# Synthetic, Spectroscopic, and X-ray Crystallographic Studies on Manganese (III) Complexes with a 14-Membered Tetraaza Macrocyclic Ligand

**Ju Chang Kim\* and Alan J. Lough[†]**

*Department of Chemistry, Pukyong National University, Pusan 608-737, Korea*
*[†]Department of Chemistry, University of Toronto, Toronto, ONT, Canada M5S 3H6*
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The structural and chemical properties of cyclam (1,4,8,11-tetraazacyclotetradecane, **L1**)-like metal complexes appear to depend on the nature of the central metal ion as well as the structure of the ligand. Typically, chromium (III), iron (III), and cobalt (III) complexes of **L1** have been observed to exist as two forms, planar *trans* and folded *cis*.[1] Recent studies of manganese (III) complex of **L1** have shown *cis-trans* isomerization, based on infrared and electrochemical analysis.[2] The introduction of C- or N-substituents on **L1** affects the structures and reactivities in a variety of transition metal systems. The addition of substituents onto the ring is generally reflected by loss of ligand flexibility, which is manifested in metal ion complexation behavior that is usually slower relative to **L1**.[1e,3] Unlike **L1**, N-methylated **L1** is known to prefer to have five-coordinate metal complexes.[4] Recently, the nickel (II), copper (II), and zinc (II) complexes of **L** in which two cyclohexane rings and two methyl groups are introduced on the C-C and C-C-C linkages of **L1**, respectively, have been prepared and structurally characterized.[5] The ligand **L**, which closely resembles **L1**, has been proved to afford somewhat different coordination environments with the aforementioned metal ions.
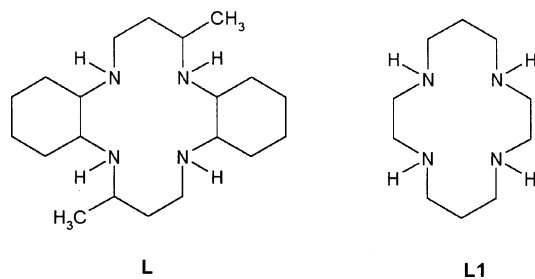


Continuing the transition metal chemistry of **L**, we have prepared and characterized a series of manganese (III) complexes of **L**. Herein, we report three new complexes of *trans*-[MnCl₂(**L**)]Cl · 4H₂O (**1**), *trans*-[Mn(H₂O)₂(**L**)]Cl₃ · 2H₂O · 0.5HCl (**2**), and *trans*-[Mn(N₃)₂(**L**)]N₃ · 2H₂O (**3**). To elucidate the metal ion environments, we carried out a single crystal X-ray determination of **2** and **3**.

## Experimental Section

**Materials and physical measurements**. All chemicals

*Author to whom correspondence should be addressed. Phone: 82-51-620-6382, Fax: 82-51-628-8147, Email: kimjc@dolphin.pknu.ac.kr

obtained from commercial sources were reagent grade and were used without further purification. Distilled water was used for all procedures. Infrared spectra of solid samples were recorded on a Perkin-Elmer Paragon 1000 FT-IR spectrophotometer between 4000 cm$^{-1}$ and 400 cm$^{-1}$ as Nujol mulls on KBr discs. Solid state electronic spectra by diffuse reflectance method were measured on a Shimadzu 2401-PC UV/vis spectrophotometer. Elemental analyses were performed by Korea Research Institute of Chemical Technology (Taejon, Korea). The free ligand **L** was synthesized by Kang's method.[3d]

**Preparation of *trans*-[MnCl₂(L)]Cl · 4H₂O (1)**.  A 2.0 g (6.0 mmol) of **L** in methanol (50 mL) was added to a 1.2 g (6.1 mmol) of MnCl₂ · 4H₂O in methanol (100 mL). Air was bubbled through the brownish solution for 24 hr, the color gradually darkening. Addition of concentrated hydrochloric acid (5 mL) gave the desired yellow solid, which was filtered off, washed with methanol, and dried at 25 °C *in vacuo* for 5 hr. IR (Nujol, KBr), cm$^{-1}$: $\nu$ (OH) 3346, $\nu$ (NH) 3098. Anal. Calcd. for C₂₀H₄₀N₄Cl₃Mn · 4H₂O (**1**): C, 42.14; H, 8.43; N, 9.83. Found C, 42.42; H, 8.22; N, 9.83.

**Preparation of *trans*-[Mn(H₂O)₂(L)]Cl₃ · 2H₂O · 0.5HCl (2)**. **1** was dissolved in a minimum amount of a dilute hydrochloric acid solution, which was allowed to stand in an open beaker at room temperature. After 2 days, the diaqua complex **2** was separated out as dark blue crystals before the solution dried up. Anal. Calcd. for C₂₀H₄₈Cl₃MnN₄O₄ · 0.5HCl (**2**): C, 40.95; H, 8.19; N, 9.55. Found C, 40.80; H, 8.37; N, 9.43.

**Preparation of *trans*-[Mn(N₃)₂(L)]N₃ · 2H₂O (3)**. This complex was prepared by treating a concentrated aqueous solution of **1** with an aqueous solution of NaN₃. Addition of a solution of NaN₃ to an aqueous solution of **1** gave immediately the desired brown color, which on standing overnight afforded brown crystals. The crystals were collected under the microscope and dried in air. Anal. Calcd. for C₂₀H₄₀N₁₃Mn · 2H₂O (**3**): C, 43.40; H, 7.96; N, 32.91. Found C, 43.76; H, 8.52; N, 32.47.

**X-ray crystallography**. A summary of selected crystallographic data for **2** and **3** is given in Table 1. Data were collected on a Nonius KappaCCD diffractometer, using graphite monochromated MoK$\alpha$ radiation ($\lambda = 0.71073$ Å). A combination of 1° phi and omega (with kappa offsets) scans were used to collect sufficient data. The data frames were integrated and scaled using the Denzo-SMN package.[6]

The structures were solved and refined, using the

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*Notes*

**Table 1**. Crystal Data and Structure Refinement for *trans*-[Mn(H$_2$O)$_2$(**L**)]Cl$_3$ · 2H$_2$O · 0.5HCl (**2**) and *trans*-[Mn(N$_3$)$_2$(**L**)]-N$_3$ · 2H$_2$O (**3**)

| | 2 | 3 |
|---|---|---|
| formula | C$_{20}$H$_{44}$Cl$_3$MnN$_4$O$_2$ · 2H$_2$O · 0.5HCl | C$_{20}$H$_{44}$MnN$_{13}$O$_2$ |
| fw | 586.13 | 553.62 |
| T, K | 100.0(1) | 100.0(1) |
| $\lambda$, Å | 0.71073 | 0.71073 |
| cryst system | monoclinic | monoclinic |
| space group | $P2(1)/n$ | $P2(1)/c$ |
| a, Å | 7.9371(2) | 9.6137(5) |
| b, Å | 17.7940(6) | 19.5541(4) |
| c, Å | 9.6531(3) | 14.2222(6) |
| $\beta$, deg | 92.370(18) | 100.589(2) |
| V, Å$^3$ | 1362.17(7) | 2628.06(18) |
| Z | 2 | 4 |
| D$_{calcd}$, Mg/m$^3$ | 1.429 | 1.399 |
| absorption coeff, mm$^{-1}$ | 0.860 | 0.548 |
| final R indices[I > 2$\sigma$(I)] | R1 = 0.0394, wR2 = 0.0981 | R1 = 0.0437, wR2 = 0.1101 |
| R indices (all data) | R1 = 0.0603, wR2 = 0.1052 | R1 = 0.0830, wR2 = 0.1199 |

R1 = $\Sigma$ || F$_o$-F$_c$ || / $\Sigma$ | F$_o$ | and wR2 = [$\Sigma$[w(F$_o^2$-F$_c^2$)$^2$]/$\Sigma$[w(F$_o^2$)$^2$]]$^{1/2}$.

