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An Inclusion Complex with $[Gd(dmf)_8]^{3+}$ Ions Encapsulated in Pockets of an Anionic Array of $[\{Cu_6(CN)_9\}^{3-}]_\infty$ Units; A Cyanide-Bridged Cu–Gd Layer Structure**

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Lanthanide–transition-metal complexes are attracting increasing attention because of their novel structures and the realization of applications in materials science[1,2] and catalysis.[3] It is of interest to not only continue preparing materials for which applications are known, but also to expand structural and chemical knowledge through the preparation and evaluation of new types of lanthanide–transition-metal complexes. With this goal in mind, we have extended our lanthanide–transition-metal studies from Group 10 transition metals[4] to Group 11 Cu^I complexes. Herein, we report the synthesis and structural characterization of an extended three-dimensional ionic inclusion complex, $[\{Gd(dmf)_8Cu_6(CN)_9\}\cdot 2\,DMF]_\infty$,[5] which contains sequestered lanthanide cations, and an extended layered complex, $[Gd_2(dmf)_8Cu_4(CN)_{10}]_\infty$.[6] These complexes constitute new structural classes of lanthanide–transition metal systems.

Although ionic inclusion complexes are known,[7] examples of an encapsulated ion within a charged cage are rare. The new inclusion complex is prepared by a three-component metathesis reaction [Equation (1)]. The anionic three-dimensional host lattice, $[\{Cu_6(CN)_9\}^{3-}]_\infty$, sequesters a cationic guest, $[Gd(dmf)_8]^{3+}$, and two free DMF solvent molecules in each "pocket" (Figure 1). In a slightly modified procedure [Equation (2)], the two-dimensional, infinite, puckered-layer complex $[Gd_2(dmf)_8Cu_4(CN)_{10}]_\infty$ (Figure 2) is formed in which the two Gd^{III} and three Cu^I atoms are bridged by cyanide ligands to form pentagonal rings. Either complex can be prepared in near-quantitative yield.

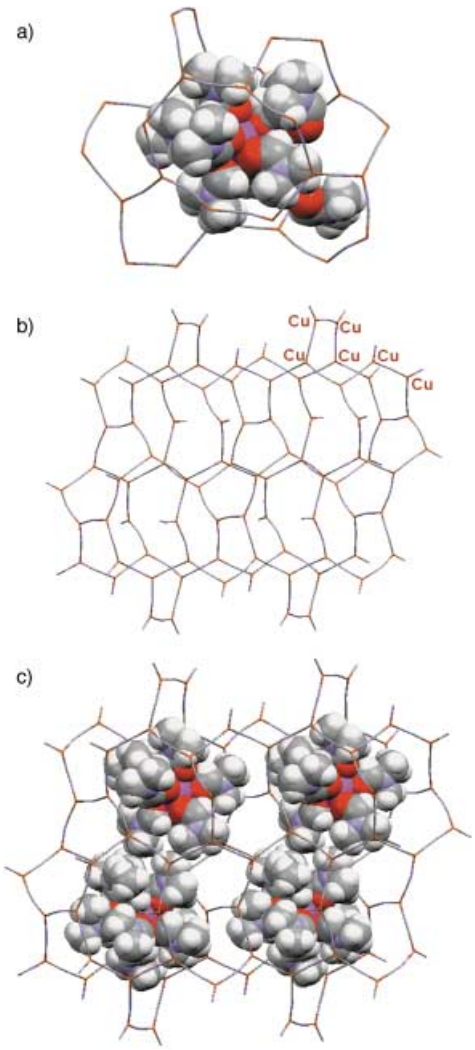

Figure 1. The structure of $[Gd(dmf)_8Cu_6(CN)_9]_\infty$. a) One pocket with an encapsulated $[Gd(dmf)_8]^{3+}$ ion and two DMF molecules. b) The partial structure of the anionic network with four vacant pockets; connections between Cu atoms represent cyanide bridges. c) Four pockets with trapped $[Gd(dmf)_8]^{3+}$ ionic guests.

$$GdCl_3 + 6\,CuCN + 3\,KCN \xrightarrow{DMF} [\{Gd(dmf)_8Cu_6(CN)_9\}\cdot 2\,DMF]_\infty + 3\,KCl \quad (1)$$

$$CuCN + KCN \xrightarrow{DMFDMF} K[Cu(CN)_2] \quad (2a)$$

$$2\,GdCl_3 + 6\,K[Cu(CN)_2] \xrightarrow{DMFDMFDMF} [Gd_2(dmf)_8Cu_4(CN)_{10}]_\infty + 6\,KCl + 2\,CuCN \quad (2b)$$

