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# Synthesis and Structural Properties of the Binary Framework C–N Compounds of Be, Mg, Al, and Tl

Darrick Williams, Brett Pleune, Kurt Leinenweber, and J. Kouvetakis[1]

*Department of Chemistry, Arizona State University, Tempe, Arizona 85287*

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**The synthesis of crystalline $Be(CN)_2$ and $Mg(CN)_2$ has been demonstrated and X-ray diffraction studies indicate simple-cubic structures with four-coordinate metal atoms surrounded by an average of two N and two C atoms. The symmetry of $Be(CN)_2$ is $Pn\bar{3}m$, $a = 5.339(1)$ Å, $Z = 2$. The symmetry of $Mg(CN)_2$ is also $Pn\bar{3}m$, $a = 6.122(1)$ Å, $Z = 2$. A thallium cyanide with composition $Tl(CN)_2$ was prepared and was shown to have a similar simple-cubic structure with $a = 6.660(1)$ Å. On the basis of the X-ray diffraction pattern, IR spectra, and combustion analysis, this material is assigned the formula $Tl^{I}Tl^{III}(CN)_4$. Crystalline $Al(CN)_3$ with simple-cubic structure has been prepared for the first time. Rietveld refinement indicated that the structure incorporates CN groups with orientational disorder in a Prussian-blue-like octahedral network. $^{27}$Al NMR spectroscopy confirmed C,N disorder in cubic $Al(CN)_3$. The symmetry for $Al(CN)_3$ is $Pm\bar{3}m$, $a = 5.205(1)$ Å.** © 2001 Academic Press

***Key Words:*** **main-group cyanides; Prussian blue; framework structures.**

## INTRODUCTION

Despite the great interest in cyanides in recent years (1) there are still some surprising gaps of knowledge concerning main-group element binary cyanides, including those of beryllium, magnesium, aluminum, and thallium. Recent work on development of superhard materials and related refractory ceramics has stimulated interest in synthesis of cyanides particularly those that are isoelectronic to diamond and incorporate light elements such as Li, Be, B, C, N, Mg, Al, and Si (2–4). The stoichiometric cyanides $Be(CN)_2$ and $Mg(CN)_2$ have an average number of four valence electrons per atom and are attractive precursors for high-pressure synthesis of dense tetrahedral materials of the same stoichiometry that have properties related to those of diamond.

A previously reported cyanide of beryllium with composition close to $Be(CN)_2$ was not characterized to any extent (5). This compound was obtained from the reaction of $Be(CH_3)_2$ with HCN and was only described as a polymeric colorless solid. Little is known about $Mg(CN)_2$, which was purportedly obtained from the reaction of finely divided magnesium with HCN in liquid ammonia. This synthesis was reported in a 1947 U.S. patent (6). In this study we describe a practical synthetic method for crystalline $Mg(CN)_2$ and $Be(CN)_2$ and report characterization of their structures using powder X-ray diffraction. Both compounds form diamond-like tetrahedral networks related to that of $Zn(CN)_2$.

Synthesis of octahedrally coordinated main-group analogs with composition $M(CN)_3$ (where $M$ is a group 13 element: B, Al, Ga, In, or Tl) that have large pores in the structure is also of interest because these systems may posses interesting zeolitic and adsorption properties. Known examples of such materials include the binary $Ga(CN)_3$, and $In(CN)_3$ cyanides, which have Prussian-blue-type structures that incorporate large cavities in the center of the simple-cubic cell (7, 8). Very recently, crystalline $B(CN)_3$ was isolated for the first time as a molecular Lewis acid–base complex with bases such as $N(CH_3)_3$ and $Si(CH_3)_3CN$ (4). The existence of crystalline $Al(CN)_3$ and $Tl(CN)_3$, however, has not been established to date. In the current study we focus on preparation and structural characterization of the missing $Al(CN)_3$ and related Tl compounds to complete the entire family of binary $M(CN)_3$ compounds of group 13 elements. Previous attempts to prepare aluminum cyanide have produced only uncharacterized materials with compositions purportedly close to the desired $Al(CN)_3$ product (9, 10). TlCN is the only known and well characterized cyano compound of Tl and has a disordered CsCl-type structure (11).

## RESULTS AND DISCUSSION

The synthesis of $M(CN)_2$ ($M =$ Be, Mg) utilizes a common reagent, $(CH_3)_3SiCN$, which undergoes metathesis with $MCl_2$ to produce the desired composition at low

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[1] To whom correspondence should be addressed.

