

Novel Examples of High-Dimensional Mixed-Valence Copper Cyanide Complexes

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The first examples of high-dimensional mixed-valence homometallic cyano-bridged copper complexes were synthesized and characterized: net-structured $[\text{Cu}(\text{CN})_4\{\text{Cu}(\text{cyclam})\}_{1.5}]_n(\text{H}_2\text{O})_{5n}$ (**1**), ladder-type double-chain-structured $[\text{Cu}(\text{CN})_2\{\text{Cu}(\text{CN})_2\text{Cu}(\text{cyclam})\}]_n(\text{H}_2\text{O})_n$ (**2**), layer-structured $[\{\text{Cu}(\text{CN})_2\}_2\text{Cu}(\text{cycalm})]_n$ (**3**), and hydrogen-bond-based 2-D $[\text{Cu}(\text{CN})_3\text{Cu}(\text{cyclam})]_n(\text{CH}_3\text{OH})_n$ (**4**) (cyclam = 1,4,8,11-tetraazacyclotetradecane). **1** crystallizes in triclinic space group $P\bar{1}$ with $a = 8.3589(11)$ Å, $b = 13.478(2)$ Å, $c = 14.828(2)$ Å, $\alpha = 66.895(2)^\circ$, $\beta = 77.916(3)^\circ$, $\gamma = 85.939(3)^\circ$, and $Z = 1$; **2** crystallizes in triclinic space group $P\bar{1}$ with $a = 8.2305(12)$ Å, $b = 9.8861(15)$ Å, $c = 13.219(2)$ Å, $\alpha = 84.863(3)^\circ$, $\beta = 75.744(3)^\circ$, $\gamma = 89.818(3)^\circ$, and $Z = 2$; **3** crystallizes in monoclinic space group $P2_1/c$ with $a = 6.830(2)$ Å, $b = 8.482(2)$ Å, $c = 17.306(4)$ Å, $\beta = 98.144(4)^\circ$, and $Z = 2$; **4** crystallizes in triclinic space group $P\bar{1}$ with $a = 9.470(1)$ Å, $b = 10.034(1)$ Å, $c = 12.064(1)$ Å, $\alpha = 67.325(2)^\circ$, $\beta = 75.593(2)^\circ$, $\gamma = 70.672(2)^\circ$, and $Z = 2$. The coordination sphere of Cu^I sites in the complexes shows diverse structures: tetrahedral $[\text{CuC}_4]$ for **1**, tetrahedral $[\text{CuC}_3\text{N}]$ and triangular $[\text{CuC}_2\text{N}]$ for **2**, triangular $[\text{CuC}_2\text{N}]$ for **3**, and triangular $[\text{CuC}_3]$ for **4**. In particular, **1** constitutes the first example of a structurally characterized system containing a bridging tetrahedral $[\text{Cu}(\text{CN})_4]^{3-}$ unit. The diverse structural nature of these complexes is governed by the capping amines and the content of water in the reaction media. The magnetic interactions are negligible in these mixed-valence complexes.

Introduction

High-dimensional network systems have emerged as important synthetic targets because of the possibility that they lead to a wide range of purpose-built materials with predetermined structures and useful properties.¹ In particular, cyano-bridged transition-metal complexes have drawn much attention because of their structural diversity and strong tendency to construct rigid coordination bonding networks.^{2–7} Most of the known cyano-bridged transition-metal complexes in which cyanide anions bridge two transition-metal cations⁸ M and M' are heterometallic, and the examples of homometallic systems are limited to $M/M' = \text{Mo}^0/\text{Mo}^0$,^{2j} $\text{Mn}^{\text{II}}/\text{Mn}^{\text{II}}$,^{3h} $\text{Co}^{\text{III}}/\text{Co}^{\text{II}}$,^{2h} $\text{Rh}^{\text{III}}/\text{Rh}^{\text{III}}$,^{2k} $\text{Ni}^{\text{II}}/\text{Ni}^{\text{II}}$,²ⁱ $\text{Cu}^{\text{I}}/\text{Cu}^{\text{I}}$,^{9–11} Cu^{I}

Cu^{II} ,¹² $\text{Zn}^{\text{II}}/\text{Zn}^{\text{II}}$,^{7a} and $\text{Cd}^{\text{II}}/\text{Cd}^{\text{II}}$.^{6a} For the cyano-bridged homocopper(I) systems, the diverse structural feature, initially observed in the spiral polymer chain system $\text{KCu}(\text{CN})_2$ ^{9a} and the polymer sheets $\text{KCu}_2(\text{CN})_3 \cdot \text{H}_2\text{O}$ ^{9b} and $\text{CuCN} \cdot \text{NH}_3$,^{9c} has recently become more evident through the works of Zubietta et al.¹⁰ and other groups¹¹ who exploited the chemistry of

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(1) Batten, S. R.; Robson, R. *Angew. Chem.* **1998**, *110*, 1558; *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1460 and references therein.

(2) Cluster systems: (a) Van Langenberg, K.; Batten, S. R.; Berry, K. J.; Hockless, D. C. R.; Moubaraki, B.; Murray, K. S. *Inorg. Chem.* **1997**, *36*, 5006. (b) Kou, H.-Z.; Gao, S.; Ma, B.-Q.; Liao, D.-Z. *Chem. Commun.* **2000**, 713. (c) Zhong, Z. J.; Seino, H.; Mizobe, Y.; Hida, M.; Fujishima, A.; Ohkoshi, S.; Hashimoto, K. *J. Am. Chem. Soc.* **2000**, *122*, 2952. (d) Larionova, J.; Gross, M.; Pilkington, M.; Andres, H.; Stoeckli-Evans, H.; Güdel, H. U.; Decurtins, S. *Angew. Chem., Int. Ed.* **2000**, *39*, 1605. (e) Berseth, P. A.; Sokol, J. J.; Shores, M. P.; Heinrich, J. L.; Long, J. R. *J. Am. Chem. Soc.* **2000**, *122*, 9655. (f) Sokol, J. J.; Shores, M. P.; Long, J. R. *Angew. Chem., Int. Ed.* **2001**, *40*, 236. (g) Parker, R. J.; Spiccia, L.; Berry, K. J.; Fallon, G. D.; Moubaraki, B.; Murray, K. S. *Chem. Commun.* **2001**, 333. (h) Heinrich, J. L.; Berseth, P. A.; Long, J. R. *Chem. Commun.* **1998**, 1231. (i) Meyer, F.; Winter, R. F.; Kaifer, E. *Inorg. Chem.* **2001**, *40*, 4597. (j) Contakes, S. M.; Rauchfuss, T. B. *Angew. Chem., Int. Ed.* **2000**, *39*, 1984. (k) Contakes, S. M.; Klausmeyer, K. K.; Milberg, R. M.; Wilson, S. R.; Rauchfuss, T. B. *Organometallics* **1998**, *17*, 3633.

copper(I) cyanide in the presence of organic Lewis base ligands. In contrast to the foregoing rich Cu^I/Cu^I cyanide chemistry, the mixed-valence Cu^I/Cu^{II} systems are rare^{12–14} and the Cu^{II}/Cu^{II} cyanide system lacks an example.¹⁵

To expand the system of homometallic cyano-bridged copper complexes involving Cu^{II} units, we have employed Cu(II) cations as a copper source and cyclam (= 1,4,8,11-tetraazacyclotetradecane) as an organic Lewis base capping ligand in different solvents, resulting in the observation of novel mixed-valence homometallic cyano-bridged copper

complexes such as 2-D [Cu(CN)₄{Cu(cyclam)}_{1.5}]_{2n}(H₂O)_{5n} (**1**), ladder-type double-chain-structured [Cu(CN)₂{Cu(CN)₂Cu(cyclam)}_n](H₂O)_n (**2**), 2-D [{Cu(CN)₂}₂Cu(cyclam)]_n (**3**), and hydrogen-bond-based 2-D [Cu(CN)₃Cu(cyclam)]_n·(CH₃OH)_n (**4**). In addition, the characterization of the compounds reveals that the structural tuning can be achieved via inducing the change in coordination sphere around a metal center bonded to a bridging cyano-carbon atom. Furthermore, complex **1** constitutes the first example of a high-dimensional compound based on a bridging tetrahedral [Cu(CN)₄]³⁻ unit of which a discrete form is known as a potassium salt.¹⁶ Reported herein are the details of the synthesis, characterization, and properties of the foregoing four novel mixed-valence cyano-bridged copper complexes.