SHELXTL\PC V5.1 package.[7] Refinement was by full-matrix least-squares on $F^2$, using all data (negative intensities included). For **2**, hydrogen atoms were included in calculated positions, except for the hydrogen atoms of the coordinated water molecule, which was refined with isotropic thermal parameters. The water molecule of crystallization is disordered over 3 sites in a solvent void of approximately 60 Å$^3$. The cation molecule has crystallographic inversion symmetry. The Cl atoms in the asymmetric unit refine to an occupancy of 0.75. Thus, in the asymmetric unit of the structure there are 0.5 of a cation molecule, 1.5 Cl anions, 0.25 of an HCl molecule and one water molecule. The full occupancy Cl anion is Cl(1) and the site that shares the 0.5 Cl anion atom and the 0.25 HCl atom is Cl(2). The Cl(2) site is between 2.6 Å and 3.0 Å from the three disordered oxygen sites. The hydrogen atoms from the water molecule and the HCl molecule were neither located nor included in the refinement. For **3**, the H atoms on the H$_2$O molecules were not located, as the H atoms are disordered.

### Results and Discussion

Yellow complex **1** was obtained from stoichiometric amounts of **L** and manganese dichloride in methanol. Under similar experimental conditions with **L1**, Létumier and coworkers observed a mixed-valence di-$\mu$-oxo-dimanganese (III, IV) species and a *cis*-[MnCl$_2$(**L1**)]Cl in addition to a *trans*-[MnCl$_2$(**L1**)]Cl.[2] The present ligand **L** with manganese dichloride gave only a *trans* species **1**. **1** dissolved in a dilute hydrochloric acid solution led to the formation of dark
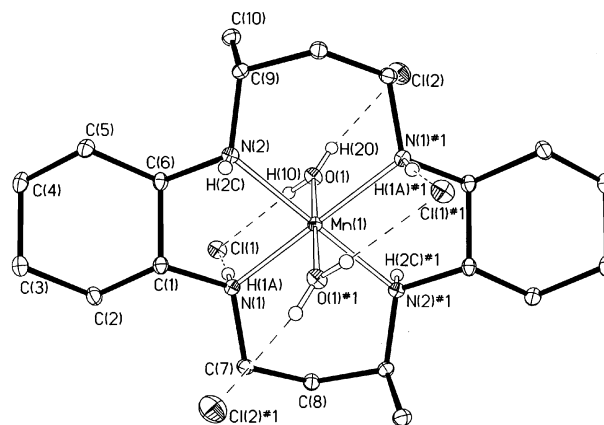


**Figure 1**. Molecular structure of [Mn(H$_2$O)$_2$(**L**)]Cl$_3$ · 2H$_2$O · 0.5 HCl (**2**) with atomic labeling scheme. Dashed lines indicate hydrogen bonds.

blue crystals **2** when the solution was nearly dried up. **1** was never recovered during this process. **2** was stable over a month exposed to air.

Figure 1 shows the structure of **2** determined by single-crystal X-ray crystallography. The selected bond lengths and angles are listed in Table 2. The coordination environment around manganese (III) ion in **2** is similar to those of related complexes reported earlier.[5b,8] The ligand skeleton of **2** adopts the most stable "*trans* III (*R,R,S,S*)" conformation with two chair form six-membered and two gauche five-membered chelate rings.[9] The bond lengths of 2.0363(16) Å and 2.0694(16) Å for the Mn-N (macrocycle) are comparable to those found in other six-coordinate manganese(III) tetraaza macrocyclic complexes (*trans*-[Mn(N$_3$)$_2$(**L1**)]ClO$_4$; 2.043(3) Å, *trans*-[MnCl$_2$(**L1**)]Cl; 2.036(3) Å, 2.031(2) Å, *trans*-[Mn(NO$_3$)$_2$(**L1**)]NO$_3$; 2.041(4) Å, 2.031(4) Å, *trans*-[MnCl$_2$(**L1**)]NO$_3$; 2.036(1) Å, 2.033(1) Å).[2,8b,8c] The long Mn-O bond lengths of 2.1787(15) Å are indicative of an elongated Jahn-Teller axis along H$_2$O-Mn-OH$_2$ that are mutually *trans* to each other. The Mn-O contact is believed to be stabilized by hydrogenbonding chelate rings composed of chlorides, water molecules, secondary amines of the macrocycle, and the central manganese (III) ion (Table 4). Similar types of hydrogen bonding are found in other metal complexes of 14-membered tetraaza macrocyclic ligands.[5c,8a,10]

When an aqueous solution of **1** is treated with an excess amount of NaN$_3$, a brown solution is obtained immediately,

