Inorg. Chem. **2000,** *39,* 4639−4645 **4639**

Direct Evidence for O−H···NC Hydrogen Bonding in a Cyanide-Bridged Lanthanide−Transition-Metal Complex $(H_2O)_6(DMF)_6Ho_2[Ni(CN)_4]_3$: An Eight-Coordinated Holmium Center with a Bicapped (Square Face) Trigonal Prismatic Geometry[†]

Bin Du, Edward A. Meyers, and Sheldon G. Shore*

Evans Laboratory, Department of Chemistry, The Ohio State University, Columbus, Ohio 43210

Received February 24, 2000

The lanthanide−transition-metal complex $(H_2O)_6(DMF)_6Ho_2[Ni(CN)_4]_3$, **1**, was prepared from the reaction of $Ho(NO_3)_3{\cdot}6.5H_2O$ with $K_2[Ni(CN)_4]$ at a 2:3 molar ratio in DMF (DMF = *N*,*N*-dimethylformamide). This compound is a model compound for studying the effects of H_2O ligands on the coordination geometry of lanthanide centers and the tendency to form oligomers rather than extended arrays with cyanide bridges. The presence of multiple hydrate water molecules appears to inhibit the formation of an extended array complex containing cyanide bridges but favors intermolecular hydrogen bonds between oligomers. The Ho centers are trans-bridged through a $[Ni(CN)_4]^{2-}$ unit. Each Ho center also forms an isocyanide linkage with a terminal $[Ni(CN)_4]^{2-}$ unit. Holmium is eight-coordinated. It is bound to three DMF molecules and three H_2O molecules in addition to two $[Ni(CN)_4]^{2-}$ units. The coordination geometry of Ho is a distorted bicapped (square face) trigonal prism. The X-ray crystal structure and IR spectra support the presence of strong-to-moderate O−H···NC hydrogen bonds. Crystal data for **1**: monoclinic space group $P2_1/n$, $a = 8.907(1)$ Å, $b = 25.579(1)$ Å, $c = 11.761(1)$ Å, $\beta = 105.138(1)°$, $Z = 2$.

Introduction

There has been continued interest in cyanide-bridged lanthanide−transition-metal complexes because of their applications as precursors in the preparation of rare earth orthoferrites (perovskite-type oxides),[1] oxide fuel cells,[2] electroceramic materials,[3,4] and chemical sensor materials;[5] in the preparation of fluorescent materials[6] and zeolitic-type materials;[5,7] in high-pressure tunable nonradiative energy-transfer processes;[8] as semipermeable solid membranes in reverse osmosis desalination of seawater;[7,9] as the catalysts in carbonylation reactions and chiral selective ring-opening reactions;[10] in the medical treatment of heavy-metal poisoning and the environmental cleanup of radioactive materials and heavy metals;[3] and in analytical ion-exchange columns for selective metal separation.[11]

We have developed a general nonaqueous synthetic procedure for the preparation of cyanide-bridged lanthanide−transition-metal arrays as potential precursors for homogeneous and heterogeneous catalysts.[12] We have also prepared water-free two- and three-dimensional cyanide-bridged lanthanide−transition-metal arrays and are investigating their potential as mo-

---

[†] Dedicated to Professor Dr. Heinrich Varhrenkamp on the occasion of his 60th birthday.

(1) (a) Gallagher, P. K. *Mater. Res. Bull.* **1968**, *3*, 225. (b) Nakayama, S.; Sakamoto, M.; