Silver(II) Bis(pyridine-2,6-dicarboxylate) Monohydrate. A Novel Six-Coordinate Structure[1]

Sir:

The strong oxidizing nature of compounds of silver(II) and their magnetic and spectral properties make these d^9 systems of considerable interest. Studies are at present frustrated by the scarcity of silver(II) complexes and the lack of structural data for those derivatives which have been prepared. Most known silver(II) complexes almost certainly owe their stability to their low solubility in the reaction medium and subsequent ease of isolation. One such class of compounds, namely the derivatives with the pyridinecarboxylic acids,[2,3] has recently been investigated in detail by us.[4] Of particular interest is the complex formed with pyridine-2,6-dicarboxylic acid, which can be isolated as a monohydrate,[4] dihydrate,[2] or tetrahydrate.[3,4] We have now succeeded in obtaining silver(II) bis(pyridine-2,6-dicarboxylate) monohydrate as fine black needles,[5] and a three-dimensional X-ray analysis has shown this molecule to have a novel six-coordinate structure, the main features of which we now report.

$Ag(C_7H_4NO_4)_2 \cdot H_2O$ crystallizes in the orthorhombic system, space group P_{nna}, with dimensions a = 7.874 (6), b = 10.942 (7), c = 17.734 (12) Å, Z = 4, V = 1527.9 Å^3, mol wt = 451.5, d_m = 1.97 (1) g/cc, d_c = 1.99 g/cc. These lattice dimensions and diffraction intensities were measured with a General Electric XRD-5 diffractometer, equipped with a manual goniostat and scintillation counter, using nickel-filtered copper radiation (Cu Kα 1.54178 Å). Intensities of 1459 independent reflections ($2\theta \leq 140°$) were measured using the stationary crystal–stationary counter technique. The structure was solved by Patterson and Fourier syntheses and the 1043 nonzero reflections have been refined (Ag, N, C, O anisotropic) to a conventional R value of 0.10.

The structure is shown in Figure 1, together with the appropriate bond lengths. The Ag and two N atoms are in special positions (4c) with coordinates ($^1/_4$, 0, z); the molecule therefore has imposed twofold symmetry. Standard deviations for the bond lengths are Ag–O and Ag–N 0.01, C–C, C–N, and C–O 0.015 Å, and for the O–Ag–N angles, 0.3°.

The silver atom is six-coordinate, being bonded to the nitrogen and two oxygens from each of the tridentate ligand molecules. However, the two ligands coordinate in a strikingly different manner, the coordination best being described as from anionic (A) and neutral (B) ligand molecules. For ligand A, the silver atom forms single bonds to the nitrogen (2.08 Å) and to the two negatively charged oxygen atoms at 2.20 Å. For ligand B, the silver atom is bonded less strongly to the nitrogen (2.20 Å) and to the two ketonic oxygen atoms at 2.54 Å.

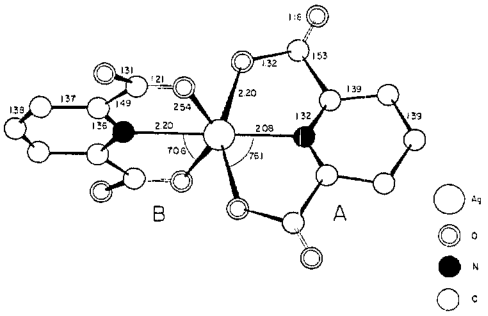

Figure 1. The molecular structure of silver(II) bis(pyridine-2,6-dicarboxylate) monohydrate, showing the principal bond lengths.

The identity of the oxygen atoms in each ligand is satisfactory confirmed by the disparity in the C–O bond lengths (see Figure 1). The structure is best considered as a very distorted octahedron with the angles around the silver showing the extent of this distortion, $(O\text{–}Ag\text{–}N)_a$ being 76.1° and $(O\text{–}Ag\text{–}N)_b$ being 70.6°. The two ligand molecules are approximately planar and intersect at 84.6°, and the largest distance of an atom from either of the two least-squares planes is 0.09 Å for the oxygen atoms in ligand **B**. The packing of the molecules is facilitated by hydrogen bonds formed between the water molecule and oxygen atoms in adjacent molecules. The electronic absorption spectrum of the tetrahydrate is very similar to that of the monohydrate, and it is probable that it has an equivalent gross structure. Both spectra are significantly more complex in the visible region (28–10 kK) than are the spectra of related square-planar silver(II) species;[4] they have absorption maxima at ~25 and ~17 kK in the diffuse-reflectance spectra, and a further absorption band at 10 kK in aqueous solution; the latter is not located in the solid-state spectra. The correlation of these spectra with the distorted stereochemistry of these derivatives will be discussed in more detail in a subsequent publication.

