

Silver Complexes with Succinimide as Models for the Interaction of Silver(I) with the Uracil Residue

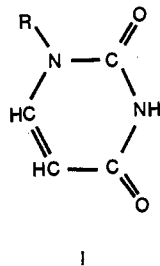
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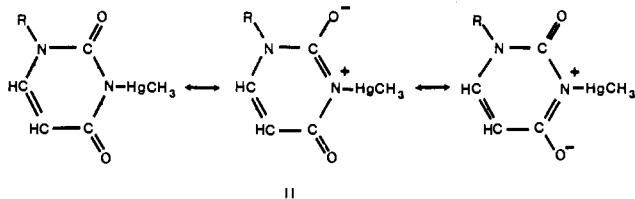
Succinimide (HSuc) forms silver complexes of compositions AgSuc and $\text{M}[\text{Ag}(\text{Suc})_2]$ (with $\text{M} = \text{Na}$ and Li). The crystals of the 1:1 complex belong to the monoclinic space group $P2_1/c$, with $a = 8.031$ (4) Å, $b = 13.306$ (7) Å, $c = 10.345$ (2) Å, $\beta = 97.16$ (3)°, and $Z = 4 \text{ Ag}_2(\text{Suc})_2 \cdot \text{H}_2\text{O}$ units per cell. The structure was refined on 1671 non-zero reflections ($I > 2.5\sigma(I)$) to $R = 0.038$. This compound is best formulated as the Ag^+ salt of the $[\text{Suc-Ag-Suc}]^-$ ion, in which silver is approximately linearly coordinated to deprotonated nitrogen atoms of two succinimide anions. The other half of silver atoms form moderately strong bonds with two carbonyl groups of one anion, one carbonyl group of another anion, and one water molecule, in a roughly tetrahedral pattern. $\text{Li}[\text{Ag}(\text{Suc})_2] \cdot 4\text{H}_2\text{O}$ is orthorhombic, space group $Pnma$, with $a = 12.091$ (2) Å, $b = 8.934$ (1) Å, $c = 12.981$ (2) Å, and $Z = 4$. The structure was refined on 1351 non-zero reflections ($I > 2.5\sigma(I)$) to $R = 0.026$. The unit cell contains the linear $[\text{Suc-Ag-Suc}]^-$ ion observed in the previous compound. The Li^+ ion is surrounded by four water molecules in a roughly tetrahedral arrangement. These water molecules form H bonds with the carbonyl groups of the anions. The ^1H and ^{13}C NMR spectra of the succinimide complexes are consistent with the presence of two-coordinate $[\text{Suc-Ag-Suc}]^-$ anions in solution, and the close similarity in the spectra of the $\text{M}[\text{Ag}(\text{Suc})_2]$ complexes for $\text{M} = \text{Li}^+$, Na^+ , and Ag^+ suggests that, in the last case, the Ag-O interactions found in the crystal are not maintained in solution. Various regions of the IR spectra can be used to detect metal complexation to the deprotonated nitrogen site of succinimide, but direct binding of silver to the carbonyl groups in $\text{Ag}[\text{Ag}(\text{Suc})_2]$ produces no obvious diagnostic signals in the spectra.

Introduction

As part of our general interest in the reactions of linearly coordinated $\text{Ag}(\text{I})$ and $\text{Hg}(\text{II})$ with nucleic acid components, we have prepared and structurally characterized several complexes with derivatives of uracil (I, $\text{R} = \text{H}$). By using the



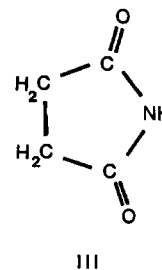
CH_3Hg^+ ion, we have shown that the primary reactions take place by substitution of the weakly acidic N-H proton, producing a neutral CH_3HgL complex, where $\text{HL} = 1$ -methylthymine (I, $\text{R} = \text{CH}_3$)¹ or thymidine (I, $\text{R} = \text{deoxyribose}$).² Hydrogen displacement by the less electron-attracting metal ion releases electron density into the ring, thereby increasing the nucleophilic character of the adjacent carbonyl groups (II).



Enhanced basicity of the carbonyl groups is evidenced from the obtainment of "adducts" with alkali salts, such as $\text{CH}_3\text{HgL} \cdot \frac{1}{2}\text{NaNO}_3$ ¹ and $\text{CH}_3\text{HgL} \cdot \text{NaClO}_4$.² However, we have been unable to isolate compounds in which Hg would be bonded to oxygen. On the other hand, for the 1:1 silver complex with 1-methylthymine,³ it was shown that half of the Ag atoms joined two ligands by N-Ag-N bonds, whereas the

other half were surrounded by carbonyl oxygens from two adjacent molecules. Compounds of the type $\text{M}[\text{L-Ag-L}]$, in which cation M is different from Ag^+ , have been prepared.² They probably retain only the N-Ag-N coordination, but no suitable crystalline samples were obtained to ascertain the structure by X-ray diffraction.

Succinimide (HSuc, III) was considered as a suitable model compound for the uracil residue, since it contains the same potential donor atoms $-\text{C}(\text{O})\text{N}(\text{H})\text{C}(\text{O})-$ similarly arranged in the rings. Furthermore, recent work by Huot, Serve, and



Lessard⁴ on Ag-imide systems in acetonitrile indicated the same reactivity pattern as for the Ag-uridine system. The present paper describes the characterization of silver complexes with succinimide by NMR and IR spectroscopy and X-ray diffraction.

Experimental Section

Methods. The potentiometric measurements were carried out with a locally made digital potentiometer, equipped with a glass or a silver electrode and a double-junction calomel reference electrode (0.1 M KNO_3 in the outside jacket). The NMR spectra were recorded at ambient probe temperature with a Bruker WH-90 (^1H spectra) or WH-80 (^{13}C spectra, 20.11 MHz). The solvent used was $\text{Me}_2\text{SO}-d_6$ (Merck Sharp and Dohme Canada) with Me_4Si as internal standard. The IR spectra were obtained with a Digilab FTS-15 C/D Fourier transform spectrometer equipped with a wide-range high-sensitivity Hg/Cd telluride detector (Infrared Associates). Typically, 250 interferograms of 2048 points recorded with an optical velocity of 1.2 cm s^{-1} and maximum optical retardation of 0.25 cm were coadded, apodized with a triangular function, and Fourier transformed with four levels of zero filling, resulting in a spectral resolution of 4 cm^{-1} .

(1) Guay, F.; Beauchamp, A. L. *Inorg. Chim. Acta* 1982, 66, 57-63.

(2) Guay, F.; Beauchamp, A. L., to be submitted for publication.

(3) Guay, F.; Beauchamp, A. L. *J. Am. Chem. Soc.* 1979, 101, 6260-6263.

(4) Huot, J. Y.; Serve, D.; Lessard, J. *Can. J. Chem.* 1983, 61, 1890-1898.

