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Improved Syntheses of One-Dimensional Cyanide-Bridged Lanthanide−Transition-Metal Arrays

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We have been interested in synthesizing cyanide-bridged lanthanide−transition-metal arrays.[1] A number of applications of such materials have been reported in the literature,[2] and we have recently examined such materials as bimetallic catalyst precursors and magnetic materials.[3] The usual synthesis[1a,d,h] employs anhydrous MCl_3 (M = Sm, Eu, Er, Yb), $K_2[M'(CN)_4]$ (M′ = Ni, Pd, Pt), and dry DMF solvent to prevent the formation of hydrate products.The primary drawback of this method is the long reaction time ranging from 1 to 2 weeks.[1c] This is the result of the small stepwise dissociation constants of MCl_3 in DMF.[4] The formation of complex ions $[(DMF)_{8-x}MCl_x]^{(3-x)+}$ is ultimately responsible for the long reaction times.[1] We recently found that the reaction times were reduced to within 15−30 min when lanthanide nitrates were used in place of the chlorides. Lanthanide nitrates are strong electrolytes, and they dissociate completely in DMF to form simple $[(DMF)_8M]^{3+}$ ions.

Complexes $\{(DMF)_{10}Gd_2[Ni(CN)_4]_3\}_\infty$ and $\{(DMF)_{10}Ho_2[Ni(CN)_4]_3\}_\infty$ were prepared quantitatively through metathesis reactions in 3:2 molar ratios of $K_2[Ni(CN)_4]$ with Gd(III) and Ho(III) nitrates in DMF at room temperature.[5] The reactions were complete within 15−30 min. The procedure described here yielded the desired water-free products, on the basis of infrared spectra and single-crystal X-ray analyses, when the lanthanide nitrate was heated in a vacuum at 100 °C for 12 h. With excess water the reactions may yield hydrate complexes.[6] Lanthanide nitrates are highly hygroscopic and can quickly pick up a considerable amount of water. Therefore, only fresh lanthanide nitrate reagents were used, and heating them in dynamic vacuum is necessary.[6] Although some coordinated water is retained by the lanthanide nitrate after this heating procedure, it is replaced by DMF in the preparation and workup of the lanthanide−nickel complex.

Complexes $\{(DMF)_{10}Ho_2[Ni(CN)_4]_3\}_\infty$ and $\{(DMF)_{10}Gd_2[Ni(CN)_4]_3\}_\infty$ were crystallized as one-dimensional double-stranded extended arrays, designated as type B structures in earlier reports.[1b,c] Figure 1 is an ORTEP drawing of a portion of the structure for $\{(DMF)_{10}Ho_2[Ni(CN)_4]_3\}_\infty$. [7] A detailed description of the type B structure is provided in an earlier report.[1c] Both Ho and Gd atoms are eight-coordinated to three nitrogen atoms from bridging $[Ni(CN)_4]^{2-}$ units and five oxygen atoms from ligating DMF molecules. Like other complexes of the series, the coordination geometry of Gd is a square antiprism.[1] Its coordination geometry is given in the Supporting Information. On the other hand, the coordination geometry of Ho is a severely distorted bicapped trigonal prism (Figure 2), a type not usually observed for eight-coordinated lanthanide complexes.[8] The choice of one coordination geometry over the others is likely determined by a combination of several factors including the crystal packing forces and steric effects. Each of the two triangular bases of the prism consists of two oxygen atoms from DMF molecules and one nitrogen atom from an $[Ni(CN)_4]^{2-}$ unit. The two capping ligating groups are one DMF and one $[Ni(CN)_4]^{2-}$. The edge shared by two $[Ni(CN)_4]^{2-}$ units is not the one shared by the two capped faces even though the Ho−N bonds are longer than the Ho−O bonds.

The Ho−O bond distances are within 3σ of the Ho−O($CH_3CO_2^-$) bond distances (averages of 2.32(3) Å) reported for $Ho(AcO)_3(H_2O)_2$, also an eight-coordinate complex.[9] The Ho−O

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(1) Earlier, related publications in this series: (a) Knoeppel, D. W.; Shore, S. G. *Inorg. Chem.* **1996**, *35*, 1747. (b) Shore, S. G.; Deng, H.; Knoeppel, D. W.; Liu, J.; White, J. P., III; Chun, S.-H. *J. Alloys Compd.* **1997**, *249*, 25. (c) Knoeppel, D. W.; Shore, S. G. *Inorg. Chem.* **1996**, *35*, 5328. (d) Knoeppel, D. W.; Liu, J.; Meyers, E. A.; Shore, S. G *Inorg. Chem.* **1998**, *37*, 4828. (e) Liu, J.; Meyers, E. A.; Cowan, J. A.; Shore, S. G. *Chem. Commun.* **1998**, 2043. (f) Liu, J.; Meyers, E. A.; Shore, S. G. *Inorg. Chem.* **1998**, *37*, 5410. (g) Du, B.; Meyers, E. A.; Shore, S. G. *Inorg. Chem.* **2000**, *39*, 4639.

(2) See ref 1e for references to selected applications.

(3) (a) Rath, A.; Liu, J.; Shore, S. G.; Aceves, E.; Mitome, J.; Ozkan U. S. *J. Mol. Catal.* **2001**, *165*, 103−111. (b) Du, B. Ph.D. Dissertation, The Ohio State University, Columbus, OH, 2000. (c) Du, B.; Ebels, U. S.; Wigen, P. E.; Shore S. G. Manuscript in preparation.

(4) Ishiguro, S.-I.; Takahashi, R. *Inorg. Chem.* **1991**, *30*, 1854.

(5) For the preparations of $\{(DMF)_{10}Gd_2[Ni(CN)_4]_3\}_\infty$ and $\{(DMF)_{10}Ho_2[Ni(CN)_4]_3\}_\infty$, fresh samples (Aldrich) of the complexes $Gd(NO_3)_3 \cdot 6H_2O$ and $Ho(NO_3)_3 \cdot 3.4H_2O$ were heated under dynamic vacuum at 100 °C for 12 h, which yielded $Gd(NO_3)_3 \cdot 1.74H_2O$ and $Ho(NO_3)_3 \cdot 1.25H_2O$, respectively. In a drybox, 90 mg (0.2 mmol) of $Gd(NO_3)_3 \cdot 1.74H_2O$ and 73 mg (0.3 mmol) of $K_2[Ni(CN)_4]$ (Aldrich) were added to 25 mL of dry DMF in a 50 mL flask with a magnetic stirring bar. The reactants dissolved in DMF in 5 min to give a maroon solution. The mixture was stirred for another 20 min at room temperature. The solution was reduced to 2 mL under dynamic vacuum on a high-vacuum line. Colorless cubic KNO_3 crystals were removed by filtration through a pipet stuffed with tissue paper. The solution was further reduced to 0.5 mL under static vacuum. The viscous solution was allowed to stand overnight. X-ray-quality orange-colored cubic single crystals of $\{(DMF)_{10}Gd_2[Ni(CN)_4]_3\}_\infty$ were obtained. Yield: 151 mg (98%). Drying of the crystals under dynamic vacuum for 12−14 h resulted in the loss of two DMF molecules per empirical unit as determined by elemental analysis. Anal. Calcd for $C_{36}H_{56}N_{20}O_8Gd_2Ni_3$: C, 31.16; H, 4.07; N, 20.19. Found: C, 31.37; H, 4.54; N, 19.48. IR (Nujol mull, ν_{CN}, cm^{-1}): 2143 (vs), 2123 (s, sh), 2116 (vs), 2102 (m, sh). IR (DMF solution, ν_{CN}, cm^{-1}): 2147 (m), 2123 (s), 2116 (vs). Complex $\{(DMF)_{10}Ho_2[Ni(CN)_4]_3\}_\infty$ was prepared in an identical manner, employing $Ho(NO_3)_3 \cdot 1.25H_2O$, 88 mg (0.2 mmol), and $K_2[Ni(CN)_4]$, 72 mg (0.3 mmol). Yield: 153 mg (99%). Drying of the crystals under dynamic vacuum for 12−14 h resulted in the loss of two DMF molecules per empirical unit as determined by elemental analysis. Anal. Calcd for $C_{36}H_{56}N_{20}O_8Ho_2Ni_3$: C, 30.82; H, 4.02; N, 19.97. Found: C, 30.68; H, 4.27; N, 19.92. IR (Nujol mull, ν_{CN}, cm^{-1}): 2158 (m, sh), 2146 (vs), 2127 (s), 2121 (s), 2117 (ms). IR (DMF solution, ν_{CN}, cm^{-1}): 2149 (m), 2123 (s), 2116 (vs).