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temperatures in nonaqueous solvents (Eq. [1]):

$$MCl_2 + 2(CH_3)_3SiCN \rightarrow M(CN)_2 + 2(CH_3)_3SiCl$$
$$M = \text{Be, Mg.} \qquad [1]$$

$Be(CN)_2$ was initially amorphous and an annealing step at 500°C was necessary to obtain crystalline material. The preparation of crystalline $Mg(CN)_2$ also required a brief annealing step at 375°C. Pure $Be(CN)_2$ is a colorless, air-stable solid which is thermally stable up to 700°C. $Mg(CN)_2$ is also colorless and highly moisture sensitive. The IR spectrum of $Be(CN)_2$ is very simple and shows only two peaks: $\nu$ C–N at 2233 $cm^{-1}$ and $\nu$ $M$–CN at 756 $cm^{-1}$. The corresponding peaks for $Mg(CN)_2$ appear at 2197 and 492 $cm^{-1}$, respectively. The absence of any vibrational modes above 3000 $cm^{-1}$ in the IR spectra of both compounds indicates that they do not contain any CH, NH, or OH contamination.

The X-ray diffraction pattern of $Be(CN)_2$ revealed a simple-cubic structure with a lattice parameter $a = 5.339(1)$ Å. Rietveld refinement using a model similar to that of $Zn(CN)_2$ with $Pn\bar{3}m$ symmetry gave an average Be–(C, N) bond length of 1.718(1) Å and a C–N bond length of 1.187(1) Å, which compare well with reported values (4). X-ray diffraction shows that $Mg(CN)_2$ has the same simple-cubic structure with $a = 6.122$ (1) Å. The structure was refined in $Pn\bar{3}m$ and the bond lengths of C–N and Mg–(C,N) were found to be 1.085(7) and 2.108(4) Å, respectively. The observed and calculated profiles for $Be(CN)_2$ and $Mg(CN)_2$ are shown in Figs. 1 and 2, respectively. Atomic positions, displacement factors, and a summary of Rietveld refinement for these compounds are shown in Tables 1 and 2, respectively. There are no ordering reflections in the X-ray patterns of either compound (for instance, (100) is absent in both patterns). Consequently, disorder of the C–N groups results in an average structure in which $M(C,N)_4$ ($M$ = Be, Mg) tetrahedra are joined at the vertices by C–N bonds. This is in contrast to the ordered arrangement observed in the structurally related $LiB(CN)_4$ material, which has the Li atoms exclusively bonded to N atoms and the B atoms bonded to C atoms to form two interpenetrating lattices of $LiN_4$ and $BC_4$ tetrahedra joined by C–N bonds (4). A sketch of the structure of $Mg(CN)_2$ and $Be(CN)_2$ is shown in Fig. 3.

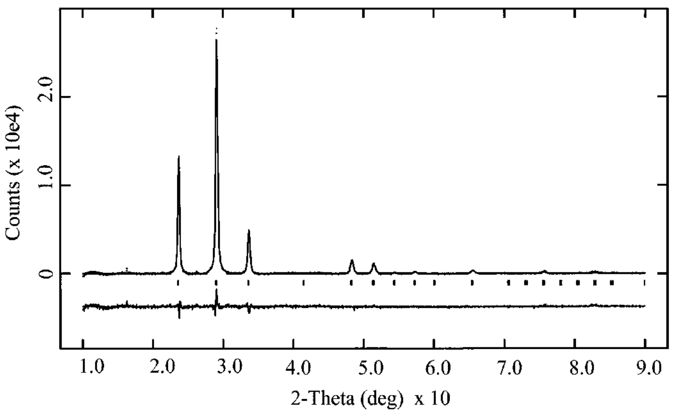

**FIG. 1.** X-ray powder diffraction profile for $Be(CN)_2$. The top line is the experimental data and the bottom one is the difference between the experimental and calculated data on the same scale.