**Table 2**. Selected Bond Lengths (Å) and Angles ($^o$) for *trans*-[Mn(H$_2$O)$_2$(**L**)]Cl$_3$ · 2H$_2$O · 0.5HCl (**2**)

| | | | |
|---|---|---|---|
| Mn(1)-N(1) | 2.0363(16) | Mn(1)-N(2) | 2.0694(16) |
| Mn(1)-O(1) | 2.1787(15) | | |

| | | | |
|---|---|---|---|
| N(1)#1-Mn (1)-N(1) | 180.0 | N(1)#1-Mn(1)-N(2)#1 | 84.78(6) |
| N(1)-Mn(1)-N(2)#1 | 95.22(6) | N(2)#1-Mn(1)-N(2) | 180.0 |
| N(1)#1-Mn(1)-O(1) | 92.70(6) | N(1)-Mn(1)-O(1) | 87.30(6) |
| N(2)#1-Mn(1)-O(1) | 87.15(6) | N(2)-Mn(1)-O(1) | 92.85(6) |
| O(1)-Mn(1)-O(1)#1 | 180.00(4) | | |

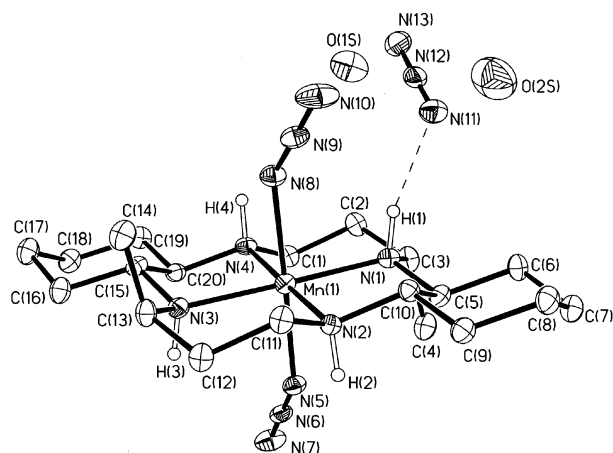Symmetry transformations used to generate equivalent atoms: #1−x+1, -y, -z+1

*Notes*

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**Figure 2**. Molecular structure of $[Mn(N_3)_2(\mathbf{L})]N_3 \cdot 2H_2O$ (**3**) with atomic labeling scheme.

and on standing at ambient temperature for a day this solution resulted in brown crystals of **3**. Complex **3** is stable in the solid state; however, an aqueous solution of this compound decomposes under light leading an unidentified product. Wieghardt and coworkers recently prepared a nitrido-manganese complex, *trans*-$[Mn(N)(\mathbf{L1})]ClO_4$ from corresponding azido precursors, using the decomposition process under light.[8b] The crystal structure of **3** consists of monomeric cations, water molecules, and azide anions. A perspective drawing of the molecule is shown in Figure 2. The manganese atom is six-coordinate as a consequence of the coordination of the four secondary amine nitrogen atoms and two axially arranged azido nitrogen atoms. The ligand skeleton in **3** is identical to that of complex **2**. Selected bond lengths and angles for **3** are summarized in Table 3. Bond distances between manganese and nitrogen atoms range from 2.0816(18) Å to 2.039(2) Å, and the average of the four distances is ~2.061 Å. This value falls within the range of similar reports for such a geometry.[2,8b,8c] The two *trans*-azido ligands are end bonded to the central manganese ion and are bent (N6-N5-Mn and N9-N8-Mn angles are 141.21(17)° and 138.77(18)°, respectively). As is usual in the 14-membered tetraaza macrocyclic complexes, the N-Mn-N angles of the six-membered chelate rings (95.19(7)° and

