Synthesis, Structure, and Properties of [(tmeda)Cu[Hg(CN)$_2$]$_2$][HgCl$_4$]: A Non-Centrosymmetric 2-D Layered System that Shows Strong Optical Anisotropy

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The first coordination polymer incorporating $Hg(CN)_2$ units as building blocks is reported. The reaction of the labile transition-metal halide $CuCl_2$, the soft Lewis acidic $Hg(CN)_2$, and N,N,N′,N′-tetramethylethylenediamine (tmeda) formed large single crystals of [(tmeda)Cu[Hg(CN)$_2$]$_2$][HgCl$_4$] (**1**). The migration of two labile chloride ligands from harder Cu(II) to softer Hg(II) drives the formation of **1**, which self-assembles in high yield from several combinations of reagents. Complex **1** crystallizes in the tetragonal, noncentric $P\bar{4}2_1m$ space group, $Z = 2$, with $a = b = 10.9576(12)$ Å and $c = 9.8516(13)$ Å. The structure is composed of a 2-D cationic layer of [(tmeda)Cu[Hg(CN)$_2$]$_2$]$^{2+}$ units in which the six-coordinate Cu(II) centers are bridged by four $Hg(CN)_2$ groups and capped by a tmeda ligand. This array is interspersed with a layer of $[HgCl_4]^{2-}$ anions, which form bridging Hg−Cl bonds with the $Hg(CN)_2$ units. At 300 K, *a*- or *b*-oriented single-crystal plates of **1** are strongly birefringent with a birefringence value of $\Delta n = 6.38 \times 10^{-2}$, as measured at $\lambda = 546.1$ nm. The strongly anisotropic crystal structure, including the highly polarizable Hg(II) ions, is responsible for this significant optical birefringence. Upon cooling, the birefringence of **1** decreases slightly to $\Delta n = 6.12 \times 10^{-2}$ at 90 K.

Introduction.

Recently, there has been tremendous interest in the design and synthesis of multidimensional inorganic coordination polymers from the self-assembly of simple molecular building blocks.[1] In particular, cyanometalate units have been widely employed in the synthesis of a variety of supramolecular structures, including chains, planes, and 3-D arrays.[2] These systems have attracted interest because the alteration of the metal center in $[M(CN)_n]^{x-}$ building blocks, and the consequent adjustment of the geometric, magnetic, and electronic properties, provides the control and flexibility necessary to assemble solids with potentially tunable properties. This is illustrated by Prussian blue analogues, some of which exhibit bulk magnetic ordering at or above room temperature.[3] Cyanometalates have also been employed extensively to generate inclusion compounds, clathrates, and zeolite-type systems using square-planar or tetrahedral $[M(CN)_4]^{2-}$ (M = Ni, Pt, Pd, Cd) units in conjunction with cationic transition metal−ligand complexes.[4] Although the tetrahedral $[Hg(CN)_4]^{2-}$ moiety has seen some limited use in the construction of inclusion compounds that are mineralmimetic (resembling SiO_2, clay-layer, and zeolite-cage structures),[5] the *linear* $Hg(CN)_2$ molecule has not been investigated as a building block to create supramolecular architectures; a few simple double-salt adducts are known.[6] The coordinatively unsaturated Hg(II) center provides an interesting design possibility: not only could linear, bridging $Hg(CN)_2$ units be incorporated into coordination polymers, but they could also form the basis for in-situ generated trigonal or tetrahedral moieties by accepting compatible ligands during polymer formation.[7] This process could potentially increase the structural dimensionality in the supramolecular polymer,[8] an important

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(1) (a) Moulton, B.; Zaworotko, M. J. *Chem. Rev.* **2001**, *101*, 1629. (b) Eddaoudi, M.; Moler, D. B.; Li, H.; Chen, B.; Reineke, T. M.; O'Keeffe, M.; Yaghi, O. M. *Acc. Chem. Res.* **2001**, *34*, 319. (c) Holliday, B. J.; Mirkin, C. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 2022. (d) Decurtins, S.; Pellaux, R.; Antorrena, G.; Palacio, F. *Coord. Chem. Rev.* **1999**, *190−192*, 841.

(2) Dunbar, K. R.; Heintz, R. A. *Prog. Inorg. Chem*. **1997**, *45*, 288.