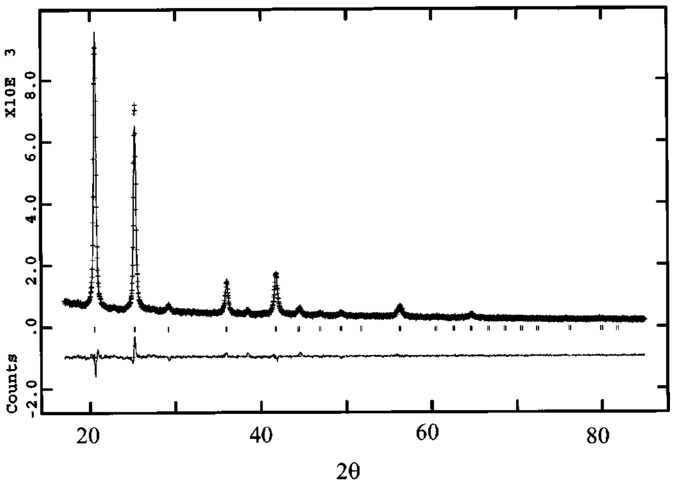

**FIG. 2.** X-ray diffraction profile fit for $Mg(CN)_2$. The data shown as + and the tick marks are the Bragg positions. The solid line is the calculated profile and the difference curve is at the bottom on the same scale.

The synthesis of $Al(CN)_3$ was accomplished via a metathesis reaction involving interaction between of $LiAlCl_4$ and $(CH_3)_3SiCN$. The reaction proceeds essentially quantitatively according to

$$LiAlCl_4 + 3(CH_3)_3SiCN \rightarrow Al(CN)_3 + 3(CH_3)_3SiCl + LiCl. \qquad [2]$$

Removal of the volatiles from the reaction mixture gave a colorless residue that was extracted with THF to remove LiCl and yield the desired cyanide product. The compound

### TABLE 1
### Atomic Positions and Displacement Factors ($U$) for $Be(CN)_2$, and $Mg(CN)_2$ with $Pn\bar{3}m$ Symmetry and $Al(CN)_3$ with $Pm\bar{3}m$ Symmetry

| Atoms | Wyc. | $x$ | $y$ | $z$ | $U$(Å$^2$) |
|---|---|---|---|---|---|
| Be | 2$a$ | 0.25 | 0.25 | 0.25 | 0.064(3) |
| (C, N) | 8$e$ | 0.4358(1) | 0.4358(1) | 0.4358(1) | 0.103(3) |
| Mg | 2$a$ | 0.25 | 0.25 | 0.25 | 0.104(3) |
| (C, N) | 8$e$ | 0.4462(3) | 0.4462(3) | 0.4462(3) | 0.101(3) |
| Al | 1$a$ | 0.0 | 0.0 | 0.0 | 0.0423(1) |
| (C, N) | 6$e$ | 0.3882(4) | 0.0 | 0.0 | 0.0399(1) |

*Note.* The C, N positions are occupied by 0.5 C and 0.5 N.

**TABLE 2**
**Summary of Rietveld Refinement for $Mg(CN)_2$, $Be(CN)_2$, and $Al(CN)_3$**

| | $Mg(CN)_2$ | $Be(CN)_2$ | $Al(CN)_3$ |
|---|---|---|---|
| Space group | $Pn\bar{3}m$ | $Pn\bar{3}m$ | $Pm\bar{3}m$ |
| Unit cell parameter (Å) | $a = 6.122(1)$ | $a = 5.339(1)$ | $a = 5.205(3)$ |
| Volume (Å$^3$) | 229.45(1) | 151.2(1) | 141.09(24) |
| No. of reflections | 22 | 46 | 46 |
| No. of refined parameters | 14 | 15 | 17 |
| $\chi^2$ | 1.82 | 6.87 | 2.485 |
| $R_p$ | 4.72 | 4.54 | 3.30 |
| $R_{wp}$ | 5.99 | 6.64 | 4.36 |

was initially amorphous but it crystallized upon heating at temperatures in excess of 400°C. The pure material is a colorless solid, stable in air, and insoluble in polar organic solvents. The IR spectrum reveals strong absorptions at 2220 and 530 $cm^{-1}$, corresponding to $\nu$ C–N and $\nu$ Al–(C–N), respectively. These values compare well with the corresponding values of the related aluminum cyanide $[(CH_3)_2Al(CN)]_4$ which were observed at 2224 and 510 $cm^{-1}$, respectively (5). The X-ray diffraction pattern (Fig. 4) revealed a simple cubic unit cell with $Pm\bar{3}m$ symmetry and $a = 5.205(1)$ Å. Rietveld refinement indicated a disordered structure with respect to the orientation of the C, N ligands. The Al atoms in the structure occupy the cell corners and are octahedrally coordinated by C, N ligands, which are aligned at the cell edges (Fig. 5). The C–N bond length was found to be 1.164(5) Å, a value normal for metal cyanides, and the Al–(C,N) distance is 2.021(2) Å. A summary of the crystallographic data for $Al(CN)_3$ is shown in Tables 1 and 2.

