Synthetic Routes to Ga(CN)$_3$ and MGa(CN)$_4$ (M = Li, Cu) Framework Structures

Louis C. Brousseau, Darrick Williams, J. Kouvetakis,* and M. O'Keeffe

Contribution from the Department of Chemistry and Biochemistry, Arizona State University, Tempe, Arizona 85287

Received January 21, 1997[⊗]

Abstract: Ga(CN)$_3$ has been prepared for the first time with a new method for preparation of inorganic cyanides. Pure crystalline material is formed by reaction of Cl$_2$GaN$_3$ with SiMe$_3$CN via elimination of SiMe$_3$N$_3$ and SiMe$_3$Cl. Reaction of GaCl$_3$ with SiMe$_3$CN also provides Ga(CN)$_3$. A new convenient route to GeMe$_3$CN and SnMe$_3$CN is described, but reactions of GaCl$_3$ with these compounds result in Lewis acid−base adducts. The composition of Ga(CN)$_3$ was confirmed by spectroscopic and elemental analysis. Quantitative X-ray powder diffraction was used to refine the cubic structure, which has CN groups with orientational disorder in a Prussian-blue-like network structure. The symmetry is $Pm\bar{3}m$, a = 5.295(2) Å. Ga is octahedrally surrounded by on average three C and three N atoms with a Ga−(C,N) bond length of 2.072(2) Å, and the C−N bond length is 1.148(1) Å. LiGa(CN)$_4$ was prepared by reaction of Ga(CN)$_3$ with LiCN and was characterized by quantitative X-ray diffraction. The symmetry is $P\bar{4}3m$, a = 5.874(2) Å, and the structure consists of LiN$_4$ and GaC$_4$ tetrahedra linked by C−N bonds to form two interpenetrating networks of the Zn(CN)$_2$ type. CuGa(CN)$_4$ has a similar structure with a = 5.729(5) Å, but Cu,Ga and/or C,N disorder cannot be ruled out.

Introduction

Cyanide inclusion compounds have attracted considerable interest since the discovery of the "Hofmann compounds" one hundred years ago.[1] In particular there has been much recent interest[2] in compounds containing open frameworks with stoichiometry M(CN)$_2$ with M having a d^{10} configuration in its normal oxidation state, such as Cu(I) and Zn(II),[2a,b] and particularly Cd(II).[2a,c−i] Hydrated transition metal cyanide compounds also form well-known structures[3] with open frameworks of ideal stoichiometry M(CN)$_3$ and with water and additional cations in the cavities; the classical examples are pigments such as Prussian blue, which has been formulated[3c] as Fe$_{2−x}$(CN)$_6$·nH$_2$O. The Cr analogs[3d,e] with compositions Cr$_{2.4}$(CN)$_6$·6.1H$_2$O and Cr$_{2.1}$(CN)$_6$·2.8 H$_2$O are interesting high-T_c ferrimagnets. Anhydrous CdPd(CN)$_6$ with an empty M(CN)$_3$ framework has been described[4] and ScIn(CN)$_6$ is believed to be isostructural.[5] Except for brief reports (without structures)

of In(CN)$_3$[6] and alkylcyano complexes of Ga and In,[7] no cyanides of column 13 elements have been described.[8] Here we report the synthetic routes to, and characterization of, crystalline anhydrous Ga(CN)$_3$, which has an empty Prussian blue framework structure (Figure 1). LiGa(CN)$_4$, with a structure consisting of GaC$_4$ and LiN$_4$ tetrahedra linked together by C−N bonds to form a simple cubic structure (Figure 2) similar to that of Zn(CN)$_2$, has also been prepared and characterized. CuGa(CN)$_4$ is shown to have the same structure. The synthetic routes to these new phases are simple and are expected to lead to a general preparation of other anhydrous cyanide frameworks.

Results and Discussion

Synthesis of Ga(CN)$_3$ by Reaction of Me$_3$SiCN and Cl$_2$GaN$_3$. We initially prepared Ga(CN)$_3$ by an unusual synthetic route involving direct interaction of azidodichlorogallane, Cl$_2$GaN$_3$, with Me$_3$SiCN. This reaction takes place via displacement of the azide group and the chlorine ligands by cyanides at room temperature according to the procedure summarized in reaction 1.

$$3Me_3SiCN + Cl_2GaN_3 \rightarrow$$
$$2Me_3SiCl + Me_3SiN_3 + Ga(CN)_3 \quad (1)$$
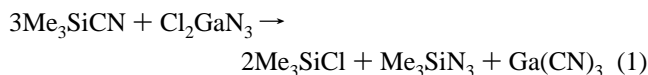
The Me$_3$SiCl and Me$_3$SiN$_3$ byproducts were readily removed by vacuum distillation, and the residue was collected at nearly quantitative yield to give Ga(CN)$_3$ as a colorless solid that is soluble in highly polar solvents such as tetrahydrofuran (THF)