(6) When $Ho(NO_3)_3 \cdot 6.5H_2O$ was used as received without the drying procedure described above, the hydrated complex $(H_2O)_6(DMF)_6Ho_2[Ni(CN)_4]_3$ was produced. Du, B.; Meyers, E, A.; Shore, S. G. *Inorg. Chem.* **2000**, *39*, 4639.

(7) Diffraction data were collected on a Nonius Kappa CCD diffractometer using Mo Kα radiation. Data integrations were carried out using the Denzo-SMN package. Absorption corrections were applied using the SORTAV program. The structures were solved by the DIRECT method using the SHELXTL-97 structure solution package. Crystal data for $\{(DMF)_{10}Gd_2[Ni(CN)_4]_3\}_\infty$: triclinic space group $P\bar{1}$, $a = 9.0408(1)$ Å, $b = 11.7363(2)$ Å, $c = 16.01975(3)$ Å, $\alpha = 80.206(1)°$, $\beta = 74.592(1)°$, $\gamma = 80.882(1)°$, $Z = 1$. Crystal data for $\{(DMF)_{10}Ho_2[Ni(CN)_4]_3\}_\infty$: triclinic space group $P\bar{1}$, $a = 9.074(1)$ Å, $b = 11.298(1)$ Å, $c = 16.196(1)$ Å, $\alpha = 81.270(2)°$, $\beta = 77.101(2)°$, $\gamma = 83.223(2)°$, $Z = 1$.

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10.1021/ic001340o CCC: $20.00

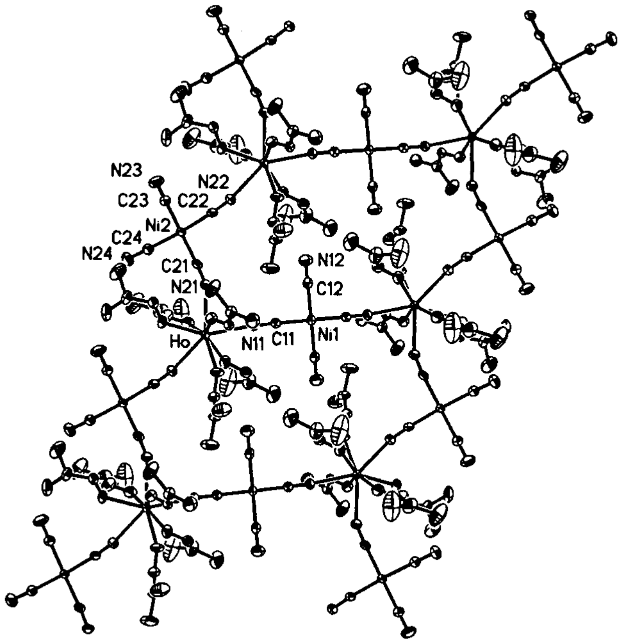

Figure 1. ORTEP drawing (50% thermal ellipsoids) of a portion of the "ladder-like" type B complex $\{(DMF)_{10}Ho_2[Ni(CN)_4]_3\}_\infty$. Only oxygen atoms from the ligating DMF molecules are shown for clarity. Selected bond distances (Å) for $\{(DMF)_{10}Gd_2[Ni(CN)_4]_3\}_\infty$: Gd−O, 2.344(4)−2.373(3); Gd−N, 2.481(4)−2.518(4); Ni−C, 1.861(5)−1.868(5); C≡N, 1.143(6)−1.160(5). $\{(DMF)_{10}Ho_2[Ni(CN)_4]_3\}_\infty$: Ho−O, 2.299(4)-2.386(2); Ho−N, 2.439(3)−2.490(3); Ni−C, 1.862(3)−1.878(4); CN, 1.145(5)−1.150(4). Selected bond angles (deg) for $\{(DMF)_{10}Gd_2[Ni(CN)_4]_3\}_\infty$: N11−Gd−N21, 77.1(1); N21−Gd−N22, 137.2(1); N11−Gd−N22, 142.8(1); Gd−N11−C11, 173.0(3); Gd−N21−C21, 151.2(3); Gd−N22−C22, 169.2(3); C−Ni−C, 89.0(2)−91.6(2); Ni−C−N, 176.9(4)−179.2(4). Selected bond angles (deg) for $\{(DMF)_{10}Ho_2[Ni(CN)_4]_3\}_\infty$: N11−Ho−N21, 78.4(1); N21−Ho−N22, 135.3(1); N11−Ho−N22, 143.0(1); Ho−N11−C11, 165.3(3); Ho−N21−C21, 155.7(3); Ho−N22−C22, 169.3(3); C−Ni−C, 88.1(2)−92.3(1); Ni−C−N, 174.6(3)-179.1(4).