(3) (a) Ferlay, S.; Mallah, T.; Ouahès, R.; Veillet, P.; Verdaguer, M. *Nature* **1995**, *378*, 710. (b) Hatlevik, Ø.; Buschmann, W. E.; Zhang, J.; Manson, J. L.; Miller, J. S. *Adv. Mater.* **1999**, *11*, 914. (c) Holmes, S. M.; Girolami, G. S. *J. Am. Chem. Soc.* **1999**, *121*, 5593.

(4) Iwamoto T. In *Inclusion Compounds, Vol. 5*; Atwood, J. L., Davies, J. E. D.; MacNicol, D. D., Eds.; Oxford University Press: New York, 1991; Chapter 6.

(5) (a) Iwamoto, T., In *Comprehensive Supramolecular Chemistry, Vol. 7*; Lehn, J. M., Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Vögtle, F., Alberti, G., Bein, T., Eds.; Pergamon Press: Oxford, 1996; pp 643−690 and references therein. b) Miyasaka, H.; Matsumoto, N. *Chem. Lett.* **1997**, 427.

(6) (a) Thiele, G.; Brodersen, K.; Frohring, H. *Z. Naturforsch.* **1981**, *36b*, 180. (b) Brodersen, K.; Hummel, H.-U. *Z. Anorg. Allg. Chem*. **1983**, *500*, 171. (c) Thiele, G.; Hilfrich, P. *Z. Anorg. Allg. Chem*. **1980**, *461*, 109. (d) Mahon, C. *Inorg. Chem*. **1971**, *10*, 1813. (e) Mahon, C.; Britton, D. *Inorg. Chem*. **1971**, *10*, 586.

(7) (a) Sharpe, A. G. *The Chemistry of Cyano Complexes of the Transition Metals*; Academic Press Inc.: London, 1976; Chapter 11. (b) Penneman, R. A.; Jones, L. H. *J. Inorg. Nucl. Chem*. **1961**, *20*, 19.

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goal for synthesizing materials with potentially useful bulk properties.

Of particular interest are the properties related to noncentrosymmetrical arrangements of molecules in the structure. Crystals with this feature may exhibit both piezoelectric effects and optical nonlinearity. The latter is potentially useful for frequency doubling into short wavelengths via the so-called second harmonic generation (SHG), that is desirable for high-density information storage and telecommunication. Another important property of crystals is the birefringence, especially the principal birefringence which is defined as the difference in the refractive indices of two waves vibrating in the same plane along two different crystallographic axes. Birefringence can be useful in SHG materials. Greatly amplified harmonics are possible if the velocities of the fundamental and harmonic waves are made equal. This kind of phase matching is possible if the difference in refractive indices due to dispersion can be matched by birefringence.[9] Birefringence is characteristic of the anisotropy of the crystals. For instance, low dimensional polymers have been shown to exhibit high birefringence because of the structural anisotropy.[10] The use of mercury(II) cyanide, with its highly polarizable Hg(II) ions, is particularly appealing with respect to generating high anisotropy and thereby strong birefringence.

We hereby report that by employing the labile transition metal halide $CuCl_2$ in conjunction with a soft, coordinately unsaturated Hg(II) acceptor, we synthesized $[(tmeda)Cu[Hg(CN)_2]_2][HgCl_4]$ (**1**), a high dimensionality coordination polymer with a 2-D layered structure that shows strong optical birefringence related to the structural anisotropy. Complex **1** represents the first supramolecular system that incorporates $Hg(CN)_2$ as a building block.

Experimental

General Procedures and Physical Measurements. All manipulations were performed in air using purified solvents. All reagents were obtained from commercial sources and used as received.

IR spectra were obtained using a Thermo Nicolet Nexus 670 FT-IR spectrometer. Microanalyses (C, H, N) were performed at Simon Fraser University by Mr. Miki Yang. Variable temperature magnetic susceptibility data were collected on powdered samples at 10 000 G between 2 and 300 K using a Quantum Design MPMS-5S SQUID magnetometer. All data were corrected for TIP, the diamagnetism of the sample holder, and the constituent atoms (by use of Pascal constants).[11] Thermogravimetric analysis data were collected using a Shimadzu TGA-50 instrument. Solid-state visible spectra were obtained using a diode-array HP 8453 spectrometer and a suspension of sample in a customized cell.