Acknowledgment. We thank the University of Reading for a grant (to R. W. M.), and Imperial Chemical Industries for a fellowship (to M. G. B. D.)

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(1) Part II of the series Studies on Coordination Compounds of Silver(II).

(2) B. Banerjee and P. Ray, *J. Indian Chem. Soc.*, 33, 503 (1956).

(3) B. Banerjee and P. Ray, *ibid.*, 34, 207, 859 (1957).

(4) G. W. A. Fowles, R. W. Matthews, and R. A. Walton, *J. Chem. Soc.*, *A*, 1108 (1968).

(5) *Anal.* Calcd for $C_{14}H_{10}N_2O_9Ag$: C, 36.70; H, 2.20; N, 6.12. Found: C, 36.56; H, 2.24; N, 5.97. In our preparation we were also able to separate some dark green wedge-shaped plates whose diffraction pattern we have found too weak to interpret, but which is clearly different from the black monohydrate.

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(*cis*)^4-Oxonin and Its Geometrical Isomer

Sir:

Quite recently Anastassiou and Cellura[1] have reported that thermolysis of (*cis*)^4-oxonin (**1**) "appears to follow a path contrary to that prescribed by orbital symmetry" and suggested that "the arrangement of minimum skeletal strain is ideally disposed for Möbius interaction between four planar ethylene segments of **1**." The claim for such a rare and important anomaly demands an unequivocal stereochemical proof of the product. Apparently these authors were misled by

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(1) A. G. Anastassiou and R. P. Cellura, *Chem. Commun.*, 903 (1969).

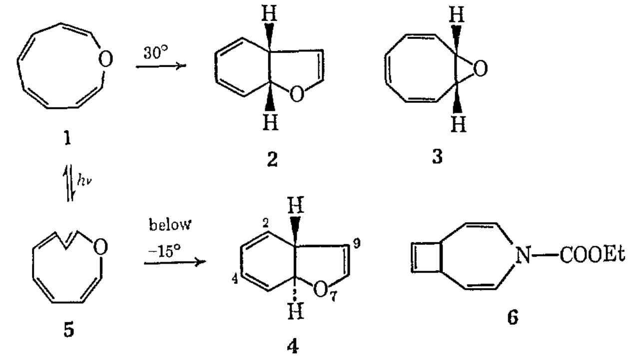

Figure 1.

erroneous stereochemical assignments in the literature,[2] and we now find that the thermal product of **1** is *not* *trans*-8,9-dihydrobenzofuran as they supposed, but rather its *cis* isomer (**2**); thus, **1** follows the Woodward–Hoffmann selection rule. Furthermore, we wish to show that direct photolysis[3a–c] of cyclooctatetraene epoxide (**3**) at −80° with a low-pressure mercury lamp (2537 Å) involves, in addition to **1**, an extremely (thermally) labile geometrical isomer [very likely $(cis)^3$,-*trans*] of **1**, and that this isomer isomerizes to *true* *trans*-8,9-dihydrobenzofuran (**4**). These two thermolysis products, **2** and **4**, were previously reported and proposed to possess structures *trans*-8,9-dihydrobenzofuran and 8-oxabicyclo[5.2.0]nona-3,5,9-triene, respectively[2,4] (see Figure 1; the corresponding nitrogen (O = NCOOEt) compounds are numbered **1a**, **2a**, **3a**, **4a**, and **5a**).

Compounds **2** and **4** (III and V of ref 2) were prepared as described previously and hydrogenated with rhodium catalyst to provide the corresponding perhydro compounds **2′** and **4′**, respectively. That **2′** and **4′** are *cis*- and *trans*-7-oxabicyclo[4.3.0]nonane was proven beyond doubt by comparison [glpc (UCW-98 and Reoplex), ir, nmr, mass spectrum] with the authentic samples prepared according to the procedure described briefly in the footnote.[5] While the nmr spectral assignment to **2** is obvious, signals at τ 3.60, 4.75, 5.86, and 6.77 in a spectrum of **4**[2] are now assigned to C(8)-H, (9)-H, (6)-H, and (1)-H of **4**, respectively. The coupling constant observed for C(1)-H and (6)-H is very large (23.5 Hz)[2] but compounds possessing a similar structural feature such as *trans*-8,9-dihydroindene (20 Hz)[6] and *trans*-N-carbethoxy-7-azabicyclo[4.3.0]nona-2,4,8-triene (**4a**) (24 Hz)[7] exhibited coupling constants of the same magnitude.[8]