Experimental Section

Reagents and General Procedures. All reagents were purchased from Aldrich, Fluka, or Strem and used without further purification. Elemental analyses for C, H, and N were performed on a CE Instruments model Flash EA 1112 Series analyzer at the Elemental Analysis Service Center of the Korea Basic Science Institute. Infrared spectra were obtained from KBr pellets with a Bruker EQUINOX-55 spectrometer.

Synthesis. [Cu(CN)₄{Cu(cyclam)}_{1.5}]_{2n}(H₂O)_{5n} (**1**) and [Cu(CN)₂{Cu(CN)₂Cu(cyclam)}_n](H₂O)_n (**2**). To a methanolic solution (20 mL) of Cu(SO₄)·5H₂O (0.25 g, 1.0 mmol) was added a methanolic solution (10 mL) of cyclam (0.12 g, 0.60 mmol). Heating of the resulting purple solution to 60 °C was followed by dropwise addition of a methanolic solution (20 mL) of KCN (0.13 g, 2.0 mmol). The reaction mixture was stirred for 1 h, the white precipitate was filtered off, and the filtrate was left undisturbed, affording purple crystals of **1** in 55% yield based on Cu. After the collection of **1** by filtration, the resulting filtrate was further left undisturbed in the air, giving blue crystals of **2** in 36% yield based on Cu.

Data for **1**. Elem Anal. Calcd (%) for C₃₈H₈₂N₂₀O₅Cu₅ (1216.9): C, 37.51; H, 6.79; N, 23.02. Found: C, 37.59; H, 7.01;

- (3) 1-D systems: (a) Ohba, M.; Maruono, N.; Okawa, H.; Enoki, T.; Latour, J.-M. *J. Am. Chem. Soc.* **1994**, *116*, 11566. (b) Re, N.; Gallo, E.; Floriani, C.; Miyasaka, H.; Matsumoto, N. *Inorg. Chem.* **1996**, *35*, 6004. (c) Fu, D. G.; Chen, J.; Tan, X. S.; Jiang, L. J.; Zhang, S. W.; Zheng, P. J.; Tang, W. X. *Inorg. Chem.* **1997**, *36*, 220. (d) Ohba, M.; Fukita, N.; Okawa, H. *J. Chem. Soc., Dalton Trans.* **1997**, 1733. (e) Colacio, E.; Domínguez-Vera, J. M.; Ghazi, M.; Kivekäs, R.; Klinga, M.; Moreno, J. M. *Chem. Commun.* **1998**, 1071. (f) Ohba, M.; Usuki, N.; Fukita, N.; Okawa, H. *Inorg. Chem.* **1998**, *37*, 3349. (g) Knoepfel, D. W.; Liu, J.; Meyers, E. A.; Shores, S. G. *Inorg. Chem.* **1998**, *37*, 4828. (h) Matsumoto, N.; Sunatsuki, Y.; Miyasaka, H.; Hashimoto, Y.; Luneau, D.; Tuchagues, J.-P. *Angew. Chem., Int. Ed.* **1999**, *38*, 171.
- (4) 2-D systems: (a) Chen, Z. N.; Wang, J. L.; Qiu, J.; Miao, F. M.; Tang, W. X. *Inorg. Chem.* **1995**, *34*, 2255. (b) Miyasaka, H.; Matsumoto, N.; Okawa, H.; Re, N.; Gallo, E.; Floriani, C. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1446. (c) Ferlay, S.; Mallah, T.; Vaissermann, J.; Bartholomé, F.; Veillet, P.; Verdaguer, M. *Chem. Commun.* **1996**, 2481. (d) Miyasaka, H.; Matsumoto, N.; Re, N.; Gallo, E.; Floriani, C. *Inorg. Chem.* **1997**, *36*, 670. (e) Ohba, M.; Okawa, H.; Fukita, N.; Hashimoto, Y. *J. Am. Chem. Soc.* **1997**, *119*, 1011. (f) Kou, H.-Z.; Liao, D.-Z.; Cheng, P.; Jiang, Z.-H.; Yan, S.-P.; Wang, G.-L.; Yao, X.-K.; Wang, H.-G. *J. Chem. Soc., Dalton Trans.* **1997**, 1503. (g) Re, N.; Crescenzi, R.; Floriani, C.; Miyasaka, H.; Matsumoto, N. *Inorg. Chem.* **1998**, *37*, 2717. (h) Kou, H.-Z.; Bu, W.-M.; Liao, D.-Z.; Jiang, Z.-H.; Yan, S.-P.; Fan, Y.-G.; Wang, G.-L. *J. Chem. Soc., Dalton Trans.* **1998**, 4161. (i) Miyasaka, H.; Okawa, H.; Miyazaki, A.; Enoki, T. *Inorg. Chem.* **1998**, *37*, 4878. (j) Colacio, E.; Domínguez-Vera, J. M.; Ghazi, M.; Kivekäs, R.; Lloret, F.; Moreno, J. M.; Stoeckli-Evans, H. *Chem. Commun.* **1999**, 987. (k) Sra, A. K.; Andruh, M.; Kahn, O.; Golhen, S.; Ouahab, L.; Yakhmi, J. V. *Angew. Chem., Int. Ed.* **1999**, *38*, 2606. (l) Ma, B.-Q.; Gao, S.; Su, G.; Xu, G.-X. *Angew. Chem., Int. Ed.* **2001**, *40*, 434.
- (5) 3-D systems: (a) Fallah, M. S. E.; Rentschler, E.; Caneschi, A.; Sessoli, R.; Gatteschi, D. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1947. (b) Fukita, N.; Ohba, M.; Okawa, H.; Matsuda, K.; Iwamura, H. *Inorg. Chem.* **1998**, *37*, 842. (c) Larionova, J.; Sanchiz, J.; Golhen, S.; Ouahab, L.; Kahn, O. *Chem. Commun.* **1998**, 953. (d) Ohba, M.; Usuki, N.; Fukita, N.; Okawa, H. *Angew. Chem., Int. Ed.* **1999**, *38*, 1795. (e) Sra, A. K.; Rombaut, G.; Lahitête, F.; Golhen, S.; Ouahab, L.; Mathonière, C.; Yakhmi, J. V.; Kahn, O. *New J. Chem.* **2000**, *24*, 871. (f) Zhang, S.-W.; Fu, D.-G.; Sun, W.-Y.; Hu, Z.; Yu, K.-B.; Tang, W.-X. *Inorg. Chem.* **2000**, *39*, 1142.
- (6) Zeolite-like porous systems: (a) Nishikiori, S.; Iwamoto, T.; Yoshino, Y. *Chem. Lett.* **1979**, 1509. (b) Gable, R. W.; Hoskins, B. F.; Robson, R. *J. Chem. Soc. Chem. Commun.* **1990**, 762. (c) Brimah, A. K.; Siebel, E.; Fischer, R. D.; Davis, N. A.; Apperley, D. C.; Harris, R. K. *J. Organomet. Chem.* **1994**, *475*, 85. (d) Kitazawa, T.; Nishikiori, S.; Kuroda, R.; Iwamoto, T. *J. Chem. Soc., Dalton Trans.* **1994**, 1029. (e) Soma, T.; Iwamoto, T. *Chem. Lett.* **1994**, 821. (f) Janiak, C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1431. (g) Brousseau, L. C.; Williams, D.; Kouvetakis, J.; O'Keefe, M. *J. Am. Chem. Soc.* **1997**, *119*, 6292. (h) Ibrahim, A. M. A. *J. Organomet. Chem.* **1998**, *556*, 1. (i) Shores, M. P.; Beauvais, L. G.; Long, J. R. *J. Am. Chem. Soc.* **1999**, *121*, 775. (j) Kitazawa, T. *Chem. Commun.* **1999**, 891.
- (7) Network systems: (a) Hoskins, B. F.; Robson, R. *J. Am. Chem. Soc.* **1990**, *112*, 1546. (b) Soma, T.; Yuge, H.; Iwamoto, T. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1665. (c) Soma, T.; Iwamoto, T. *Chem. Lett.* **1995**, 271. (d) Hoskins, B. F.; Robson, R.; Scarlett, N. V. *Y. Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1203. (e) Batten, S. R.; Hoskins, B. F.; Robson, R. *J. Am. Chem. Soc.* **1995**, *117*, 5385. (f) Hirsh, K. A.; Wilson, S. C.; Moore, J. S. *Chem.—Eur. J.* **1997**, *3*, 765.
- (8) Only a few examples of compounds with μ₃-cyanide, bridging two copper(I) ions via carbon terminal and another metal ion via nitrogen terminal, have been reported so far. (a) Cromer, D. T.; Larson, A. C.; Roof, R. B., Jr. *Acta Crystallogr.* **1965**, *19*, 192. (b) Ibrahim, A. M. A.; Siebel, E.; Fischer, R. D. *Inorg. Chem.* **1998**, *37*, 3521.
- (9) (a) Cromer, D. T. *J. Phys. Chem.* **1957**, *61*, 1388. (b) Cromer, D. T.; Larson, A. C. *Acta Crystallogr.* **1962**, *15*, 397. (c) Cromer, D. T.; Larson, A. C.; Roof, R. B., Jr. *Acta Crystallogr.* **1965**, *19*, 192.
- (10) (a) Chesnut, D. J.; Zubieta, J. *Chem. Commun.* **1998**, 1707. (b) Chesnut, D. J.; Kusnetzow, A.; Zubieta, J. *J. Chem. Soc., Dalton Trans.* **1998**, 4081. (c) Chesnut, D. J.; Kusnetzow, A.; Birge, R.; Zubieta, J. *Inorg. Chem.* **1999**, *38*, 5484. (d) Chesnut, D. J.; Plewak, D.; Zubieta, J. *J. Chem. Soc., Dalton Trans.* **2001**, 2567. (e) Chesnut, D. J.; Kusnetzow, A.; Birge, R.; Zubieta, J. *J. Chem. Soc., Dalton Trans.* **2001**, 2581.
- (11) (a) Zhao, Y.; Hong, M.; Su, W.; Cao, R.; Zhou, Z.; Chan, A. S. C. *J. Chem. Soc., Dalton Trans.* **2000**, 1685. (b) Yu, J.-H.; Xu, J.-Q.; Yang, Q.-X.; Pan, L.-Y.; Wang, T.-G.; Lü, C.-H.; Ma, T.-H. *J. Mol. Struct.* **2003**, *658*, 1.
- (12) Nondiscrete Cu^ICu^{II}(NH₃)₃(CN)₄: (a) Williams, R. J.; Cromer, D. T.; Larson, A. C. *Acta Crystallogr., Sect. B* **1971**, *B27*, 1701. (b) Vrabel, V.; Garaj, J.; Sivxoc6, J.; Oktavec, D. *Acta Crystallogr., Sect. C* **1999**, *C55*, 1381.
- (13) Nondiscrete Cu^ICu^{II}(CN)₆(DMF): (a) Peng, S. M.; Liaw, D. S. *Inorg. Chim. Acta* **1986**, *113*, L11. (b) Zhao, X.-J.; Batten, S.; Du, M. *Acta Crystallogr., Sect. E* **2004**, *E60*, m1237.
- (14) Discrete [Cu^{II}(en)₂(H₂O)]₂[Cu^I(CN)₄]: Williams, R. J.; Larson, A. C.; Cromer, D. T. *Acta Crystallogr., Sect. B* **1972**, *B28*, 858.
- (15) Octa-^{15a} and decacopper(II)^{15b} clusters, bearing two and four cyano-bridged Cu(II) units, respectively, were derived from the metallasiloxane cage [Cu₆{(PhSiO₂)₆}₂(*n*-BuOH)_n] and might be considered as closely related examples: (a) Abbati, G. L.; Cornia, A.; Caneschi, A.; Fabretti, A. C.; Mortalò, C. *Inorg. Chem.* **2004**, *43*, 4540. (b) Abbati, G. L.; Caneschi, A.; Cornia, A.; Fabretti, A. C.; Pozdniakova, Y. A.; Shchegolikhina, O. I. *Angew. Chem., Int. Ed.* **2002**, *41*, 4517.
- (16) Cox, E. G.; Wardlaw, W.; Webster, K. C. *J. Chem. Soc.* **1936**, 775.