The spectra were taken with KBr pellets for the free ligands and with Nujol and hexachlorobutadiene mulls for the silver complexes, which slowly reacted with KBr.

Silver was analyzed potentiometrically by AgCl precipitation with 0.14 M HCl. The samples were dissolved in dilute HNO₃ to eliminate secondary interactions of Ag⁺ with free succinimide. Succinimide was estimated by pH metric titration. A sample of the complex was dissolved in a known amount of 0.192 M HNO₃, and excess acid was titrated by 1.018 M NaOH.

Synthesis. Ag₂(Suc)₂·H₂O. This compound was prepared according to the procedures used by Ley and Schaefer⁵ and by Huot, Serve, and Lessard.⁴ Anal. Calcd for C₈H₁₀Ag₂N₂O₅: Ag, 50.2; Suc, 45.6. Found: Ag, 49.9; Suc, 46.0.

Li[Ag(Suc)₂]₂·4H₂O. Succinimide (2.8 g, 28 mmol) and AgNO₃ (1.8 g, 10 mmol) are dissolved in a minimum volume of water at room temperature. A solution of 1.0 g (24 mmol) of LiOH·H₂O in water is slowly added. The white precipitate of Ag₂(Suc)₂·H₂O first formed redissolves upon further addition of LiOH. After the solution is cooled, the white precipitate is filtered and recrystallized from hot water. A second crop of pure compound is obtained by spontaneous evaporation of ~2/3 of the filtrate at room temperature. Anal. Calcd for C₈H₁₆AgLiN₂O₈: Ag, 28.2; Suc, 51.2. Found: Ag, 27.4; Suc, 51.3.

Na[Ag(Suc)₂]₂·5H₂O. The procedure used is the same as above for the Li⁺ salt, after replacing LiOH by NaOH. Anal. Calcd for C₈H₁₈AgNaN₂O₉: Ag, 25.9; Suc, 47.0. Found: Ag, 26.3; Suc, 46.6.

Ag₂(Pht)₂·H₂O. The compound was prepared by the method of Heller and Jacobsohn,⁶ from phthalimide (Pht) and silver acetate. The white solid was recrystallized from hot acetonitrile. Anal. Calcd for C₁₆H₁₀Ag₂O₅N₂: Ag, 41.0. Found: Ag, 40.6.

K(Pht). The compound from Eastman was used without purification.

Crystallographic Measurements and Structure Resolution. The X-ray data were collected with an Enraf-Nonius CAD-4 diffractometer, according to a procedure described previously.⁷ Crystal data for Ag₂(Suc)₂·H₂O, C₈H₁₀Ag₂N₂O₅: *M*_r = 429.91, monoclinic, *P*2₁/*c*, *a* = 8.031 (4) Å, *b* = 13.306 (7) Å, *c* = 10.345 (2) Å, β = 97.16 (3)°, *V* = 1096.8 Å³, *D*_{obsd} = 2.59 (1) g cm⁻³, *D*_{calcd} = 2.603 g cm⁻³, *Z* = 4 Ag₂(Suc)₂·H₂O formula units per cell, λ = 0.71069 Å (graphite monochromator), *t* = 23 °C, crystal dimensions 0.15 × 0.19 × 0.58 mm³, μ = 35.5 cm⁻¹, transmission range 0.49–0.63.

This compound crystallized as well-shaped colorless crystals, most of which were twinned. The specimen used was the only one showing only a few extraneous spots due to a second individual on the precession photographs. Despite these spots, space group *P*2₁/*c* was unambiguously determined from precession and cone axis photographs. This small amount of twinning did not hinder structure determination, but a dozen reflections were rejected at the end of the refinement for this reason.

A total of 2330 independent *hkl* and *hk̄l* reflections (2θ ≤ 50°) were measured, of which 1671 were retained for structure determination (*I*/σ(*I*) > 2.5). These data were corrected for hte effects of Lorentz, polarization, and absorption (Gaussian integration, grid 8 × 8 × 8). The structure was solved by the heavy-atom method and refined by full-matrix least squares. Individual weights based on counting statistics were applied in the refinement. Both nonequivalent Ag atoms were located from a Patterson synthesis. The remaining atoms were found from structure factor calculation and difference Fourier (Δ*F*) synthesis. The hydrogens of the water molecule were refined isotropically and the non-hydrogen atoms anisotropically. A secondary extinction coefficient was also refined. The aliphatic hydrogens of succinimide were fixed at their calculated position with *B* = 4.0 Å². The final residuals were *R* = ∑||*F*_o|| - ||*F*_c|| / ∑||*F*_o|| = 0.038 and *R*_w = [∑w(|*F*_o|| - ||*F*_c||)² / ∑w||*F*_o||²]^{1/2} = 0.054. The goodness-of-fit ratio was 2.13. The final Δ*F* map was essentially featureless: general background ±0.4 e/Å³, maximum peaks in the range ±0.5–0.8 e/Å³ near Ag.

Crystal data for Li[Ag(Suc)₂]₂·4H₂O, C₈H₁₆AgLiN₂O₈: *M*_r = 383.03, orthorhombic, *Pnma*, *a* = 12.091 (2) Å, *b* = 8.934 (1) Å, *c* = 12.981 (2) Å, *V* = 1402.11 Å³, *D*_{obsd} = 1.82 (1) g cm⁻³, *D*_{calcd} = 1.814 g cm⁻³, *Z* = 4, λ = 0.71069 Å, *t* = 23 °C, crystal dimensions 0.22 mm × 0.53 mm × 0.20 mm, μ = 14.6 cm⁻¹, transmission range 0.63–0.83.