⊗ Abstract published in *Advance ACS Abstracts,* June 1, 1997.
(1) (a) Hofmann, K. A.; Küspert, F. A. *Z. Anorg. Allg. Chem.* **1897**, *15*, 204. Reviews of early work are by: (a) Iwamoto, T. In *Inclusion Compounds*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D.) Academic Press: New York, 1984; Vol. 1, pp 29−57. Oxford University Press: Oxford, 1991; Vol 5, pp 172−212. (b) Dunbar, K. R.; Heintz, R. A. *Progress in Inorganic Chemistry* **1996**, *45*, in press.
(2) Some recent papers, which give references to earlier work are: (a) Hoskins, B. F.; Robson, R. *J. Am. Chem. Soc.* **1990**, *102*, 1546−1554. (b) Bu, X.; Gier, T. E.; Stucky, G. D. *Acta Crystallogr.* **1996**, *C52*, 14−16. (c) Kitazawa, T.; Nishikori, S.; Kuroda, R.; Iwamoto, T. *Chem. Lett.* **1988**, 1729−1732. (d) Abrahams, B. F.; Hoskins, B. F.; Liu, J.; Robson, R. *J. Am. Chem. Soc.* **1991** *113*, 3045−3051. (e) Kitazawa, T.; Nishikori, S.; Yamagishi, A.; Kuroda, R.; Iwamoto, T. *J. Chem. Soc., Chem. Commun.* **1992**, 413−415. (f) Nishikiori, S.; Ratcliffe, C. I.; Ripmeester, J. A. *J. Am. Chem. Soc.* **1992**, *114*, 8590−8595. (g) Kim, J.; Whang, D.; Lee, J. I.; Kim, K. *J. Chem. Soc., Chem. Commun.* **1993**, 1400−1402. (h) Yuge, Y.; Iwamoto, T. *J. Chem. Soc. Dalton Trans.* **1993**, 2841−2847. (i) Kim, J.; Whang, D.; Koh, Y.-S.; Kim, K. *J. Chem. Soc., Chem. Commun.* **1994**, 637−638.
(3) (a) Ludi, A.; Güdel, H.-U. *Helv. Chim. Acta* **1968**, *51*, 2006−2016. (b) Ludi, A.; Güdel, H.-U.; Rüegg, M. *Inorg. Chem.* **1970**, *9*, 2224−2227. (c) Herren, F.; Fischer, P.; Ludi, A.; Haelg, W. *Inorg. Chem.* **1980**, *19*, 956−949. (d) Mallah, T.; Thiébaut, S.; Verdaguer, M.; Viellet, P. *Science* **1993**, *262*, 1554−1557. (e) Sato, O.; Iyoda, T.; Fujishima, A.; Hashimoto, K. *Science* **1996**, *271*, 49−51.
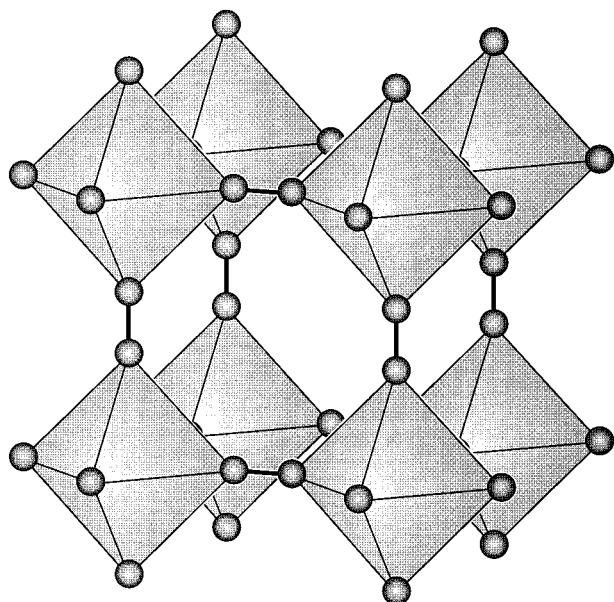
(4) Buser, H.-J.; Ron, G.; Ludi, A.; Engel, P. *J. Chem. Soc., Dalton Trans.* **1974**, 2473−2474.
(5) Hulliger, F.; Vetsch, H. , *Eur. J. Solid State Chem.* **1996**, *33*, 33−39.
(6) Goggin, P. L.; McColm, I. J.; Shore, R. *J. Chem. Soc. A* **1966**, 1314−1317 (1966).
(7) Müller, P.; Schmock, F.; Klopsch, A.; Dehnicke, K. *Chem. Ber.* **1975**, *108*, 664−672.
(8) Downs, A. J., Ed. *Chemistry of Aluminium, Gallium, Indium and Thallium*, Blackie Academic and Professional, New York, 1993.

