Pergamon

Polyhedron Vol. 16, No. 16, pp. 2893–2895, 1997

0277-5387/97 $17.00+0.00

PII: S0277-5387(97)00022-3

COMMUNICATION

A simple helix based on 2,2′-biimidazole. Crystal and molecular structure of $[Ag(NO_3)(H_2biim)]_n$

Colin A. Hester,[a] Russell G. Baughman[b] and Harvest L. Collier[a]*

[a]Department of Chemistry, University of Missouri-Rolla, Rolla, MO 65401, U.S.A.

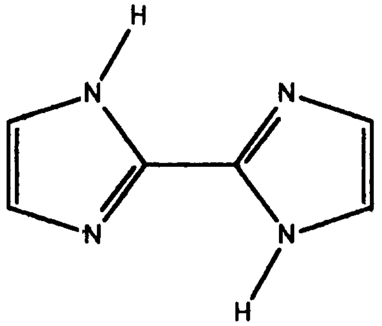
[b]Division of Science, Truman State University, Kirksville, MO 63501, U.S.A.

(Received 9 September 1996; accepted 6 January 1997)

Abstract—Silver(I) nitrate and 2,2′-biimidazole (H_2biim) crystallize from an aqueous solution to afford a single-strand helix, as evidenced by X-ray crystallography. This assemblage is based on an approximate *cis* conformation of H_2biim acting in concert with the preferred linear two-coordinate nature of the ligated silver(I) atom. © 1997 Elsevier Science Ltd

Keywords: 2,2′-biimidazole; silver(I) nitrate; helix; self-assembly; crystal structure.

Our initial interest in the silver chemistry of 2,2′-biimidazole (H_2biim, **1**) was spurred by a report describing the preparation of its disilver salt, Ag_2biim [1]. It was hoped this compound would be a viable alternative (i.e. lower toxicity) to the dithallium salt of H_2biim [2a], which has been used as a precursor in metathetical reactions involving halo-bound metal centers [2a–d].



(1)

Attempts were made to prepare Ag_2biim as previously described: H_2biim was solubilized in dilute HNO_3 (aq) and 2 equiv. of silver(I) nitrate added directly as a solid, resulting in the formation of a white precipitate.† This precipitate can be resolubilized if the solution is made sufficiently acidic. Likewise, if the initial solution is too acidic no precipitate is formed on the addition of $AgNO_3$. In either case, golden columnar crystals are deposited upon slow evaporation of the respective solutions. IR analyses of the initial precipitate and the deposited crystalline compound are identical, both showing the characteristic N—H stretch (3141–2810 cm^{-1}, m) of H_2biim and the ionic nitrate absorption (1360 m^{-1}, s), clearly indicating that neither product is the desired disilver salt, but rather a complex involving both $AgNO_3$ and H_2biim. Elemental analyses and solution conductivity studies confirm this and imply an empirical formula commensurate with a 1 : 1 $AgNO_3$: H_2biim stoichiometry, which has been reported [3].

---

[*] Author to whom correspondence should be addressed.

[†] Anal. Found: C, 24.0; H, 2.0; N, 22.9; Ag 35.9. Calc. for $C_6H_6AgN_5O_3$: C, 23.7; H, 2.0; N, 23.0; Ag, 35.5%. ^1H NMR (100 MHz, D_2O): δ 4.82 (2H, s, C—H), 7.38 (1H, s, N—H).

