A NEW HOST LATTICE BUILT OF THE WERNER-TYPE COPPER(I,II) CYANIDE COMPLEX INVOLVING A MACROCYCLIC LIGAND

Hidetaka YUGE[1], Takayoshi SOMA[2] and Takeshi Ken MIYAMOTO[3]

Department of Chemistry, School of Science, Kitasato University, Kitasato, Sagamihara, Kanagawa 228-8555, Japan; e-mail: [1] yuge@kitasato-u.ac.jp, [2] soma@kitasato-u.ac.jp, [3] tkmiyamo@kitasato-u.ac.jp

Received June 19, 1997
Accepted March 11, 1998

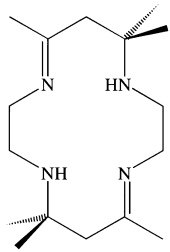
Crystals of a new clathrate $[Cu^{II}(hmtd)Cu^{I}(CN)_3]\cdot CH_2Cl_2$ were afforded from a Me_2CO–EtOH–CH_2Cl_2 solution of a macrocyclic complex $Cu^{II}(hmtd)Cu^{I}(CN)_3\cdot 2\ H_2O$ (hmtd = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene). It crystallizes in the monoclinic space group $P2_1/n$, a = 7.936(5), b = 18.717(4), c = 17.783(6) Å, β = 98.55(4)°, Z = 4, R = 0.0558 for 1 870 reflections. Unprecedentedly, only one of the three nitrogen-ends of a $Cu^{I}(CN)_3$ moiety is coordinated to the square-pyramidal Cu(II) center. The guest CH_2Cl_2 molecules are captured in the channel between the potlid-shaped $[Cu^{II}(hmtd)Cu^{I}(CN)_3]$ molecules.

Key words: Copper complexes; Copper(I,II) cyanide; Macrocyclic ligands; Werner complex host; Clathrates; Crystal structure.

A number of transition metal cyanide complexes involved with various am(m)ine ligands have been developed as hosts of inclusion compounds[1]. Among them, the three-dimensional host structures of the Hofmann-diam-type clathrates $[Cd(diam)Ni(CN)_4]\cdot x$ G (diam = $NH_2(CH_2)_nNH_2$, n = 2–9, x = 0.5–2, G is aromatic guest species)[2] have topologies identical to the two-dimensional Hofmann-type host $[Cd(NH_3)_2Ni(CN)_4]$, in which tetracyanonickelate anions coordinate to the octahedral Cd cations through all of the four cyano groups to form the electrically neutral network. Without enclathration of guest molecules but H_2O, a series of the complexes $CdNi(CN)_4\cdot 2$ diam$\cdot x\ H_2O$ (n = 2–7 and 9, x = 0–2) have crystallized in variegated multidimensional structures owing to the differences in the number of their methylene groups[3].

Cyanocuprate(I) complexes have been known to have various multidimensional structures since the structure determination of $K[Cu(CN)_2]$ by Cromer[4] in 1957. We have recently reported the crystal structure of $[(aepipzH)_2H][Cu_4(CN)_7]$ (aepipz = *N*-(2-aminoethyl)piperazine)[5]; a dimeric guest of $[(aepipzH)_2H]^{3+}$ cations protonated at each 4-NH end of piperazine ring and 2-NH_2 of 2-aminoethyl group sharing H^+ are captured in the three-dimensional framework. At this stage we attempted to obtain other negatively-charged cyanocuprate(I) skeletons including some macrocyclic Cu(II) complexes as larger countercations, *e.g.* 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene (hmtd), which is one of the macrocyclic ligands developed by Curtis[6]. Accom-

modation of a Cu(II) complex of hmtd, followed by recrystallization from a Me_2CO–EtOH–CH_2Cl_2 solution gave a new inclusion compound $[Cu(hmtd)Cu(CN)_3]\cdot CH_2Cl_2$ (**1**). The discrete molecular host of **1** consists of square-pyramidal $[Cu^{II}(hmtd)]$ and trigonal $[Cu^{I}(CN)_3]$ moieties spanned by one of the three cyano groups.