Further evidence for the C,N static disorder in $Al(CN)_3$ is provided by the solid-state $^{27}$Al NMR spectrum of the compound which reveals a multiplet consisting of at least seven narrow and closely spaced peaks as shown in Fig. 6. This pattern indicates the presence of seven possible Al sites, which are likely to be created by the orientational static disorder of bridging cyanides in the structure. The seven site possibilities are (Al)C6, (Al)C5N, (Al)C4N2, (Al)C3N3, (Al)C2N4, (Al)CN5, and (Al)N6 and correspond to the number of possible ways of arranging the C and N atoms in an octahedron. We speculate that the resonances with peak maxima at $-37.95$, $-39.59$, $-41.46$, $-43.81$, $-47.32$, $-50.84$, and $-54.35$ ppm correspond to those sites, respectively. As illustrated in the $^{27}$Al NMR spectrum in Fig. 6 the resonances downfield are better resolved than those upfield; i.e., the peak separation increases as one moves from Al sites predominately surrounded by C (downfield) to those surrounded by N (upfield). The $^{27}$Al NMR spectrum is consistent with the reported $^{13}$Cd NMR spectrum of $Cd(CN)_2$, which shows five resonances corresponding to the five possible distributions of C and N about Cd in a $Cd(C,N)_4$ tetrahedron (12). The $CdC_4$ site in the disordered $Cd(CN)_2$ structure was assigned the largest downfield shift and the $CdN_4$ the smallest. The separation between peaks also decreases downfield in the NMR spectrum.

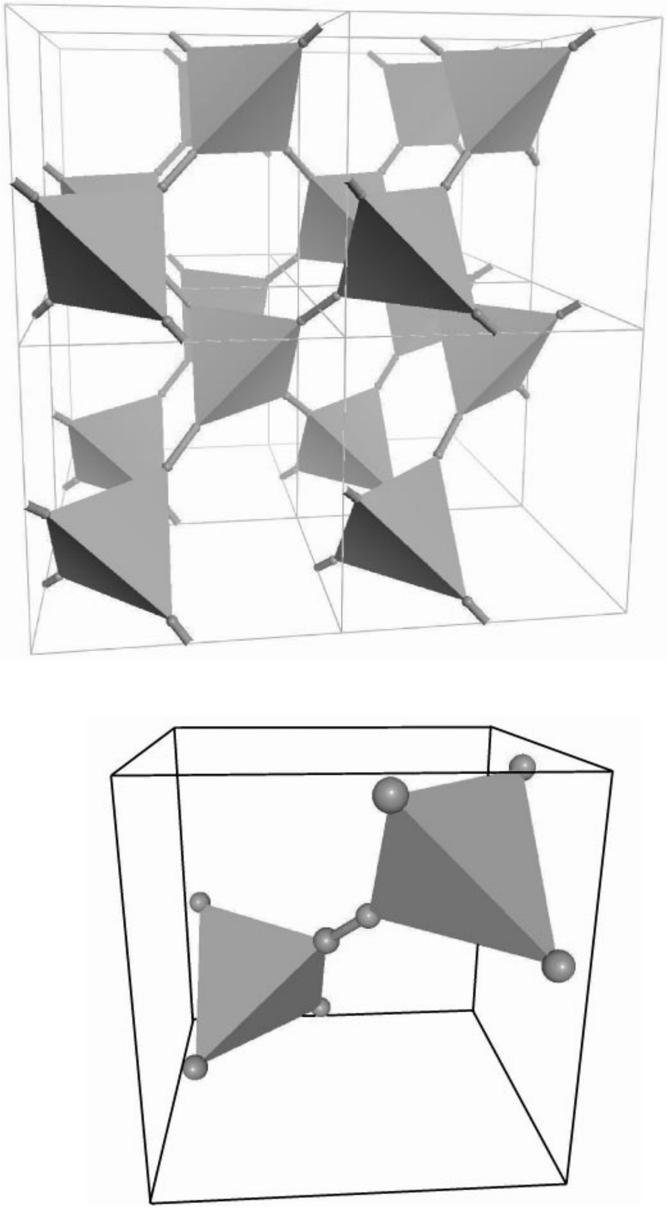

**FIG. 3.** (Top) Schematic of structure of $M(CN)_2$ ($M$ = Be, Mg) shown as $M(C,N)_4$ tetrahedra. (Bottom) Unit cell of $M(CN)_2$.