Table I. Refined Coordinates

| atom | x | y | z |
|---|------------|-----------|-----------|
| Ag ₂ (Suc) ₂ ·H ₂ O (× 10 ⁴ , Ag × 10 ⁵ , H × 10 ³) | | | |
| Ag(1) | 4061 (5) | 39731 (4) | -7745 (4) |
| Ag(2) | -26721 (6) | 41400 (4) | 5299 (5) |
| O(1) | -3258 (6) | 5258 (4) | 2195 (5) |
| O(11) | -3574 (5) | 3815 (4) | -1687 (4) |
| O(12) | 873 (6) | 3895 (4) | -3964 (5) |
| O(21) | -564 (5) | 3554 (4) | 2169 (4) |
| O(22) | 4359 (6) | 3709 (5) | 493 (4) |
| N(1) | -1106 (6) | 3935 (4) | -2558 (5) |
| N(2) | 1704 (6) | 3748 (4) | 1057 (5) |
| C(11) | -2762 (7) | 3809 (5) | -2632 (6) |
| C(12) | -3563 (8) | 3667 (6) | -4042 (7) |
| C(13) | -2055 (9) | 3678 (6) | -4789 (6) |
| C(14) | -586 (8) | 3847 (5) | -3758 (6) |
| C(21) | 944 (8) | 3550 (5) | 2125 (6) |
| C(22) | 2219 (8) | 3329 (6) | 3277 (6) |
| C(23) | 3899 (8) | 3401 (5) | 2739 (6) |
| C(24) | 3394 (7) | 3629 (5) | 1326 (6) |
| H(221) | 215 | 380 | 395 |
| H(222) | 206 | 267 | 360 |
| H(231) | 456 | 394 | 315 |
| H(232) | 452 | 280 | 286 |
| H(121) | -412 | 303 | -415 |
| H(122) | -433 | 418 | -431 |
| H(131) | -195 | 307 | -524 |
| H(132) | -215 | 422 | -541 |
| H(1) | -412 (10) | 564 (7) | 225 (8) |
| H(2) | 261 (14) | 454 (9) | -262 (11) |
| Li[Ag(Suc) ₂] ₂ ·4H ₂ O (× 10 ⁴ , Ag × 10 ⁵ , H × 10 ³) | | | |
| Ag | 17156 (2) | 25000 | 11602 (2) |
| O(1) | -1817 (2) | 7500 | 1319 (2) |
| O(2) | 5249 (2) | 7500 | 1411 (2) |
| O(3) | -3283 (1) | 9267 (2) | 2865 (2) |
| O(11) | 3726 (1) | 5040 (2) | 1205 (1) |
| O(21) | -306 (1) | 5034 (2) | 1188 (1) |
| N(1) | 3441 (2) | 2500 | 1221 (2) |
| N(2) | -10 (2) | 2500 | 1142 (2) |
| C(11) | 4085 (2) | 3743 (3) | 1190 (2) |
| C(12) | 5302 (2) | 3342 (3) | 1142 (2) |
| C(21) | -652 (2) | 3750 (3) | 1085 (2) |
| C(22) | -1853 (2) | 3355 (4) | 921 (2) |
| Li | -3272 (5) | 7500 | 2021 (5) |
| H(11) | -138 (3) | 828 (5) | 135 (2) |
| H(21) | 481 (2) | 675 (4) | 138 (2) |
| H(31) | -282 (2) | 943 (3) | 311 (2) |
| H(32) | -379 (2) | 947 (3) | 315 (2) |
| H(121) | 558 (2) | 375 (3) | 53 (2) |
| H(122) | 565 (2) | 374 (4) | 177 (2) |
| H(221) | -222 (3) | 371 (4) | 158 (2) |
| H(222) | -209 (2) | 371 (4) | 37 (2) |

Space group *Pnma* was obtained from precession and cone axis photographs. A set of 1994 independent *hkl* reflections (2θ ≤ 55°) was collected, of which 1351 were retained for structure resolution (*I*/σ(*I*) > 2.5). The Ag atom was located on a crystallographic mirror plane (equipoint 4c) from a Patterson map. The remaining atoms including all hydrogens were located and refined as above. Full-matrix least squares converged to *R* = 0.026, *R*_w = 0.033, and a goodness-of-fit ratio of 1.29. The final Δ*F* map had a general background of ±0.27 e/Å³, with maximum peaks of ±(0.4–0.5) e/Å³ near silver.

The refined coordinates for both structures are listed in Table I. The refined temperature factors and the tables of structure factors are part of the supplementary material.

The scattering curves used were those of Cromer and Waber,⁸ except for hydrogen.⁹ The *f*' and *f*'' contributions to anomalous scattering of Ag were taken into account.¹⁰ The programs used are listed elsewhere.¹¹

(5) Ley, H.; Schaefer, K. *Ber. Dtsch. Chem. Ges.* **1906**, *39*, 1259–1266.

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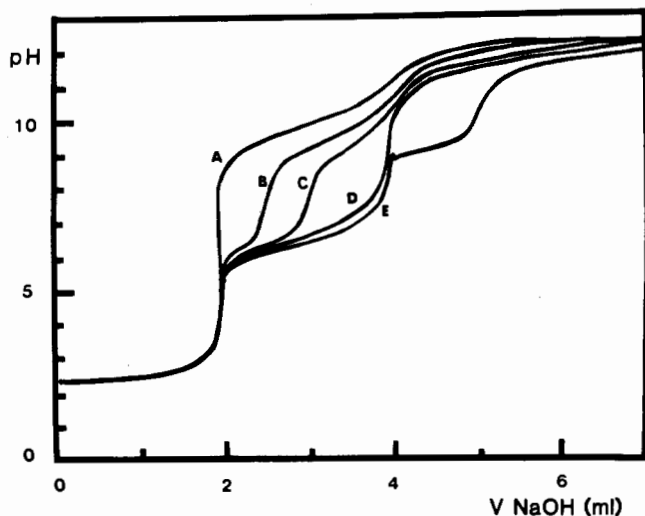
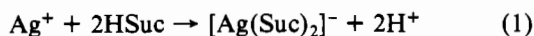


Figure 1. pH metric titration curves with 1.018 M NaOH. The solutions consisted of 0.192 M HNO₃ (10 mL), 0.202 M succinimide (10 mL), and the following volumes of 0.204 M AgNO₃: (A) 0; (B) 1.25 mL; (C) 2.50 mL; (D) 5.0 mL; (E) 10.0 mL. They correspond to Ag/succinimide ratios of 0, 1/8, 1/4, 1/2 and 1, respectively. The total initial volume was completed to 150 mL with water.

Results and Discussion

pH Metric Measurements. Succinimide and uridine possess N-H protons of comparable acidities ($pK_a = 9.1$ (uridine³), 9.6 (succinimide¹²)), and both adjacent ring positions bear carbonyl groups in each case. Thus, the similar reaction patterns with Ag⁺ noted in acetonitrile solution⁴ were expected to show for water solutions as well. This is borne out by the set of neutralization curves shown in Figure 1. The solutions contained a fixed amount of succinimide (2.02 mmol) and increasing quantities of AgNO₃ (0–2 mmol). A constant amount of HNO₃ (1.92 mmol), titrated between 0 and 2.0 mL, was also added to obtain a homogeneous solution at the starting point in all cases. Curve A between 2.0 and 4.0 mL is typical of the neutralization of an acid of $pK_a = 9.6$. The pH in the same portions of curves B–E is much lower than in A, indicating that Ag⁺ complexes are formed with proton displacement. When no precipitate is present, the data points in these regions can be satisfactorily fitted by using the formation constants reported by Blais, Enea, and Berthon for 1:1 and 1:2 complexes.¹³ The main reaction taking place involves a displacement of two protons per Ag⁺ ion (eq 1). This is



definitely the predominant species present at the end points of curves B (2.5 mL), C (3.0 mL), and D (4.0 mL). For B and C, excess succinimide is titrated as a weak acid between pH 9 and 10.5. When similar conditions are used at higher concentration to prepare salts of the [Ag(Suc)₂]⁻ ion, a precipitate appears shortly after the first end point. It was identified as Ag₂(Suc)₂·H₂O by an X-ray powder pattern. Thus, the free Ag⁺ ions act as the counteraction to precipitate the Ag⁺ salt of [Ag(Suc)₂]⁻ (eq 2). The precipitate redissolves



as the external Ag⁺ ion is used to bind to deprotonated succinimide upon further addition of NaOH. Curve E, where the reactants are in a 1:1 ratio, should correspond to maximum formation of Ag[Ag(Suc)₂] at 4.0 mL. However, this system further reacts upon addition of excess NaOH (eq 3). At 5.0

