, is nearly compensated for by an increase of the s character in the C(1)-C(2) and C(1)-