The optical birefringence was measured along different crystallographic directions by means of polarized light microscopy (Olympus BX60) on platelets of different orientations polished using fine alumina powder (3 μm) mixed with silicon oil. The optical retardation was measured using a tilting compensator (3λ) at the wavelength of $\lambda = 546.1$ nm (e-line), and the birefringence was calculated by dividing the measured retardation by the crystal thickness. A heating/cooling stage (Linkam HTMS600) mounted on the microscope was used for studying the temperature dependence of the birefringence.

Table 1. Summary of Crystallographic Data

	1[a]
formula	$C_{10}H_{16}N_6Hg_3CuCl_4$
fw, g/mol	1027.40
space group	$P\bar{4}2_1m$ (No. 113)
a, Å	10.9576(12)
b, Å	10.9576(12)
c, Å	9.8516(13)
α, deg	90
β, deg	90
γ, deg	90
V, Å^3	1182.87(20)
Z	2
ρ_{calc}, g/cm^3	2.885
μ, cm^{-1}	207.6
T, K	293
R, Rw ($I > 2.5\sigma(I)$)[b]	0.022, 0.024

[a] Enraf-Nonius CAD-4 diffractometer, Mo Kα radiation (λ = 0.71069 Å), graphite monochromator. [b] Function minimized $\Sigma w(|F_o| - |F_c|)^2$ where $w^{-1} = \sigma^2(F_o) + 0.0002F_o^2$, $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R_w = (\Sigma w(|F_o| - |F_c|^2)/\Sigma w|F_o|^2)^{1/2}$.

Synthetic Procedures. CAUTION. Although we have experienced no difficulties, perchlorate salts are potentially explosive and should be used only in small quantities and handled with care.

$[(tmeda)Cu[Hg(CN)_2]_2][HgCl_4]$ (1). *Reaction 1.* A 10-mL methanolic solution of $Hg(CN)_2$ (0.100 g, 0.396 mmol) was added to a solution of $CuCl_2{\cdot}2H_2O$ (0.067 g, 0.396 mmol) and tmeda (0.046 g, 0.396 mmol) in methanol at room temperature. The blue solution was decanted after the precipitation of a green side-product. Dark blue blocklike crystals of **1** were obtained by slow evaporation of the solvent, collected, and washed with cold MeOH. Yield: 0.198 g (49%).

Reaction 2. A 10-mL aqueous solution of $Hg(CN)_2$ (0.200 g, 0.791 mmol), $HgCl_2$ (0.107 g, 0.396 mmol), and KCl (0.059 g, 0.791 mmol) was added to a 10-mL aqueous solution of $Cu(ClO_4)_2{\cdot}6H_2O$ (0.147 g, 0.396 mmol) and tmeda (0.046 g, 0.396 mmol) at room temperature. Dark blue platelike crystals of **1** were obtained. Yield: 0.321 g (79%).

Reaction 3. A 10-mL methanolic solution of $Hg(CN)_2$ (0.200 g, 0.791 mmol) and $HgCl_2$ (0.107 g, 0.396 mmol) was added to a methanolic solution of $CuCl_2{\cdot}2H_2O$ (0.067 g, 0.396 mmol) and tmeda (0.046 g, 0.396 mmol) at room temperature. Dark blue blocklike crystals of **1** were obtained as in reaction 1. Yield: 0.370 g (91%). Anal. Calcd. for $C_{10}H_{16}N_6Cl_4CuHg_3$: C, 11.69; H, 1.57; N, 8.18. Found: C, 11.72; H, 1.57; N, 8.01. IR (KBr): ν_{CN} 2247(s), 2197(w), ν_{HgC} 426 cm^{-1}.

X-ray Crystallographic Analysis of $[(tmeda)Cu[Hg(CN)_2]_2][HgCl_4]$ (1). Crystallographic data are collected in Table 1. A blue block-shaped crystal of **1** was mounted on a glass fiber. Using the diffractometer control program DIFRAC[12] and an Enraf Nonius CAD4F diffractometer, data from 4° ≤ 2θ ≤ 52° were recorded. The data were corrected by integration for the effects of absorption (0.0399−0.1430 minimum/maximum transmission). Data reduction included corrections for Lorentz and polarization effects. Final unit-cell dimensions were determined based on 48 well-centered reflection with a range of 40° ≤ 2θ ≤ 49°. The programs used for absorption correction and data reduction were from the NRCVAX Crystal Structure System.[13] The structure was solved and refined using CRYSTALS.[14] Complex scattering

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(8) (a) Leznoff, D. B.; Xue, B.-Y.; Patrick, B. O.; Sanchez, V.; Thompson, R. C. *Chem. Commun.* **2001**, 259. (b) Leznoff, D. B.; Xue, B.-Y.; Batchelor, R. J.; Einstein, F. W. B.; Patrick, B. O. *Inorg. Chem.* **2001**, *40*, 6026 and references therein. (c) Shorrock, C. J.; Xue, B.-Y.; Kim, P. B.; Batchelor, R. J.; Patrick, B. O.; Leznoff, D. B. *Inorg. Chem.* **2002**, *41*, 6743−6753.