Figure 1. The structure of $Ga(CN)_3$. The octahedra of six (C,N) atoms (spheres) are shown connected by heavy lines representing C—N bonds.
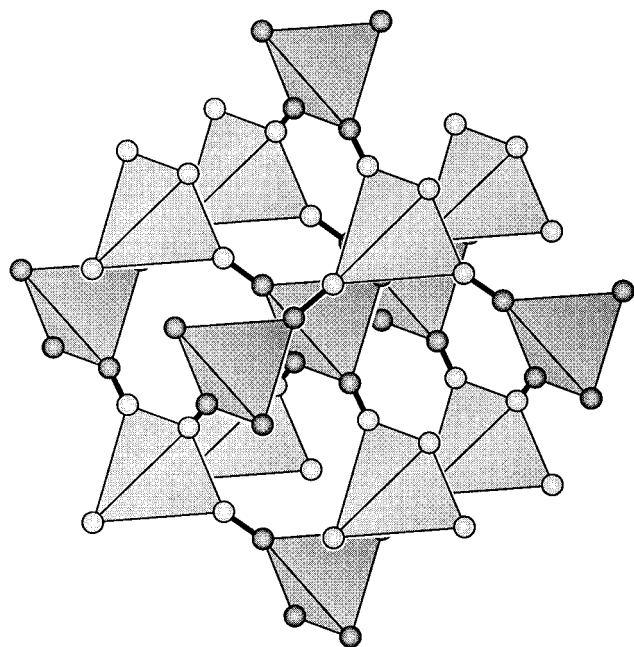

Figure 2. The structure of $LiGa(CN)_3$. The structure is shown as LiN_4 tetrahedra (lighter) and GaC_4 tetrahedra (darker) and the heavy lines are the C—N bonds.

and dimethylformamide (DMF), and which decomposes to a black amorphous solid when heated above 450 °C. Samples left exposed to the air rapidly deteriorated to an amorphous material that was shown by IR not to be a cyanide.

The infrared spectrum of the solid is simple, with strong absorptions at 2215 [ν(CN)] and 440 cm^{-1} [ν(M—CN)]. These values should be compared with those for dimethylgallium cyanide,[8] which has corresponding absorbances at 2207 and 429 cm^{-1}. The absence of any absorption above 3000 cm^{-1} indicates that the solid does not contain C—H, N—H, or O—H groups. The compound is volatile in the mass spectrometer. Mass spectra obtained by direct vaporization of the solid at 225 °C reveal the molecular $Ga(CN)_3$ species at m/z 147 and 149 corresponding to the 69 and 71 amu gallium isotopes of the compound. C, H, and N elemental analysis confirmed the phase purity.
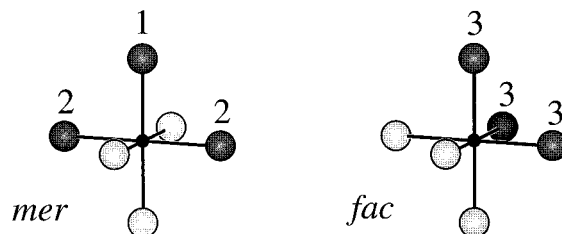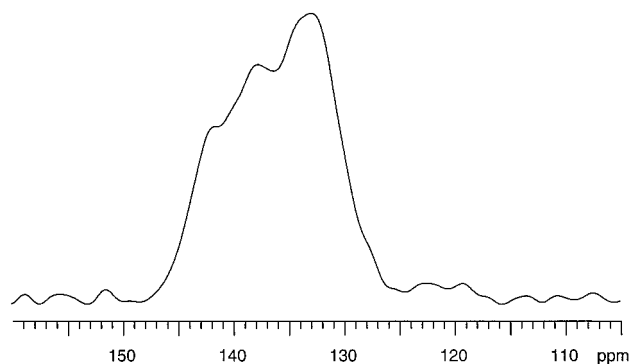

Figure 3. (Top) Solid state (magic angle spinning) ^{13}C spectrum of $Ga(CN)_3$. (Bottom) The *mer* and *fac* isomers of an octahedral GaC_3N_3 (C is darker shaded). If the *mer* and *fac* isomers occur in equal amounts, the three types of C environments labeled 1, 2, and 3 should occur in the ratio 1:2:3.