Figure 1 b shows the anionic network $[\{Cu_6(CN)_9\}^{3-}]_\infty$, while Figure 1 a illustrates a pocket that contains a trapped $[Gd(dmf)_8]^{3+}$ ion and two free DMF molecules. All of the

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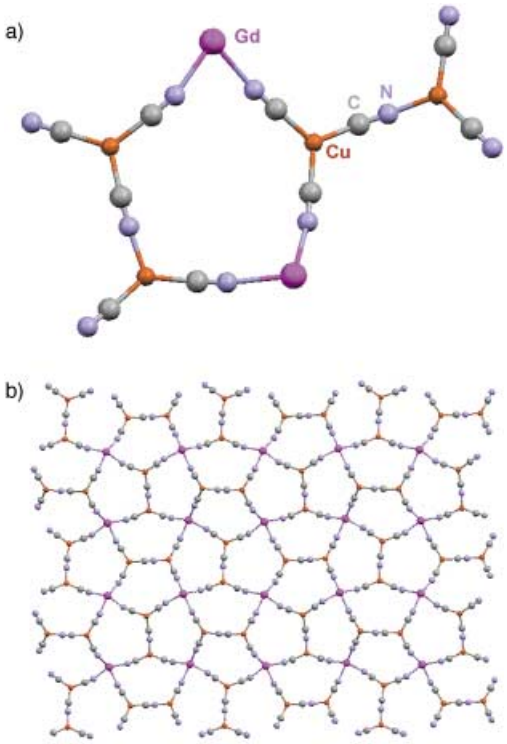

Figure 2. Molecular structure of $[Gd_2(dmf)_8Cu_4(CN)_{10}]_\infty$. a) The repeating unit of $[Gd_2(dmf)_8Cu_4(CN)_{10}]_2$; DMF molecules are omitted for clarity. b) A single layer of the two-dimensional complex; DMF molecules are omitted for clarity.

Cu atoms are coordinated to three cyanide groups. The three-dimensional anionic framework of pockets is formed through Cu-CN-Cu bridges. This is in contrast to previously reported three-dimensional arrays, which consist of four-coordinate copper centers.[7a] Each pocket has 30 copper atoms connected to 36 cyanide linkages and is irregular in shape; the approximate dimensions of the enclosure are $16 \times 11 \times 24$ Å. Each pocket is associated with 14 neighboring pockets. The coordination geometry of the Gd center in $[Gd(dmf)_8]^{3+}$ is square–antiprismatic. The approximate diameter of the cation (greater than 12.0 Å) is wider than the width of the largest window (less than 10.2 Å) of the pocket, thus trapping the cation in the pocket along with two DMF molecules. This structure differs from interpenetrating networks.[7c–f]

Figure 2a reveals the repeating unit ($[Gd(dmf)_4Cu_2(CN)_5]_2$) of the extended, layer-structured complex $[Gd_2(dmf)_8Cu_4(CN)_{10}]_\infty$. In this unit, two Cu^I atoms are linked through a cyanide bridge with each Cu^I atom joined to two Gd^{III} atoms through cyanide bridges. This generates the five-membered-ring building block. Each Gd^{III} atom is bonded to four DMF molecules and four bridging cyanide ligands, which leads to a square–antiprismatic coordination geometry. In our previous structural studies of lanthanide–transition-metal cyanide complexes,[4] we have not encountered arrays composed of pentagons. Figure 2b shows a single puckered layer of the two-dimensional complex with DMF molecules omitted for clarity. Adjacent layers are eclipsed and the interlayer distance is about 6.9 Å.

The two compounds reported here are prepared under different conditions. For the following reasons, we account for the variation in the products based on the difference in procedures. The inclusion complex is formed from an initial reaction mixture that contains CuCN, KCN, and $GdCl_3$. It is believed that the low solubility of CuCN in DMF results in a low concentration of $K[Cu(CN)_2]$ at any given time. This favors the probability for preferentially forming $[Gd(dmf)_8]^{3+}$ over Cu-CN-Gd bridges. Such a situation would allow for the slow assembly of the copper–cyanide anionic pocket around the solvated gadolinium cation. It should be noted that the formation of the crystalline inclusion complex requires several weeks. On the other hand, the layer complex is produced when CuCN and KCN are first allowed to form $K[Cu(CN)_2]$ [Reaction (2a)] and then the $GdCl_3$ is added to the reaction mixture [Reaction (2b)]. $K[Cu(CN)_2]$ has significant solubility in DMF and contains CN-Cu-CN-Cu-CN[8] linkages that can couple to Gd atoms to generate the CN-Gd-CN-Cu-CN-Cu-CN-Gd building units that are the basic units of the layer structure. The layer structure crystallizes from a solution in DMF after about one day. It will be worthwhile to determine if these procedures can be generalized for lanthanide(III)–copper(I)systems of the types described here.