(9) Newhnam, R. E. *Structure−Property Relations*; Springer-Verlag: Berlin, 1975; Chapter V.

(10) Fromm, K. M.; Gueneau, E. D.; Rivera, J.-P.; Bernardinelli, G.; Goesmann, H. *Z. Anorg. Allg. Chem.* **2002**, *628*, 171.

(11) Kahn, O. *Molecular Magnetism*; VCH: Weinheim, Germany, 1993.

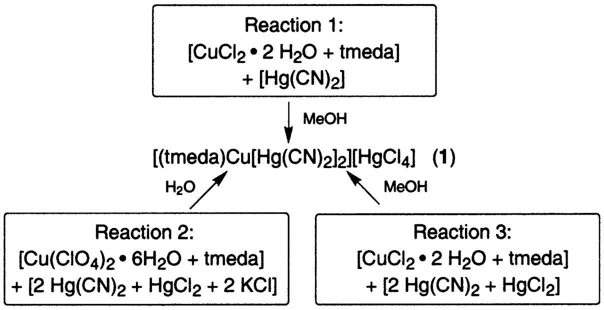
(12) Gabe, E. J.; White, P. S.; Enright, G. D. DIFRAC: A Fortran 77 Control Routine for 4-Circle Diffractometers; N. R. C.: Ottawa, ON, 1995.

(13) Gabe, E. J.; LePage, Y.; Charland, J.-P.; Lee, F. L.; White, P. S. *J. Appl. Crystallogr.* **1989**, *22*, 384.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $[(tmeda)Cu[Hg(CN)_2]_2][HgCl_4]$ (1)

Cu(1)−N(1)	2.050(7)	Hg(1)−C(3)	2.049(13)
Cu(1)−N(3)	1.975(11)	Hg(1)−C(4)	2.014(12)
Cu(1)−N(4)*	2.583(13)	Hg(1)−Cl	3.0514(21)
N(1)−C(1)	1.500(10)	Hg(1)*−Cl	3.217(2)
N(3)−C(3)	1.120(17)	Hg(2)−Cl	2.4807(23)
C(1)−C(1)*	1.540(10)	Hg(1)−Hg(1)*	5.5505(6)
C(4)−N(4)	1.116(17)	Hg(1)−Hg(2)	3.9094(4)
Cu(1)−Cu(1)*	10.353(2)		
N(1)−Cu(1)−N(3)	90.3(4))	C(3)−Hg(1)−C(4)	172.4(4)
N(1)−Cu(1)−N(3)*	178.3(4))	Hg(1)−Cl−Hg(2)	89.31(6)
N(1)−Cu(1)−N(1)*	88.0(5)	Hg(1)−Cl*−Hg(2)	85.6(2)
N(1)−Cu(1)−N(4)*	97.75(17)	Cl−Hg(1)−C(3)	85.9(2)
N(3)−Cu(1)−N(4)	100.56(9)	Cl−Hg(1)−Cl*	85.91(7)
N(3)−Cu(1)−N(3)*	91.3(3)	Cl−Hg(1)−C(4)	99.6(2)
N(3)−Cu(1)−N(4)*	82.48(16)	Cl−Hg(2)−Cl*	105.52(5)
N(4)−Cu(1)−N(4)*	158.4(5)	Cl*−Hg(2)−Cl*	117.70(11)

Scheme 1. Three Reaction Pathways for the Synthesis of 1



factors for neutral atoms[15] were used in the calculation of structure factors.

Coordinates for all non-hydrogen atoms, anisotropic displacement parameters for the ordered non-hydrogen atoms, and isotropic displacement parameters for the disordered carbon atoms of the tmeda ligand were refined. Hydrogen atoms were placed in calculated positions (*d* C−H 0.95 Å) and their coordinate shifts were linked with those of the respective carbon atoms during refinement. Two isotropic thermal parameters for the methylene and methyl hydrogen atoms were refined. An extinction parameter was included in the final cycles of full-matrix least-squares refinement. The final refinement using observed data ($I_o \geq 2.5\sigma(I_o)$) included 65 parameters for 1081 data. Selected bond lengths and angles for **1** are found in Table 2.