N, 23.15. Selected IR data (cm^{-1} , KBr pellet): 3595 (s), 3405 (m, broad), 3207 (s), 2939 (m), 2877 (m), 2096 (shoulder), 2088 (s, ν_{CN}), 1626 (m), 1466 (w), 1430 (m), 1319 (w), 1098 (m), 1070 (w), 1022 (w), 983 (m), 889 (w), 658 (w), 503 (w), 483 (w), 472 (w).

Data for **2**. Elem Anal. Calcd (%) for $\text{C}_{14}\text{H}_{26}\text{N}_8\text{OCu}_3$ (513.04): C, 32.78; H, 5.11; N, 21.84. Found: C, 33.22; H, 4.78; N, 23.15. Selected IR data (cm^{-1} , KBr pellet): 3584 (s), 3414(m), 3223 (s), 2938 (m), 2113 (m), 2090 (s, ν_{CN}), 2078 (shoulder), 2066 (s, ν_{CN}), 1637 (w), 1487 (w), 1436 (w), 1103 (m), 1081 (m), 1034 (m), 986 (m).

$\{[\text{Cu}(\text{CN})_2]_2\text{Cu}(\text{cyclam})\}_n$ (**3**). This compound was obtained during the recrystallization process of **1** in water. A small amount of **1** was dissolved in water, and the purple solution in the open container was left undisturbed for a few days. Well-shaped purple crystals of **3** were formed in 61% yield. Elem Anal. Calcd (%) for $\text{C}_{14}\text{H}_{24}\text{N}_8\text{Cu}_3$ (495.03): C, 33.97; H, 4.89; N, 22.64. Found: C, 34.12; H, 5.01; N, 22.48. Selected IR data (cm^{-1} , KBr pellet): 3432 (m), 3240 (s), 2956 (m), 2927 (m), 2871 (m), 2126 (m), 2098 (s ν_{CN}), 1637 (w), 1467 (w), 1428 (w), 1093 (m), 1067 (m), 1024 (m), 986 (m), 885 (w).

$[\text{Cu}(\text{CN})_3\text{Cu}(\text{cyclam})]_n(\text{CH}_3\text{OH})_n$ (**4**). To a methanolic solution (20 mL) of anhydrous $\text{Cu}^{\text{II}}(\text{SO}_4)$ (0.16 g, 1.0 mmol) was added a methanolic solution (10 mL) of cyclam (0.12 g, 0.60 mmol). The resulting purple solution was heated to 60 °C, treated with a methanolic solution (20 mL) of KCN (0.13 g, 2.0 mmol) in a dropwise manner, and stirred for 12 h. The white precipitate was filtered off, and the filtrate was left undisturbed, affording purple needle-shaped crystals of **4**. The yield was 67% based on Cu. Elem Anal. Calcd (%) for $\text{C}_{14}\text{H}_{28}\text{N}_7\text{OCu}_2$ (437.51): C, 38.43; H, 6.45; N, 22.41. Found: C, 38.35; H, 6.11; N, 23.17. Selected IR peaks (cm^{-1} , KBr pellet): 3325 (m), 3204 (s), 2939 (m), 2877 (s), 2528 (w), 2204 (w), 2126 (w), 2097 (vs, ν_{CN}), 2089 (vs, ν_{CN}), 1625 (m), 1429 (s), 1262 (s), 1101 (m), 1028 (m), 985 (m), 804 (m).