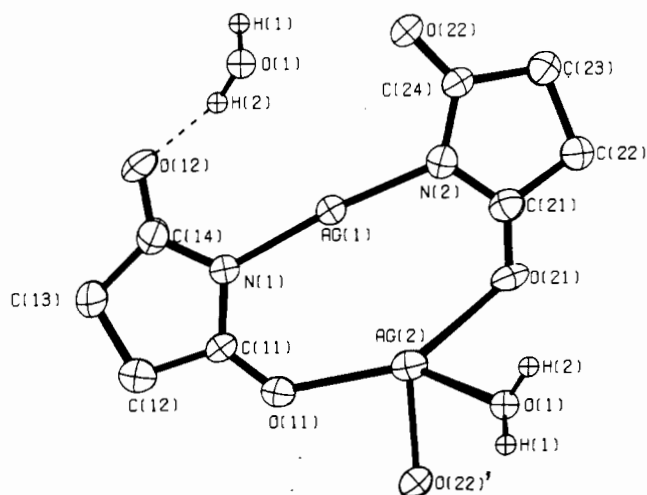


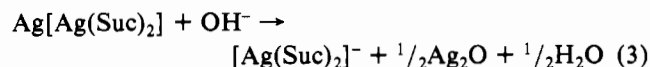
Figure 2. Numbering scheme for the asymmetric unit of Ag₂(Suc)₂·H₂O.

Table II. Interatomic Distances and Bond Angles in Ag₂(Suc)₂·H₂O

| Distances (Å) | | | |
|--------------------------------|------------|---|-----------|
| Ag(1)–N(1) | 2.079 (5) | C(11)–O(11) | 1.241 (7) |
| Ag(1)–N(2) | 2.067 (5) | C(14)–O(12) | 1.218 (8) |
| Ag(2)–O(11) | 2.357 (5) | N(2)–C(21) | 1.353 (8) |
| Ag(2)–O(21) | 2.374 (4) | N(2)–C(24) | 1.360 (8) |
| Ag(2)–O(22) | 2.448 (5) | C(21)–C(22) | 1.500 (9) |
| Ag(2)–O(1) | 2.367 (6) | C(22)–C(23) | 1.525 (9) |
| N(1)–C(11) | 1.333 (8) | C(23)–C(24) | 1.498 (9) |
| N(1)–C(14) | 1.363 (8) | C(21)–O(21) | 1.218 (7) |
| C(11)–C(12) | 1.531 (9) | C(24)–O(22) | 1.233 (7) |
| C(12)–C(13) | 1.516 (10) | O(1)–O(11) | 2.817 (7) |
| C(13)–C(14) | 1.505 (9) | O(1)–O(12) | 2.723 (7) |
| Angles (deg) | | | |
| N(1)–Ag(1)–N(2) | 169.0 (2) | N(1)–C(14)–O(12) | 124.4 (6) |
| O(11)–Ag(2)–O(21) | 137.7 (2) | Ag(1)–N(2)–C(21) | 123.3 (4) |
| O(11)–Ag(2)–O(22) ^a | 76.2 (2) | Ag(1)–N(2)–C(24) | 125.5 (4) |
| O(11)–Ag(2)–O(1) | 139.3 (2) | C(21)–N(2)–C(24) | 110.5 (5) |
| O(21)–Ag(2)–O(22) ^a | 122.7 (2) | N(2)–C(21)–C(22) | 110.7 (5) |
| O(21)–Ag(2)–O(1) | 82.8 (2) | N(2)–C(21)–O(21) | 125.6 (6) |
| O(22) ^a –Ag(2)–O(1) | 82.9 (2) | C(22)–C(21)–O(21) | 123.7 (6) |
| Ag(1)–N(1)–C(11) | 121.5 (4) | C(21)–C(22)–C(23) | 104.2 (5) |
| Ag(1)–N(1)–C(14) | 126.8 (4) | C(22)–C(23)–C(24) | 103.0 (5) |
| C(11)–N(1)–C(14) | 110.7 (5) | C(23)–C(24)–O(22) | 125.6 (6) |
| N(1)–C(11)–C(12) | 111.6 (5) | C(23)–C(24)–N(2) | 111.4 (5) |
| N(1)–C(11)–O(11) | 124.9 (6) | N(2)–C(24)–O(22) | 123.0 (6) |
| C(12)–C(11)–O(11) | 123.5 (6) | C(14)–O(12)–O(1) ^b | 121.0 (5) |
| C(11)–C(12)–C(13) | 102.5 (5) | C(24)–O(22)–O(11) ^c | 174.6 (4) |
| C(12)–C(13)–C(14) | 104.2 (6) | O(11) ^d –O(1)–O(12) ^b | 119.2 (2) |
| C(13)–C(14)–O(12) | 124.7 (6) | Ag(2)–O(1)–O(11) ^d | 113.3 (2) |
| C(13)–C(14)–N(1) | 110.9 (6) | Ag(2)–O(1)–O(12) ^b | 124.2 (2) |

^a Symmetry transformation: $-1 + x, y, z$. ^b Symmetry transformation: $-x, 1 - y, -z$. ^c Symmetry transformation: $1 + x, y, z$. ^d Symmetry transformation: $-1 - x, 1 - y, -z$.

mL, half of the Ag⁺ ions present have precipitated as brown Ag₂O, whereas the other half exists as [Ag(Suc)₂]⁻ anions. This is the stable high-pH form of silver in the presence of succinimide.



Description of the Structures. Ag₂(Suc)₂·H₂O. The compound contains two nonequivalent Ag atoms. The numbering scheme is shown in Figure 2. Interatomic distances and bond angles are listed in Table II. One of the Ag atoms is two-coordinated, with very short Ag–N distances (2.079 (5) and 2.067 (5) Å) comparable to those found in the complex with 1-methylthymine (2.081 (4) Å).³ Distances in the range 2.14–2.23 Å are more common with this type of N-donor ligand.¹⁴ The departure from linearity is highly significant

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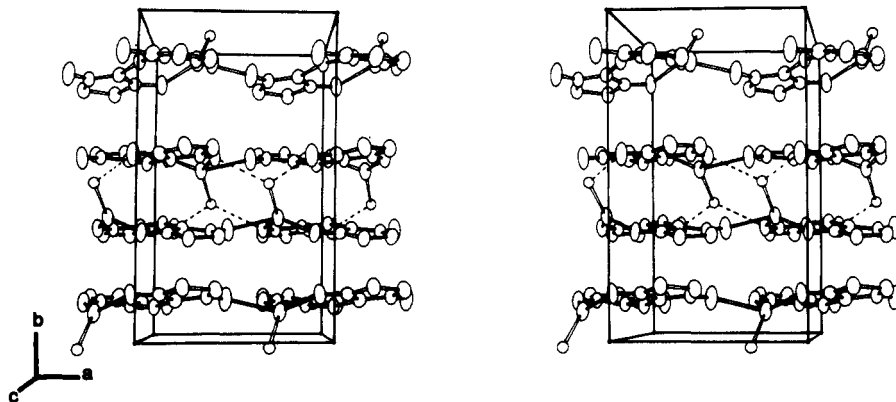


Figure 3. Stereoview of the unit cell of $\text{Ag}_2(\text{Suc})_2 \cdot 4\text{H}_2\text{O}$ down the c axis. Dashed lines correspond to hydrogen bonds.