Results and Discussion

Synthesis and Solid-State Structure. Complex **1** spontaneously self-assembles in good yields (49−91%) from several different starting points (Scheme 1), indicating that it is the most thermodynamically stable product. In reactions 1 and 3, the migration of two labile chloride ligands from Cu(II) to Hg(II) drives the formation of the product;[16] in reaction 2, additional chloride is added. This halide migration from the harder Cu(II) to the softer Hg(II), that effectively opens two coordination sites on the Cu(II) for cyano-nitrogen binding, may potentially be used to design coordination polymers in other geometries. The IR spectrum clearly shows a blue-shifted ν_{CN} (2247 cm^{-1}) band consistent with the formation of a bridging cyanide ligand. Interestingly, the crystal morphology of **1** ranges from blocklike (reactions 1, 3) to plate-shaped (reaction 2).

A single X-ray diffraction study performed on **1** reveals a 2-D cationic $[(tmeda)Cu[Hg(CN)_2]_2]^{2+}$ network consisting of six-coordinate Cu(II) centers and bridging $Hg(CN)_2$ groups, impregnated with a layer of $[HgCl_4]^{2-}$ anions (Figure 1). Complex **1** crystallizes in the noncentrosymmetric, tetragonal space group $P\bar{4}2_1m$. The Cu(II) center adopts a Jahn−Teller distorted octahedral geometry by coordinating to one tmeda molecule and four cyanide bridged $Hg(CN)_2$ moieties. Each $Hg(CN)_2$ unit bridges in an axial/equatorial fashion to a different $[(tmeda)Cu]^{2+}$ center, thus propagating the corrugated 2-D array that lies in the *ab* plane (Figure 1a, Cu−N(3, eq-CN) = 1.975(11) Å; Cu−N(4, ax-CN) = 2.583(13) Å; Cu−N(1,tmeda) = 2.050(7) Å). The approximately 11 Å diameter cavities delineated by four Cu(II) centers (Figure 1a) are filled by tetrahedral $[HgCl_4]^{2-}$ anions (Hg(2)−Cl = 2.4807(23) Å), thus stabilizing the cationic 2-D array (Figure 1b). Each Cl atom further interacts with its two closest bridging Hg atoms with bond distances of 3.0514(21) Å and 3.217(2) Å respectively (weakest interaction shown as dashed lines), resulting in a distorted octahedral geometry about each mercury cyanide's metal center; all are within the sum of the van der Waals radii of 3.30 Å.[17]

These bonding interactions can be compared with the pseudo-octahedral chain structure of $K_2HgCl_4 \cdot H_2O$, which has two short Hg−Cl distances of 2.383(1) Å and two longer pairs at 2.897(1) and 3.251(1) Å.[18] The 2-D sheets in **1** are stacked together in a corrugated fashion, held together only by weak hydrophobic interactions between tmeda ligands, forming zigzag channels (∼4 Å) between each sheet, as shown in Figure 2. This unusual structure, containing two different 2-D layers embedded in each other, is perhaps more closely related to some organic−inorganic hybrid materials[19a] than to interpenetrated coordination polymers, which normally involve interpenetration of one network with itself.[19b]

A variety of physical properties have been investigated. The magnetic susceptibility of **1** as a function of temperature was measured. However, despite the 2-D structural nature, $\mu_{eff} = 1.87(1)\ \mu_B$ at 300 K and is temperature independent until 5 K, below which weak antiferromagnetic coupling is observed. The Jahn−Teller distorted weak axial bonding of the cyanides effectively disrupts coupling interactions between Cu(II) centers.[20] From thermogravimetric analysis, **1** decomposes from 133 to 138 °C with loss of all material except $CuCl_2$ (86.91% calculated weight loss, 86.07% observed).

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(14) Watkin, D. J.; Prout, C. K.; Carruthers, J. R.; Betteridge, P. W.; Cooper, R. I. *CRYSTALS Issue 11.67*; Chemical Crystallography Laboratory, University of Oxford: Oxford, U.K., 2001.

(15) (a) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K. (present distributor Kluwer Academic Publishers: Boston, MA), 1974; Vol. IV, p 99. (b) *International Tables for Crystallography*; Kluwer Academic Publishers: Boston, MA, 1992; Vol. C, p 200.