A 0.015 *M* solution of **3** in diethyl ether or pentane was irradiated at −80° with a spiral low-pressure (2537 Å) mercury lamp (1.8 m, 120 mA) for 40 min, the photolysate was distilled at −50 to −45° (10^{-6} mm), and a fraction[9] was treated in the following ways: (i) a portion was kept at −80°, (ii) two portions were maintained at −15° for 1 hr and 2 hr, respectively, and (iii) the last portion was, after process ii, warmed to 40°. All the four samples were hydrogenated at −80° with rhodium catalyst under the conditions successfully applied for similar carbocyclic and azacyclic compounds.[3] Since **2** and **4** were hydrogenated under these conditions to give in *ca.* 90% yield **2′** and **4′**,[10] and **3** provided a 90% yield of a mixture of *cis*-cyclooctene epoxide and cyclooctanol (ratio was somewhat variable) but none gave oxacyclononane (**1′**),[11] this analytical method was satisfactory for the present purpose. The product distribution of perhydro compounds summarized in Table I clearly demonstrates that an oxacyclononane precursor (X) was converted into **4** at −15° at least mainly (if not quantitatively) and that the other (Y) was rather stable and isomerized only after heating at 40°. That Y is indeed $(cis)^4$-oxonin was proven by isolating it in pure state and measuring the kinetics of its thermal conversion.

Table I

Thermolysis conditions	Product distribution (%) of perhydro compounds				
	1′	*a*	*b*	*c*	*d*
−80°	43	4	3	35	15
−15°, 1 hr	15	5	25	36	15
−15°, 2 hr	15	4	25	35	18
40°, 1 hr	0	17	26	35	19

[a] Mixture of 2′ and 2-cyclohexylethanol.[10] [b] Mixture of 4′ and *trans*-2-ethylcyclohexanol.[10] [c] Mixture of *cis*-cyclooctene epoxide and cyclooctanol. [d] Mixture of as yet uncharacterized compounds. Hexan-2-ol used throughout as standard. F & M 5750, Reoplex (6 ft × 3/16 in.), and yields not corrected for the sensitivity of the detector.

The photolysate obtained as described above, by careful fractional distillation through a 25-cm column with a temperature-controlled jacket, provided a small fraction (bp −20° (0.01 mm)) of pure **1** which showed the following spectral data: calcd mass for C_8H_8O, 120.0575; found *m/e*, M, 120.0572, M − 29 (base peak); $\lambda_{max}^{pentane}$ 251 nm (log ε 3.32), λ_{min} 241 (3.31); nmr (100 MHz, CD_2Cl_2, −20°) τ 3.79 (d, *J* = 7.2 Hz, 2 H), 4.14 (br s, 2 H),[12] 4.24 (br d, *J* = 4.0, 2 H),[12] and 4.92 (br

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[2] J. M. Holovka, P. D. Gardner, C. B. Strow, M. L. Hill, and T. V. Van Auken, *J. Amer. Chem. Soc.*, 90, 5041 (1968).

[3] For low-temperature photolysis of $(CH)_{10}$ (a), C_9H_{10} hydrocarbons (b), and the nitrogen analog (c and d), see: (a) S. Masamune and R. T. Seidner, *Chem. Commun.*, 542 (1969); (b) S. Masamune, P. M. Baker, and K. Hojo, *ibid.*, 1203 (1969); (c) S. Masamune, K. Hojo, and S. Takada, *ibid.*, 1204 (1969); and (d) A. G. Anastassiou and J. H. Grebrian, *J. Amer. Chem. Soc.*, **91**, 4011 (1969). For thermal rearrangements of **3**, see (e) G. Büchi and E. M. Burges, *ibid.*, **84**, 3104 (1962).

[4] Our doubt about the correctness of the structures proposed for these compounds and subsequent structural and stereochemical work on several photoproducts delayed our announcement of the synthesis of **1** by some months.