The synthesis of the tricyanide of thallium was attempted by reaction of $TlCl_3$ with a stoichiometric amount of $(CH_3)_3SiCN$ in ether. A colorless solid was isolated from this reaction and was identified by IR spectroscopy to be a cyanide. The vibrational spectrum showed a broad absorption at 392 $cm^{-1}$, corresponding to $\nu$ Tl–(C,N), and two

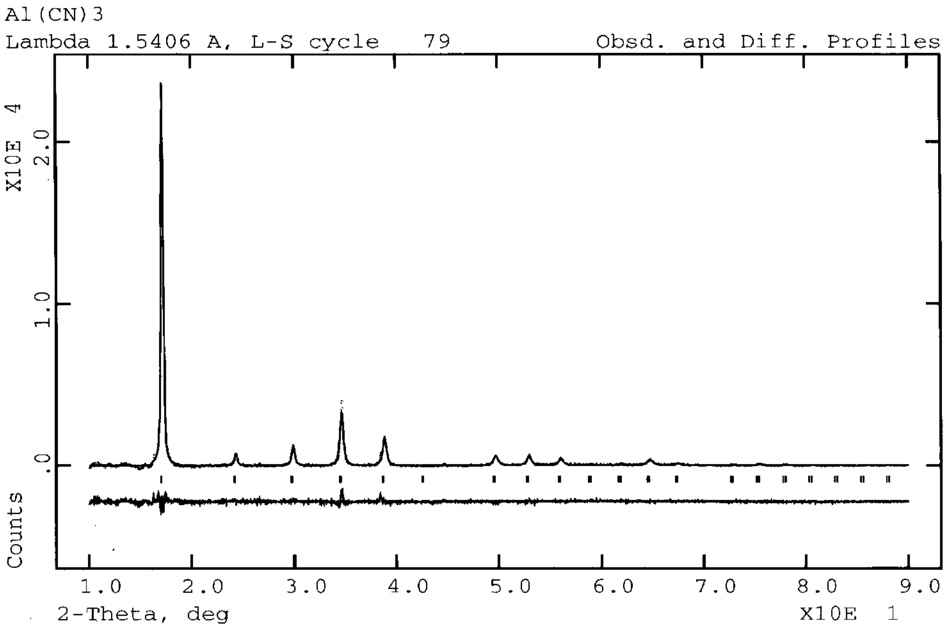

**FIG. 4.** X-ray diffraction profile fit for $Al(CN)_3$. The top line is the experimental data and the bottom one is the difference between the experimental and calculated data on the same scale.

closely spaced and sharp C–N absorptions at 2209 and 2198 $cm^{-1}$. A comparison of these stretches with that of $(CH_3)_2TlCN$ (2100 $cm^{-1}$) (5), in which C–N appears to be non bridging, shows an increase in C–N stretching frequency. Since bridging C–N groups are known to exhibit higher stretching frequencies (7, 13), we attribute both of the 2209 and 2198 $cm^{-1}$ frequencies to stretching modes of bridging C–N groups. The absence of any absorptions above 3000 $cm^{-1}$ is indicative that the solid did not contain any CH, NH, and OH impurity groups. Elemental analysis for C, H, N, and Cl confirmed that the material was free of H and Cl impurities and also indicated a composition close to $TlC_2N_2$.

The X-ray diffraction pattern was very simple and suggested single-phase material. All diffraction data were indexed

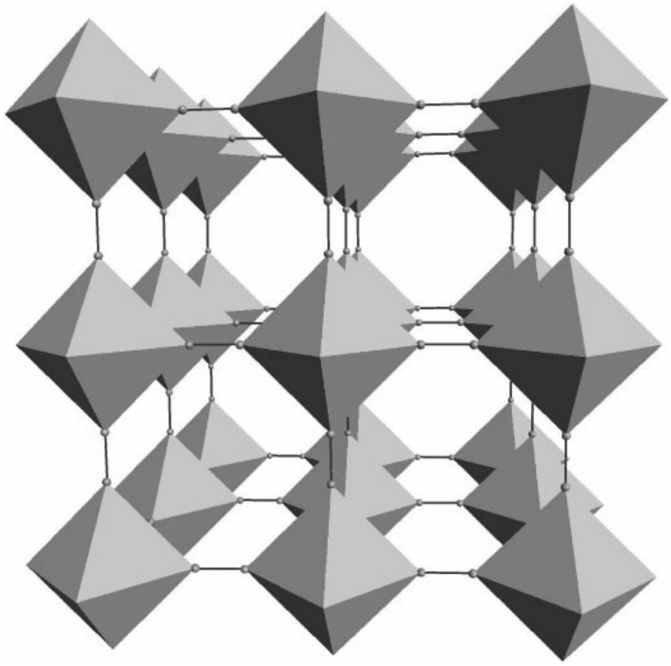

**FIG. 5.** Structure of $Al(CN)_3$ shown as interconnected $Al(C,N)_6$ octahedra. The Al atoms, in the centers of the octahedra, are surrounded by six (C,N) atoms (small spheres), which are shown to be linked by lines representing C–N bonds.

