

Alkali Cation Ligating Iodocuprate(I)-Based Coordination Networks with the Thiocrown Ether 1,10-Dithia-18-crown-6

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The lamellar coordination polymer $\infty[\text{CuI}(\text{1,10DT18C6})]$ (1) (1,10DT18C6 = 1,10-dithia-18-crown-6) may be prepared by reaction of CuI with the thiocrown ether in acetonitrile. 1 crystallizes in the monoclinic space group $P2_1/n$ with $a = 10.764(2)$, $b = 14.317(3)$, and $c = 12.335(3)$ Å, $\beta = 98.08(3)^\circ$, $V = 1882.0(7)$ Å³, $Z = 4$, $R = 0.041$, $wR_2 = 0.102$ for 5480 reflections and contains (CuI)₂ rhomboid dimers as characteristic building units. Performing the reaction in the presence of an equimolar quantity of alkali metal halide MI ($M^+ = \text{Na}^+, \text{K}^+$) in acetonitrile solution at 100°C leads to formation of ion-ligating iodocuprate(I)-based two-dimensional coordination networks in $\infty[\{\text{Na}(\text{CH}_3\text{CN})\}\{\text{Cu}_5\text{I}_6(\text{1,10DT18C6})\}]$ (2) and $\infty[\text{K}\{\text{Cu}_4\text{I}_5(\text{1,10DT18C6})_2\}]$ (3). Both anionic frameworks contain characteristic iodocuprate(I) chains that are bridged in a $\mu\text{-S1,S10}$ manner by 1,10DT18C6 macrocycles. However, the structure-directing influence of the alkali metal cation manifests itself in both the connectivity pattern and the stoichiometry of the resulting CuI-based network. 2 is chiral and crystallizes in the monoclinic space group $P2_1$ with $a = 10.456(4)$, $b = 13.674(6)$, and $c = 11.535(5)$ Å, $\beta = 92.82(3)^\circ$, $V = 1647.3(12)$ Å³, $Z = 2$, $R = 0.049$, $wR_2 = 0.110$ for 3018 reflections. 3 is likewise monoclinic, space group $P2/n$ with $a = 11.418(6)$, $b = 12.521(7)$, and $c = 15.398(7)$ Å, $\beta = 96.58(3)^\circ$, $V = 2187(2)$ Å³, $Z = 2$, $R = 0.064$, $wR_2 = 0.176$ for 3858 reflections. After losing their coordinated acetonitrile molecules at 180°C, the lamellar coordination networks of 2 retain their integrity up to 230°C before loss of their bridging thiocrown ethers. © 2000 Academic Press

Key Words: iodocuprates (I); 1,10-dithia-18-crown-6; coordination polymers; lamellar networks; crystal engineering.

INTRODUCTION

The construction of porous solid-state coordination networks capable of reversibly hosting selected guest molecules or ions in their voids is a topic of considerable current interest (1–4). Although a number of known examples do contain 4,4'-bipyridine (5–11), attempts to design two- or three-dimensional frameworks with larger channels have

often been foiled when employing rigid organic spacer molecules by the self-interpenetration of multiple networks, so as to eliminate the void space (12). Rational crystal engineering strategies to enable a systematic modification of cavity size and chemical environment must, therefore, also prevent lattice interweaving, while retaining a given supramolecular architecture.

In the past, rigid bi- and tridentate N-donor ligands such as pyrazine or 4,4'-bipyridine have often been chosen as molecular building blocks for the design of network topologies. However, a few encouraging reports on the employment of more flexible connecting ligands such as methylene-bridged dichalcogenoethers (13), thioether macrocycles (14–16), or functionalized pendant-arm derivatives of 1,4,7-triazacyclononane (17) have appeared in the recent literature. In analogy to the porous networks of zeolites, the resulting layers or frameworks might be expected to be capable of undergoing elastic deformations in response to structure-directing agents or imbibed molecular guests.

The characteristic ability of alkylcycloarsoxanes (RAsO_n , $n = 4, 5$; $R = \text{CH}_3, \text{C}_2\text{H}_5$) to bridge tetrahedrally coordinated metal atoms, taken together with their pronounced conformational flexibility and their confirmed selective ligating properties for alkali cations (18), suggested to us that such macrocyclic ligands would exhibit considerable potential as spacer molecules for the construction of functional porous networks. These considerations led us to prepare a series of one- to three-dimensional polymers (19–21), in which copper(I) halides were employed to render tailored complementary building blocks such as (CuX)₂ rhomboid dimers or $\infty[\text{CuX}]$ single and double chains under self-assembly conditions (22). Both neutral and anionic coordination networks can be generated in this manner. For instance, discrete $[\text{Cu}_6\text{I}_8]^{2-}$ units are linked by tetrameric *cyclo*-(CH₃AsO)₄ into infinite anionic chains that coordinate the Cs⁺ counterions in a $\kappa^8\text{O}$ manner in the layered structure of $[\text{Cs}(\text{H}_2\text{O})_2][\text{Cu}_3\text{I}_4\{\text{cyclo}-(\text{CH}_3\text{AsO})_4\}_2]$ (23). We have now extended this design strategy to the crown ether 1,10-dithia-18-crown-6 (1,10DT18C6) (24) and report the preparation, structure, and properties of the two-

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dimensional coordination polymers $\frac{2}{\infty}[\text{CuI}(1,10\text{DT}18\text{C}6)]$ (**1**), $\frac{2}{\infty}[\{\text{Na}(\text{CH}_3\text{CN})\}\{\text{Cu}_5\text{I}_6(1,10\text{DT}18\text{C}6)\}]$ (**2**), and $\frac{2}{\infty}[\text{K}\{\text{Cu}_4\text{I}_5(1,10\text{DT}18\text{C}6)_2\}]$ (**3**).

EXPERIMENTAL SECTION

1,10-Dithia-18-crown-6 (1,10DT18C6) was prepared according to the literature procedure (24). Elementary analyses for C,H,N were performed on a Vario El (Elementar Analysen-systeme GmbH), the thermogravimetric analysis (TGA/DTA) on an Exstar 6000 (Seiko Instruments), and the powder X-ray diffraction study on a Bruker AXS D8 Advance.