[5] *cis* Isomer: according to the procedure of W. E. Harvey and D. S. Tarbell, *J. Org. Chem.*, **32**, 1679 (1967); *trans* isomer: cyclohexene epoxide ($^-CH_2CN$) → *trans*-1,2-cyanomethylcyclohexanol (OH^-, $LiAlH_4$, 1 mol of TsCl, and solvolysis) → **4′**; *cf.* M. Mousseron and M. Canot, *Bull. Soc. Chim. Fr.*, 192 (1952).

[6] S. W. Staley and T. J. Henry, *J. Amer. Chem. Soc.*, **91**, 1239 (1969).

[7] S. Masamune and K. Hojo, unpublished results.

[8] Professor Gardner has reached the same conclusion concerning the structures and stereochemistry of 2 and 4 as those described herein and will publish his results soon. We are grateful to him for sending us spectra pertinent to the present work.

[9] This fraction represented *ca.* 20% of the total photolysate and constituted a major fraction containing C_8H_8O compounds (*ca.* 3/4 of the total C_8H_8O's).

[10] The remaining *ca.* 10% of the products were mainly 2-cyclohexylethanol and *trans*-2-ethylcyclohexanol from 2 and 4, respectively.

[11] J. K. Crandall and R. J. Watkins, *Tetrahedron Lett.*, 1717 (1967).

[12] Weak multiplets appeared at τ 4.0 and 4.35, ascribable to these four protons. Spectra of 1 (CS_2 + THF-d_8) virtually remained unchanged in a range of −20 to −130°.

dd, $J = 7.2, 4.0, 2$ H).[13] Quantitative thermal conversion of **1** into **2** but not **3** was confirmed by nmr and ir spectroscopy and provided the following kinetic parameters: k (at 10.7°) = $(7.8 \pm 0.3) \times 10^{-5}$ sec^{-1}; k (at 32.3°) = $(9.3 \pm 0.5) \times 10^{-4}$ sec^{-1}; $\Delta H^{\ddagger} = 19$ kcal/mol; $\Delta S^{\ddagger} = -10$ eu (*cf.* the rate of thermolysis of cyclononatetraene and azonin[3b,c]). Catalytic hydrogenation (Rh, *vide supra*) of **1** provided **1′** quantitatively. All these results are consistent with the assignment of all-*cis* structure **1** to Y and further suggest that X is a geometrical isomer, very likely $(cis)^3$,*trans*-oxonin (**5**) assuming X is a single compound[14] and the selection rule is applicable to the thermolysis.

Preliminary photochemical experiments with the irradiation of **1** and other isomers by 2537-Å light at −80° indicated that a certain number of compounds set up a photochemical "pool," monocyclic tetraenes representing major constituents. Although the exact composition is difficult to estimate due to substantial leakage leading to polymeric material (unlike $(CH)_{10}$ and C_9H_{10} hydrocarbons[3a,b]), geometrical isomerization of a double bond of an oxonin is undoubtedly an important photochemical process.[3a,b] This situation is very similar to that observed for its nitrogen analog as we found that both **3a** and **6**[3c,15] provided N-carbethoxyazonin (**1a** and possibly **5a**) upon low-temperature irradiation and that the photolysate upon warming afforded **2a** and **4a**.[7] Each set of C_9H_{10}, $(CH)_{10}$, C_8H_8O, and C_8H_8N–R appears to behave photochemically in a similar fashion and the relative thermal stability of all *cis*- and mono-*trans*-monocyclic compounds is comparable in, at least, the first three series.[3]

Acknowledgment. The authors are grateful to Mr. H. Ona for his skillful technical assistance and to the National Research Council of Canada and Defense Research Board for financial support.

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[13] If these nmr signals exhibited by **1** are compared with those of furan (H-2, τ 2.58, H-3, 3.36) (Varian Analytical Instrument Division, High Resolution Nmr Catalog, Sample No. 50, 1962), γ-pyran (H-2, 3.84, H-3, 5.37) [S. Masamune and N. T. Castellucci, *J. Amer. Chem. Soc.*, **84**, 2452 (1962)] and oxepin (3.8, 4.4, 4.86) [E. Vogel, W. A. Böll, and H. Günther, *Tetrahedron Lett.*, 609 (1965)], it is obvious that there is no clear evidence for the presence of any significant diamagnetic ring current.

[14] We have not yet excluded the possibility that a second double bond isomer of **1** in addition to **5** was produced and isomerized to an as yet uncharacterized C_8H_8O compound. The structural assignment of **5** is solely on the basis of the selection rule.

[15] S. Masamune and N. T. Castellucci, *Angew. Chem. Intern. Ed. Engl.*, **3**, 582 (1964).