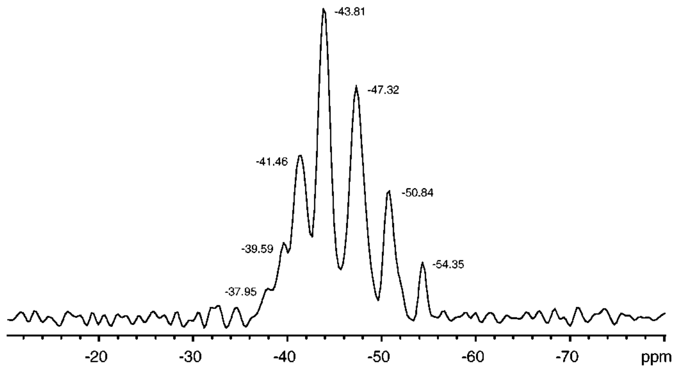

**FIG. 6.** Solid-state (magic angle spinning) $^{27}Al$ spectrum of $Al(CN)_3$ illustrating seven resonances. These suggest that Al in the structure is in seven different environments of (Al)C6, (Al)C5N, (Al)C4N2, (Al)C3N3, (Al)C2N4, (Al)CN5, and (Al)N6.

**TABLE 3**
**Observed and Calculated *d* spacings (Å) and Relative Intensities in the X-ray Diffraction Powder Pattern for $Tl(CN)_2$**

| *h* | *k* | *l* | $d_{obs}$ | $I/I_{o\ obs}$ | $d_{calc}$ | $I/I_{o\ calc}$ |
|---|---|---|---|---|---|---|
| 1 | 0 | 0 | | | 6.600 | < 1 |
| 1 | 1 | 0 | 4.662 | 100.0 | 4.666 | 100.0 |
| 1 | 1 | 1 | | | 3.810 | 2 |
| 2 | 0 | 0 | 3.282 | 15 | 3.300 | 12 |
| 2 | 1 | 0 | | | 2.970 | < 1 |
| 2 | 1 | 1 | 2.687 | 43 | 2.694 | 41 |
| 2 | 2 | 0 | 2.328 | 19 | 2.333 | 17 |
| 2 | 2 | 1 | | | 2.220 | < 1 |
| 3 | 1 | 0 | 2.087 | 14 | 2.087 | < 17 |
| 3 | 1 | 1 | | | 2.000 | < 1 |
| 3 | 1 | 1 | | | 2.000 | < 1 |
| 2 | 2 | 2 | 1.903 | 9 | 1.905 | 4 |
| 3 | 2 | 0 | | | 1.84 | < 1 |
| 3 | 2 | 1 | 1.761 | 19 | 1.764 | 20 |
| 3 | 3 | 0 | 1.551 | 8 | 1.555 | 8 |
| 4 | 2 | 0 | 1.477 | 7 | 1.476 | 20 |
| 3 | 3 | 2 | 1.406 | 8 | 1.407 | 3 |
| 4 | 2 | 2 | 1.356 | 6 | 1.347 | 3 |

*Note.* The small C, N contribution to $I/I_o$ calc has been included in the calculation.

by using a primitive cubic cell with $a = 6.660(1)$ Å. The results were consistent with a tetrahedral structure of $Pn\bar{3}m$ symmetry similar to that observed in the previously described $Be(CN)_2$ and $Mg(CN)_2$ compounds. The observed and calculated diffraction patterns for this topology are in good agreement, and the calculated and observed intensities of the X-ray lines are compared in Table 3. The X-ray analysis clearly points to a structure that consists of $Tl(C,N)_4$ tetrahedra joined at the vertices by bridging C–N groups to form a network that is isomorphic and compositionally analogous to the disordered $Cd(CN)_2$ phase of $Pn\bar{3}m$ symmetry. However, because of the high contrast between Tl and (C, N) it is not possible to tell whether the C, N atoms are ordered or disordered in this material. Based on the structural and the combustion analysis results we conclude that this material has a $Tl(CN)_2$ empirical formula and should incorporate the Tl cations in two different oxidation states, i.e., $Tl^{I}Tl^{III}(CN)_4$.