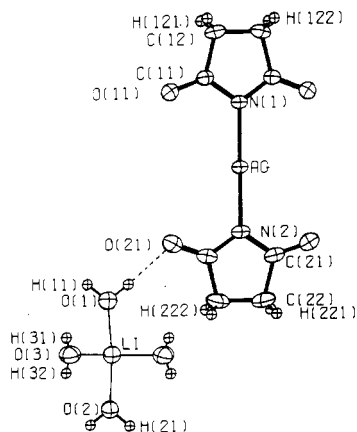


Figure 4. Numbering scheme for the asymmetric unit $\text{Li}[\text{Ag}(\text{Suc})_2] \cdot 4\text{H}_2\text{O}$. There are crystallographic mirror planes through $\text{N}(1)\text{--Ag--N}(2)$ and $\text{O}(1)\text{--Li--O}(2)$.

$\text{N}(1)\text{--Ag}(1)\text{--N}(2) = 169.0(2)^\circ$, although not unusually large. This distortion is required to optimize the bonding of carbonyl oxygens $\text{O}(11)$ and $\text{O}(21)$ with $\text{Ag}(2)$. Indeed, the $[\text{Suc}\text{--Ag}\text{--Suc}]^-$ unit with roughly coplanar succinimide rings could in principle act as a bidentate donor through a pair of carbonyl oxygens on either side. However, with a N--Ag--N angle of 180° , the $\text{O}\cdots\text{O}$ bite would be too wide to produce efficient interactions with a single metal ion. This is made possible, however, by carbonyl groups $\text{O}(11)$ and $\text{O}(21)$ moving toward each other, reducing the N--Ag--N angle by 11° . This leads to moderately strong $\text{Ag}(2)\text{--O}$ bonds of 2.357 (4) and 2.374 (4) Å. Meanwhile, the opposite pair of carbonyl groups have moved apart, so that they can no longer bind to a common Ag^+ ion. Only $\text{O}(22)$ is bound to a $\text{Ag}(2)$ atom at 2.448 (5) Å, which is already bonded to $\text{O}(11)$ and $\text{O}(21)$ of an adjacent unit. Water molecule $\text{O}(1)$ at 2.367 (6) Å completes the roughly tetrahedral environment of $\text{Ag}(2)$.

In the packing diagram of Figure 3, the $[\text{Suc}\text{--Ag}\text{--Suc}]^-$ units are seen edgewise. The water molecule coordinated to a $\text{Ag}(2)$ atom of one layer is H bonded to two carbonyl groups of the layer above (or below) with moderately strong H bonds ($\text{O}\cdots\text{O} = 2.817(7)$ and $2.723(7)$ Å). These double layers are superimposed in the b direction and interact by normal van der Waals contacts.

$\text{Li}[\text{Ag}(\text{Suc})_2] \cdot 4\text{H}_2\text{O}$. This structure consists of well-separated $[\text{Suc}\text{--Ag}\text{--Suc}]^-$ anions and $[\text{Li}(\text{H}_2\text{O})_4]^+$ cations (Figure 4). The complex anion has a crystallographic mirror plane running

Table III. Interatomic Distances and Bond Angles for $\text{Li}[\text{Ag}(\text{Suc})_2] \cdot 4\text{H}_2\text{O}$

| Distances (Å) | | | |
|--|------------|---|-----------|
| $\text{Ag}(1)\text{--N}(1)$ | 2.088 (2) | $\text{C}(21)\text{--O}(21)$ | 1.228 (3) |
| $\text{Ag}(1)\text{--N}(2)$ | 2.087 (2) | $\text{Li--O}(1)$ | 1.981 (6) |
| $\text{N}(1)\text{--C}(11)$ | 1.357 (3) | $\text{Li--O}(2)^b$ | 1.956 (6) |
| $\text{C}(11)\text{--C}(12)$ | 1.516 (3) | $\text{Li--O}(3)$ | 1.922 (4) |
| $\text{C}(12)\text{--C}(12)^a$ | 1.504 (4) | $\text{Li--O}(3)^c$ | 1.922 (5) |
| $\text{N}(2)\text{--C}(21)$ | 1.362 (3) | $\text{O}(11)\text{--O}(3)^d$ | 2.782 (2) |
| $\text{C}(21)\text{--C}(22)$ | 1.509 (3) | $\text{O}(21)\text{--O}(3)^d$ | 2.808 (2) |
| $\text{C}(22)\text{--C}(22)^a$ | 1.528 (5) | $\text{O}(21)\text{--O}(1)$ | 2.867 (2) |
| $\text{C}(11)\text{--O}(11)$ | 1.238 (3) | $\text{O}(11)\text{--O}(2)$ | 2.880 (2) |
| Angles (deg) | | | |
| $\text{N}(1)\text{--Ag--N}(2)$ | 178.48 (8) | $\text{O}(1)\text{--Li--O}(3)$ | 105.6 (2) |
| $\text{Ag--N}(1)\text{--C}(11)$ | 124.9 (2) | $\text{O}(2)^b\text{--Li--O}(3)$ | 103.0 (2) |
| $\text{Ag--N}(2)\text{--C}(21)$ | 124.8 (2) | $\text{O}(3)\text{--Li--O}(3)^c$ | 110.5 (2) |
| $\text{C}(11)\text{--N}(1)\text{--C}(11)^a$ | 109.8 (2) | $\text{Li--O}(1)\text{--O}(21)$ | 126.4 (2) |
| $\text{N}(1)\text{--C}(11)\text{--C}(12)$ | 111.4 (2) | $\text{Li}^e\text{--O}(2)\text{--O}(11)$ | 128.5 (2) |
| $\text{N}(1)\text{--C}(11)\text{--O}(11)$ | 124.4 (2) | $\text{Li--O}(3)\text{--O}(21)^f$ | 116.0 (2) |
| $\text{C}(12)\text{--C}(11)\text{--O}(11)$ | 124.2 (2) | $\text{Li--O}(3)\text{--O}(11)^f$ | 115.1 (2) |
| $\text{C}(11)\text{--C}(12)\text{--C}(12)^a$ | 103.7 (2) | $\text{O}(21)\text{--O}(1)\text{--O}(21)^c$ | 100.4 (1) |
| $\text{C}(21)\text{--N}(2)\text{--C}(22)^a$ | 110.1 (2) | $\text{O}(1)\text{--O}(21)\text{--C}(21)$ | 120.5 (2) |
| $\text{N}(2)\text{--C}(21)\text{--C}(22)$ | 111.4 (2) | $\text{O}(11)\text{--O}(2)\text{--O}(11)^c$ | 99.5 (1) |
| $\text{N}(2)\text{--C}(21)\text{--O}(21)$ | 124.4 (2) | $\text{O}(2)\text{--O}(11)\text{--C}(11)$ | 119.5 (2) |
| $\text{C}(22)\text{--C}(21)\text{--O}(21)$ | 124.2 (2) | $\text{O}(11)^f\text{--O}(3)\text{--O}(21)^f$ | 121.4 (1) |
| $\text{C}(21)\text{--C}(22)\text{--C}(22)^a$ | 103.5 (2) | $\text{O}(3)^d\text{--O}(11)\text{--C}(11)$ | 121.4 (2) |
| $\text{O}(1)\text{--Li--O}(2)^b$ | 128.7 (3) | $\text{O}(3)^d\text{--O}(21)\text{--C}(21)$ | 123.5 (2) |