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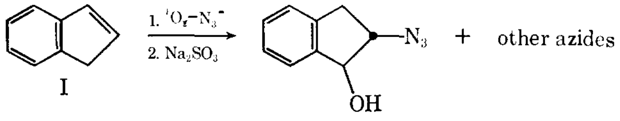
Mechanism of the Reaction of $^1\Delta_g$ Excited Oxygen with Olefins. II. Elimination of the Concerted "Ene" Mechanism as the Route to Allylic Hydroperoxides[1]

Sir:

In a previous communication we furnished chemical evidence for the existence of 1,2-dioxetanes as intermediates in carbonyl-forming reactions of $^1\Delta_g$ oxygen with olefins.[2] Subsequently, Kopecky has isolated stable dioxetanes of alkyl-substituted olefins and shown that they thermally decompose to the expected carbonyl fragments.[3] We have pointed out that allylic hydroperoxides could arise also from the dioxetane *via* a stereospecific, intramolecular hydrogen abstraction as an alternative route to the generally accepted "ene" mechanism.[2] In this communication, we show conclusively that allylic hydroperoxides are not formed *via* a concerted "ene" mechanism and furthermore furnish additional evidence for the existence of a discrete intermediate which leads to the production of allylic hydroperoxides in $^1\Delta_g$ additions to olefins.

Our earlier observation that an intermediate in the dye-sensitized photooxidation of indene could be intercepted by nucleophilic attack of methanol prompted us to examine the effects of other nucleophiles on these reactions. When indene (I) was photooxidized with methylene blue at 25° in 40% aqueous acetone, 1.0 M in sodium azide,[4] a sensitive mixture of azido hydroperoxides was obtained. Sulfite reduction of the mixture led to the isolation of II, *trans*-2-azido-1-indanol,[5] and two other azide-containing compounds which were not identified. The complete absence of the normal reaction product, homophthalaldehyde, is consistent with the enhanced nucleophilicity of azide ion over methanol.



I

II

2,3-Dimethyl-2-butene (III) reacts with $^1\Delta_g$ oxygen under a wide variety of conditions to yield only the corresponding rearranged allylic hydroperoxide (V),[6] but when III was photooxidized with methylene blue in the presence of sodium azide (1.0 M in 40% aqueous methanol) only 3% of V was obtained; 97% of the mixture consisted of the azido hydroperoxide IV.[7] IV is not a secondary reaction product since V was completely unreactive when subjected to the identical conditions required for the formation of IV. Photoreactions of azide ion were also discounted since III was

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[1] This work was supported by grants from the American Cancer Society, California Division, the National Science Foundation, GP-12050 (to D. R. K.), and the Petroleum Research Fund (to P. R.), administered by the American Chemical Society.

[2] W. Fenical, D. R. Kearns, and P. Radlick, *J. Am. Chem. Soc.*, **91** 3396 (1969).

[3] K. R. Kopecky and C. Mumford, *Can. J. Chem.*, **47**, 709 (1969), and personal communication.

[4] The photooxidations of I, III, and VI were conducted as 0.1 M solutions with the described sensitizers and solvent systems. Irradiation times varied from 48 hr with indene to 5 hr with 2,3-dimethyl-2-butene.

[5] The structure of II was confirmed as *trans*-2-azido-1-indanol by its infrared absorptions at 3450 and 2140 cm^{-1} and by its nmr spectrum which consisted of a multiplet at τ 2.80 (4 H), a broad singlet at 5.00 (1 H), a multiplet at 6.08 (1 H), a double doublet ($J = 7.5$ Hz) at 6.77 (1 H), a double doublet ($J = 7.5$ Hz) at 7.30 (1 H), and a broad solvent-dependent band at 7.10 (1 H) (10% solution in $CDCl_3$).

[6] K. Gollnick, *Advan. Photochem.*, **6**, 1 (1968).

[7] The structure of IV was indicated by its infrared spectrum with absorptions at 3430 and 2130 cm^{-1}, its nmr spectrum which showed two sharp singlets at τ 8.69 and 8.74, and its reduction with sulfite ion to a new compound, 2-azido-2,3-dimethyl-2-butanol. The latter compound had an nmr spectrum of two equal-intensity singlets at τ 8.71 and 8.82. The azido alcohol was synthesized independently by reaction of 2,3-dimethyl-2,3-epoxybutane with azide ion in aqueous methanol and the two were shown to be identical by comparison of their nmr and infrared spectra.