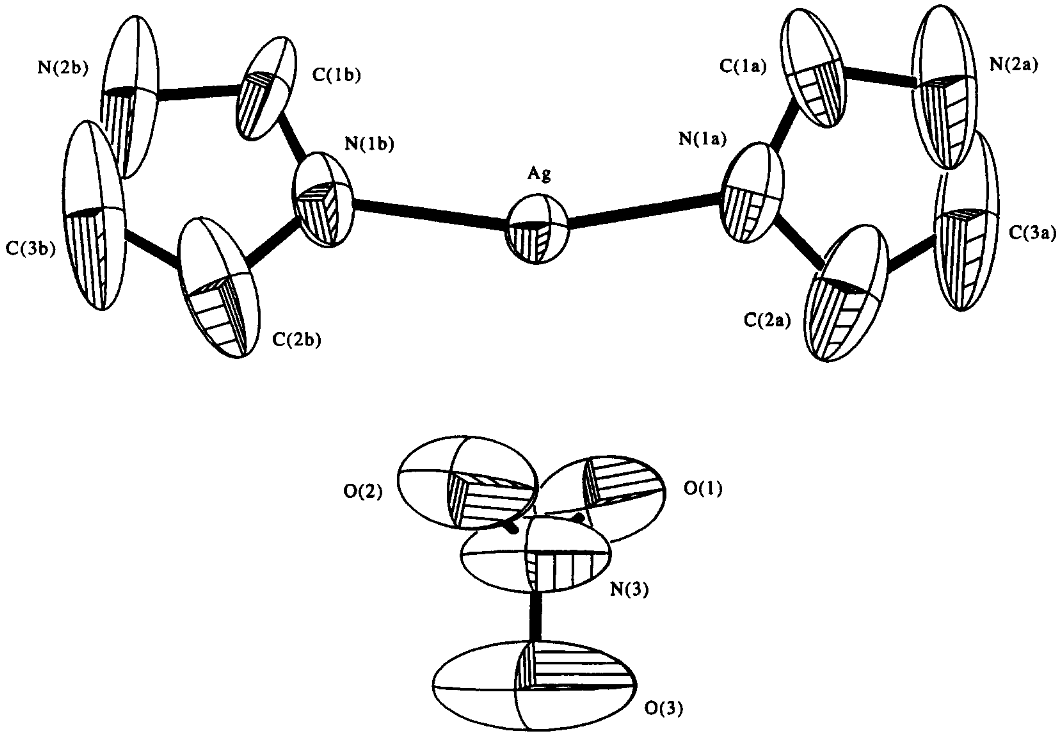


Fig. 1. Asymmetric unit (50% ellipsoids) showing the two major species resulting from the libration about Ag. C1a is bound to a C1b *via* $2-y$, $x-y+1$, $z-1/3$; C1b to a C1 a *via* $-x+y+1$, $2-x$, $z+1/3$.

X-ray crystallography was employed to better understand this complex.* The asymmetric unit consists of two imidazolyl moieties, one silver atom and one nitrate group. Although of no chemical significance, in order to obtain an acceptable crystallographic agreement factor, the asymmetric unit was deconvoluted into two major moieties ("a" and "b") which appear to librate about a nearly isotropic silver atom (Fig. 1).

The single-strand helical nature of this structure is very surprising for its sheer simplicity (Fig. 2). Recent literature demonstrates that the current thrust of supramolecular chemistry is based on either higher order helices (double or triple strands) [6] or intricate arrangements of intertwined threads [7]. The overall (at least most common) theme tying these assemblies together is that the point of metal–ligand contact is based on either the imidazolyl or pyridyl moiety, these being incorporated into monomeric or oligomeric units. So it should come as no surprise that H_2biim can be the foundation upon which supramolecular assemblies may be constructed.

The bond distances and angles of the complexed H_2biim are unexceptional and compare well with the free ligand [8]. Of note is the dihedral angle between the two imidazole rings. The free ligand is found to crystallize in a *trans* disposition, as expected, but in the title complex H_2biim takes on a *cis* conformation with a dihedral angle of 23.2(2)°. This angle presumably minimizes the proton–proton (N—H $\cdots$ H—N) and silver–silver interactions, whilst preserving the favourable pi overlap between the two bridging atoms of the aromatic rings, albeit somewhat