EXPERIMENTAL

Preparation

$CuSO_4\cdot 5\ H_2O$ (2.50 g, 0.010 mol) and hmtd·2 HBr (5.30 g, 0.012 mol; ref.[6b]) were dissolved in H_2O (50 ml) and KOH pellets (1.30 g) were added. The resulting solution was poured into 50 ml of an aqueous solution containing CuCN (0.90 g, 0.010 mol) and KCN (1.96 g, 0.030 mol); after standing overnight at 5 °C, the purple precipitate of $Cu(hmtd)Cu(CN)_3\cdot 2\ H_2O$ was obtained; yield 2.14 g (0.0041 mol, 41%). For $C_{19}H_{36}Cu_2N_7O_2$ (521.6) calculated: 43.75% C, 6.96% H, 18.80% N; found: 43.34% C, 6.88% H, 18.73% N.

The precipitate (0.50 g) was dissolved in a 1 : 1 (v/v) mixture of Me_2CO and EtOH (100 ml) and CH_2Cl_2 (50 ml) was added to the resulting solution. Blue plate-like crystals of $[Cu^{II}(hmtd)Cu^{I}(CN)_3]\cdot CH_2Cl_2$ (**1**) were obtained after a few days standing at 5 °C. For $C_{19.5}H_{33}N_7ClCu_2$ (528.1) calculated: 44.35% C, 6.30% H, 18.57% N; found: 44.32% C, 6.29% H, 19.26% N. The partial liberation of the guest CH_2Cl_2 appears to cause discrepancies in the analytical results. Hence, the composition was determined from the density value and the results of the X-ray structure.

X-Ray Crystallography

A thin plate-like single crystal of **1** with dimensions 0.05 × 0.10 × 0.25 mm coated with epoxy resin was subjected to intensity data collection on a Rigaku AFC-7R diffractometer (MoKα: λ = 0.71069 Å) at 293 K by 2θ–ω technique. The cell dimensions were refined using 25 reflections in $30.67 \le 2\theta \le 34.09°$. The crystal data are: $C_{20}H_{34}Cl_2Cu_2N_7$, M = 570.52, monoclinic, $P2_1/n$ (No. 14), a = 7.936(5), b = 18.717(4), c = 17.783(6) Å, β = 98.55(4)°, U = 2 584(2) Å^3, Z = 4, D_m = 1.436 g cm^{-3} (flotation method in bromoform–mesitylene), D_x = 1.466 g cm^{-3}, μ(MoKα) = 1.874 mm^{-1}. Three standard reflections were monitored after every 150; no remarkable decay was observed during data collection. The intensity data were corrected for Lp and absorption[7]; transmission factors range from 0.6516 to 0.9121.

The structure was solved by the direct method using SHELXS86 (ref.[8]). Non-H atoms were refined anisotropically with H atoms at calculated positions through the full-matrix least-squares on F^2 using SHELXL93 (ref.[9]). The final values are: $(\Delta/\sigma)_{max}$ = 0.000, $\Delta\rho_{max}$ = 0.758, $\Delta\rho_{min}$ = –0.838 e Å^{-3};

the peak and the hole are located at 0.99 and 1.08 Å from Cu1, respectively. R = 0.0558 and $wR(F^2)$ = 0.0994 for 1 870 observed reflections with $F_o^2 > 2\sigma(F_o^2)$, and R = 0.2008 and $wR(F^2)$ = 0.1458 for 4 546 independent reflections among the 4 901 measured in $4 < 2\theta < 55°$ for 280 parameters. Atomic scattering factors including those for real and imaginary anomalous dispersion corrections were taken from ref.[10].