Crystallographic Data Collection and Structure Determination. A suitable single crystal of each compound was carefully selected under a polarizing microscope, coated with Paraton-N oil, and mounted on a glass fiber. Crystallographic data for all compounds were collected on a Bruker SMART 1K CCD-equipped diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 293 K. The hemispheres of diffraction data were collected as ω -scan frames with a width of $0.3^\circ/\text{frame}$ and an exposure time of 10 s/frame. Cell parameters were determined and refined by the SMART program.¹⁷ Data reduction and Lorentz polarization correction were performed using the SAINT software.¹⁸ Empirical absorption corrections were applied with the SADABS program.¹⁹ Totals of 6662 (**1**), 4664 (**2**), 2261 (**3**), and 4363 (**4**) reflections with the maximum θ values of 28.00° (**1**), 28.00° (**2**), 27.98° (**3**), and 28.30° (**4**) were measured, and 3335 (**1**), 2184 (**2**), 1612 (**3**), and 3346 (**4**) reflections were assumed to be observed by applying the condition $F_o > 4\sigma(F_o)$. The structures were solved by Peterson's heavy atom method using the SHELXS-86 program²⁰ for **1**, **3**, and **4** and the SHELXTL software package²¹ for **2**. All

Table 1. Crystallographic Data for **1** and **2**

	1	2
empirical formula	$\text{C}_{38}\text{H}_{82}\text{N}_{20}\text{O}_5\text{Cu}_5$	$\text{C}_{14}\text{H}_{26}\text{N}_8\text{OCu}_3$
fw	1216.91	513.04
cryst syst	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a (\AA)	8.3589(11)	8.2305(12)
b (\AA)	13.478(2)	9.8861(15)
c (\AA)	14.828(2)	13.219(2)
α (deg)	66.895(2)	84.863(3)
β (deg)	77.916(3)	75.744(3)
γ (deg)	85.939(3)	89.818(3)
V (\AA^3)	1502.4(4)	1038.1(3)
Z	1	2
d_{calcd} (g cm^{-3})	1.345	1.641
μ (mm^{-1})	1.792	3.064
λ (\AA)	0.71073	0.71073
total reflns	6662	4664
obsd reflns ^a	3335	2184
params	309	244
$R1^b$	0.0529	0.0615
wR2 ^c	0.1369	0.1449
GOF	1.104	0.935

^a Criterion: $F_o > 2\sigma(F_o)$. ^b $R1 = \sum||F_o| - |F_c||/\sum|F_c|$. ^c $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$ and $P = (F_o^2 + 2F_c^2)/3$.

Table 2. Crystallographic Data for **3** and **4**

	3	4
empirical formula	$\text{C}_{14}\text{H}_{24}\text{N}_8\text{Cu}_3$	$\text{C}_{14}\text{H}_{28}\text{N}_7\text{OCu}_2$
fw	495.03	437.51
cryst syst	monoclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$
a (\AA)	6.830(2)	9.4699(11)
b (\AA)	8.482(2)	10.03338(12)
c (\AA)	17.306(4)	12.0635(14)
α (deg)	90.00	67.325(2)
β (deg)	98.144(4)	75.593(2)
γ (deg)	90.00	70.672(2)
V (\AA^3)	992.5(4)	988.3(2)
Z	2	2
d_{calcd} (g cm^{-3})	1.657	1.470
μ (mm^{-1})	3.199	2.167
λ (\AA)	0.71073	0.71073
total reflns	2261	4363
obsd reflns ^a	1612	3346
params	123	235
$R1^b$	0.0324	0.0401
wR2 ^c	0.0776	0.1055
GOF	1.097	1.095

^a Criterion: $F_o > 2\sigma(F_o)$. ^b $R1 = \sum||F_o| - |F_c||/\sum|F_c|$. ^c $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$ and $P = (F_o^2 + 2F_c^2)/3$.

non-hydrogen atoms, except some of the amine hydrogens, were refined by full-matrix least-squares techniques with anisotropic parameters using the SHELXL-93 program²² for **1**, **3**, and **4** and the SHELXTL software package²¹ for **2**. The packing water molecules in **1** are disordered and refined isotropically.²³ Hydrogen atoms were calculated at idealized positions and refined riding on the corresponding carbon atoms with isotropic thermal parameters. Crystallographic data and details of the data collection are listed in Tables 1 and 2.

Results and Discussions

Synthesis. The overall synthetic routes to the mixed-valence homometallic copper cyanide complexes are sum-

(17) SMART, Data Collection Software, version 5.0; Bruker AXS, Inc.: Madison, WI, 1998.

(18) SAINT, Data Integration Software, version 5.0; Bruker AXS, Inc.: Madison, WI, 1998.

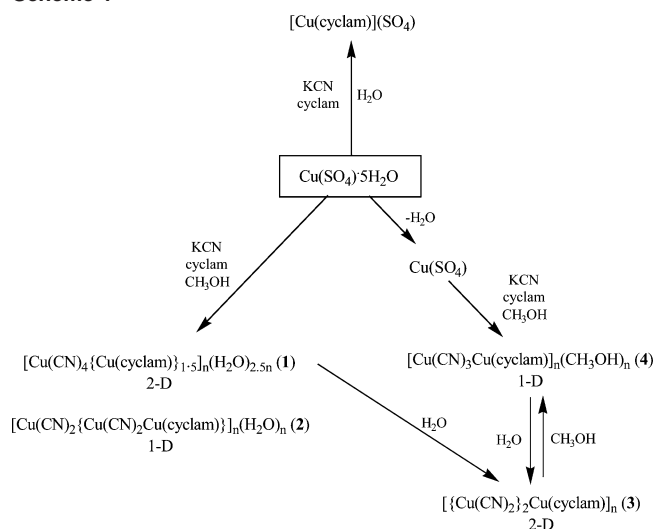
(19) Sheldrick, G. M. SADABS, A Program for Absorption Correction with the Bruker SMART System; Universität Göttingen: Göttingen, Germany, 1996.

(20) Sheldrick, G. M. SHELXS-86: Program for the Solution of Crystal Structures; Universität Göttingen: Göttingen, Germany, 1986.

(21) SHELXTL, Structure Solving Software, version 5.0; Bruker AXS, Inc.: Madison, WI, 1998.

(22) Sheldrick, G. M. SHELXL-93: Program for the Refinement of Crystal Structures; Universität Göttingen: Göttingen, Germany, 1993.

Scheme 1



marized in Scheme 1. When the reaction systems of $\text{Cu}(\text{SO}_4) \cdot 5\text{H}_2\text{O}$, cyclam, and KCN were run with four different molar ratio sets of 1:0.6:2, 1:1:1, 1:1:2, and 2:1:2 in methanol at 60 °C, both products **1** and **2** were always produced in different yields. The use of a 1:0.6:2 molar ratio gave the maximum isolated yields for both products, although the variation of the yield was more sensitive for **2**. The reaction also proceeds at room temperature, affording the same products in somewhat lower yields. The consideration of the formal charge suggests that compounds **1** and **2** have a Cu(I)/Cu(II) ratio of 0.67:1 and 2:1, respectively, indicating that part of the starting Cu(II) ions were reduced during the reaction. In fact, it is known that copper(II) dicyanide is not stable but is reduced by cyanide ions to a mixture of copper(I) cyanides with the release of cyanogen.²⁴ It was also noted that organoamines function as reducing agents in hydrothermal reactions, perhaps serving to generate a repository of reduced metal species for further aggregation.^{10a,25} Therefore, the formation of **1** and **2** from the same reaction batches with the various stoichiometric conditions is conceivable. Interestingly, in H_2O , **1** transforms into a two-dimensional assembly, **3**, with a Cu(I)/Cu(II) ratio of 2:1. An attempt to prepare **3** directly from the reaction of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, cyclam, and KCN in H_2O was unsuccessful because the known mononuclear complex $[\text{Cu}(\text{cyclam})](\text{ClO}_4)_2$ ²⁶ was