All peaks in the powder X-ray diffraction pattern could be indexed by using a primitive cubic cell with $a = 5.295(2)$ Å. The only plausible possibility for cubic $Ga(CN)_3$ is a disordered structure (C,N rotational disorder) with Ga at the cell corners, octahedrally coordinated by (C,N) and joined by C—N bonds aligned along the cell edges as in Prussian blue (see Figure 1). The structure was verified by quantitative Rietveld analysis.[9] The C—N bond length was found to be 1.148(1) Å, a value normal for metal cyanides,[10] and the Ga—(N,C) distance is 2.072(2) Å.

Solid state (magic angle spinning) ^{13}C NMR studies confirmed the presence of the CN ligands and revealed three closely spaced peaks at an approximate ratio of 1:2:3 and centered at 141.5, 137.5, and 134 ppm, respectively (Figure 3, top). The NMR data indicate the existence of at least three possible types of carbon sites in the framework structure and confirm the C,N disorder. The most plausible interpretation of the NMR data is that each Ga is bonded to three C atoms in approximately equal amounts of the *fac* and *mer* isomers; in the former the three C atoms are equivalent and in the latter there are two kinds of C environments which occur in the ratio of 2:1 (Figure 3, bottom). In $Cd(CN)_2$, which also forms a three-dimensional framework structure,[2a] a disordered structure was determined[11] from ^{113}Cd NMR; in this case Cd is four coordinated by (C,N) and evidence for CdC_4, $CdCN_3$, CdC_2N_2, $CdCN_3$, and CdN_4 was presented with CdC_2N_2 predominating. Notice that the earlier proposed[2a] ordered $Cd(CN)_2$ structure is the same as that described below for $LiGa(CN)_4$ and would contain equal amounts of CdC_4 and CdN_4 tetrahedra.

Efforts to prepare singly substituted cyanide material of the form Cl_2GaCN, analogous to Me_2GaCN, by reaction of 1 equiv each of Me_3SiCN and Cl_2GaN_3 resulted primarily in formation of the trisubstituted product, $Ga(CN)_3$, as indicated by X-ray

(9) Partin, D. E.; Williams, D.; Lincoln, F. J.;Brousseau, L.; Kouvetakis, J.; O'Keeffe, M. To be submitted for publication.

(10) Wells, A. F. *Structural Inorganic Chemistry,* 5th Ed.; Clarendon Press: Oxford, 1984.

(11) Nishikiori, S.; Ratcliffe, C. I.; Ripmeester, J. A. *Can. J. Chem.* **1990**, *68*, 2270−2273.

diffraction. (Dimethylgallium cyanide, Me_2GaCN, is a tetramer in which the metal is bound to four ligands.[12]) However, Cl_2-GaCN was formed as a minor byproduct, and it was isolated as a Lewis acid−base complex with trimethylamine, (Cl_2GaCN)·NMe$_3$. This material is a colorless solid that sublimes at 70−100 °C, and its identity was established by IR, NMR, and mass spectrometry. The ^1H NMR spectrum reveals a single resonance $\delta = 1.8$ corresponding to the NMe_3 ligand. The FTIR spectrum confirms the presence of NMe_3 by the characteristic C−H stretches at 2950 cm^{-1}, and shows a sharp cyanide stretch at 2181 cm^{-1}, as well as $\nu(Ga-CN)$ at 440 cm^{-1}. The mass spectra display the expected isotopic envelops for (M^+-Cl) and (M^+-CN), the strongest peaks, as well as peaks for $[N(CH_3)_3]^+$ and $(HCN)^+$.

It is worth noting that, unlike the reactions of Me_3SiCN with Cl_2GaN_3 which very readily produce $Ga(CN)_3$ as the major product, the reaction of Me_3SiN_3 (large excess) and $GaCl_3$ always gives the singly substituted product, Cl_2GaN_3, and any additional substitutions of Cl by N_3 with this method are not possible. These results and the facile displacement of N_3 by CN in Cl_2GaN_3 to form $Ga(CN)_3$ suggest that Ga−CN bonding may be stabilized by a metal-to-ligand π bonding interaction involving donations of electrons from the filled d orbital of the metal to empty π antibonding orbital of the ligand. This type of interaction is presumably not possible in the corresponding azides.

