

The Oxime Functionality: A Versatile Tool for Supramolecular Assembly of Metal-Containing Hydrogen-Bonded Architectures

Christer B. Aakeröy,* Alicia M. Beatty, and Destin S. Leinen

Department of Chemistry, Kansas State University
Manhattan, Kansas 66506

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To build new supramolecular architectures,¹ it is necessary to identify versatile supramolecular synthons and to utilize such connectors in the assembly of organic molecular solids and metal-containing networks.² So far, predictable assembly of metal complexes has primarily been achieved through syntheses of coordination polymers, and several 2-D and 3-D metal-containing frameworks based on ligands such as 4,4'-bipyridine and pyrazine have resulted in porous solids with channels and cavities, (although interpenetration of identical networks is commonly observed).^{3–5} Incorporation of metal ions within ordered hydrogen-bonded networks has received far less attention, although some intermolecular connectors have been utilized for linking metal complexes into a variety of hydrogen-bonded architectures.^{6,7}

The oxime moiety ($-\text{C}(\text{R})=\text{NOH}$) represents a supramolecular connector that can generate infinite low-dimensional networks through complementary hydrogen bonds involving a dimeric $\text{R}_2^2(6)$ motif.^{8,9} If the oxime functionality is combined with a

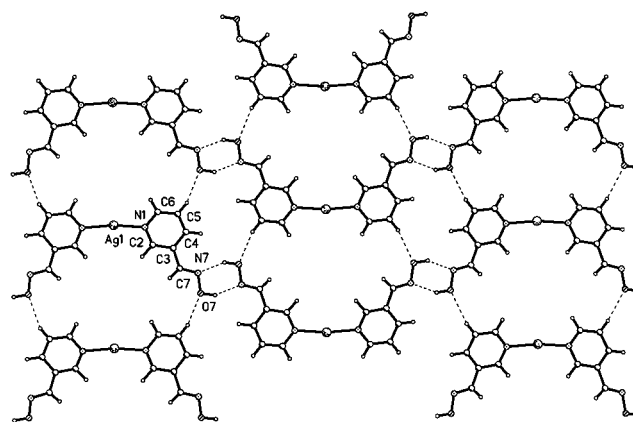


Figure 1. Hydrogen-bonded cationic sheet in **1**.

coordination site for a metal ion, we have access to a bridge between coordination complexes and supramolecular assembly. To this end, we have explored various pyridine–oxime ligands in the design of silver(I)-containing hydrogen-bonded networks where the geometry encoded in the coordination complex is propagated into low-dimensional architectures via intermolecular oxime–oxime hydrogen bonds.^{10,11}

The crystal structure of bis(3-aldoximepyridine)silver(I) hexafluorophosphate (**1**)¹² contains cations comprised of two 3-aldoximepyridine ligands coordinated through the pyridine nitrogen atoms to a silver(I) ion, [$\text{N}_{\text{py}}-\text{Ag}-\text{N}_{\text{py}}$ 171.7(1)°]. The oxime moieties are *cis* with respect to each other, and cations are linked by complementary $\text{O}-\text{H}\cdots\text{N}$ hydrogen bonds between oxime moieties on neighboring ligands, generating infinite 1-D chains. Adjacent chains are linked by two $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds, resulting in 2-D cationic sheets, Figure 1. The $[\text{PF}_6]^-$ counterions occupy the resulting “holes” within the cationic sheet, and are held in position by several $\text{C}-\text{H}\cdots\text{F}$ hydrogen bonds. The result is the anisotropic, lamellar structure shown in Figure 2.