---

*Crystal data: $M = 304.03$, trigonal, space group $P3_2$, $a = 10.147(2)$, $b = 10.147(2)$, $c = 7.765$ Å, $V = 692.3(3)$ Å^3, $Z = 3$, $D_{calc} = 2.188$ g cm^{-3}, $F(000) = 444$, μ(Mo-K_α) $= 2.179$ mm^{-1}, $T = 288(2)$ K. Two octants of data were collected on a crystal of dimensions $0.45 \times 0.30 \times 0.25$ mm with a Siemens P3 diffractometer using graphite monochromated X-radiation ($\lambda = 0.71073$ Å) operating in the $\theta/2\theta$ mode from 2.32 to 25.01° ($-12 \leqslant h \leqslant 12$, $-12 \leqslant k \leqslant 12$, $-9 \leqslant l \leqslant 9$). Unit-cell parameters were based on a least-squares fit of 40 reflections with $8.1 < \theta < 15.3°$. Absorption corrections (semi-empirical from ψ-scans) were applied ($T_{min} = 0.855$; $T_{max} = 1.000$). All non-hydrogen atoms were allowed anisotropic thermal motion. Hydrogen atoms were placed at idealized positions (C—H 0.96 Å, N—H 0.90 Å) and were assigned isotropic thermal of U(eq) $= 80$. The structure was solved using SHELXL-PC™ [4] and refined on F^2 by a full-matrix least-squares method using the weighting scheme $w = [\sigma^2(F_o^2) + (0.205P)^2 + 0.0252P]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$ with SHELXL-93 [5] to a final $R_1 = 0.0134$ ($wR_2 = 0.0336$; $S = 1.149$). The largest difference peak and hole were 0.169 and -0.290 e Å^{-3}, respectively.