Synthesis of $Ga(CN)_3$ by Reaction of Me_3SiCN and $GaCl_3$. Highly pure and crystalline $Ga(CN)_3$ is also conveniently synthesized by the reaction of $GaCl_3$ and Me_3SiCN as shown in reaction 2 below.

$$3Me_3SiCN + GaCl_3 \rightarrow 3Me_3SiCl + Ga(CN)_3 \qquad (2)$$

The formation of $Ga(CN)_3$ from $GaCl_3$ and Me_3SiCN occurs readily and completely under very mild conditions, and the material has the same composition and structure as the material obtained from the reaction of Me_3SiCN and Cl_2GaN_3. We also explored the use of the Ge and Sn organometallic cyanides to prepare $Ga(CN)_3$. Me_3GeCN had been previously[12] reacted with $GaMe_3$ to produce the tetrameric $GaMe_2CN$. The Me_3GeCN and Me_3SnCN compounds used here were prepared by a new and very efficient method involving direct interaction of the corresponding halides and Me_3SiCN:

$$Me_3SiCN + Me_3MCN \rightarrow$$
$$Me_3SiCl + Me_3MCN \qquad (M = Ge, Sn) \ (3)$$

Reactions of $GaCl_3$ with Me_3GeCN and Me_3SnCN did not yield $Ga(CN)_3$ but resulted in formation of 1:1 Lewis acid−base complexes. In particular, direct reaction of Me_3GeCN with $GaCl_3$ produces a colorless solid that melts sharply at 85 °C and sublimes unchanged at 50 °C and 10^{-3} Torr. The identity of the compound was established by elemental analysis for C and H, the results being consistent with the Me_3GeCN·$GaCl_3$ empirical formula, and by IR and ^1H NMR spectroscopies. The ^1H NMR spectrum reveals a single resonance ($\delta = 0.86$) consistent with the $GeMe_3CN$ group. The IR spectra are consistent with the assigned structure and correlate well with those in other related cyanide compounds. The IR shows the Ga−Cl stretching band at 400 cm^{-1}, confirming the presence of $GaCl_3$, and shows the C−H stretching bands associated with the $GeMe_3$ ligand at 2983 and 2994 cm^{-1}. A sharp band at 2234 cm^{-1} clearly corresponds to the C−N stretch. A comparison of this stretch with that of the $GeMe_3CN$ compound

(2189 cm^{-1}) shows an increase in the C−N stretching frequency. A similar increase was also noted when $GeMe_3CN$ forms an adduct with boron trifluoride [$\nu(CN)$ for Me_3GeCN·BF_3: 2270 cm^{-1}].[13] The stretching frequencies of the cyanide ligand in many metal cyanides have been previously discussed with particular regard to the distinction between the bridging and the terminal cyanides.[14] It was demonstrated that the bridging cyanide groups exhibit a higher absorption frequency than do terminal cyanide groups as we have also observed in this study. This is believed to be because electrons are removed from the 5σ (HOMO) orbital which is weakly antibonding with respect to the C−N bond.[14] We also noted that the Me_3GeCN·$GaCl_3$ compound is found to decompose in the mass spectrometer, as the spectrum shows the corresponding molecular ions for the $GaCl_3$ and Me_3Ge type constituents. While Me_3GeCN·$GaCl_3$ appears to be stable, the corresponding Me_3SnCN·$GaCl_3$, which forms as a viscous colorless liquid at room temperature, decomposes at higher temperatures to yield $GaCl_3$ and Me_3SnCN. Thermal decomposition of Me_3GeCN·$GaCl_3$ and reaction of Me_3SnCN with $GaCl_3$ at temperatures up to 200 °C did not provide any $Ga(CN)_3$.

The similarity in chemical bonding properties and size between aluminum and gallium prompted attempts to prepare the Al analog of $Ga(CN)_3$. However, reactions of Me_3SiCN with trihalides of aluminum consistently resulted in formation of amorphous cyanide material. A plausible explanation is that π-back-bonding from Ga to the carbon atom may promote extended bridge formation through the N atom because the creation of the bridging bond exerts an electron withdrawing effect on the CN ligand.[14] This form of π-back-bonding which involves d-orbitals should not be possible with aluminum.

Synthesis of $LiGa(CN)_4$ and $CuGa(CN)_4$

Very many fascinating structures have frameworks composed of the cyanides of Zn and (especially) Cd. We expected that similar networks of composition $LiGa(CN)_4$ and $CuGa(CN)_4$ will be formed by reaction between LiCN or CuCN and Ga-$(CN)_3$.

We synthesized $LiGa(CN)_4$ by direct reaction of pure LiCN with a sample of $Ga(CN)_3$ at 123 °C in DMF. The two-stage synthetic procedure is summarized below.