The crystal structure of bis(3-aldoximepyridine)silver(I) perchlorate (**2**)¹³ is very similar to that of **1**, even though the size of the anion has changed significantly from **1** to **2** (molecular volumes of 72 and 55 Å³, respectively¹⁴). The oxime–oxime hydrogen bonds still persist, and there are no notable changes in the way in which neighboring silver(I) complexes are held

(10) *Experimental details*: An ethanolic solution of the pyridine–oxime ligand was slowly added to an aqueous solution of the silver(I) salt. The flask was covered with aluminum foil and left to stand in ambient air. After 2–4 days, colorless crystals were formed. The ratios of ligand to silver salt in the reactions were 4:1 for **1** (mp 181–183.5 °C), 1:1 for **2** (mp 181–183 °C), 2:1 for **3** (mp 180–184 °C), and 2:1 for **4** (mp 180–183.5 °C).

(11) *X-ray crystallography*: Crystal data were collected using a Siemens P4 four-circle diffractometer with graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Crystal stabilities were monitored by measuring 3 standard reflections after every 97 reflections, with no significant decay observed. Cell parameters were obtained from 35 accurately centered reflections in the 2θ range 10–28°. Data were collected using a θ – 2θ scanning technique, and Lorentz and polarization corrections were applied. The structures were solved by heavy atom methods, with non-hydrogen atoms found by successive full matrix least squares refinement on F^2 and refined with anisotropic thermal parameters. Hydrogen atom positions were located from difference Fourier maps, and a riding model with fixed thermal parameters [$u_{ij} = 1.2U_{ij}(\text{eq})$ for the atom to which they are bonded] was used for subsequent refinements. The weighting function applied was $w^{-1} = [\sigma^2(F_o^2) + (g_1P)^2 + (g_2P)]$ where $P = [F_o^2 + 2F_c^2]/3$. The SHELXTL PC and SHELXL-93 packages were used for data reduction and structure solution and refinement {Sheldrick, G. M. SHELXL-93, University of Göttingen}.

(12) *Crystal data for 1*: $\text{C}_{12}\text{H}_{12}\text{AgF}_6\text{N}_4\text{O}_2\text{P}$, $M_r = 497.10$ g mol⁻¹, colorless, irregular prism (0.42 × 0.28 × 0.16 mm), monoclinic, space group $C2/c$, $a = 15.403(2)$ Å, $b = 8.3865(8)$ Å, $c = 13.265(1)$ Å, $\beta = 111.300(8)^\circ$, $U = 1596.5(3)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 2.068$ g cm⁻³, $\mu(\text{Mo K}\alpha) = 1.455$ mm⁻¹; of 1305 reflections collected, 1255 were independent; $T = 173$ K; Final R value 0.0211, $wR = 0.0508$, for 1182 data with $I > 2\sigma(I)$ and 119 parameters; largest difference peak and hole 0.330 and -0.544 e Å⁻³.

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(8) A search of the Cambridge Structural Database for simple aromatic aldoximes have identified three oxime–oxime intermolecular interactions resulting in dimeric $\text{R}_2^2(6)$ motifs, infinite chains $\text{C}_1^1(3)$, and one example of a tetrameric assembly generated by the $\text{C}_1^1(3)$ motif. Due to the lack of structural data, it is currently not possible to make statistically significant statements about the relative occurrence of these motifs in organic molecular solids.

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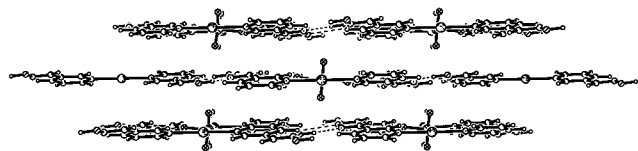


Figure 2. Edge-on view of the lamellar structure of **1**, with $[\text{PF}_6]^-$ anions positioned within cationic sheets.

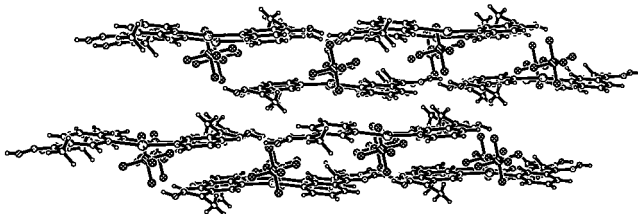


Figure 3. Edge-on view of the packing in **3**, with $[\text{PF}_6]^-$ anions positioned between cationic sheets.

together. The hydrogen bonds that generate the cationic sheets are robust, but not too rigid, and can therefore “flex” to accommodate a smaller anion within the holes while maintaining an efficient packing.