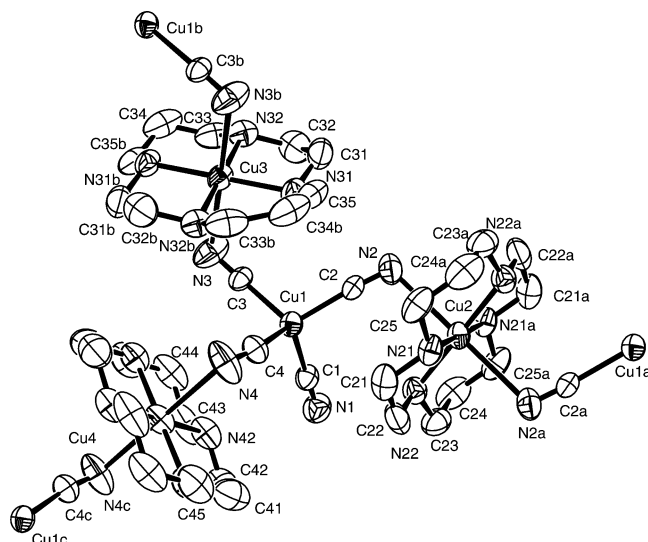


Figure 1. Asymmetric unit and part of the symmetry-generated atoms of $[\text{Cu}(\text{CN})_4\{\text{Cu}(\text{cyclam})\}_{1.5}]_{2n}(\text{H}_2\text{O})_{5n}$ (**1**). Packing water molecules are omitted for clarity.

formed. The use of $\text{Cu}(\text{SO}_4) \cdot 5\text{H}_2\text{O}$ instead of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ also resulted in the formation of $[\text{Cu}(\text{cyclam})]^{2+}$, as judged by IR spectroscopy.²⁷ An additional unusual feature of the synthetic scheme is that the use of anhydrous $\text{Cu}(\text{SO}_4)$ instead of the hydrate form gives a new assembly, **4**, with a structure totally different from those of the other three compounds. Compound **4**, which has a Cu(I)/Cu(II) ratio of 1:1, also transforms into **3** in H_2O upon stirring for 6h, and the retransformation of **3** to **4** can be effected in low yield by stirring **3** in CH_3OH for 12 h.²⁸

The set of reactions described above indicates that the formation of four mixed-valence copper complexes is greatly affected by the amount of water in the reaction media and, thus, can be controlled by the solvent composition. The extent of Cu(II) reduction and the solubility factor seem to be greatly associated with the solvent composition. The observed various Cu(I)/Cu(II) ratios were pointed out earlier. The solubility of potassium salts of the associated anions, CN^- and SO_4^{2-} , is dependent on the solvent composition and, thus, may affect the reaction conditions because KCN and K_2SO_4 are soluble and insoluble in methanol, respectively, whereas both are soluble in water.

Crystal Structures. $[\text{Cu}(\text{CN})_4\{\text{Cu}(\text{cyclam})\}_{1.5}]_{2n}(\text{H}_2\text{O})_{5n}$ (**1**). Figure 1 illustrates an asymmetric unit and part of the symmetry-generated atoms. Packing water molecules are disordered and omitted for clarity in Figure 1. Selected bond distances and angles are listed in Table 3. The Cu1 center, presumably a Cu^{I} center, has four cyanide anions in its distorted tetrahedral coordination sphere, revealing the first example of a structurally characterized bridging $[\text{Cu}(\text{CN})_4]^{3-}$ unit. Only three of the four cyanide groups participate in building the coordination network, and one remains unin-

(23) The TGA carried out under N_2 and the elemental analysis indicate the presence of 4.5 and 5 packing waters, respectively. The X-ray analysis reveals three ordered and two disordered packing waters.

(24) (a) Cooper, D.; Plane, R. A. *Inorg. Chem.* **1966**, *5*, 1677. (b) Chadwick, B. M.; Sharpe, A. G. In *Advances in Inorganic Chemistry and Radiochemistry*, Emeleus, H. J., Sharpe, A. G., Eds.; Academic Press: New York, 1966; Vol. 8, p 83.

(25) Khan, M. I.; Haushalter, R. C.; O'Connor, C. J.; Tao, C.; Zubietta, J. *Chem. Mater.* **1995**, *7*, 593.

(26) The mononuclear complex $[\text{Cu}^{\text{II}}(\text{cyclam})](\text{ClO}_4)_2$ was synthesized by the reaction of $\text{Cu}^{\text{II}}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, cyclam, and KCN in aqueous solution. Elemental analysis calcd (%) for $\text{C}_{10}\text{H}_{24}\text{N}_4\text{Cl}_2\text{O}_8\text{Cu}$ (462.78): C, 25.95; H, 5.23; N, 12.11. Found: C, 26.10; H, 5.21; N, 12.05. Crystal data [Mo $\text{K}\alpha$, 293(2) K]: triclinic, $P-1$, $a = 8.032(2)$ Å, $b = 8.304(2)$ Å, $c = 8.532(2)$ Å, $\alpha = 113.787(4)^\circ$, $\beta = 16.692(4)^\circ$, $\gamma = 94.437(4)^\circ$, $V = 441.4(2)$ Å³, $Z = 2$, purple, GOF = 1.109, $R = 3.51\%$ for 1837 observed independent reflections ($2.83^\circ < \theta < 28.06^\circ$). IR (cm^{-1} , KBr pellet): 3432 (s), 3243 (s), 2938 (m), 1637 (w), 1121 (vs, broad), 626 (m).

(27) Selected IR peaks for $[\text{Cu}^{\text{II}}(\text{cyclam})](\text{SO}_4)$ (cm^{-1} , KBr pellet): 3375-(m), 3207(m), 3130 (m), 2941 (m), 1592 (w), 1120 (vs), 1060 (m), 988 (m), 883 (w), 619 (m).

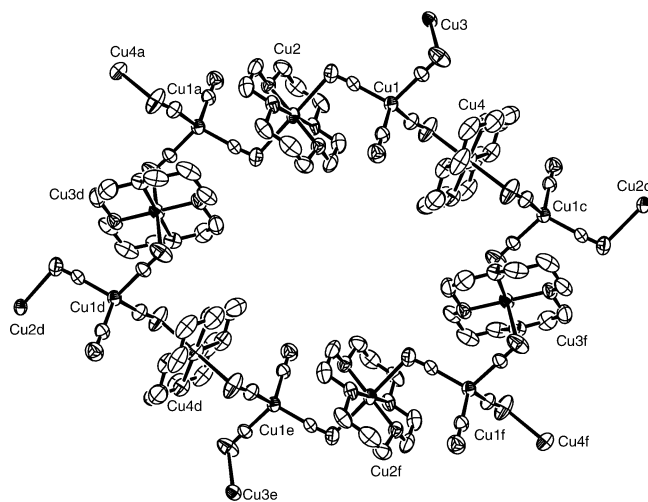
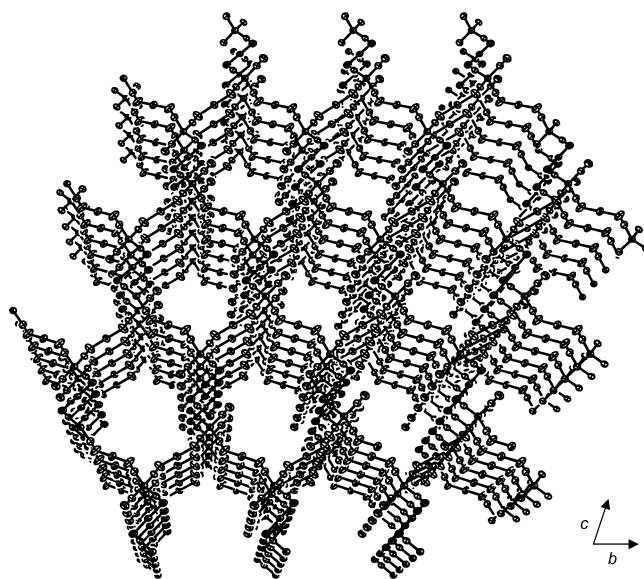
(28) The IR data and the unit cell parameters of **3** and **4** achieved in this way are identical to those described in the text, supporting the validity of such transformations.