$$MeLi + SiMe_3CN \rightarrow LiCN + SiMe_4 \qquad (4)$$

$$LiCN + Ga(CN)_3 \rightarrow LiGa(CN)_4 \qquad (5)$$

The mixture of reactants was stirred for 24 h under dry nitrogen in DMF, followed by low-pressure distillation to remove the solvent and to obtain $LiGa(CN)_4$ as a light brown solid in nearly quantitative yield. The IR spectrum of the material displayed a weak but sharp cyanide stretch at 2227 cm^{-1}. The X-ray powder diffraction spectrum revealed a simple cubic structure with lattice parameter $a = 5.874(2)$ Å. The structure was modeled after the structure of $LiCo(CO)_4$ in which[15] there is a framework of corner connected LiO_4 and CoC_4 tetrahedra. $Zn(CN)_2$ has been proposed to have the same structure; however, we have determined[9] from neutron diffraction data that this compound has C,N disorder. In the $LiGa$-$(CN)_4$ compound it is assumed that Li is bonded to four N and Ga is bonded to four C, but C,N disorder cannot be excluded (C and N cannot be distinguished by X-ray diffraction in practice). The metal-centered tetrahedra are linked by C−N bonds to form two interpenetrating networks in which LiN_4

(12) Coates, G. E.; Mukherjee, R. N. *J. Chem. Soc.* **1963**, 229−233.

(13) Seyferth, D.; Kahlen, N. *J. Am. Chem. Soc.* **1960**, *25*, 809−812.

(14) Dows, D. A.; Haim, A.; Wilmarth, W. K. *J. Inorg. Nucl. Chem.* **1961**, *21*, 33.

(15) Kluefers, P. *Z. Kristallogr.* **1984**, *167*, 275−286.

Table 1. Observed and Calculated d Spacings (Å) and Relative Intensities in the X-ray Diffraction Powder Patterns (Cu Kα radiation) of LiGa(CN)₄ and CuGa(CN)₄

	LiGa(CN)₄				CuGa(CN)₄			
hkl	d_{obs}	I_{obs}	d_{calc}	I_{calc}	d_{obs}	I_{obs}	d_{calc}	I_{calc}
100	5.855	48	5.866	59			5.729	0
110	4.145	100	4.147	100	4.044	100	4.051	100
111	3.386	73	3.387	63	3.314	19	3.308	13
200			2.933	0			2.864	3
210	2.624	32	2.623	31			2.562	0
211	2.395	29	2.395	23	2.334	26	2.339	27
220	2.075	25	2.074	26	2.025	20	2.026	17
221	1.955	15	1.955	14			1.909	1
310	1.855	7	1.855	5	1.814	9	1.812	8
311	1.769	8	1.767	9			1.727	1
222			1.693	1			1.654	1
320	1.627	4	1.627	4			1.589	0
321	1.569	14	1.568	15	1.531	18	1.531	14

tetrahedra are linked to four GaC₄ tetrahedra and *vice versa* as indicated in Figure 2. The Li–N and Ga–C bond lengths were found to be 2.021(5) and 2.00(1) Å, respectively. The C–N bond length is found to be 1.07(1) Å, which is reasonable for a metal cyanide bond length.[10]

CuGa(CN)₄ was similarly prepared by the direct combination of CuCN in DMF at 137 °C, followed by low-pressure distillation to remove the solvent. The IR spectrum of the material displayed a single sharp cyanide stretch at 2133 cm⁻¹ and indicated that no SiMe₃CN or SiMe₃Cl was present. The X-ray diffraction pattern could now be indexed as a primitive cubic structure with $a = 5.635(5)$ Å, but because of the similarity of scattering factors for Cu and Ga, and for C and N, we could not distinguish between an ordered, as for LiGa(CN)₄, or a disordered, as for Zn(CN)₂, structure; we note that CuGa-(CN)₄ and Zn(CN)₂ are exactly isoelectronic. Table 1 compares observed and calculated intensities for the first few lines of the powder patterns of LiGa(CN)₄ and CuGa(CN)₄.[16]

The lattice parameter is smaller for CuGa(CN)₄ than for LiGa-(CN)₄. We note that a similar contraction in the cubic lattice parameter (from 11.774 to 11.609 Å) is observed in going from (NMe₄)LiZn(CN)₄[2b] to (NMe₄)CuZn(CN)₄.[2a]

The change in CN stretch from 2227 cm⁻¹ in LiGa(CN)₄ to 2133 cm⁻¹ in CuGa(CN)₄ is striking. In Zn(CN)₂ the frequency was measured to be 2218 cm⁻¹; we are unable to explain the large shift in the Cu compound at this time.