Syntheses

$\frac{2}{\infty}[\text{CuI}(1,10\text{DT}18\text{C}6)]$ (**1**). In acetonitrile solution, 38.1 mg of CuI (0.2 mmol) and 59.2 mg (0.2 mmol) of 1,10DT18C6 (1,10-dithia-18-crown-6) were refluxed for 3 h. Leaving the solution to stand at room temperature over a period of 2 d led to growth of colorless crystals of **1** in 79% yield (77 mg). Elemental analysis, $\text{C}_{12}\text{H}_{24}\text{CuI}_2\text{O}_4\text{S}_2$, $M = 486.87$; C 29.3 (calc 29.6), H 4.9 (calc 4.9), S 13.4 (calc 13.2)%.

$\frac{2}{\infty}[\{\text{Na}(\text{CH}_3\text{CN})\}\{\text{Cu}_5\text{I}_6(1,10\text{DT}18\text{C}6)\}]$ (**2**). In 2 ml of CH_3CN , 38.1 mg of CuI (0.2 mmol), 59.2 mg of 1,10DT18C6 (0.2 mmol), and 30.0 mg of NaI (0.2 mmol) were dissolved and heated in a sealed glass tube (~ 10 ml capacity) at 100°C for 40 h. Slow cooling to room temperature at $1^\circ\text{C}\cdot\text{h}^{-1}$ afforded colorless crystals of **2** in 78% yield (45 mg) based on Cu. Elemental analysis, $\text{C}_{14}\text{H}_{27}\text{Cu}_5\text{I}_6\text{NNaO}_4\text{S}_2$, $M = 1439.58$; C 11.5 (calc 11.7), H 1.9 (calc 1.9), N 0.9 (calc 1.0), S 4.4 (calc 4.5)%.

$\frac{2}{\infty}[\text{K}\{\text{Cu}_4\text{I}_5(1,10\text{DT}18\text{C}6)_2\}]$ (**3**). In 2 ml of acetonitrile solution, 38.1 mg of CuI (0.2 mmol), 59.2 mg of 1,10DT18C6 (0.2 mmol), and 33.2 mg of KI (0.2 mmol) were heated at 100°C for 40 h in a sealed glass tube. Slow cooling to room temperature at $1^\circ\text{C}\cdot\text{h}^{-1}$ led to growth of colorless crystals of **3** in 83% yield (63 mg) based on Cu. Elemental analysis, $\text{C}_{24}\text{H}_{48}\text{Cu}_4\text{I}_5\text{KO}_4\text{S}_2$, $M = 1520.62$; C 19.21 (calc 19.0), H 3.1 (calc 3.2), S 8.57 (calc 8.4)%.

X-Ray Structural Analyses

Crystal and refinement data are listed for **1–3** in Table 1. Unit cell constants were obtained from least-squares fits to the settings of 25 reflections ($20^\circ \leq 2\theta \leq 30^\circ$) centered on a Siemens P4 diffractometer. Intensity data were collected on this instrument in the ω mode at 293 K. Three selected reflections, that were monitored at regular intervals during the course of data collection for each of the compounds, exhibited no significant deviations in intensity. Absorption corrections were performed for **1** and **3** on the basis of

TABLE 1
Crystal and Refinement Data for **1–3**

	1	2	3
Space group	$P2_1/n$	$P2_1$	$P2/n$
a (Å)	10.764(2)	10.456(4)	11.418(6)
b (Å)	14.317(3)	13.674(6)	12.521(7)
c (Å)	12.335(3)	11.535(5)	15.398(7)
α (°)	90	90	90
β (°)	98.08(3)	92.82(3)	96.58(3)
γ (°)	90	90	90
V (Å ³)	1882.0(7)	1647.3(12)	2187(2)
Z	4	2	2
M	486.87	1439.58	1520.62
$F(000)$	968	1312	1440
D_{calc} (g·cm ⁻³)	1.718	2.902	2.309
Radiation	MoK α	MoK α	MoK α
μ (mm ⁻¹)	3.03	8.96	5.77
Crystal size (mm)	$0.37 \times 0.30 \times 0.28$	$0.27 \times 0.25 \times 0.11$	$0.48 \times 0.39 \times 0.21$
Absorption corr.	ψ scan	Empirical	ψ scan
Max./min. transm.	0.094/0.071	1.00/0.54	0.124/0.061
$2\theta_{\text{max}}$ (°)	60	50	50
$h/k/l$ Ranges	0/15,0/20, -17/17	0/12,0/16, -13/13	-13/0,0/14, -18/18
Independ. refl.	5480	3018	3858
R_{int}	0.033	0.040	0.043
$I > 2\sigma(I)$	1675	2359	2506
Goodness-of-fit S	0.705	1.039	1.026
$R [I > 2\sigma(I)]^a$	0.041	0.049	0.064
wR_2 (all data) ^b	0.102	0.110	0.176

$$^a R = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$$

$$^b wR_2 = \frac{[\sum w(F_o^2 - F_c^2)^2 / F_c^2] / \sum w(F_o^2)^2 \sum w(F_c^2)^2]^{1/2}}{w} \text{ with weights given by } w = [\sigma^2(F_o^2) + (aP)^2 + bP]^{-1} \text{ with } P = [\max(F_o^2, 0) + 2F_c^2] / 3.$$

ψ scan data (nine chosen reflections with high χ values) and for **2** using DIFABS (25). After structure solution with SHELXS-86 (26), positional parameters and anisotropic temperature factors were refined against F_o^2 with SHELXL-93 (27). C5–C9 of one of the 1,10DT18C6 ligands in **3** are disordered with partial occupation factors of 0.667 and 0.333. Hydrogen atoms were included at calculated positions for nondisordered carbon atoms with their isotropic temperature factors coupled to those of the parent carbon atoms. Atom coordinates and equivalent isotropic temperature factors are listed for **1–3** in Table 2, selected bond lengths and angles in Tables 3–5. Crystallographic data for these compounds have been deposited with the Cambridge Crystallographic Data Centre (CCDC 135283–135285). Copies may be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1 E2, UK (fax int. code +44(0) 1223/336-033, e-mail deposit@chemcrs.cam.ac.uk).