^a Symmetry transformation: $x, 1/2 - y, z$. ^b Symmetry transformation: $-1 + x, y, z$. ^c Symmetry transformation: $x, 3/2 - y, z$. ^d Symmetry transformation: $1/2 + y, 3/2 - y, 1/2 - z$. ^e Symmetry transformation: $1 + x, y, z$. ^f Symmetry transformation: $-1/2 + x, 3/2 - y, 1/2 - z$.

through Ag , $\text{N}(1)$, $\text{N}(2)$, and the middle of the $\text{C}(\text{H}_2)\text{--C}(\text{H}_2)$ bonds. The two succinimide rings are nearly coplanar, and the N--Ag--N angle ($178.48(8)^\circ$) (Table III) is close to the ideal value for linear coordination. Again, the Ag--N bonds are short (2.087 (2) and 2.088 (2) Å).

The Li^+ ion lies on a mirror plane. It is surrounded by four water molecules, two of which also lie on the mirror plane. This approximately tetrahedral arrangement is common for Li^+ , and the Li--O distances (1.92–1.98 Å) are in the normal range.¹⁵

In contrast with $\text{Ag}_2(\text{Suc})_2 \cdot \text{H}_2\text{O}$, there are no direct Ag--carbonyl contacts in the present case. These carbonyl groups participate only in H bonds with the water molecules. A view of the unit cell is given in Figure 5. The $[\text{Suc}\text{--Ag}\text{--Suc}]^-$ ion is roughly parallel to the ab plane and oriented along the a axis. Each $\text{O}(3)$ water molecule "bridges" $\text{O}(11)$ and $\text{O}(21)$ belonging to the same anion, with hydrogen bonds. Water molecule $\text{O}(1)$ "bridges" two symmetry-equivalent $\text{O}(21)$

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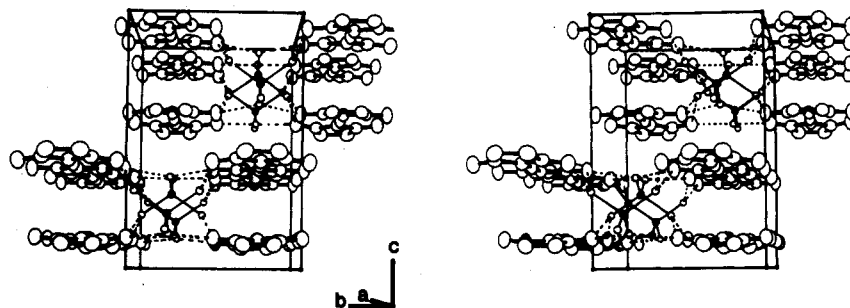


Figure 5. View of the unit cell of $\text{Li}[\text{Ag}(\text{Suc})_2] \cdot 4\text{H}_2\text{O}$ down the b axis. Dashed lines correspond to hydrogen bonds. The Li atoms are shown as black spheres.

carbonyl groups on the next $[\text{Suc}-\text{Ag}-\text{Suc}]^-$ ion along b , whereas O(2) acts similarly with respect to a pair of O(11) carbonyl groups. The four water molecules around Li^+ are H bonded to molecules above and molecules below along c . The resulting double layers, superimposed in the c direction, interact by normal van der Waals contacts.

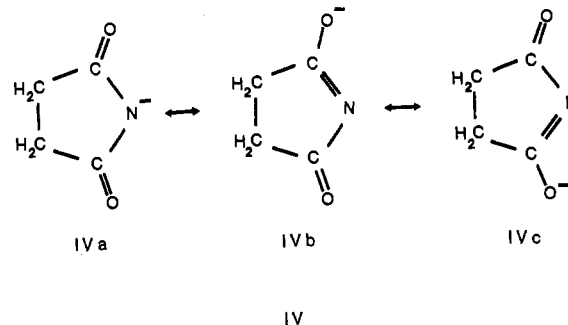
Geometry of Coordinated Succinimide. The succinimide moiety is roughly planar, but in three of the four nonequivalent ligands for these two structures, the N atom is 0.03–0.05 Å ($\sigma = 0.005$ Å) above the plane of the four carbon atoms, producing a slight “envelope” distortion in the ring. The carbonyl oxygens also show distances to the planes in the same range, presumably as a result of coordinating interactions with silver or H bonding with water (supplementary material, Tables VIII and XII).

The distances and angles in the succinimide ring for both Ag^+ complexes were compared with those of succinimide,¹⁶ its N-Br,¹⁷ N-Cl,¹⁸ and N-S¹⁹ derivatives, and complexes with Cu^{2+} ²⁰ and Ni^{2+} ²¹ (Table VI, supplementary material). No significant trends in distances can be detected. However, the C-N-C and N-C-C angles depend on the substituent on nitrogen and they are roughly correlated with the electrophilic character of this substituent. For instance, the C-N-C angle progressively decreases with decreasing substituent electrophilic character (115.0 (15)°, Cl; 111.6 (7)°, Br; 112.6 (6)°, H; 110.2 (4)°, Ag; 108.3 (4)°, Ni), whereas the adjacent N-C-C angles increase, but to a lesser extent (106.5 (15)°, Cl; 107.4 (8)°, Br; 108.3 (6)°, H; 111.2 (5)°, Ag; 112.1 (5)°, Ni). This is to be compared with the increase of $\sim 4^\circ$ of C-N-C and the decrease of $\sim 3-4^\circ$ on the adjacent angles, taking place in purines upon protonation.²²

Infrared Spectroscopy. The spectra of succinimide were investigated by Woldbaek, Klaeboe, and Christensen.^{23,24} Our results for the silver complexes are given in the supplementary material (Table IV and Figure 6). Assignments are proposed by comparison with the normal-coordinate interpretation presented by the above authors. So far, discussion of the IR spectra of metal complexes has been restricted to the stretching carbonyl region (1700 cm^{-1}).²⁵⁻²⁸

The most obvious modifications introduced by complexation are connected with the substitution of the N-bonded proton. The broad N-H stretching band ($\sim 3170 \text{ cm}^{-1}$) in succinimide disappears in the complexes, as well as the sharp band at 820 cm^{-1} assigned to the out-of-plane N-H bending mode.²³ The in-plane N-H bending vibration has been tentatively associated with a sharp peak at 1418 cm^{-1} in succinimide, with an overtone at $\sim 2800 \text{ cm}^{-1}$. The overtone is absent from the spectra of the complexes. Some simplification also occurs around 1415 cm^{-1} , but this crowded region is of little value as a diagnostic for complexation.