(16) (a) Schunk, A.; Thewalt, U. *Z. Anorg. Allg. Chem.* **2001**, *627*, 797. (b) Exarchos, G.; Robinson, S. D.; Steed, J. W. *Polyhedron* **2001**, *20*, 2951.

(17) Brodersen, K.; Hummel, H.-U. In *Comprehensive Coordination Chemistry, Vol. 5*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, 1987; Chapter 56.2.

(18) (a) Aurivillius, K.; Stalhandske, C. *Acta Chem. Scand. Ser. A* **1976**, *30*, 735. (b) Falk, M.; Knop, O. *Can. J. Chem.* **1977**, *55*, 1736.

(19) (a) Hagrman, P. J.; Hagrman, D.; Zubieta, J. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 2638. (b) Batten, S. R.; Robson, R. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1460.

(20) Leznoff, D. B.; Xue, B.-Y.; Stevens, C. L.; Storr, A.; Thompson, R. C.; Patrick, B. O. *Polyhedron* **2001**, *20*, 1247.

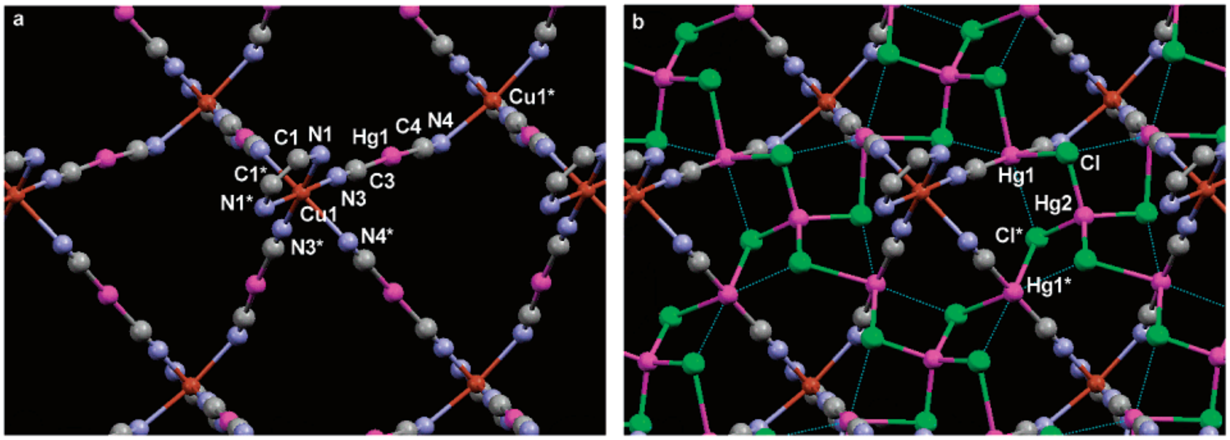

Figure 1. (a) View of the cationic 2-D framework of **1**, with its numbering scheme, down the *c* axis, showing corrugated cavities. (b) Cavities filled with $[HgCl_4]^{2-}$ anions. The tmeda methyl groups have been omitted for clarity. Color scheme: Hg, pink; Cu, red; Cl, green; N, blue; C, gray.

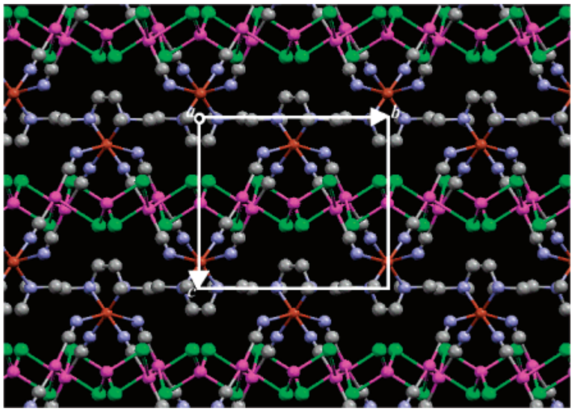

Figure 2. Packing diagram of **1** viewed down the *a*-axis, showing the unit cell. Color scheme: Hg, pink; Cu, red; Cl, green; N, blue; C, gray.