RESULTS AND DISCUSSION

The lamellar coordination polymer $\frac{2}{\infty}[\text{CuI}(1,10\text{DT}18\text{C}6)]$ (**1**) crystallizes from an equimolar CuI/1,10DT18C6

TABLE 2
Atom Positional Parameters with Equivalent Isotropic Temperature Factors U_{eq} ($\text{\AA}^2 \times 10^3$)^a

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	U_{eq}
${}^2_{\infty}[\text{CuI}(1,10\text{DT18C6})] (\mathbf{1})$				
I(1)	3730(1)	1085(1)	9095(1)	85(1)
Cu(1)	6052(1)	469(1)	9776(1)	81(1)
S(1)	7223(2)	420(1)	8341(1)	78(1)
S(10)	8236(2)	-3372(1)	3963(1)	89(1)
O(4)	5891(4)	-1852(3)	6665(3)	88(1)
O(7)	5507(4)	-2890(3)	4691(3)	92(1)
O(13)	8370(4)	-689(3)	4850(3)	91(1)
O(16)	7406(4)	864(3)	5789(3)	81(1)
C(2)	7091(6)	-646(4)	7553(5)	103(2)
C(3)	5809(6)	-932(4)	7103(6)	116(3)
C(5)	4698(5)	-2095(4)	6102(5)	86(2)
C(6)	4779(5)	-3017(4)	5555(5)	94(2)
C(8)	5686(6)	-3723(4)	4116(5)	103(2)
C(9)	6618(4)	-23517(5)	3356(5)	112(3)
C(11)	8273(6)	-2300(3)	4777(4)	87(2)
C(12)	8082(7)	-21433(4)	4112(5)	111(2)
C(14)	8131(8)	159(4)	4281(5)	115(3)
C(15)	8343(6)	931(4)	5096(5)	96(2)
C(17)	7547(6)	1571(4)	6593(4)	98(2)
C(18)	6674(6)	1355(4)	7404(4)	98(2)
${}^2_{\infty}[\{\text{Na}(\text{CH}_3\text{CN})\}\{\text{Cu}_2\text{I}_2(1,10\text{DT18C6})\}] (\mathbf{2})$				
I(1)	2698(2)	10846(1)	4199(2)	45(1)
I(2)	5042(1)	8184(1)	4696(1)	35(1)
I(3)	1670(1)	8570(1)	6612(1)	38(1)
I(4)	5296(2)	7409(1)	8454(1)	44(1)
I(5)	2994(1)	5670(1)	5843(1)	41(1)
I(6)	4915(2)	10473(1)	7477(1)	46(1)
Cu(1)	4862(3)	10174(3)	5248(3)	58(1)
Cu(2)	2697(3)	8932(2)	4636(3)	45(1)
Cu(3)	4216(3)	8705(3)	6878(3)	55(1)
Cu(4)	2992(3)	7029(2)	7508(3)	46(1)
Cu(5)	5098(3)	6718(3)	6277(3)	50(1)
S(1)	1439(5)	8227(5)	3143(5)	37(1)
S(10)	-1642(5)	11630(4)	1023(5)	38(1)
Na(1)	-39(8)	8661(7)	791(7)	43(2)
O(4)	-1037(13)	7398(11)	2036(12)	43(4)
O(7)	-2183(12)	9220(10)	1327(12)	36(4)
O(13)	714(12)	10276(12)	217(12)	42(4)
O(16)	2335(14)	8776(12)	782(13)	52(5)
N(100)	-978(19)	8592(19)	-1164(17)	61(6)
C(100)	-1433(19)	8680(18)	-2091(17)	43(6)
C(200)	-1975(22)	8832(24)	-3273(18)	70(10)
C(2)	536(22)	7186(14)	3623(16)	57(8)
C(3)	-314(19)	6713(12)	2706(17)	46(6)
C(5)	-2051(17)	7816(18)	2628(16)	55(8)
C(6)	-2855(18)	8439(14)	1816(20)	50(7)
C(8)	-3020(15)	9853(13)	694(17)	40(6)
C(9)	-2302(18)	10651(10)	120(12)	29(5)
C(11)	-250(12)	11129(16)	1810(13)	36(5)
C(12)	866(18)	11022(16)	1055(18)	49(7)
C(14)	1795(17)	10118(21)	-443(17)	58(8)
C(15)	2853(18)	9585(16)	210(22)	65(9)
C(17)	3240(15)	8297(15)	1531(15)	41(6)
C(18)	2547(18)	7583(13)	2257(16)	51(7)

TABLE 2—Continued

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	U_{eq}
${}^2_{\infty}[\text{K}\{\text{Cu}_4\text{I}_3(1,10\text{DT18C6})_2\}] (\mathbf{3})^b$				
I(1)	9350(1)	7302(1)	553(1)	50(1)
I(2)	9070(1)	7606(1)	3424(1)	59(1)
I(3)	12500	7964(1)	2500	51(1)
Cu(1)	8249(2)	8115(2)	1816(1)	53(1)
Cu(2)	10444(2)	7015(2)	2119(2)	63(1)
K(1)	7500	12069(4)	2500	51(1)
S(1)	8235(3)	9940(3)	1516(2)	45(1)
S(10)	10787(4)	15201(4)	2319(3)	61(1)
O(4)	7077(12)	11884(9)	564(7)	76(4)
O(7)	7788(11)	13760(11)	1444(7)	77(4)
O(13)	10870(10)	13119(8)	3560(8)	63(3)
O(16)	9858(12)	11251(11)	2745(8)	80(4)
C(2)	7517(17)	10036(12)	409(6)	68(5)
C(3)	7498(19)	11118(10)	2(10)	75(6)
C(5)	7140(49)	12851(14)	92(18)	88(13)
C(5A)	6668(39)	12944(16)	403(39)	88(13)
C(6)	6965(24)	13769(23)	682(14)	55(9)
C(6A)	7669(46)	13718(41)	519(9)	78(18)
C(8)	8816(23)	14363(30)	1367(17)	74(14)
C(8A)	8621(28)	14585(47)	1887(45)	126(70)
C(9)	9348(15)	14579(25)	2283(17)	61(10)
C(9A)	9895(27)	14207(28)	1701(30)	89(19)
C(11)	11165(16)	15006(12)	3480(5)	68(5)
C(12)	11697(14)	13950(10)	3748(13)	74(6)
C(14)	11379(15)	12098(10)	3710(16)	93(8)
C(15)	10420(17)	11282(15)	3614(10)	91(7)
C(17)	10427(15)	10485(17)	2261(11)	97(8)
C(18)	9727(9)	10338(18)	1390(10)	81(6)

^a U_{eq} is defined as one-third of the trace of orthogonalized U_{ij} tensor
^bC5–C9 in **3** has a partial occupation factor of 0.667, C5A–C9A of 0.333.