RESULTS AND DISCUSSION

The interatomic distances and angles are listed in Table I. ORTEP (ref.[11]) drawings of the asymmetric unit and the crystal structure of **1** are illustrated in Figs 1 and 2, respectively.

As shown in Fig. 1, the crystal structure of **1** is composed of host [Cu(hmtd)-$Cu(CN)_3$] molecules and guest CH_2Cl_2 molecules. Like as the handle of a potlid, the trigonal $Cu^I(CN)_3$ moiety coordinates to the square-pyramidal Cu^{II}(hmtd) through one nitrogen-end of the three cyano groups in the host complex. The trigonal $Cu^I(CN)_3$ moieties have been found in a number of cyanocuprate(I) complexes; that in $Na_2Cu(CN)_3 \cdot 3\ H_2O$ (ref.[12]) behaves as the discrete anion whereas those in $K[Cu(CN)_2]$ (ref.[4]) and $K[Cu_2(CN)_3] \cdot H_2O$ (ref.[13]) span the Cu atoms *via* two of the three and all three cyano groups, respectively. However, compound **1** is the first example that only one nitrogen-end of the three cyano groups ligates to the other coordination metal centers and the two others remain terminal.

The Cu1–N21 distance, 2.494(8) Å, in the apical disposition about square-pyramidal Cu(II) center is remarkably longer than the equatorial Cu1–N distances, 2.00 ± 0.03 Å. The elongation of the apical or axial bond length(s) due to the Jahn–Teller effect on the Cu(II) center has been often observed in such cyanometallate compounds as $[Cu^{II}(H_2O)(en)_2][Cu_2(CN)_4]$ (ref.[14]) and $[Cu^{II}(en)_2Ni(CN)_4]$ (ref.[15]); the relatively small Cu1–N21–C21 angle, 125.5(7)°, was also similar to that of the latter (123.6(4)°). An-

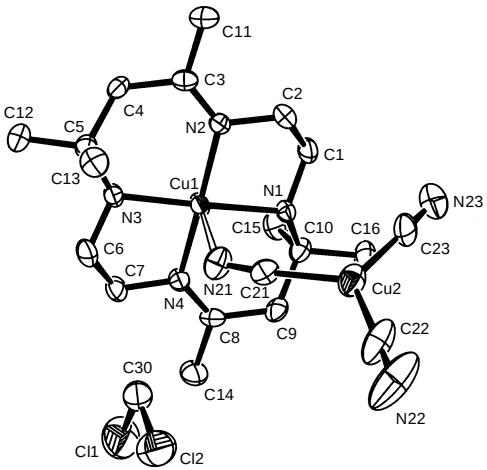


FIG. 1
Asymmetric unit of $[Cu(hmtd)Cu(CN)_3] \cdot CH_2Cl_2$ at the 30% probability ellipsoids along with the atomic notations

TABLE I
Interatomic distances (Å) and angles (°) for **1**

Distances

Cu1–N1	2.029(5)	N1–C10	1.495.(9)	C9–C10	1.532(10)
Cu1–N2	1.970(6)	N2–C2	1.469(9)	C3–C11	1.495(10)
Cu1–N3	1.970(6)	N2–C3	1.266(9)	C5–C12	1.530(10)
Cu1–N4	1.980(6)	N3–C5	1.491(9)	C5–C13	1.514(10)
Cu1–N21	2.494(8)	N3–C6	1.429(9)	C8–C14	1.500(10)
Cu2–C21	1.929(9)	N4–C7	1.463(9)	C10–C15	1.522(10)
Cu2–C22	1.933(2)	N4–C8	1.259(9)	C10–C16	1.535(10)
Cu2–C23	1.921(12)	C1–C2	1.510(10)	C11–C30	1.729(10)
N21–C21	1.133(9)	C3–C4	1.507(10)	C12–C30	1.755(11)
N22–C22	1.128(4)	C4–C5	1.525(10)	Cu1...N22^{i}	2.978(12)
N23–C23	1.143(12)	C6–C7	1.493(10)	N3...N22^{i}	2.911(12)
N1–C1	1.475(9)	C8–C9	1.508(10)	C30...N23^{ii}	3.281(13)