The crystal structure of bis(3-acetyloximepyridine)silver(I) hexafluorophosphate (**3**)¹⁵ contains cations comprised of two 3-acetyloximepyridine ligands coordinated through the pyridine nitrogen atoms to a silver(I) ion, $[\text{N}_{\text{py}}-\text{Ag}-\text{N}_{\text{py}} 170.3(1)^\circ]$. The oxime moieties are arranged trans with respect to each other and neighboring cations are linked by oxime-oxime $\text{O}-\text{H}\cdots\text{N}$ hydrogen bonds, $\text{R}_2^2(6)$, into 1-D chains. The chains are arranged within well-defined 2-D regions, connected by intermolecular hydrogen bonds. The anions, positioned *between* layers, act as “bridges”, via $\text{C}-\text{H}\cdots\text{F}$ hydrogen bonds, Figure 3. There are no short aryl \cdots aryl contacts or hydrogen bonds between cationic layers.

The crystal structure of bis(3-acetyloximepyridine)silver(I) perchlorate (**4**)¹⁶ contains cations where the pyridine nitrogen atoms are coordinated to a silver(I) ion $[\text{N}_{\text{py}}-\text{Ag}-\text{N}_{\text{py}} 165.6(1)^\circ]$ and with a trans arrangement of oxime groups. The silver complexes are again connected through $\text{O}-\text{H}\cdots\text{N}$ intermolecular $\text{R}_2^2(6)$ hydrogen bonds, resulting in 1-D chains. These chains

(13) *Crystal data for 2*: $\text{C}_{12}\text{H}_{12}\text{AgClN}_4\text{O}_6$, $M_r = 451.58 \text{ g mol}^{-1}$, colorless, irregular prism ($0.40 \times 0.38 \times 0.42 \text{ mm}$), monoclinic, space group $P2(1)/c$, $a = 15.333(2) \text{ \AA}$, $b = 8.185(1) \text{ \AA}$, $c = 13.165(2) \text{ \AA}$, $\beta = 110.681(9)^\circ$, $U = 1545.7(3) \text{ \AA}^3$, $Z = 4$, $\rho_{\text{calcd}} = 1.940 \text{ g cm}^{-3}$, $\mu(\text{Mo K}\alpha) = 1.516 \text{ mm}^{-1}$; of 2844 reflections collected, 2714 were independent; $T = 173 \text{ K}$; final R value 0.0449, $wR = 0.1212$, for 2402 data with $I > 2\sigma(I)$ and 217 parameters; largest difference peak and hole 1.636 and $-1.351 \text{ e \AA}^{-3}$.

(14) Molecular volumes were calculated as Connolly surfaces with a probe radius of 1.4 \AA .

(15) *Crystal data for 3*: $\text{C}_{14}\text{H}_{16}\text{AgF}_6\text{N}_4\text{O}_2\text{P}$, $M_r = 525.15 \text{ g mol}^{-1}$, colorless, irregular prism ($0.33 \times 0.32 \times 0.30 \text{ mm}$), triclinic, space group $P1$, $a = 8.0125(4) \text{ \AA}$, $b = 8.6411(4) \text{ \AA}$, $c = 13.5754(9) \text{ \AA}$, $\alpha = 74.133(4)^\circ$, $\beta = 86.497(4)^\circ$, $\gamma = 81.677(5)^\circ$, $U = 894.35(8) \text{ \AA}^3$, $Z = 2$, $\rho_{\text{calcd}} = 1.950 \text{ g cm}^{-3}$, $\mu(\text{Mo K}\alpha) = 1.296 \text{ mm}^{-1}$; of 4318 reflections collected, 4032 were independent; $T = 173 \text{ K}$; final R value 0.0362, $wR = 0.0985$, for 3721 data with $I > 2\sigma(I)$ and 253 parameters; largest difference peak and hole 1.240 and $-0.933 \text{ e \AA}^{-3}$.