reaction mixture in acetonitrile solution and contains $(\text{CuI})_2$ rings as characteristic building blocks (Fig. 1). These are linked by 1,10DT18C6 macrocycles in a μ -*SI*, *S10* fashion to construct corrugated sheets, whose connectivity pattern is depicted in Fig. 2. On regarding the $(\text{CuI})_2$ lozenges as junctions in the lamellar network, it is possible to recognize a simple 4^4 net similar to that previously observed in ${}^2_{\infty}[\text{Cu}_2\text{X}_2\{\text{cyclo}-(\text{CH}_3\text{AsO})_4\}_2]$ ($X = \text{Cl}, \text{Br}$ (20)). As illustrated in Fig. 3, individual thiacycrown ligands of the large 48-membered $[\text{Cu}_6\text{I}_4(1,10\text{DT18C6})_4]$ rings of **1** are alternately orientated on opposite sides of the polymeric

TABLE 3
Selected Bond Lengths (\AA) and Angles ($^\circ$) in $[\text{CuI}(1,10\text{DT18C6})] (\mathbf{1})$

Cu1–I1	2.6727(11)	Cu1–S10a	2.329(2)
Cu1–S1	2.313(2)	Cu1–I1a	2.6174(10)
I1–Cu1–I1a	117.22(3)	Cu1–I1–Cu1a	62.78(3)
I1–Cu1–S1	110.83(5)	I1–Cu1–S10a	100.38(6)
I1a–Cu1–S1	111.33(5)	I1a–Cu1–S10a	104.69(6)
S1–Cu1–S10a	111.66(7)		

TABLE 4
Selected Bond Lengths (Å) and Angles (°) in
[Na(CH₃CN)]₂[Cu₅I₆(1,10DT18C6)] (2)

Cu1-I1	2.675(4)	Cu3-I6	2.609(4)
Cu1-I2	2.803(4)	Cu4-I3	2.698(4)
Cu1-I6	2.601(4)	Cu4-I4	2.648(4)
Cu1a-I5	2.711(4)	Cu4-I5	2.672(4)
Cu2-I1	2.665(4)	Cu5-I2	2.710(4)
Cu2-I2	2.655(3)	Cu5-I4	2.681(4)
Cu2-I3	2.614(3)	Cu5-I5	2.652(4)
Cu3-I2	2.793(4)	Cu5-I1a	2.676(4)
Cu3-I3	2.671(4)	Cu2-S1	2.324(6)
Cu3-I4	2.742(4)	Cu4-S10a	2.324(6)
Cu1-I1-Cu2	65.51(11)	Cu2-I3-Cu4	104.93(10)
Cu2-I1-Cu5a	119.01(12)	Cu3-I3-Cu4	61.40(11)
Cu1-I1-Cu5a	61.85(11)	Cu3-I4-Cu4	61.11(11)
Cu2-I2-Cu5	106.96(11)	Cu3-I4-Cu5	66.21(12)
Cu2-I2-Cu3	66.37(11)	Cu4-I4-Cu5	61.17(10)
Cu3-I2-Cu5	65.11(11)	Cu4-I5-Cu5	61.22(10)
Cu1-I2-Cu2	63.86(10)	Cu1a-I5-Cu5	61.69(11)
Cu1-I2-Cu5	124.39(10)	Cu1a-I5-Cu4	122.53(12)
Cu1-I2-Cu3	61.35(10)	Cu1-I6-Cu3	66.45(12)
Cu2-I3-Cu3	68.74(11)		

TABLE 5
Selected Bond Lengths (Å) and Angles (°) in
[K{Cu₄I₅(1,10DT18C6)₂}] (3)

Cu1-I1	2.637(2)	Cu2-I2	2.788(3)
Cu1-I2	2.625(3)	Cu2-I3	2.636(3)
Cu1a-I2	2.707(3)	Cu1-S1	2.331(5)
Cu2-I1	2.610(3)	Cu2-S10a	2.319(5)
Cu1-I1-Cu2	65.81(8)	I2-Cu1-I2a	108.02(8)
Cu1-I2-Cu1a	64.94(8)	I2-Cu2-I3	106.31(9)
Cu1-I2-Cu2	63.49(7)	I1-Cu1-S1	103.03(12)
Cu1a-I2-Cu2	125.93(8)	I2-Cu1-S1	114.74(13)
Cu2-I3-Cu2a	126.46(13)	I2a-Cu1-S1	102.66(13)
I1-Cu1-I2	116.95(9)	I1-Cu2-S10a	108.2(2)
I1-Cu1-I2a	110.50(9)	I2-Cu2-S10a	105.3(2)
I1-Cu2-I2	112.34(9)	I3-Cu2-S10a	106.2(2)
I1-Cu2-I3	117.58(9)		

sheets. A marked distortion is apparent for the centrosymmetric (CuI)₂ rings, which exhibit Cu-I bond lengths of 2.617(1) and 2.673(1) Å accompanied by I1-Cu1-I1a and Cu1-I1-Cu1a angles of respectively 117.22(3) and 62.78(3)°.

Ion-Ligating Iodocuprate(I)-Based Networks

The two-dimensional network of **1** illustrates how copper(I) halides are capable of providing complementary building units that are tailored to meet the spacial requirements of their partner bridging ligand. Many types of

oligomeric and polymeric CuX substructures have been found in copper(I) halide-based coordination polymers of rigid N-donor ligands, for instance both cubane-like and tricyclic Cu₄X₄ tetramers, zigzag helical $\frac{2}{\infty}$ [CuX] single chains, and staircase or spirocyclic $\frac{2}{\infty}$ [CuX] double chains (28, 29). The formation of infinite chains in **1** is apparently prevented by both the size and conformational flexibility of the participating 1,10DT18C6 thiacycrown ligands, which successfully adjust to fill the potential voids of the resulting 4⁺ net. Inspection of Figs. 2 and 3 suggests that **1** could be capable of selectively imbibing alkali metal salts between its sheets by coordinating their hard monovalent cations M⁺ through its 1,10DT18C6 O-donor atoms. The alternative approach toward the design of ion ligating networks presented in this work involves performing the self-assembly reaction between CuX and the thiacycrown ether in the presence of MX. As illustrated in a schematic fashion for theor-