Table 3. Selected Bond Distances (Å) and Angles (deg) for **1**

Bond Distances (Å)			
Cu1—C1	1.968(6)	Cu1—C2	1.988(6)
Cu1—C3	1.982(6)	Cu1—C4	2.006(6)
C1—N1	1.155(9)	C2—N2	1.138(8)
C3—N3	1.118(9)	C4—N4	1.137(10)
Cu2—N2	2.681(5)	C3—N3	2.635(7)
Cu4—N4	2.620(7)	Cu2—N21	2.016(4)
Cu2—N22	2.029(5)	Cu3—N31	2.034(5)
Cu3—N32	2.041(5)	Cu4—N41	2.025(6)
Cu4—N42	2.010(5)		
Bond Angles (deg)			
C1—Cu1—C2	106.2(2)	C1—Cu1—	117.9(2)
C1—Cu1—C4	110.2(3)	C2—Cu1—C3	109.1(3)
C2—Cu1—C4	117.3(2)	C3—Cu1—C4	96.4(2)
N1—C1—Cu1	178.5(5)	N2—C2—Cu1	175.1(5)
N3—C3—Cu1	164.9(5)	N4—C4—Cu1	164.9(5)
C2—N2—Cu2	108.7(5)	C3—N3—Cu3	112.6(5)
C4—N4—Cu4	123.0(4)	N2—Cu2—N21	95.61(17)
N2—Cu2—N22	91.03(18)	N21—Cu2—N22	86.64(19)
N3—Cu3—N31	86.7(2)	N3—Cu3—N32	87.4(2)
N31—Cu3—N32	87.0(2)	N4—Cu4—N41	92.31
N4—Cu4—N42	93.91	N41—Cu4—N42	87.1(2)

involved. Among the bond distances between Cu1 and the cyano-carbon atoms, the uninvolved cyano group forms the shortest distance of 1.968 Å, whereas the other three cyano groups show an average distance of 1.992 Å that can be compared with the 2.003 Å found in the discrete $K_3[Cu(CN)_4]$.¹⁶ For the C—N distances of the cyano groups, the uninvolved cyano group gives the longest distance of 1.155 Å, whereas the other three cyano groups form an average distance of 1.131 Å that is similar to the 1.129 Å found in the discrete regular tetrahedral $[Cu(CN)_4]^{3-}$.¹⁶ Complex **1** has an average NC—Cu1—CN bond angle of 109.5°, but the associated standard deviation of 7.2° reflects the extent of distortion. The Cu2, Cu3, and Cu4 centers, presumably Cu^{II} centers, have distorted octahedral geometry, with the equatorial planes occupied by cyclam and the axial positions by cyano-nitrogen atoms. The distance between the adjacent Cu^I and Cu^{II} centers ranges from 4.544 to 4.672 Å. The dihedral angles between the $[CuN_4]$ square panes in **1** are 73.8(3)° for Cu2—Cu3, 74.0(3)° for Cu2—Cu4, and 49.0(3)° for Cu3—Cu4. The average bond distance between the nitrogen atoms of cyclam and the Cu^{II} centers is 2.026 Å, as usual for the Cu—N bond distances. On the other hand, the axial bond distances are extremely long so that the average distance reaches to 2.645 Å. In general, the bond distance between copper and the cyano-nitrogen atom is known to be longer, at around 2.5 Å, because of the weak overlap between the d orbital of copper and the s orbital of the cyano-nitrogen atom,^{9a} indicating that the bridging interaction in **1** is weak. This weak bridging interaction might be the reason for the instability of **1** in water. The bridging C—N—Cu^{II} angles in **1** are very small, at an average of 114.8°, which can also be explained in terms of the participation of a nondirectional s orbital in bridging.^{9a}

The extended structure of **1** is a two-dimensional netlike layer consisting of fused cyclic $[Cu^I_6Cu^{II}_6(CN)_{12}]$ pores, as shown in Figures 2 and 3. The interlayer $Cu^i—Cu^j$ ($i = 1-4$) distances are equal at 8.359 Å. The uninvolved cyanides are directed inside of the pores with a size of 9.8×8.5 Å. The crystal shape of **1** collapses with the loss of packing water

**Figure 2.** Cyclic $[Cu^I_6Cu^{II}_6(CN)_{12}]$ pore of $[Cu(CN)_4\{Cu(cyclam)\}_{1.5}]_{2n}-(H_2O)_{5n}$ (**1**). Packing water molecules are omitted for clarity.**Figure 3.** Extended 2-D net structure of $[Cu(CN)_4\{Cu(cyclam)\}_{1.5}]_{2n}-(H_2O)_{5n}$ (**1**) stacked along the a axis. Packing water molecules and capping ligands are omitted for clarity.

molecules, but the IR spectrum of the dehydrated sample of **1** shows the same cyanide stretching peaks as those of the hydrated form, indicating that the same cyano-bridged framework is maintained. This rigid framework, however, breaks down in H_2O and generates another assembly, **3**.

$[Cu(CN)_2\{Cu(CN)_2Cu(cyclam)\}]_n(H_2O)_n$ (**2**). Asymmetric units and symmetry-related atoms of **2** are illustrated in Figure 4. Selected bond distances and angles are listed in Table 4. There are three types of Cu sites in **2**: a square-pyramidal Cu1 sites, presumably a Cu^{II} center, consisting of four equatorial cyclam N atoms and one axial cyano-N atom; tetrahedral Cu2 sites, presumably a Cu^I center, being composed of three cyano-C atoms and one cyano-N atom; and triangular Cu3 sites, presumably a Cu^I center, with a $[C_2N]$ coordination sphere from three cyano groups. Two adjacent planar $(Cu_2)_2C_2$ rhombuses are parallel and are linked by two triangular Cu3 sites, leading to a ladder-type double-chain structure, as illustrated in Figure 5. System **2**

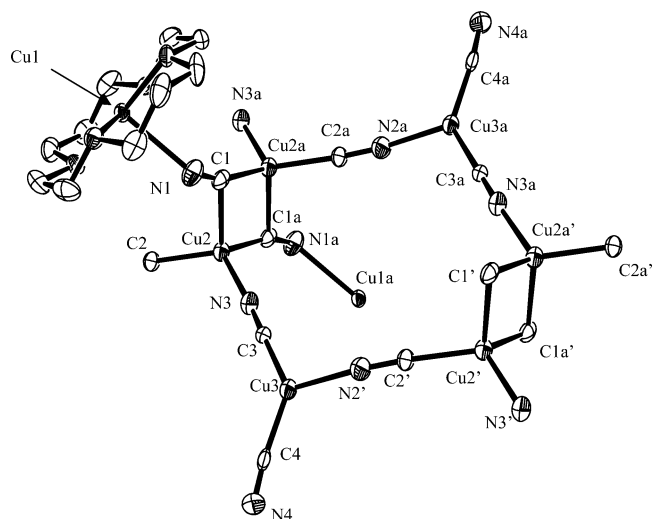


Figure 4. Asymmetric unit and symmetry-related atoms of $[\text{Cu}(\text{CN})_2\text{-}2\{\text{Cu}(\text{CN})_2\text{Cu}(\text{cyclam})\}]_n(\text{H}_2\text{O})_n$ (**2**). Packing water molecules are omitted for clarity.

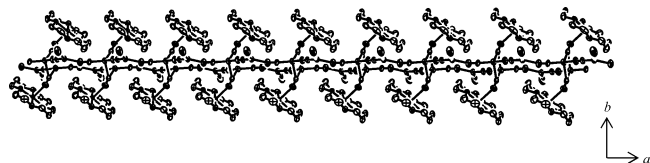


Figure 5. Extended view of $[\text{Cu}(\text{CN})_2\text{-}2\{\text{Cu}(\text{CN})_2\text{Cu}(\text{cyclam})\}]_n(\text{H}_2\text{O})_n$ (**2**) in the *ac* plane, showing a ladder-type double-chain structure. Packing water molecules are omitted for clarity.