**Table 3**. Selected Bond Lengths (Å) and Angles (°) for *trans*-$[Mn(N_3)_2(\mathbf{L})]N_3 \cdot 2H_2O$ (**3**)

| Mn(1)-N(1) | 2.0816(18) | Mn(1)-N(2) | 2.049(2) |
|---|---|---|---|
| Mn(1)-N(3) | 2.0753(17) | Mn(1)-N(4) | 2.039(2) |
| Mn(1)-N(5) | 2.148(2) | Mn(1)-N(8) | 2.176(2) |
| N(5)-N(6) | 1.196(3) | N(6)-N(7) | 1.171(3) |
| | | | |
| N(4)-Mn (1)-N(2) | 179.14(8) | N(4)-Mn(1)-N(3) | 84.33(7) |
| N(2)-Mn(1)-N(3) | 96.34(7) | N(4)-Mn(1)-N(1) | 95.19(7) |
| N(2)-Mn(1)-N(1) | 84.13(7) | N(3)-Mn(1)-N(1) | 178.89(8) |
| N(4)-Mn(1)-N(5) | 93.32(8) | N(2)-Mn(1)-N(5) | 87.26(8) |
| N(3)-Mn(1)-N(5) | 87.56(7) | N(1)-Mn(1)-N(5) | 93.47(7) |
| N(5)-Mn(1)-N(8) | 178.85(7) | N(6)-N(5)-Mn(1) | 141.21(17) |
| N(7)-N(6)-N(5) | 178.7(2) | C(3)-C(2)-C(1) | 117.3(2) |
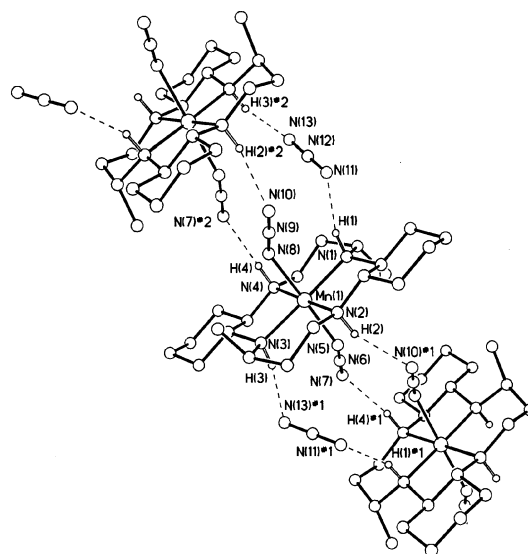


**Figure 3**. View of hydrogen bond systems between the molecular units in $[Mn(N_3)_2(\mathbf{L})]N_3 \cdot 2H_2O$ (**3**).

96.34(7)°) are larger than those of the five-membered chelate rings (84.33(7)° and 84.13(7)°). The manganese-nitrogen (axial azido) distances of 2.148(2) Å and 2.176(2) Å can be compared to that found in *trans*-$[Mn(N_3)_2(\mathbf{L1})]ClO_4$ (Mn-N = 2.171(3) Å).[8b] Again, the strong tetragonal distortion in **3** can be attributed to the well-known Jahn-Teller theorem.[11] In this connection it is interesting to compare the structural parameters around chromium(III) ion for *trans*-$[Cr(N_3)_2(\mathbf{L1})]ClO_4$, in which the average Cr-N (macrocycle) and Cr-N (axial azido) distances are 2.062(4) Å and 1.977(4) Å, respectively.[12] The opposite trend is observed in **3**, indicating that the elongated octahedron along the $N_3$-Mn-$N_3$ direction is due to the Jahn-Teller distortion. Two kinds of hydrogen bonding are observed in **3**. One is between the azido ligand coordinated to the manganese ion and the secondary amine hydrogen atoms of macrocycle, the other is between the counter anion, $N_3^-$, and the rest of the secondary amine hydrogen atoms, resulting in an infinite linear chain between each molecular unit (Figure 3). The hydrogen bonding parameters in **2** and **3** are listed in Table 4 and Table 5, respectively.

The infrared spectrum of **2** displayed bands at 3357 cm$^{-1}$ and 3269 cm$^{-1}$, which is attributable to O-H stretchings. Bands at 1650 cm$^{-1}$ and 1633 cm$^{-1}$ were assignable to H-O-H bending vibrations of the water molecules; however, it is hard to tell their origin, *i.e.*, the lattice or coordinated, due to high sensitivity to their surroundings.

The infrared spectrum of **3** contains strong absorptions at 2070 cm$^{-1}$ and 2016 cm$^{-1}$ due to antisymmetric stretchings of $N_3$ along with a symmetric stretching band at 1354 cm$^{-1}$. Weak absorptions at 3390 cm$^{-1}$ and 3058 cm$^{-1}$ were assigned to O-H (water) and N-H (secondary nitrogen) stretchings, respectively. H-O-H bending vibrations were found at ~1630 cm$^{-1}$.