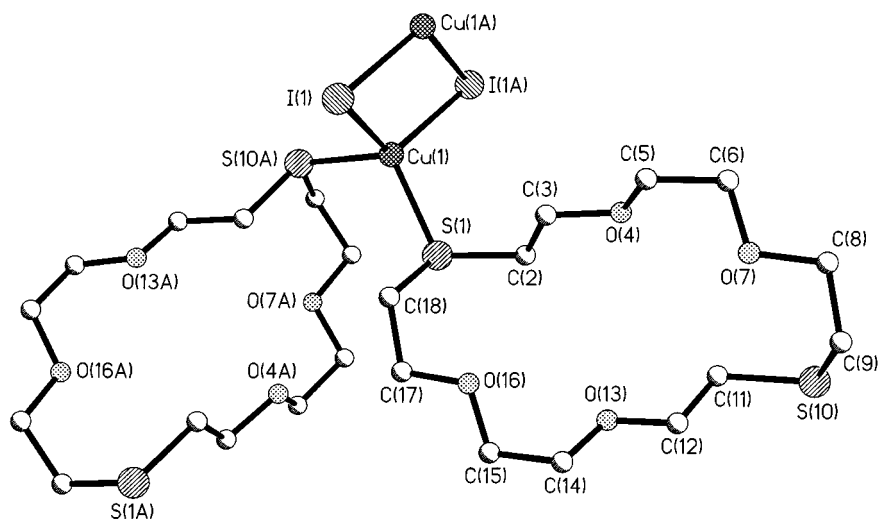


FIG. 1. Numbering scheme in the asymmetric unit of $\frac{2}{\infty}$ [Cu(1,10DT18C6)] (**1**).

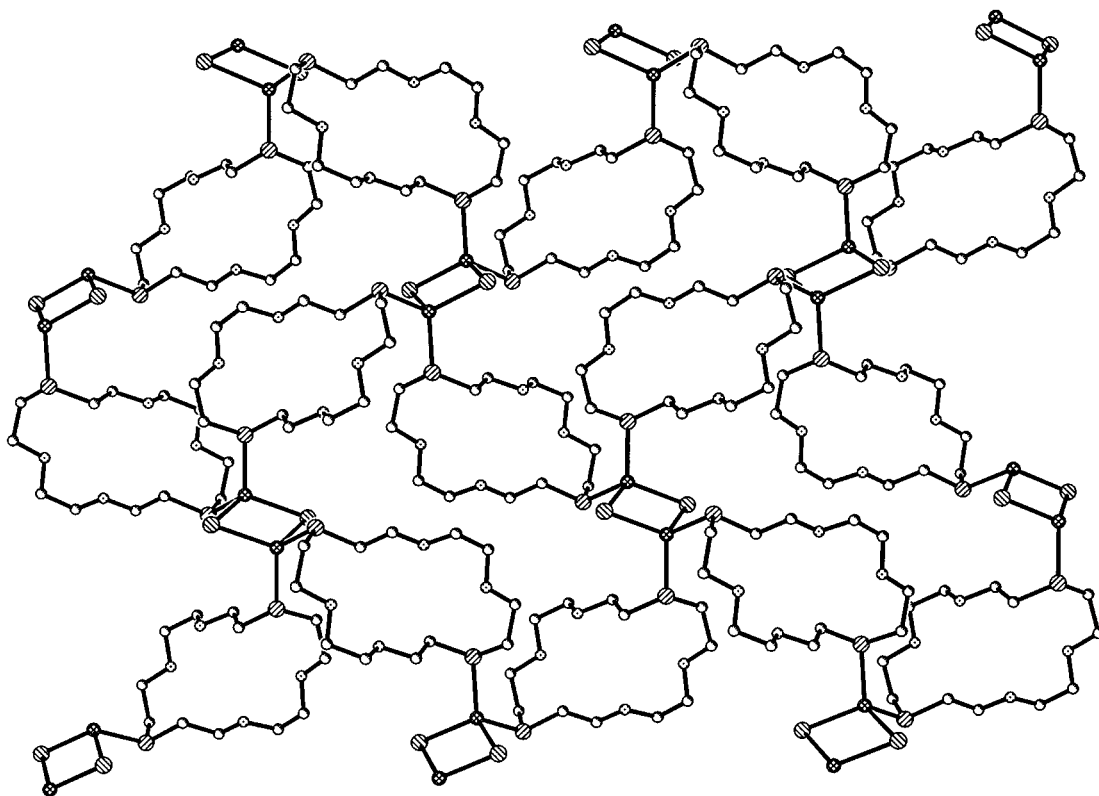


FIG. 2. Two-dimensional network of **1**.

etical examples in Fig. 4, two general types of anionic coordination polymers could potentially result from such a process: (a) infinite chains $\frac{1}{\infty}[\text{Cu}_a\text{X}_b(1,10\text{DT18C6})_c]$ with intrastrand bridging or (b) lamellar frameworks $\frac{2}{\infty}[\text{Cu}_a\text{X}_b(1,10\text{DT18C6})_c]$ with interstrand bridging. A version of the former type (Fig. 4a) has previously been found in $[\text{Cs}(\text{H}_2\text{O})_2][(\text{Cu}_3\text{I}_4\{\text{cyclo}-(\text{CH}_3\text{AsO})_4\}_2)]$, in which discrete $[\text{Cu}_6\text{I}_8]^{2-}$ units are linked by bridging methylcycloarsoxane tetramers into infinite chains (23). Both the stoichiometry and connectivity pattern of any resulting coordination polymer will, of course, be expected to intimately

depend on the size and desired coordination number of the structure-directing alkali cation M^+ , a state of affairs that is clearly reflected in the structures of **2** and **3**. A sheetlike network with interstrand bridging of the general type shown in Fig. 4b is found for both coordination polymers. However, although identical equimolar ratios of $\text{CuX}/\text{MX}/1,10\text{DT18C6}$ were employed in both cases, strikingly different stoichiometries are apparent for $\frac{2}{\infty}[\{\text{Na}(\text{CH}_3\text{CN})\}\{\text{Cu}_5\text{I}_6(1,10\text{DT18C6})\}]$ (**2**) and $\frac{2}{\infty}[\{\text{K}\{\text{Cu}_4\text{I}_5(1,10\text{DT18C6})_2\}]$ (**3**). The asymmetric unit of the former complex is depicted in Fig. 5, which highlights the coordination of the Na^+ ions