Table 4. Selected Bond Distances (Å) and Angles (deg) for **2**

Bond Distances (Å)			
Cu1–N1	2.402(8)	Cu1–N11	2.013(6)
Cu1–N14	2.012(7)	Cu1–N18	2.019(6)
Cu2–C1	2.289(8)	Cu2–C1a	1.981(10)
Cu2–C2	1.930(8)	Cu2–N3	1.981(8)
Cu3–N2	2.011(7)	Cu3–C3	1.913(8)
Cu3–N4	1.900(10)	N1–C1	1.124(10)
N2–C2a	1.145(10)	N3–C3	1.167(10)
N4–C4	1.140(10)		
Bond Angles (deg)			
C1–Cu1–C2	133.53(13)	C1–Cu1–N1	116.21(14)
N1–Cu1–N11	91.5(3)	N1–Cu1–N14	93.1(3)
N1–Cu1–N1	92.1(3)	N1–Cu1–N21	89.9(3)
Cu2–C1–N1	122.4(8)	Cu2a–C1–N1	161.2(8)
Cu2–C1–Cu2a	75.0(3)	C1–Cu2–C2	123.6(3)
C2–Cu2–N3	111.3(3)	C1–Cu2–N3	110.3(3)
C2–Cu2–C1	101.3(3)	C1–Cu2–C1a	105.0(3)
N3–Cu2–C1	102.5(3)	N2a–C2–Cu2	176.1(8)
C2a–N2–Cu3	165.6(8)	C3–N3–Cu2	175.1(7)
Cu3–C3–N3	178.5(8)	C3–Cu3–C4	133.8(3)
N2–Cu3–C4	116.4(3)	N2–Cu3–C3	109.5(3)
Cu3–C4–N4	174.2(7)	Cu1–N1–C1	129.3(7)

is unique, as compared with systems **1**, **3**, and **4**, in that the $\text{Cu}^{\text{II}}(\text{cyclam})$ unit acts as a terminal group and does not participate in building the double-chain structure.

$[\{\text{Cu}(\text{CN})_2\}_2\text{Cu}(\text{cyclam})]_n$ (**3**). The cyclic pore $[\text{Cu}_6^{\text{I}}\text{Cu}_2^{\text{II}}(\text{CN})_8]$ containing an asymmetric unit and part of the symmetry-generated atoms is illustrated in Figure 6. Selected bond distances and angles are listed in Table 5. The Cu1 site, presumably a Cu^{I} site, of this complex has triangular geometry, with the coordination sphere of $[\text{C}_2\text{N}]$ from three cyano groups and six Cu1 sites in the secondary building block serving as bridging heads, forming a net structure that

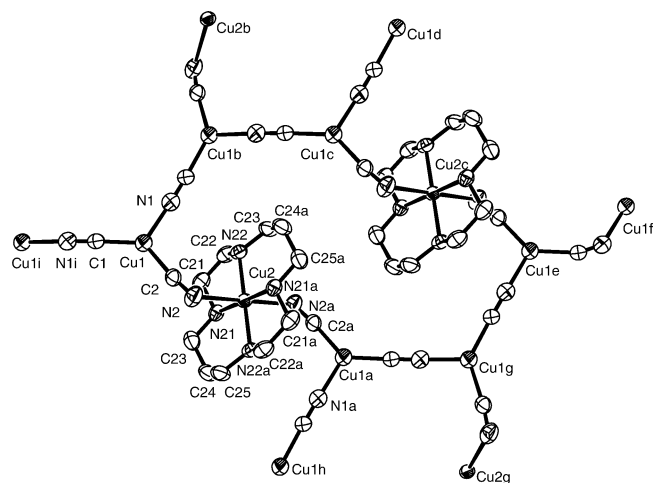


Figure 6. Cyclic pore, $[\text{Cu}_6^{\text{I}}\text{Cu}_2^{\text{II}}(\text{CN})_8]$, of $[\{\text{Cu}(\text{CN})_2\}_2\text{Cu}(\text{cyclam})]_n$ (**3**).

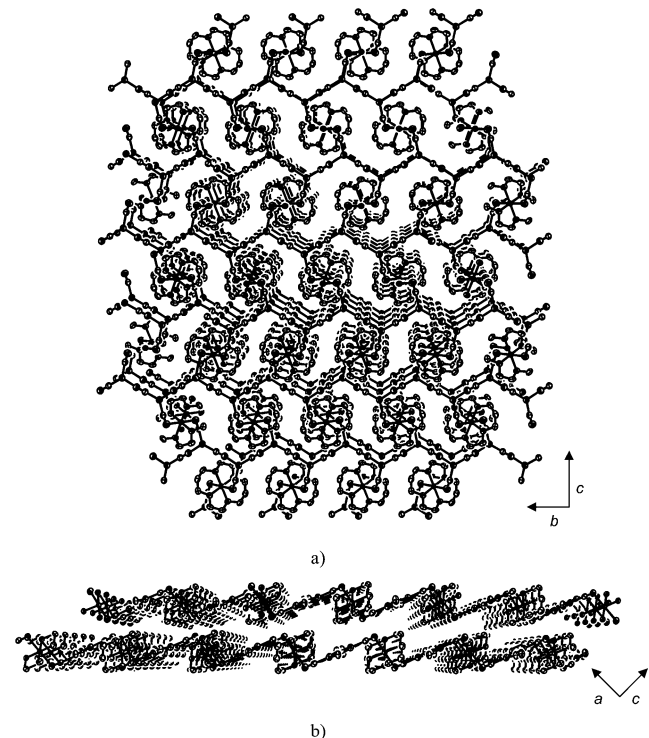


Figure 7. Extended view of **3** showing the net structure: (a) view in the *bc* plane and (b) view in the *ac* plane.

Table 5. Selected Bond Distances (Å) and Angles (deg) for **3**

Bond Distances (Å)			
Cu1–C1	1.895(3)	Cu1–C2	1.916(4)
Cu1–N1	1.970(3)	C1–N1	1.146(5)
C2–N2	1.141(4)	Cu2–N2	2.582(3)
Cu2–N21	2.012(2)	Cu2–N22	2.031(2)
Bond Angles (deg)			
C1–Cu1–C2	133.53(13)	C1–Cu1–N1	116.21(14)
C2–Cu1–N1	110.26(12)	N1i–C1–Cu1	176.9(3)
C1b–N1–Cu1	170.7(3)	N2–C2–Cu1	173.5(3)
N2–Cu2–N21	96.17(10)	N2–Cu2–N22	93.04(11)
N21–Cu2–N22	94.00(10)	C2–N2–Cu2	110.6(2)

can be viewed as one-dimensional chains $[\text{Cu}_2^{\text{I}}(\text{CN})_4]_n^{2n-}$ cross-linked by $[\text{Cu}(\text{cyclam})]$ units via cyano-bridges, as shown in Figure 7a. The 2D nets of **3** are wrinkled because of the small bridging C2–N2–Cu2 angle of $110.6(2)^\circ$ and are packed to fit each other, as shown in Figure 7b. In the

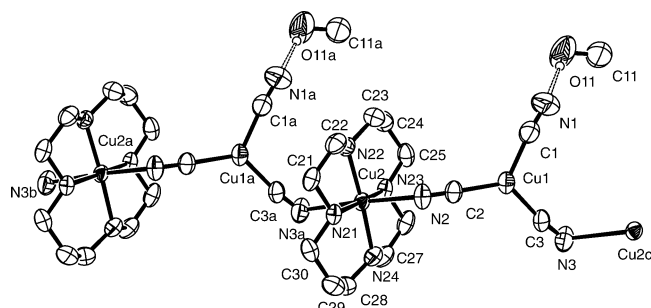


Figure 8. Repeating unit and symmetry-generated atoms of $[\text{Cu}(\text{CN})_3\text{Cu}(\text{cyclam})]_n(\text{CH}_3\text{OH})_n$ (**4**). Double dashed bonds denote hydrogen bonds.