In the 1600–1800- cm^{-1} portion, succinimide contains sharp peaks at 1773 and 1695 cm^{-1} for the in-phase and out-of-phase stretching motions of the C=O groups. In the Ag^+ complexes, these bands are found at ~ 1700 and 1570–1615 cm^{-1} , respectively. Similar differences have been observed between phthalimide and its anionic form in the K^+ salt.²⁹ These changes, which are correlated with those found for the uracil moiety,³⁰ can be ascribed to delocalization of the anionic charge into the ring and carbonyl groups, decreasing the C=O bond order (IV). Thus, the (C=O) region is very sensitive to



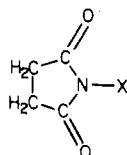
proton substitution but rather insensitive to whether the C=O groups are involved in metal coordination. Indeed, there are no dramatic differences between the spectra of $\text{Ag}_2(\text{Suc})_2$ and $\text{Li}[\text{Ag}(\text{Suc})_2] \cdot 4\text{H}_2\text{O}$, which could indicate that Ag^+ forms moderately strong bonds with the C=O groups in the former case but not in the latter.

Other ligand modes are affected by complexation. For instance, the strong 1193- cm^{-1} absorption, probably localized in the C-N-C region, appears at $\sim 1250 \text{ cm}^{-1}$ for the complexes, near the CH_2 wagging vibration at 1240 cm^{-1} . Similarly, the sharp absorption of succinimide at 935 cm^{-1} is absent from the spectra of the complexes. This effect is also a good diagnostic for succinimide complexation.

Significant shifts below 700 cm^{-1} take place in the complexes. A weak band at 420 cm^{-1} , believed to involve C=O

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Table V. ^1H and ^{13}C NMR Chemical Shifts of Succinimide and Some of Its Derivatives^a

| X | ^1H | | ^{13}C | |
|-----------------------|--------------|------|--------------------|--------------------|
| | NH | CH | C=O | C(H ₂) |
| H | 11.01 | 2.59 | 179.51 | 29.60 |
| Ag (Ag ⁺) | | 2.48 | 189.82 | 31.80 |
| Ag (Li ⁺) | | 2.42 | 189.71 | 31.58 |
| Ag (Na ⁺) | | 2.42 | 189.74 | 31.73 |
| Cl | | 2.57 | 172.5 ^b | 28.5 ^b |

^a Solvent Me₂SO-*d*₆, vs. Me₄Si. ^b Solvent dioxane.³² In dioxane, δ values for succinimide are 179.0 and 30.1.

in-plane bending, is shifted to 452–470 cm⁻¹ in the complexes. Modifications also occur in the four components at 555/564 and 639/652 cm⁻¹ due to ligand in-plane and out-of-plane skeletal motions. In this region, Ag₂(Suc)₂ and Li[Ag(Suc)₂]₂·4H₂O seem to show significant differences: the doublets are shifted to 564/585 and 662/675 cm⁻¹ in Ag₂(Suc)₂ but to 555/570 and 666/684 cm⁻¹ in the Li⁺ salt. It is possible that these differences reflect the different roles played by the C=O groups in the two compounds. However, the weakness of these bands in infrared spectra complicates their use for diagnostic purposes.

No structural information from X-rays is available for Na[Ag(Suc)₂]₂·5H₂O. Its infrared spectrum shows the effects of hydrogen substitution on nitrogen, as well as the changes mentioned above on the absorptions at 935 and 1190 cm⁻¹. These results suggest that the Na⁺ salt also contains [Ag(Suc)₂]⁻ units. In the low-wavenumber region, the weak absorptions at 452, 570, and 672 cm⁻¹ are found to differ from those observed for either Ag₂(Suc)₂ or the Li⁺ salt. This might indicate a different type of interaction for the C=O groups, such as direct Na⁺-oxygen ionic contacts similar to those found in CH₃Hg(methylthymine)₂/NaNO₃.¹

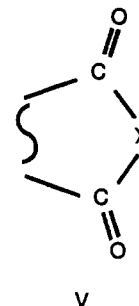
NMR Spectroscopy. The complexes were examined in Me₂SO-*d*₆ solution by means of ^1H and ^{13}C NMR spectroscopy. Our results for the succinimide complexes (Table V) are in good agreement with those of Lessard and co-workers⁴ for CD₃CN-D₂O solutions. The spectra of phthalimide and its K⁺ and Ag⁺ salts, also recorded for comparison purposes, are given in the supplementary material (Table Va).

Both imides exhibit a low-field resonance above 11 ppm for the N-bonded proton (Table V and Va), which disappears on substitution by silver. Succinimide also shows a singlet at 2.59 ppm for the four equivalent aliphatic protons. In the Ag⁺ complexes, this resonance is shifted to ~2.45 ppm. Although this shift is consistent with the reduced electrophilic character of the N-X region of the molecule (vide infra), it is much smaller than the ~1.5 ppm upfield shifts observed by Roundhill²⁷ for PPh₃-succinimide complexes of Pt and Pd. It is difficult to relate the latter results to ours, because the systems differ not only by the nature and coordination number of the metal but also by the presence of the soft phosphine in the coordination sphere and the proximity of its phenyl rings to the succinimide protons. The remote aromatic protons of phthalimide are shielded by 0.23 ppm in the Ag⁺ compounds (Table Va).

The ^{13}C spectra of succinimide were examined by Hasan³² and by Fronza and co-workers.³³ Assignment for the Ag⁺

complexes is straightforward (Table V). The ^{13}C resonances in phthalimide were assigned according to the findings of Galasso and co-workers³¹ (Table Va).

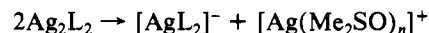
In all the complexes, the carbonyl signal undergoes a low-field shift of ~10 ppm. A series of five-membered heterocyclic dicarbonyl compounds (V) were examined by Galasso and



co-workers.³¹ An inverse correlation was found between δ for the carbonyl carbon atom and the electrophilic character of X: increasing the electronegativity of X reduces the polar character of the C=O bond (i.e. the relative weight of formulas like IVb and IVc), thereby increasing electron density at the carbon, which is shifted to high field.