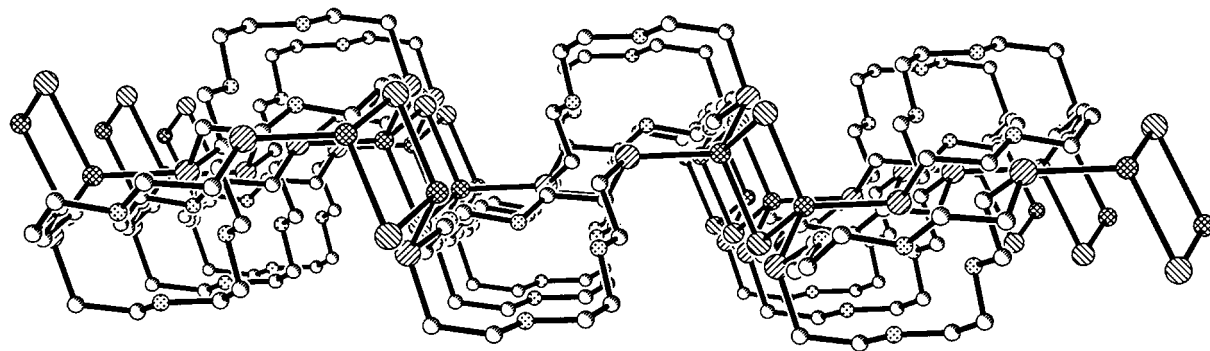


FIG. 3. Lamellar coordination polymer **1** viewed from the side.

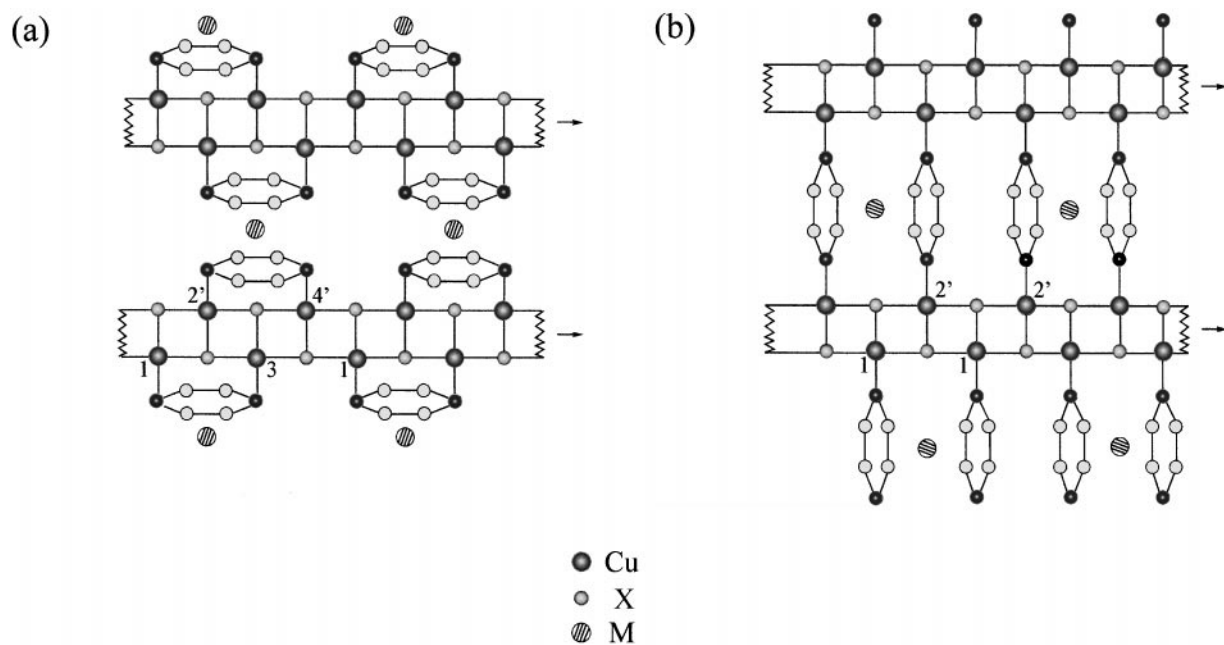


FIG. 4. Two possible types of halocuprate(I)-based networks with ion ligating 1,10DT18C6 thiocrown ethers: (a) single chains with 1,3:2',4' intrastrand bridging, (b) sheets with 1:2' interstrand bridging. Numbers refer to the position of copper atoms in the sequence of the $\frac{1}{\infty}[\text{CuX}]$ staircase and dashes to the opposite side of the backbone. Additional halogen atoms, that would be required to provide the halocuprate(I) chains with a negative charge, have been omitted.

through four O and one S atom of a single 1,10DT18C6 macrocycle. The sixth position *trans* to S1 in a distorted octahedron is occupied by the N atom of a guest acetonitrile molecule. S1 and S10 of the thiocrown ether coordinate respectively Cu2 und Cu4 of adjacent iodocuprate(I) pillars $\frac{1}{\infty}[\{\text{Cu}_5\text{I}_6\}^-]$ which contain a helical $\frac{1}{\infty}[\text{CuI}]$ double chain as their structural backbone. Completion of the distorted

tetrahedral coordination spheres of Cu1 and Cu3 is achieved through the presence of an additional bridging iodine atom I6, that of Cu5 by I2 of the double chain.

Figure 6 illustrates the connectivity pattern within the chiral two-dimensional framework of **2**, whose absolute structure was established on the basis of its Flack parameter (30) of $-0.03(7)$. Propagation of the asymmetric unit by the

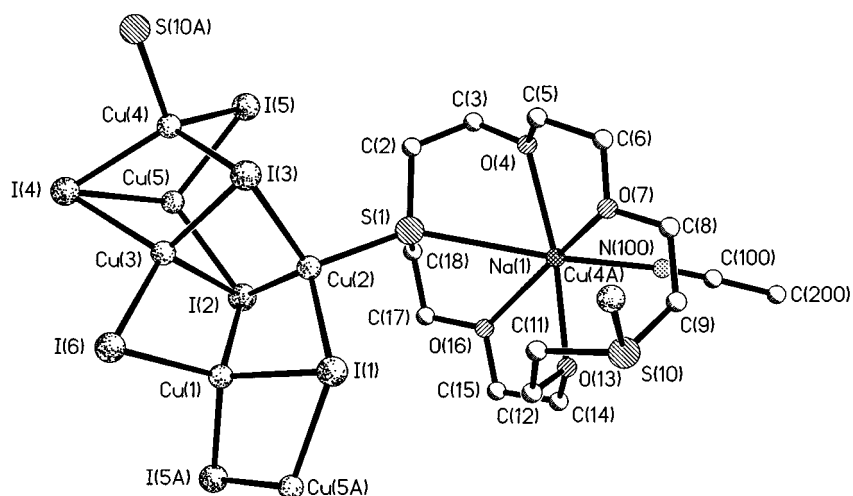


FIG. 5. Asymmetric unit and numbering scheme of $\frac{1}{\infty}[\{\text{Na}(\text{CH}_3\text{CN})\}\{\text{Cu}_5\text{I}_6(1,10\text{DT18C6})\}]$ (**2**). Selected bond lengths (Å) and angles (°) in the octahedral Na^+ coordination sphere: Na1–S1 3.11(1), Na1–O4 2.51(2), Na1–O7 2.48(2), Na1–O13 2.45(2), Na1–O16 2.49(2), Na1–N100 2.42(2), N100–Na1–S1 165.3(7), O4–Na1–O13 157.8(6), O7–Na1–O16 153.8(7).