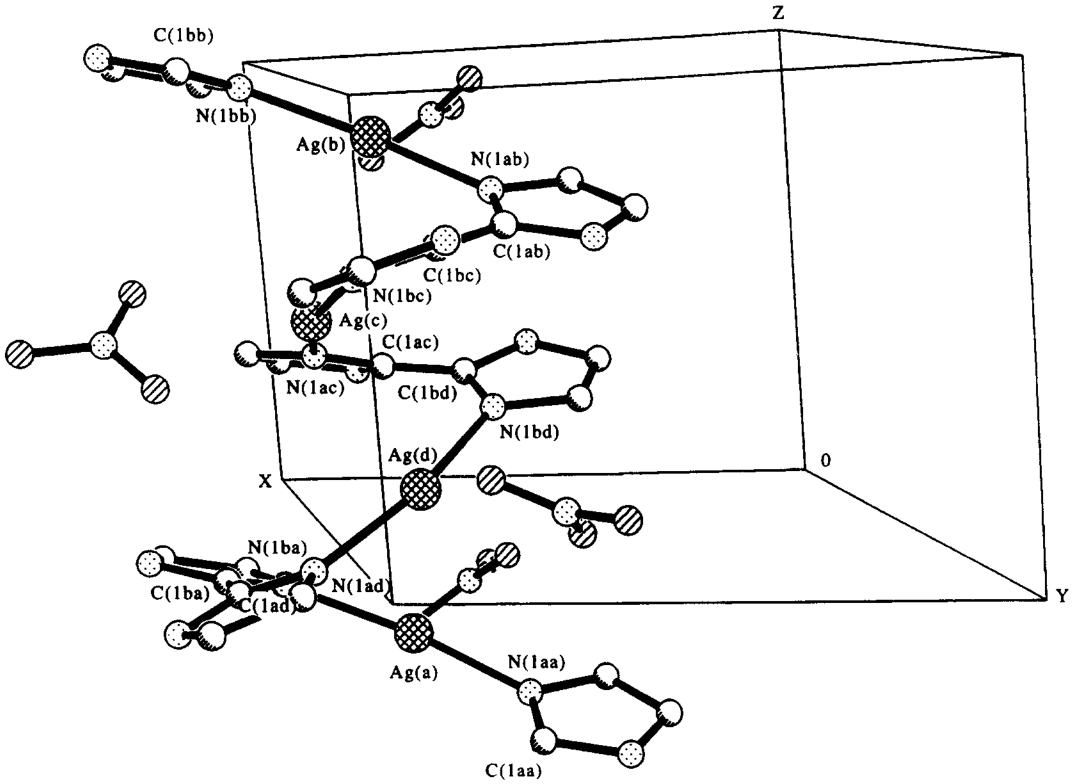


Fig. 2. View of the unit cell illustrating the right-hand nature of the helix. Displayed atoms are of arbitrary size; hydrogen atoms omitted for clarity.

reduced from the optimum coplanar arrangement [9]. This *cis* conformation constrains neighboring silver atoms into fairly close contact, $Ag—Ag^1 = 3.0029(6)$ Å, $(1 = -x+y+1, -x+2, z+1/3)$ resulting in a $Ag^1—Ag—Ag^2$ $(2 = -y+2, x-y+1, z-1/3)$ angle of 127.90(2)°. The geometry about the silver atom is best described as linear two-coordinate [N(1B)—Ag—N(2A) = 162.32(11)°]. The angles about the nitrate anion sum to 360°, within experimental error and the N—O bond lengths range from 1.19(2) [N(3b)—O(2b)] to 1.27(2) [N(3a)—O(2a)]. The planar nitrate moieties ("a" and "b") are tilted by 57.3(3) and 56.1(3)° with respect to the N(1B)—Ag—N(2A) plane and the nitrate's oxygen atoms contact the silver atom most closely at distances of 2.79(1), 2.73(1), 2.77(1), and 2.81(1) Å for O1a, O2a, O1b, and O2b, respectively. Overall, the basic structure is quite similar to that seen in the related monomeric complex $[Ag(im)_2NO_3]$ (im = imidazole) [10].

Supplementary material

Tables of atomic coordinates, thermal parameters, observed and calculated structure factors, as well as selected distances and angles (9 pages) are available from the authors upon request.

REFERENCES

1. Lehmstedt, K., *Liebigs Ann. Chem.*, 1927, **456,** 253.
2. (a) Uson, R., Gimeno, J., Fornies, J. and Martinez, F., *Inorg. Chim. Acta*, 1981, **50,** 173; (b) Uson, R. and Gimeno, J., *J. Organomet. Chem.*, 1981, **220,** 173; (c) Uson, R., Gimeno, J., Oro, L. A., Aznar, M. A. and Cabeza, J. A., *Polyhedron*, 1983, **2,** 163. (d) Oro, L. A., Pinillos, M. T., Tejel, C., Foces-Foces, C. and Cano, F. H., *J. Chem. Soc. Dalton Trans.*, 1986, 2193.
3. Wyss, G., *Chem. Ber.*, 1877, **10,** 1365.
4. Sheldrick, G. M., *SHELXTL/PC*. Siemens Analytical X-Ray Instruments, Inc., Madison, WI, 1990.
5. Sheldrick, G. M., *SHELXL-93*. *Program for the Refinement of Crystal Structures*. Institut für Anorganische Chemie, Universität Göttingen, Bundesrepublik, Germany, 1993.
6. Constable, E. C., in *Progress in Inorganic Chemistry*, Vol. 42, p. 67, ed. K. D. Karlin. John Wiley & Sons, Inc., New York, 1994.
7. Amabilino, D. B. and Stoddart, J. F., *Chem. Rev.*, 1995, **95,** 2725.
8. Cromer, D. T., Ryan, R. R. and Storm, C. B., *Acta Cryst.*, 1987, **C43,** 1435.
9. Constable, E. C., *Tetrahedron*, 1992, **48,** 10013.
10. Antti, C.-J. and Lundberg, B. K. S., *Acta Chem. Scand.*, 1971, **25,** 1758.