and Ho−N bond distances are significantly shorter than those reported for $Na[Ho(EDTA)(H_2O)_3]$ (averages of 2.453(5) and 2.633(6) Å, respectively), a nine-coordinated complex.[10] The Gd−O and Gd−N bond distances are significantly shorter than those reported for Gd−O ($CH_3CO_2^-$) and Gd−N (averages of 2.399(4) and 2.655(4) Å, respectively) of $Na[Gd(AcO)_2(H_2O)_3]$, a nine-coordinate complex.[11] Compared to other cyanide-bridged lanthanide−transition-metal complexes that contain DMF ligands of the type A or type B structures, the averages of the Ln−O and Ln−N (Ln = Gd, Ho) bond distances fit into the shortening trend for Ln−O and Ln−N distances with increasing atomic number.[1]

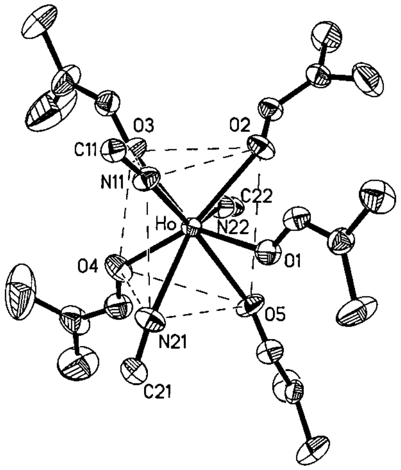

Figure 2. Distorted bicapped trigonal prism coordination geometry of the $HoN_3(DMF)_5$ group in the complex $\{(DMF)_{10}Ho_2[Ni(CN)_4]_3\}_\infty$.

Nujol mull FT-IR spectra for complexes $\{(DMF)_{10}Ho_2[Ni(CN)_4]_3\}_\infty$ and $\{(DMF)_{10}Gd_2[Ni(CN)_4]_3\}_\infty$ show a strong broad absorption band centered at 2143 and 2145 cm^{-1}, respectively. This band is assigned to the CN stretching vibration of the isocyanide linkages.[12,13] The absorption bands for the nonbridging CN ligands of the $[Ni(CN)_4]^{2-}$ units appeared at 2116, 2123, and 2102 cm^{-1} for $\{(DMF)_{10}Ho_2[Ni(CN)_4]_3\}_\infty$ and 2127, 2121, and 2116 cm^{-1} for $\{(DMF)_{10}Gd_2[Ni(CN)_4]_3\}_\infty$.[12,14] The CN stretching regions are similar to those observed for other type B complexes.[1c] The shifting to higher wavenumber for isocyanide linkages in $\{(DMF)_{10}Ho_2[Ni(CN)_4]_3\}_\infty$ is smaller than that in $\{(DMF)_{10}Gd_2[Ni(CN)_4]_3\}_\infty$. This follows the general trend observed for the frequency shifts:[1d] the shift increases accordingly as the size of Ln(III) decreases. This reflects the increased interactions between lanthanide cations and the lone pair electrons on the nitrogen atoms of the $[Ni(CN)_4]^{2-}$ units when the size of Ln(III) decreases.[13]

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Supporting Information Available: Tables listing additional X-ray experimental details and anisotropic parameters for complexes $\{(DMF)_{10}Ho_2[Ni(CN)_4]_3\}_\infty$ and $\{(DMF)_{10}Gd_2[Ni(CN)_4]_3\}_\infty$. These materials are available free of charge via the Internet at http://pubs.acs.org.

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