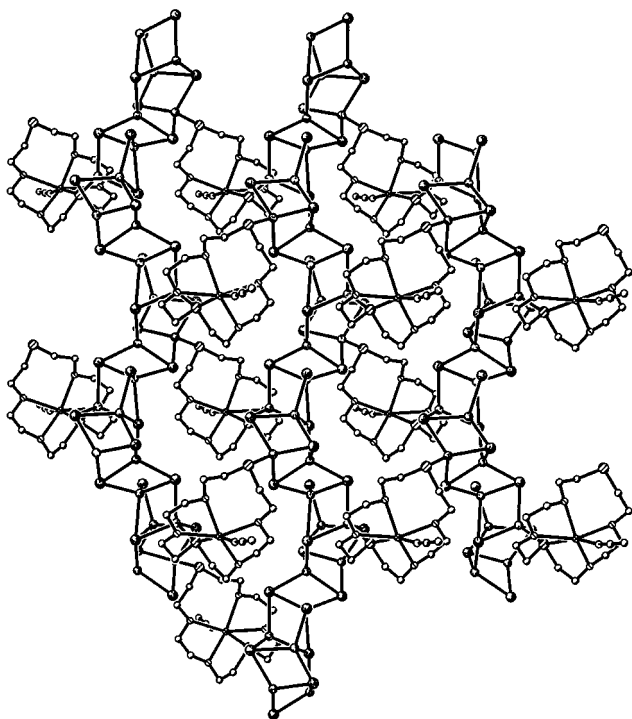


FIG. 6. Two-dimensional coordination network of **2** with highlighting of the $\frac{1}{\infty}[\text{Cu}_5\text{I}_6]^-$ chains.

crystallographic screw diads of the monoclinic space group $P2_1$ generates helical $\frac{1}{\infty}[\text{Cu}_5\text{I}_6]^-$ chains that are alternately linked to their left and right neighbors by pairs of 1,10DT18C6 thiacycrown ligands attached to Cu2 and Cu4. Using the nomenclature depicted in Fig. 4, the interstrand bridging pattern may be described as 2,4:7',9' for a pen-

tanuclear Cu_5I_5 backbone repeating unit. The adoption of this unusual connectivity mode coupled with the presence of severely twisted $\frac{1}{\infty}[\text{Cu}_5\text{I}_6]^-$ pillars (Figs. 6 and 7) reduces the potential void space to such an extent that only the coordinated acetonitrile molecules cocrystallize with the iodocuprate(I)-based coordination polymer. As may be seen in Fig. 7, these solvent molecules point away from the corrugated sheets of **2**, whose CuI core is effectively covered by the ionophoric 1,10DT18C6 macrocycles.

The coordination requirements of the larger potassium cations lead to the self-assembly of the two-dimensional coordination polymer **3** with its two thiacycrown ligands per K^+ ion. This allows the adoption of an eight-fold distorted cubelike coordination sphere by the alkali atoms, in which they themselves lie on the diad axes of the monoclinic space group $P2/n$ (Fig. 8). In contrast to **2**, for which five thiacycrown donor atoms participate in metal ion coordination, one less oxygen is required per macrocycle in the potassium iodocuprate(I) **3**. As depicted in Fig. 9, the anionic pillars of this lamellar coordination polymer contain individual tetranuclear $[\text{Cu}_4\text{I}_4]$ units, that are linked together by bridging iodine atoms I3/I3a. The symmetry-related inner copper atoms Cu1/Cu1a of these building blocks are coordinated by S1/S1a of thiacycrown ligands, whose S10/S10a sulfur atoms participate in the tetrahedral coordination spheres of the outer copper atoms Cu2/Cu2a of an adjacent iodocuprate(I) chain. This means that the interstrand bridging mode of **3** may be described as 1,4:2',3' in terms of the nomenclature introduced in Fig. 4. Inspection of Fig. 9 suggests that larger Cs^+ cation might possibly direct the assembly of a related 1;3:2',4' connectivity pattern, as this should allow five or six donor atoms of each of the participating thiacycrown macrocycles in $[\text{Cs}(1,10\text{DT18C6})_2]^+$ sandwiches to coordinate the central alkali atom.

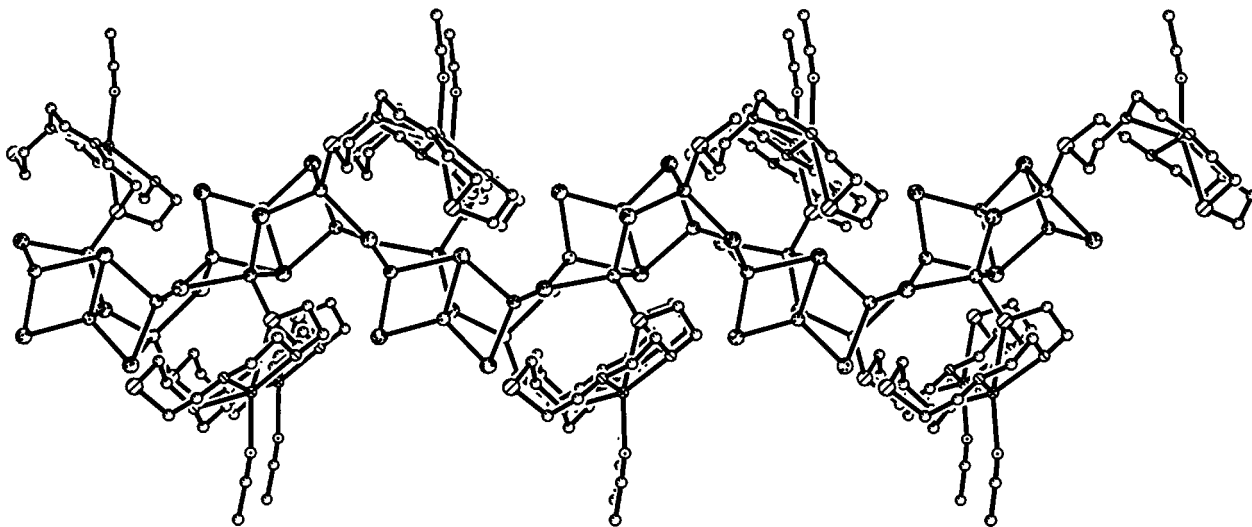


FIG. 7. Individual iodocuprate(I) chains in **2** as viewed from the side of lamellar coordination polymer.