With succinimide, spectral data are given in Table V for the N-Ag, N-H, and N-Cl compounds and, according to the above discussion, the resonances should appear in this order. This is indeed the case for both types of carbons. For the ^1H spectra, the signals of the aliphatic protons of succinimide and its N-chloro derivative are very close.

Structural information concerning the Ag⁺ species present in Me₂SO can be deduced from these spectral data. In none of the complexes was it possible to detect splitting of the signals arising from pairs of mirror-related atoms in the free ligands. The same observation was noted by Lessard et al.⁴ for CD₃CN solutions. Thus, the ligand mirror plane is maintained in the dissolved complexes. This is expected for the M[AgL₂] compounds, which should liberate [AgL₂]⁻ ions in solution. For Ag[AgL₂], if appreciable Ag-carbonyl binding is retained, signal splitting should take place. Indeed, it was shown that the presence of Ag-O bonds with a pair of CO groups on one side of the [Ag(Suc)₂]⁻ ion makes it impossible for another Ag⁺ ion to interact with the pair of CO groups on the other side, because they had to move away from each other in order to permit the interaction first mentioned. Consequently, Ag-O bonds should destroy the mirror plane of the ligands and split the corresponding NMR signals. The fact that the spectra of the Ag₂L₂ and M[AgL₂] compounds are so similar suggests that the following dissociation equilibrium of the Ag₂L₂ compounds takes place in solution, thereby destroying most of the Ag-O interactions found in the solid:



However, Lessard and co-workers⁴ noted that the loosely bound silver atoms of Ag₂L₂ were more difficult to reduce electrochemically than free Ag⁺ ions in acetonitrile, and they concluded that some Ag-carbonyl bonding remains. This would imply that averaging is achieved by fast rotation of the succinimide plane about the N-Ag-N direction⁴ and/or exchange of Ag⁺ between the four carbonyl groups. Both mechanisms are not unreasonable.

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Mayer (NMR spectra) is also acknowledged. We are grateful to J. Y. Huot for valuable advice concerning the preparation of $\text{Ag}_2(\text{Suc})_2 \cdot \text{H}_2\text{O}$ and to J. Lessard for making available a preprint of his paper.

Registry No. $(\text{Suc})_2\text{Ag}_2 \cdot \text{H}_2\text{O}$, 91191-42-3; $\text{Ag}_2(\text{Suc})_2 \cdot \text{H}_2\text{O}$ complex, 91191-44-5; $\text{Li}[\text{Ag}(\text{Suc})_2]$, 91191-41-2; $\text{Na}[\text{Ag}(\text{Suc})_2]$, 91191-43-4; $\text{Ag}_2(\text{Pht})_2$, 41505-30-0; $\text{K}(\text{Pht})$, 1074-82-4.

Supplementary Material Available: Infrared wavenumbers of succinimide and the silver complexes (Table IV), ^1H and ^{13}C NMR

chemical shifts of phthalimide and some of its derivatives (Table V), geometries of various succinimide compounds (Table VI), details on the $\text{Ag}_2(\text{Suc})_2 \cdot \text{H}_2\text{O}$ crystal structure including refined temperature factors (Table VII), weighted least-squares planes (Table VIII), distances involving the hydrogen atoms (Table IX), and observed and calculated structure factor amplitudes (Table X), details on the $\text{Li}[\text{Ag}(\text{Suc})_2] \cdot 4\text{H}_2\text{O}$ structure including refined temperature factors (Table XI), weighted least-squares planes (Table XII), distances involving the hydrogen atoms (Table XIII), and observed and calculated structure factor amplitudes (Table XIV), and infrared spectra of succinimide and its silver complexes (Figure 6) (36 pages). Ordering information is given on any current masthead page.

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An INDO Study of [1.1]Ferrocenophane as a Catalyst for Hydrogen Liberation from Aqueous Acidic Media

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INDO-SCF calculations with constrained geometry optimization have been carried out to help elucidate the mechanism by which hydrogen gas is liberated when [1.1]ferrocenophane is dissolved in acid media. The calculated equilibrium geometries correspond to protonation at ring carbon atoms. The calculated electronic structures of these species indicate large electron transfer from the rings to the protons. In order to more completely model the protonation and hydrogen liberation processes, single-point energies and electronic structures were obtained for other selected protonated species consisting of various positions of the protons relative to the crystal geometry of the [1.1]ferrocenophane. The results indicate that proton transfers around the rings and between the rings and the metal centers are necessary for these processes. Hydrogen liberation appears to occur by homolytic cleavage of metal-hydrogen bonds from a higher energy conformation, different from the crystal geometry, obtained from twisting of the molecule, leading to the formation of molecular hydrogen and a stable dication.

Introduction

The compound [1.1]ferrocenophane shows several unusual properties due to (a) the proximity of its two ferrocene units, which are linked together by two bridging methylene groups, and (b) the high degree of flexibility of the molecule around these methylene bridges. NMR studies of [1.1]ferrocenophane¹ show that the molecule undergoes a rapid syn-syn exchange, which, due to a small activation barrier, occurs at a fast rate on the NMR time scale even at low temperatures. Clearly, the exceptional ability of the molecule to undergo rapid conformational change and to accommodate charge relaxations, mediated by the metal centers, is crucial to its function and properties.

An important property of [1.1]ferrocenophane is that the compound dissolves in strong nonoxidizing acids with evolution of hydrogen gas, leaving a stable dication that can be quantitatively reduced to the neutral species.² This property, together with the feasibility of large-quantity production of the compound by new synthetic routes,^{1,3,4} makes [1.1]ferrocenophane an attractive candidate as a semiconductor surface modifier^{5,6} for use in the photochemical splitting of water in solar energy systems.

Since the oxidation of [1.1]ferrocenophane in aqueous acids is immediate, no direct observation of the intermediates in the protonation and hydrogen-liberation pathways has been possible. It has been suggested² that protonation of [1.1]ferrocenophane occurs at both iron atoms of the ferrocenyl moieties, consistent with the metal protonation of ferrocenes,^{2,7,8} substituted ferrocenes,^{8,9} and [*n*]ferrocenophanes.¹⁰ Elimination of H_2 could then follow by a twisting of the

molecule into a conformation that would place the hydrogen atoms within bonding distance. However, the exact protonation pathways in ferrocenes and ferrocenophanes and, in particular, the relative importance of the metal and cyclopentadienyl rings in this process have been the subject of much controversy.¹¹⁻¹⁴ Proton transfer to the ring is evidenced by the "rapid" (\gg benzene) deuteration of ferrocene in deuterated acid $\text{BF}_3 \cdot \text{D}_2\text{O}$ and by observed isotopic ratios of 10:3:1 for H_2 :HD:D₂ liberation by [1.1]ferrocenophane in deuterated acid.¹⁵

In view of the importance of the mechanisms of protonation and hydrogen liberation to the function of [1.1]ferrocenophane as a semiconductor surface modifier, and in the absence of direct experimental evidence, characterization of these path-

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