Angles

N1–Cu1–N2	85.1(2)	Cu1–N2–C2	110.0(5)	N3–C5–C13	109.0(6)
N1–Cu1–N3	175.4(3)	Cu1–N2–C3	128.9(5)	N3–C6–C7	110.6(7)
N1–Cu1–N4	94.8(2)	Cu1–N3–C5	122.1(5)	N4–C7–C6	109.7(6)
N2–Cu1–N3	94.8(3)	Cu1–N3–C6	108.4(5)	N4–C8–C9	121.7(7)
N2–Cu1–N4	175.0(3)	Cu1–N4–C7	110.9(5)	N4–C8–C14	124.5(8)
N3–Cu1–N4	84.9(3)	Cu1–N4–C8	127.8(6)	C4–C3–C11	115.0(7)
N1–Cu1–N21	89.3(3)	C1–N1–C10	117.5(6)	C3–C4–C5	120.6(6)
N2–Cu1–N21	98.0(3)	C2–N2–C3	121.1(6)	C4–C5–C12	107.7(6)
N3–Cu1–N21	95.3(3)	C5–N3–C6	119.3(6)	C4–C5–C13	110.1(7)
N4–Cu1–N21	87.0(3)	C7–N4–C8	121.0(7)	C12–C5–C13	110.2(7)
Cu1–N21–C21	125.5(7)	N1–C1–C2	107.3(6)	C9–C8–C14	113.8(7)
C21–Cu2–C22	119.5(4)	N1–C10–C9	107.7(6)	C8–C9–C10	118.7(6)
C21–Cu2–C23	113.6(4)	N1–C10–C15	109.9(6)	C9–C10–C15	111.6(7)
C22–Cu2–C23	126.9(5)	N1–C10–C16	110.5(6)	C9–C10–C16	107.3(7)
Cu2–C21–N21	171.3(8)	N2–C2–C1	107.1(6)	C15–C10–C16	109.9(7)
Cu2–C22–N22	178.1(4)	N2–C3–C4	119.4(7)	C11–C30–C12	111.1(5)
Cu2–C23–N23	176.0(11)	N2–C3–C11	125.5(8)	Cu1...N22^{i}–C22^{i}	172.0(10)
Cu1–N1–C1	105.8(4)	N3–C5–C4	107.8(6)	N3–H8...N22^{i}	139
Cu1–N1–C10	117.1(4)	N3–C5–C12	112.1(7)	C30–H33...N23^{ii}	173

Symmetry codes: (i): $x - 1/2, -y + 1/2, z + 1/2$; (ii): $-x + 1/2, y - 1/2, -z + 1/2$.

other nitrogen-end N22 is relatively close to Cu1 and N3; the Cu1···N22 distance, 2.978(12) Å, is too long for coordination bond while the N3···N22, 2.911(12) Å, is short enough but the N3–H8···N22 angle, 139°, is a little acute for hydrogen bond. The competition of these electrostatic interactions seems to cause the larger displacement parameter of N22. The disordered model of the cyano group was not adopted because of its worse convergence. An electrostatic interaction is also observed between the host and the guest: C30···N23 = 3.281(13) Å and C30–H33···N23 = 173°.

The host molecules accommodating the CH_2Cl_2 guest in the channel (Fig. 2) can be considered to belong to a kind of the Werner complexes. The host complexes of the so-called "Werner-type" clathrates have $M^{II}X_2A_4$ (X = SCN^-, I^-, *etc*., A = pyridine derivatives) compositions in the octahedral geometries[16]. Both hosts of **1** and the general "Werner-type" clathrates are so bulky that their three-dimensional structures in the crystalline state have the void space favourable for accommodation of some guest molecules, although they do not form multidimensional infinite structures such as the Hofmann-type and analogous hosts. Therefore the compound **1** can be regarded as a member of a new family of the inclusion compounds involved with the Werner complex hosts.