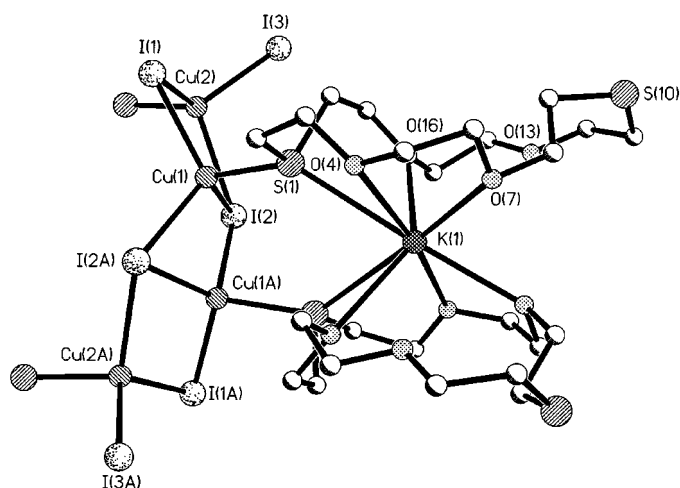


FIG. 8. Asymmetric unit and numbering scheme of $\frac{2}{\infty}[\{K\{Cu_4I_5(1,10DT18C6)_2\}]_2$ (**3**). Selected bond lengths (Å) and angles ($^\circ$) in the eight-fold coordination sphere of K1: K1–O4 2.973(11), K1–O7 2.713(12), K1–O16 2.865(13), O4–K1–O4a 171.1(5), S1–K1–O7a 169.4(2), O16–K1–O16a 138.1(6)

Thermal Gravimetric Analyses

A TGA/DTA trace of **2** performed at a speed of $2^\circ\text{C}/\text{min}$ reveals a mass reduction of 2.5% at 180°C corresponding to the loss of the coordinated acetonitrile molecule (calculated 2.8%). This is followed by gradual loss of the bridging 1,10DT18C6 ligands between 230 and 280°C (weight loss 21.6%, calculated 20.4%). **2** also rapidly loses its acetonitrile molecule under vacuum at room temperature to afford a colorless solid **2'** whose powder diffraction pattern confirms the retention of crystallinity. Its close similarity to that of **2** indicates that the integrity of the lamellar host network

is retained on loss of the solvent molecules, which subsequently can be reimbibed by covering **2** with acetonitrile. A thermal stability range comparable to that of **2** is observed for the neutral lamellar coordination polymer **1** whose network loses its bridging thiacycrown macrocycles between 240 and 280°C (weight loss 59.4%, calculated 60.9%).

CONCLUSIONS

Our studies demonstrate that a new class of lamellar coordination polymers with ion-ligating properties can be constructed by reaction of copper(I) iodide CuI with the thiacycrown ether 1,10DT18C6 in the presence of an alkali metal iodide MI. A decisive influence of the structure-directing alkali cation M^+ on both the stoichiometry and connectivity pattern of the resulting lamellar coordination polymer is apparent for $\frac{2}{\infty}[\{Na(CH_3CN)\}\{Cu_5I_6(1,10DT18C6)\}]_2$ (**2**) and $\frac{2}{\infty}[\{K\{Cu_4I_5(1,10DT18C6)_2\}]_2$ (**3**). However, both compounds contain one-dimensional iodocuprate(I) ribbons with infinite or oligomeric CuI double chains as characteristic substructures. This state of affairs underlines the ability of such copper(I) halides to generate complementary building units in coordination polymers that are tailored to meet both the charge and spacial requirements of their partner bridging ligands, in these cases complex $[M(1,10DT18C6)_n]^+$ cations.

As the thiacycrown 1,10DT18C6 contains a total of six donor atoms for alkali cation ($2 \times S$, $4 \times O$) it should be well-suited to coordinate the larger alkali cations Rb^+ and Cs^+ in lamellar compounds of the type $\frac{2}{\infty}[M\{Cu_xI_{x+1}(1,10DT18C6)_2\}]_2$ and studies on the preparation of such coordination polymers are currently in progress. Attempts to exchange K^+ in **3** by other cations have, as yet, proved unsuccessful.

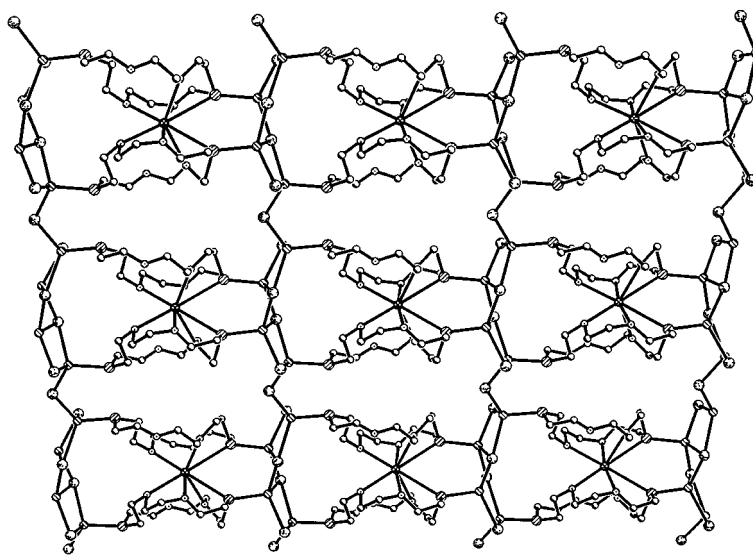


FIG. 9. Lamellar coordination network of **3** in projection perpendicular to $[001]$.

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