Experimental Section

All manipulations were carried out on a standard high-vacuum line or in a dry-box under an atmosphere of dry, pure nitrogen. The purification of dimethylformamide (Baker) and the activation of molecular sieves (4 Å, Linde) are described in a previous publication.[4d] FTIR spectra were recorded on a Mattson Polaris Fourier-transform spectrometer at 2 cm^{-1} resolution. All samples were prepared in the dry-box. Elemental analyses of materials were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Single-crystal X-ray diffraction data for $[\{Gd(dmf)_8Cu_6(CN)_9\}\cdot 2DMF]_\infty$ and $[Gd_2(dmf)_8Cu_4(CN)_{10}]_\infty$ were collected on an Enraf-Nonius KappaCCD diffraction system, which employs graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). Data integration was carried out for Lorenz and polarization effects using the Denzo-SMN package (Nonius BV, 1999).[9] Absorption corrections were applied using the SORTAV program[10] provided by MaXus software.[11] The structure was solved by direct methods and refined using the SHELXL-97 (difference electron-density calculation, full-matrix least-squares refinements) structure solution package.[12] Data merging was performed using the data preparation program supplied by SHELXL-97. After all nonhydrogen atoms were located and refined anisotropically, hydrogen atoms on DMF molecules were calculated assuming standard CH geometries. Two DMF solvent molecules crystallize with one molecule of $[Gd(dmf)_8Cu_6(CN)_9]$ in the formation of the inclusion complex, $[\{Gd(dmf)_8Cu_6(CN)_9\}\cdot 2DMF]_\infty$. CCDC-184355 and -184356 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

$[\{Gd(dmf)_8Cu_6(CN)_9\}\cdot 2DMF]_\infty$: $GdCl_3$ (178 mg, 0.674 mmol), CuCN (362 mg, 4.04 mmol), and KCN (132 mg, 2.02 mmol) were stirred in DMF (ca. 25 mL) at room temperature over 14 days. The resulting solution was filtered, leaving a white precipitate (KCl) and a colorless filtrate. Colorless crystals suitable for X-ray analysis precipitated from the solution after three weeks in near-quantitative yield. IR (KBr): $\tilde{\nu} = 2115$(s) cm^{-1} (CN). Samples for elemental analysis were obtained by washing the crystals with dry hexane in a dry-box and then drying under vacuum for 30 min. 4.5 DMF molecules per empirical unit were lost after washing and drying, as determined by the elemental analysis. Elemental analysis (%) calcd for $C_{25.5}H_{38.5}N_{14.5}O_{5.5}Cu_6Gd$: C 26.07, H 3.30, N 17.29; found: C 26.27, H 3.77, N 17.12.

$K[Cu(CN)_2]$: A flask was charged with KCN (0.73 g, 11.2 mmol), CuCN (1.00 g, 11.2 mmol), and DMF (30 mL) in a dry-box. After stirring for one

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week the solvent was removed under vacuum. A white crystalline powder (in near-quantitative yield) was obtained.

$[Gd_2(dmf)_8Cu_4(CN)_{10}]_\infty$: $GdCl_3$ (120 mg, 0.455 mmol) and $K[Cu(CN)_2]$ (210 mg, 1.36 mmol) were stirred in DMF (ca. 25 mL) at room temperature over 7 days. The resulting solution was filtered, leaving a white precipitate (KCl) and a colorless filtrate. The solution was concentrated under vacuum, from which colorless crystals (in near-quantitative yield) were obtained the following day. IR (KBr): $\tilde{\nu} = 2112$(s) cm^{-1} (CN).

Samples for elemental analysis were obtained by washing the crystals with hexane in a dry-box and then drying under vacuum for 30 min (there was no loss of solvent). Elemental analysis (%) calcd for $C_{17}H_{28}N_9O_4Cu_2Gd$: C 28.89, H 3.99, N 17.84; found: C 28.86, H 4.08, N 17.69.

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[6] Crystal data of $[Gd_2(dmf)_8Cu_4(CN)_{10}]_\infty$: $0.15 \times 0.12 \times 0.12$ mm, monoclinic, space group $P2_1$, $a = 9.101(1)$, $b = 18.024(1)$, $c = 16.349(1)$ Å, $\beta = 95.88(1)°$, $V = 2667.6(4)$ Å^3, $\rho_{cald} = 1.760$ mg m^{-3}, $2\theta_{max} = 50.02$, ω at 55/−55°, $T = -73$ °C, $\mu = 4.075$ mm^{-1}, min/max transmission = 0.5800/0.6405, 16640 measured reflections of which 10428 reflections are independent, 597 parameters, $R_1 = 0.0485$, $wR_2 = 0.1041$ (all data, refined against $|F^2|$), largest residual peak = 1.713 e Å^3.

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