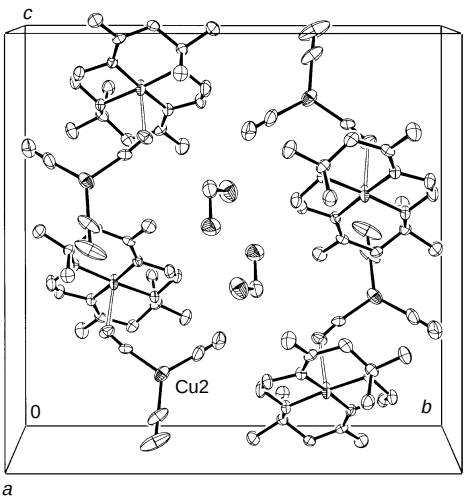


FIG. 2
The perspective view of $[Cu(hmtd)Cu(CN)_3]\cdot CH_2Cl_2$ along the *a* axis

This work was supported by Kanagawa Academy and Technology Research Grants 9961115 and Kitasato University Research Grant for Young Researchers.

REFERENCES

1. a) Iwamoto T. in: *Inclusion Compounds* (J. L. Atwood, J. E. D. Davies and D. D. MacNicol, Eds), Vol. 1, p. 29. Academic Press, London 1984; b) Iwamoto T. in: *Inclusion Compounds*

(J. L. Atwood, J. E. D. Davies and D. D. MacNicol, Eds), Vol. 5, p. 177. Oxford University Press, Oxford 1991.
2. Yuge H., Asai M., Mamada A., Nishikiori S., Iwamoto T.: *J. Inclusion Phenom. Mol. Recogn. Chem*. **1995**, *22*, 71; and references therein.
3. a) Yuge H., Mamada A., Asai M., Nishikiori S., Iwamoto T.: *J. Chem. Soc., Dalton Trans*. **1995**, 3195; b) Yuge H., Nishikiori S., Iwamoto T.: *Acta Crystallogr., Sect. C: Cryst. Struct. Commun*. **1996**, *52*, 575.
4. Cromer D. T.: *J. Phys. Chem*. **1957**, *61*, 1388.
5. Yuge H., Iwamoto T.: *J. Inclusion Phenom. Mol. Recogn. Chem*. **1996**, *26*, 119.
6. a) Curtis N. F.: *J. Chem. Soc*. **1964**, 2644; b) Hay R. W., Lawrance G. A., Curtis N. F.: *J. Chem. Soc., Perkin Trans. 1* **1975**, 591.
7. North A. T. C., Phillips D. C., Mathews F. S.: *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr*. **1968**, *24*, 351.
8. Sheldrick G. M.: *Acta Crystallogr., Sect. A: Fundam. Crystallogr*. **1990**, *46*, 467.
9. Sheldrick G. M.: *SHELXL93. Program for the Refinement of Crystal Structures*. University of Gottingen, Gottingen 1993.
10. *International Tables for Crystallography*, Vol. C, p. 500. Kluwer Academic Publishers, Dordrecht 1995.
11. Johnson C. K.: *ORTEPII. Report ORNL-5138*. Oak Ridge National Laboratory, Tennessee U.S.A. 1976.
12. Kappenstein C., Hugel R. P.: *Inorg. Chem*. **1978**, *17*, 1945.
13. Cromer D. T., Larson A. C.: *Acta Crystallogr*. **1962**, *15*, 397.
14. Williams R. J., Larson A. C., Cromer D. T.: *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem*. **1972**, *28*, 858.
15. Lokaj J., Gyerova K., Sopkova A., Sivy J., Kettmann V., Vrabel V.: *Acta Crystallogr., Sect. C: Cryst. Struct. Commun*. **1991**, *47*, 2447.
16. Lipkowski J. in: Ref.[1a], p. 59.