The existence of $Tl^{+3}$ and $Tl^{+1}$ cations in the lattice is also shown by the presence of the two C–N stretching modes at 2209 and 2198 $cm^{-1}$ in the IR spectrum, the higher frequency corresponding to $Tl^{3+}$–(C–N) and the lower to $Tl^{1+}$–(C–N) stretching modes. This assignment can be rationalized by the concept of backdonation of electron density from the metal into the $\pi^*$ (antibonding) orbital of the C–N ligand. Such backdonation would tend to be substantially higher from the less positive $Tl^{1+}$ than from the more positive $Tl^{3+}$ metal center. The net result should then be a lower bond order and thus a lower stretching frequency for the C–N bond in $Tl^{1+}$–(C–N) relative to that in $Tl^{3+}$–(C–N). The IR spectrum of $Tl(CN)_2$ also correlates well with the IR spectra of well-known transition metal cyanides with cations in two oxidation states. Such compounds have been shown in previous studies to exhibit two stretching C–N absorptions (14). It is worth noting that the tetrahedral coordination observed in $Tl^{I}Tl^{III}(CN)_4$ is not common for the oxidation state $Tl^{1+}$, although there are many examples of the oxidation state $Tl^{3+}$ in tetrahedral coordination (15). Another point to make is that the lattice parameter of $Tl^{I}Tl^{III}(CN)_4$ [6.660(1) Å] is one of the largest observed in binary $Zn(CN)_2$ structure types.

A previously reported material with formula close to $Tl(CN)_2$ was not characterized to any extent. The synthesis was carried out in aqueous media and the material was described to be stable in air. The anhydrous cyanide $Tl(CN)_2$ prepared using our method interacts readily with air and moisture. X-ray diffraction of samples exposed to air show conversion of the compound into a pollycrystalline powder of an unknown structure. Anhydrous $Tl(CN)_2$ also decomposes readily to TlCN and cyanogen gas (see Eq. [3]) with mild heating either under static or dynamic vacuum conditions.

$$Tl^{III}Tl^{I}(CN)_4 \rightarrow 2TlCN + (CN)_2. \qquad [3]$$

This facile elimination of CN resulting in reduction of $Tl^{3+}$ to form the more stable oxidation state $Tl^{1+}$ indicates that a solid-state $Tl(CN)_3$ cyanide with a Prussian-blue structure analogous to that of $Al(CN)_3$ will be very difficult to isolate as a stable phase at room temperature. Thallium (III) cyano complexes, however, with the general formula $Tl(CN)_n^{(3-n)+}$, where $n = 2$, 3, and 4, are known to exist in solution and their properties have been extensively investigated in recent studies (16, 17). This leads us to believe that stoichiometric $Tl(CN)_3$ might also exist as a soluble intermediate in route to $Tl(CN)_2$, according to our synthetic procedure summarized below:

$$TlCl_3 + 3(CH_3)_3SiCN \rightarrow \text{“}Tl(CN)_3\text{”} + 3(CH_3)_3SiCl \qquad [4]$$

$$\text{“}Tl(CN)_3\text{”} \rightarrow Tl(CN)_2 + 1/2(CN)_2. \qquad [5]$$

We attempted to isolated $Tl(CN)_3$ as a Lewis acid–base complex with a wide variety of Lewis bases but our efforts were unsuccessful.

## SUMMARY

The simple compounds $Al(CN)_3$, $Be(CN)_2$, and $Mg(CN)_2$ have been prepared by use of a novel synthetic method, and their structures have been determined by X-ray powder diffraction. $Al(CN)_3$ has an octahedral Prussian-blue-type structure and it is shown to have C, N disorder by $^{27}$Al MAS-NMR spectroscopy. $Be(CN)_2$ and $Mg(CN)_2$ form diamond-like tetrahedral networks with twofold interpenetration similar to that observed in the classical $Zn(CN)_2$ and $Cd(CN)_2$ compounds. The search for $Tl(CN)_3$, analogous to $Al(CN)_3$, has led to the synthesis of the mixed-oxidation phase $Tl^{I}Tl^{III}(CN)_4$. X-ray powder diffraction suggests that this material is isostructural to $Zn(CN)_2$.