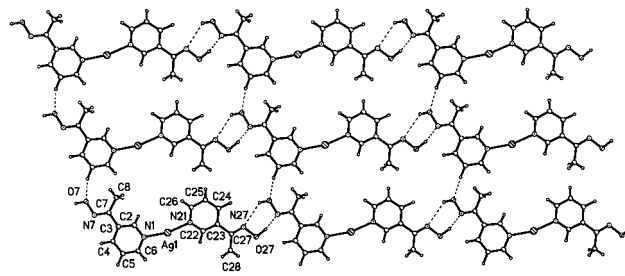


Figure 4. Hydrogen-bonded cationic sheet in **4**.

are propagated into 2-D sheets via $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds, Figure 4. The $[\text{ClO}_4]^-$ counterions are positioned between the cationic layers, and participate in several hydrogen bonds to the layer above and below.

The assembly of 1-D chains into 2-D sheets is facilitated in all four structures **1–4** through a $\text{C}-\text{H}\cdots\text{O}$ hydrogen bond to the available oxime oxygen acceptor site. Although $\text{C}(5)-\text{H}(5)$ is not the most acidic site, it is sterically more accessible than either $\text{C}(2)-\text{H}(2)$ or $\text{C}(4)-\text{H}(4)$. An interchain hydrogen bond involving $\text{C}(6)-\text{H}(6)$ would not allow the chains to pack together as efficiently, and for these reasons, $\text{C}(5)-\text{H}(5)$ becomes the most likely donor moiety for an intermolecular hydrogen bond to the oxime oxygen, thus linking 1-D chains into 2-D layers.

The persistence of the intermolecular $\text{R}_2^2(6)$ motif in the presence of different counterions and ligand substituents in the crystal structures of **1–4** is testimony to the utility of the oxime moiety as a versatile intermolecular connector which can allow coordination complexes to be directed into ordered networks such as chains (1-D motifs).¹⁷ This supramolecular synthon is particularly appealing since the oxime moiety is electronically and sterically “tunable”; the R group can be modified to include a wide range of electron donors/acceptors or “inert” spacers, and these functional groups are accessible through well-known synthetic methods.¹⁸

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Supporting Information Available: Tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths and angles, hydrogen bond geometries, and anisotropic thermal parameters for **1–4** (25 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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(16) *Crystal data for 4*: $\text{C}_{14}\text{H}_{16}\text{AgClN}_4\text{O}_6$, $M_r = 479.63 \text{ g mol}^{-1}$, colorless, irregular prism ($0.16 \times 0.25 \times 0.18 \text{ mm}$), triclinic, space group $P1$, $a = 7.6377(6) \text{ \AA}$, $b = 8.2315(8) \text{ \AA}$, $c = 13.9875(9) \text{ \AA}$, $\alpha = 75.902(6)^\circ$, $\beta = 88.767(6)^\circ$, $\gamma = 82.683(8)^\circ$, $U = 845.9(1) \text{ \AA}^3$, $Z = 2$, $\rho_{\text{calcd}} = 1.883 \text{ g cm}^{-3}$, $\mu(\text{Mo K}\alpha) = 1.391 \text{ mm}^{-1}$; of 2395 reflections collected, 2195 were independent; $T = 173 \text{ K}$; final R value 0.0229, $wR = 0.0554$, for 1994 data with $I > 2\sigma(I)$ and 235 parameters; largest difference peak and hole 0.321 and $-0.308 \text{ e \AA}^{-3}$.

(17) We are currently examining how the position of the oxime functionality affects the supramolecular assembly.

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