Table 6. Selected Bond Distances (Å) and Angles (deg) for **4**

Bond Distances (Å)			
Cu1–C1	1.932(4)	Cu1–C2	1.934(3)
Cu1–C3	1.949(3)	C1–N1	1.135(5)
C2–N2	1.134(4)	C3–N3	1.139(4)
Cu2–N2	2.414(3)	Cu2–N3a	2.752(3)
Cu2–N21	2.023(2)	Cu2–N22	2.025(2)
Cu2–N23	2.020(2)	Cu2–N24	2.024(3)
O11–C11	1.359(6)		
Bond Angles (deg)			
C1–Cu1–C2	122.4(1)	C2–Cu1–C3	126.5(1)
C1–Cu1–C3	111.0(1)	N1–C1–Cu1	172.7(4)
N2–C2–Cu1	178.7(3)	N3–C3–Cu1	172.4(3)
C2–N2–Cu2	135.8(3)	C3–N3–Cu2	108.9(3)
N21–Cu2–N2	90.1(1)	N22–Cu2–N2	93.6(1)
N23–Cu2–N2	94.1(1)	N24–Cu2–N2	90.5(1)
N21–Cu2–N22	86.0(1)	N23–Cu2–N22	93.5(1)
N23–Cu2–N24	86.0(1)	N23–Cu2–N21	175.8(1)
N21–Cu2–N24	94.3(1)	N24–Cu2–N22	175.9(1)

$[\text{Cu}^I_2(\text{CN})_4]_n^{2n-}$ chain, the average bond distance of the cyano-carbon atoms to Cu1 is 1.906 Å, which is shorter than the distance (1.970 Å) of the cyano-nitrogen atom to Cu1. A similar bonding trend was seen for the helical chain complex $\text{K}[\text{Cu}^I(\text{CN})_2]$.^{9a} The average bridging N–C–Cu1 angle is 175.2°, closer to 180° than the bridging C–N–Cu1 angle of 170.7(3)° because of the participation of an s orbital in the Cu–N bond, as mentioned above.

The Cu2 center, presumably a Cu^{II} center, has distorted octahedral geometry similar to that of **1**, however, with a shorter copper–cyano-nitrogen bond distance, of 2.582(3) Å, than those of **1**. The cyclam-based $[\text{CuN}_4]$ coordination planes of each Cu^{II} center in **3** are parallel. The shortest inter- and intranet $\text{Cu}^{\text{II}}\text{--Cu}^{\text{II}}$ separations are 6.830 and 8.482 Å, respectively.

$[\text{Cu}(\text{CN})_3\text{Cu}(\text{cyclam})]_n(\text{CH}_3\text{OH})_n$ (**4**). The repeating unit and symmetry-generated atoms of **4** are shown in Figure 8, and the selected bond distances and angles are listed in Table 6. In this complex, the $\text{Cu}(\text{CN})_3$ and $\text{Cu}(\text{cyclam})$ units are alternatively disposed to form a chain structure. The Cu1 center, likely a Cu^{I} center, has a triangular coordination sphere of $[\text{CuC}_3]$ with an average Cu1–C bond distance of 1.908 Å and a NC–Cu1–CN angle of 120.0°. One of the three cyano groups around the Cu^{I} center remains as a nonbridging unit.

The coordination sphere of the Cu2, presumably a Cu^{II} center, is similar to those observed in **1** and **3**, with the usual average bond distance of 2.023 Å between Cu2 and the cyclam-nitrogen atoms but with unusual bond distances between Cu2 and the cyano-nitrogen atoms. The interactions

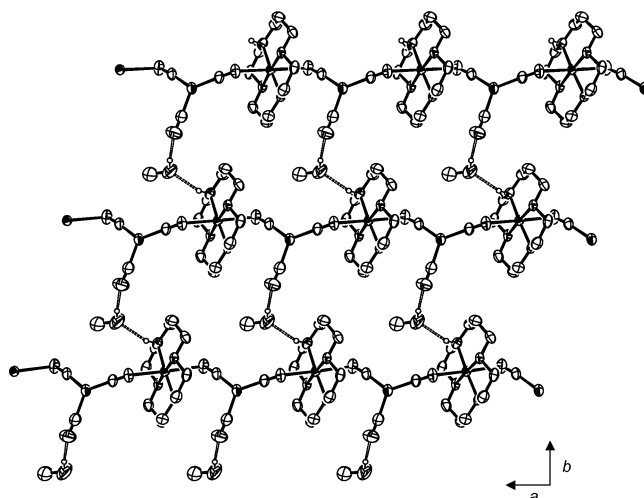


Figure 9. Extended view of $[\text{Cu}(\text{CN})_3\text{Cu}(\text{cyclam})]_n(\text{CH}_3\text{OH})_n$ (**4**) showing the two-dimensional superstructure. Double dashed bonds denote hydrogen bonds.

between Cu2 and the cyano-nitrogen atoms are asymmetric, with distances of 2.414(3) and 2.752(3) Å. In particular, the latter distance is considered as long when compared with other corresponding values, implying that the chain structure might be fragile. In fact, the dissolution of **4** in water results in the collapse of the chain structure and the transformation to **3**, as confirmed by IR spectroscopy. The bridging angles of Cu2–N–C are also asymmetric at 135.8(3)° for Cu2–N2–C2 and 108.9(3)° for Cu2–N3–C3.

The packing methanol molecules locate between the adjacent chains and form hydrogen bonds with the nonbridging cyano-nitrogen atoms and the cyclam ligands. The related bond distances and angles are 2.717(7) Å and 169(7)° for methanol–O–H–cyano–N and 2.900(6) Å and 151(3)° for cyclam–N–H–methanol–O. As a consequence of these hydrogen-bonding interactions, the chains and the methanol molecules form a two-dimensional superstructure, as shown in Figure 9. The shortest intra- and interchain $\text{Cu}^{\text{II}}\text{--Cu}^{\text{II}}$ distances are 9.470 and 10.034 Å, respectively.

The foregoing structural analyses reveal that the open-shell unit $\text{Cu}^{\text{II}}(\text{cyclam})$ in 2-D **1**, **3**, and **4** serves as a bridging group and is separated from the adjacent open-shell unit by at least one cuprous cyanide unit, whereas in **2**, it acts as a terminal group and does not participate in building the double-chain structure. Therefore, the magnetic interactions are expected to be negligible, which was confirmed experimentally for compounds **1**, **3**, and **4**.

Conclusions

The first examples of mixed-valence cyano-bridged copper complexes $[\text{Cu}^{\text{I}}(\text{CN})_4\{\text{Cu}^{\text{II}}(\text{cyclam})\}_{1.5}]_{2n}(\text{H}_2\text{O})_{5n}$ (**1**), $[\text{Cu}^{\text{I}}(\text{CN})_2\{\text{Cu}^{\text{II}}(\text{CN})_2\text{Cu}^{\text{II}}(\text{cyclam})\}]_n(\text{H}_2\text{O})_n$ (**2**), $[\{\text{Cu}^{\text{I}}(\text{CN})_2\}_2\text{Cu}^{\text{II}}(\text{cyclam})]_n$ (**3**), and $[\text{Cu}^{\text{I}}(\text{CN})_3\text{Cu}^{\text{II}}(\text{cyclam})]_n(\text{CH}_3\text{OH})_n$ (**4**), showing various structural properties, have been prepared via partial reduction of Cu^{II} ions with cyanide anions and self-assembly. The formation of these compounds is strongly affected by the amount of water in the reaction media and, thus, can be controlled by the solvent composition. In addition, the use of cyclam seems to be critical in observing

such structural variation because the use of other multidentate amines such as *N,N'*-(2-aminoethyl)-1,3-propanediamine and *N*-(3-aminopropyl)-1,3-propanediamine did not result in a similar structure variation.²⁹ Complexes **1** and **3** show net structures consisting of fused cyclic $[\text{Cu}^{\text{I}}_6\text{Cu}^{\text{II}}_6(\text{CN})_{12}]$ and $[\text{Cu}^{\text{I}}_6\text{Cu}^{\text{II}}_2(\text{CN})_8]$ pores, respectively. In particular, complex **1** constitutes a novel example of a high-dimensional compound containing a bridging tetrahedral $[\text{Cu}(\text{CN})_4]^{3-}$ unit. In the case of **4**, packing methanol molecules mediate hydrogen-bonding interactions between chains, leading to a

layer structure. Complex **2** forms a ladder-type double-chain structure whose chain skeleton does not include the Cu^{II} - (cyclam) unit. The magnetic interactions are negligible in these mixed-valence complexes.

Supporting Information Available: Crystallographic data in CIF format for the structures of **1**, **2**, **3**, and **4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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