## EXPERIMENTAL

*General considerations.* All preparations were performed under prepurified $N_2$ using standard Schlenk and drybox techniques. Solvents were dried and distilled prior to use. The FTIR spectra were recorded on a Nicolet-Magna-IR 550 spectrometer from Nujol and fluorolube mulls. $^{27}$Al NMR spectra were recorded on a Varian Unity 500 spectrometer and were referenced to the resonance of a 1 M solution of $AlCl_3$. Samples for X-ray powder diffraction were loaded in an environmental cell with a Kapton window and the data were collected on a Siemens D5000 X-ray diffractometer using Cu$K\alpha$ radiation. The refined data consisted of a single scan with 0.02° steps at a rate of 0.67° per minute. Refinement of the data was performed using the Generalized Structural Analysis System (GSAS), a Rietveld refinement code (18). $(CH_3)_3SiCN$ (Aldrich 98%) was purified by distillation prior to use. $BeCl_2$ (Cerac 99.5%), $MgCl_2$ (Aldrich 98%), $AlCl_3$ (Aldrich 99.98%), and $TlCl_3$ (Alfa) were used as received.

*Synthesis of Be(CN)$_2$.* $(CH_3)_3SiCN$ (2.9 g, 0.029 mol) was added dropwise to a stirring suspension of $BeCl_2$ (1.0 g, 0.013 mol) in butyl ether (30 mL) at $-20$°C. The mixture was warmed to room temperature, stirred for 18 h, then heated to 100°C for an additional 12 h. The mixture was filtered and the resulting solid was dried and then heated to 500°C for 48 h under vacuum to yield a colorless solid. Yield: 0.554 g (70%). IR (Nujol, cm$^{-1}$): 2233 (m), 756 (s, br). The observed and calculated X-ray diffraction patterns of $Be(CN)_2$ are shown in Fig. 1. A structure determination summary is shown in Table 2.

*Synthesis of Mg(CN)$_2$.* $(CH_3)_3SiCN$ (1.3 g, 0.013 mol) was added dropwise to a stirring suspension of $MgCl_2$ (0.5 g, 0.005 mol) in butyl ether (30 mL) at room temperature. The mixture was refluxed for 18 h and filtered, and the resulting solid was dried in vacuum. The product was combined with $(CH_3)_3SiCN$ (1.3 g, 0.013 mol) and the mixture was heated in a closed Schlenk tube under an atmosphere of nitrogen at 200°C for about 12 h. The resulting material was annealed at 375°C for 4 h to yield $Mg(CN)_2$ as a colorless solid. Yield: 0.240 g (63%). IR (nujol, cm$^{-1}$): 2197 (m), 492 (s, br). The observed and calculated X-ray diffraction patterns of $Mg(CN)_2$ are shown in Fig. 2, and a structure determination summary is shown in Table 2.

*Synthesis of Al(CN)$_3$.* $(CH_3)_3SiCN$ (2.227 g, 0.0225 mol) was added dropwise to a stirring solution of $LiAlCl_4$ (0.5 g, 0.005 mol) in 30 mL of dry ether at $-78$°C. The reaction was warmed to 22°C and a colorless precipitate was immediately formed. After stirring for an additional 12 h the precipitate was collected, dried under vacuum, and examined by powder X-ray diffraction. The powder diffraction pattern revealed crystalline LiCl and also indicated the presence of an amorphous component that was identified by IR spectroscopy to be a cyanide ($\nu$ C–N 2220 cm$^{-1}$). The product was annealed at 400°C under nitrogen for 18 h to yield crystalline $Al(CN)_3$ ($\nu$ C–N 2220 cm$^{-1}$) and LiCl. Pure $Al(CN)_3$ was isolated by extraction of LiCl from the mixture with warm $H_2O$ or tetrahydrofuran. A structure determination summary is shown in Table 2.

*Synthesis of Tl(CN)$_2$.* An ether solution of $(CH_3)_3SiCN$ (1.851 g, 0.0187 mol) was added dropwise to a stirring solution of $TlCl_3$ (1.21 g, 0.0060 mmol) in 20 mL of ether at 0°C. The solution was then heated under reflux for 24 h, after which time its total volume was reduced to 15 mL, and it was stored for several days at $-5$°C. During this time a colorless solid formed. This material was isolated by filtration and it was washed with a hot hexane/benzene solution. It was dried for several hours under vacuum. Calcd for $Tl(CN)_2$: C, 9.4; H, 0; N, 12.2; Cl, 0. Found C, 10.5; H, $<0.05$; N, 11.0; Cl, 0.80.

## ACKNOWLEDGMENTS

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