Experimental Section

General Procedures. Reactions were performed under prepurified nitrogen with standard Schlenk and drybox techniques. Solvents were dried and distilled prior to use. ¹H (300 MHz) and ¹³C (125.7 MHz) NMR spectra were collected on a Varian Gemini 300 spectrometer and were referenced to the solvent resonances (C₆D₆, ¹H, δ 7.17; ¹³C, δ 128.0). FTIR spectra were recorded on a Nicolet Magna-IR spectrometer either in Nujol mull or in a 10-cm gas cell with KBr windows. Elemental analyses were performed by Galbraith laboratories (Knoxville, TN); samples were combusted at 1050 °C in the presence of a V₂O₅ catalyst and then analyzed by FTIR (for C and H) and by thermal conductivity (for N). Electron impact mass spectra were collected on a Finnigan-MAT Model 312 spectrometer (IE = 70 eV, source $T = 225$ °C). Gallium trichloride, copper cyanide, and trimethylsilyl cyanide (Aldrich) were used as received. Trimethylsilyl azide (Aldrich) was purified and distilled and trimethylethylamine (Aldrich) was

purified over P₂O₅ and then distilled. Single-phase magic angle spinning (MAS) ¹³C NMR spectra were collected at 9.4 T on a Varian Unit Plus spectrometer. Samples were placed in a 5-mm (OD) silicon nitride rotor with Torlon caps and were spun at 10 500 Hz in a 5-mm Varian CP-MAS probe. The spectra were obtained with a single pulse train, 2000 and 10000 transients, a recycle time of 10 s/transient, and 32° pulse width.

Synthesis of Ga(CN)₃. GaCl₃ (2.0 g, 11 mmol) was placed into a Schlenk flask with a magnetic stirbar, and Me₃SiCN (6 mL, 45 mmol) was added dropwise. Gas was evolved as the mixture was stirred at room temperature and it was shown by vapor-phase FTIR to be Me₃-SiCl. The mixture was stirred at room temperature for 6 h, and then at 60 °C for another 60 h, during which time the mixture gradually darkened to deep brown. The temperature was then raised to 75 °C for 4 h to complete the reaction. The reaction flask was pumped to remove Me₃SiCl and excess Me₃SiCN, which were collected in quantitative yields and identified by vapor-phase FTIR. The light brown solid product was washed with dry hexane to remove the soluble impurities and then pumped for several hours to remove any remaining volatile components. The resulting product is a white solid that is obtained in nearly quantitative yield.

In a similar manner a suspension of Cl₂GaN₃ (3.344 g, 18 mmol) in 10 mL of hexane was treated dropwise with SiMe₃CN (7.4 mL, 55 mol). Initially the mixture becomes clear and the Cl₂GaN₃ completely dissolves. The solution is then stirred for 12 h over which time a colorless precipitate is formed. The solid is isolated by filtration and washed several times with hexane to yield Ga(CN)₃ quantitatively. IR (Nujol): 2215 cm⁻¹ ν(CN), and 440 cm⁻¹ ν(M–CN). EIMS (m/z): 147 and 149 [Ga(CN)₃]⁺. Anal. Calcd for Ga(CN)₃: C, 24.4; N, 28.4. Found: C, 24.6; N, 26.2; H, 0.7.

Structure of Ga(CN)₃. Samples for X-ray powder diffraction were loaded into an environmental cell with a kapton window and data were collected with a Rigaku D/max IIB diffractometer using Cu Kα radiation. The diffraction peaks could all be indexed by using a primitive cubic unit cell with $a = 5.295(2)$ Å. The data refined consisted of two sets, each being a sum of 10 step scans, one of 0.02° steps at a rate of 3.0°/min for the $2\theta = 5°$ to 90° set, and the other of 0.04° steps at a rate of 3.0°/min for the $2\theta = 80°$ to 140° set. The refinement with *GSAS*, a Rietveld refinement code,[17] fitted 5498 data points for 35 reflections. For the final refinement $\chi^2 = 2.0$, $R_p = 5.9\%$, $R_{wp} = 7.4\%$ for a total of 23 parameters.

Reactions of GaCl₃ with Me₃GeCN and Me₃SnCN. The GeMe₃-CN and SnMe₃CN compounds used in this study have been previously synthesized by reactions of the corresponding halides and AgCN.[13] We discovered a new and much more efficient preparation method involving reactions of the halides with SiMe₃CN to produce the cyanides via elimination of Me₃SiCl. In a typical experiment a hexane solution of Me₃MCl (M = Ge, Sn) was treated dropwise with a hexane solution of Me₃SiCN at 0 °C. Upon addition a colorless precipitate formed and the resulting mixture was stirred at room temperature for 24 h. The solvent was then removed by distillation to yield a colorless solid, which was further purified by sublimation to yield Me₃GeCN (40%) or Me₃SnCN (90%). Freshly sublimed Me₃GeCN (0.49 g, 3.4 mol) in hexane is slowly treated with a solution of GaCl₃ (0.60 g, 3.4 mol) in hexane at 0 °C. The resulting mixture was stirred for 24 h and the solvent was removed in vacuo to yield a colorless solid (0.85 g, 77% yield) which was purified by sublimation at 75 °C and melts sharply at 85 °C. IR (Nujol): 2978 (m, ν_{as} CH), 2932 (w, ν_s CH), 2234 (m, ν CN), 1265, (w), 863 (s), 785 (m), 636 (s), 481 (s, ν GeC), 399 (vs, ν GaCl) cm⁻¹. ¹H NMR (C₆D₆, 25 °C) δ 0.838. EIMS (m/z): 214 (GaCl₃)⁺. Anal. Calcd for Cl₃GaNCGeMe₃: C, 15.12; H 2.84; Found: C, 15.01; H, 2.65.