Electronic spectra of **1**, **2**, and **3**, which were obtained by the diffuse reflectance method, are depicted in Figure 4.

**Table 4**. Hydrogen Bonds for *trans*-[Mn(H$_2$O)$_2$(**L**)]Cl$_3$ · 2H$_2$O · 0.5HCl(**2**) [(Å) and (°)]

| D-H···A | d(D-H) | d(H···A) | d(D···A) | <(DHA) |
|---|---|---|---|---|
| N(1)-H(1A)···Cl(1) | 0.86(3) | 2.39(3) | 3.2516(17) | 175(2) |
| N(2)-H(2C)···Cl(1)#2 | 0.82(2) | 2.58(2) | 3.3384(17) | 156(2) |
| O(1)-H(1O)···Cl(1) | 0.80(3) | 2.26(3) | 3.0468(17) | 168(3) |
| O(1)-H(2O)···Cl(2) | 0.74(3) | 2.13(3) | 2.8664(19) | 169(3) |

Symmetry transformations used to generate equivalent atoms: #1 -x+1, -y, -z+1. #2 x-1, y, z

**Table 5**. Hydrogen Bonds for *trans*-[Mn(N$_3$)$_2$(**L**)]N$_3$ · 2H$_2$O (**3**) [(Å) and (°)]

| D-H···A | d(D-H) | d(H···A) | d(D···A) | <(DHA) |
|---|---|---|---|---|
| N(1)-H(1)···N(11) | 0.93 | 2.06 | 2.947(3) | 158.9 |
| N(2)-H(2)···N(10)#1 | 0.93 | 2.24 | 3.124(3) | 159.2 |
| N(3)-H(3)···N(13)#1 | 0.93 | 2.09 | 2.997(3) | 165.5 |
| N(4)-H(4)···N(7)#2 | 0.93 | 2.11 | 3.024(3) | 166.0 |

Symmetry transformations used to generate equivalent atoms: #1 x, -y+3/2, z-1/2. #2 x, -y+3/2, z+1/2
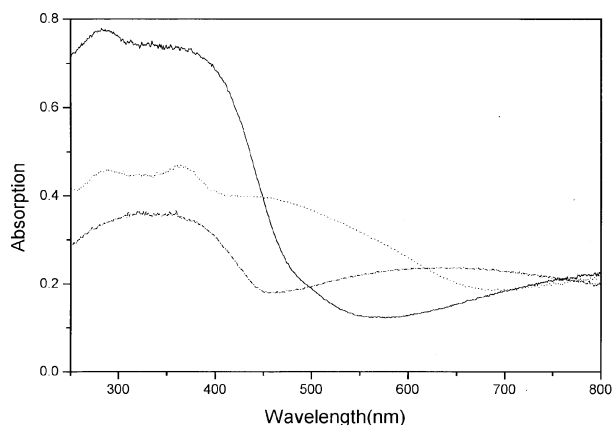


**Figure 4**. Solid state electronic absorption spectra of **1** ( — ), **2** (-·-·-), and **3** ( ······ ) in BaSO$_4$ by diffuse reflectance method at room temperature.

Qualitatively all the complexes are similar in shape, indicating similar Mn-ligand environments.

All the spectra taken over the range 250-800 nm are composed of strong broad bands at ~250-400 nm. These are tentatively assigned to ligand to metal charge transfer transitions associated with the axially ligating donors. In **2**, the d-d transitions at 620 nm in the visible region of the spectrum is believed to be a composite of the three possible transitions $d_{xy}$, $d_{xz}$, $d_{yz} \rightarrow d_{x^2-y^2}$. In **3**, the strong broad band over the range 450-550 nm is probably $\pi$-$\pi^*$ transitions of coordinated azido ligands in nature.[8b] The expected $d_{z^2} \rightarrow d_{x^2-y^2}$ transitions arising from the tetragonal splitting of the formally octahedral $e_g$ orbitals were not observed in the visible region in any of the three complexes.

**Supplementary Material Available**. Full crystal data and structure refinement details, atomic coordinates and equivalent isotropic displacement parameters, full interatomic distances and angles, anisotropic displacement parameters, hydrogen coordinates and isotropic displacement parameters, listings of observed and calculated structure factor tables, and hydrogen bond parameters for **2** and **3** are available from Ju Chang Kim.

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