The birefringence of the crystal is an important characteristic of the material. The unusual structural feature of the $[(tmeda)Cu[Hg(CN)_2]_2][HgCl_4]$ crystal, as described above, provides an ideal case to study the optical properties related to the structural anisotropy due to the stacking of 2-D sheets. To investigate such a structure−property relationship, the optical birefringence of **1** was measured along different crystallographic directions by means of polarized light microscopy. The *c*-oriented crystal plates are optically isotropic when observed along the [001] direction, with extinction at any positions between the crossed polarizers, consistent with the tetragonal point group. The *a*- or *b*-oriented crystal plates (with the *c*-axis lying in the plane of the platelets) are strongly birefringent with a birefringence value of $\Delta n = 6.38 \times 10^{-2}$ at room temperature, as measured at $\lambda = 546.1$ nm. The blue crystals of **1** absorb light at 625 nm, hence the birefringence measurement is unimpeded by the optical absorption profile. This value of birefringence can be compared with 0.105 for the coordination polymer [hydrotris(1,2,4-triazolyl)borato]silver(I)[21] and 0.0155 for [Na⊂(dibenzo-24-crown-8)(I(1,3-dioxolane)][10] or even with the value of very strongly birefringent inorganic crystals, e.g. $KNbO_3$ ($\Delta n = n_b - n_a = 0.171$).[22] Upon cooling, the birefringence of **1** decreases slightly to reach a value of $\Delta n = 6.12 \times 10^{-2}$ at 90 K, indicating a diminution of the structural anisotropy at low temperature, probably due to a thermal contraction of the polymer interlayers.

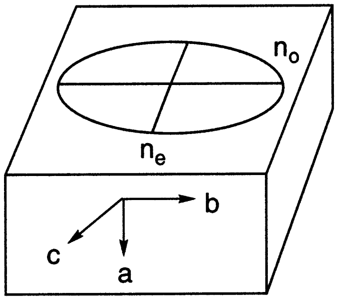

Figure 3. Orientation of the *b*−*c* section of the optical indicatrix with respect to the crystallographic axes, illustrating the optical anisotropy along the *a*-axis and the optically negative character of the $[(tmeda)Cu[Hg(CN)_2]_2][HgCl_4]$ crystals.

The correlation between the optical indicatrix and the crystallographic axes shows that the refractive index along the *a*- or *b*-axis (n_o, for the ordinary beam component) is larger than that along the *c*-axis, which is also the optical axis (n_e, for the extraordinary beam component), as indicated in Figure 3. Therefore, the birefringence corresponds to $\Delta n = n_o - n_e$, the principal birefringence of the tetragonal crystal. Since $n_e < n_o$, **1** exhibits an optically negative indicatrix.[23]

The optical character of the $[(tmeda)Cu[Hg(CN)_2]_2][HgCl_4]$ crystals can be understood with respect to the crystal structure and chemical bonding. It is known that the refractive index *n* of a crystal depends on its packing density and atomic or ionic polarizability, with a large *n* arising from a dense packing of highly polarizable atoms or ionic groups.[9] Figure 2 clearly shows that the *ab* plane contains densely packed layers of $[HgCl_4]^{2-}$ anions and the $[(tmeda)Cu[Hg(CN)_2]_2]^{2+}$ moieties; the 2-D sheets are only weakly packed along the *c*-axis. The electric vector of light propagating along the *a*- or *b*-axis encounters stronger interactions through the dense

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[21] Janiak, C.; Scharmann, T. G.; Albrecht, P.; Marlow, F.; Macdonald, R. *J. Am. Chem. Soc.* **1996**, *118*, 6307.

[22] Weber, K. *Bergmann-Shaefer, Lehrbuch der Experimentalphysik*, Bd. 3, Optik, 9th ed.; de Gruyter: Berlin, 1993; Chapters 4.6, 4.8, 4.9, 4.11.

[23] Nye, J. F. *Physical Properties of Crystals*; Oxford University Press: London, 1985; Chapter XIII.

layers of highly polarizable Hg(II) ionic groups, giving rise to a substantially larger value of the refractive index n_o (along the *a*- or *b*-axis) than n_e (along the *c*-axis) resulting in the high birefringence and the optically negative character.

Conclusions

A self-assembled Cu(II)/Hg(II) coordination polymer has been prepared using halide migration from harder Cu(II) to a coordinatively unsaturated, softer Hg(II) center. Its complex, anisotropic crystal structure leads to a significant optical birefringence. We are currently exploring the breadth of this synthetic route in terms of ligand and metal modification and the materials properties of the resulting products.

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Supporting Information Available: Complete crystallographic data in CIF format for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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