Synthesis and Structure of LiGa(CN)₄. Ga(CN)₃ (1.242 g, 8.0 mmol) and LiCN (0.5 M in DMF; 20 mL; 10.0 mmol) were combined in a Schlenk flask with a magnetic stirbar and refluxed for 24 h. The mixture was then filtered, leaving behind a pale yellow solid. The solvent was removed from the filtrate in vacuo to give the excess LiCN. The pale brown residue was completely dried by heating under high vacuum to provide LiGa(CN)₄ (1.49 g, 98% yield). The X-ray powder sample was loaded into the environmental cell and the data were collected with a Rigaku D/max IIB diffractometer using Cu Kα radiation. All reflections could be indexed by using a primitive cubic

(16) The calculation reported in Table 1 for LiGa(CN)₄ used the structural data from the full profile (Rietfeld) refinement, which is described below and which provides a much closer fit to the experimental data. The CuGa-(CN)₄ calculation used the same C–N bond length and is for the ordered model with Cu–N and Ga–C bonds. For the low-angle data reported here, the calculated data are not very sensitive to the atomic displacement ("thermal") parameters used.

unit cell with $a = 5.874(2)$ Å. The initial trial structure was modeled after that of LiCo(CO)$_4$,[15] which has symmetry $P\bar{4}3m$ ($a = 5.542$ Å); in this model Ga replaces Co and N replaces O. The X-ray data used for refinement consisted of two sets collected in the same manner as described for Ga(CN)$_3$. The structure refinement of 5498 data points was again performed with GSAS[17] and proceeded smoothly, confirming the original model. For the final refinement $\chi^2 = 7.0$, $R_p = 6.44\%$, and $R_{wp} = 9.08$ for 40 variables.

Synthesis and Structure of CuGa(CN)$_4$. Ga(CN)$_3$ (0.317 g, 2.0 mmol) and CuCN (0.183 g, 2.0 mmol) were combined in 20 mL of DMF in a Schlenk flask with a magnetic stirbar and heated at 137 °C for 24 h. The solvent was then pumped off and the remaining brown solid further annealed at 130 °C for 60 h under a dynamic vacuum. The X-ray powder sample was loaded into the environmental cell and the data were collected with a Rigaku D/max IIB diffractometer using Cu Kα radiation. All reflections could be indexed by using a primitive cubic unit cell with $a = 5.729(5)$ Å. Reflections $hk0$ with $h + k$ odd were unobserved, suggesting the possibility of disorder and $Pn\bar{3}m$ symmetry (see Table 1).

Conclusion

We have prepared the previously unknown Ga(CN)$_3$ phase that has a cubic Prussian-blue framework structure. This structure is well established in many transition metal compounds; however, in most well-characterized systems, larger alkali metals and/or water fill the spaces in the center of the

simple cubic cell and the framework metal atoms form an ordered array such as that in the K$_2$MFe(CN)$_6$ family with M = Ni, Co, and Cu. The empty framework found here for Ga-(CN)$_3$ is less common and has only been characterized earlier for the ordered CdPd(CN)$_6$ compound.[4]

Our synthetic reactions include facile displacement of azide and chloride ligands from GaCl$_3$ and Cl$_2$GaN$_3$ by CN with SiMe$_3$CN as the cyanide source, a method that can be potentially applied to prepare other inorganic cyanides. In similar reactions, the related GeMe$_3$CN and SnMe$_3$CN reagents do not generate Ga(CN)$_3$ but rather combine with GaCl$_3$ to produce Lewis base adducts; the same trend has been previously reported for the system MMe$_3$CN/BF$_3$ with M = Si, Ge, Sn.

We have also shown that Ga(CN)$_3$ can combine to form framework structures MGa(CN)$_4$ (M = Li or Cu), and we note that it should prove possible to prepare inclusion compounds in which guest molecules (such as CCl$_4$) replace one of the networks in a manner analogous to the situation in N(CH$_3$)$_4$·MZn(CN)$_4$ (M = Cu[2a] or Li[2b]) [MGa(CN)$_4$ and MZn(CN)$_4^-$ are isoelectronic].

(17) Larson, A. C.; Von Dreele, R. B. *GSAS Generalized Structure Analysis System*; LANSCE, MS-H805, Manual Lujan Neutron Scattering Center: Los Alamos, NM, 1989.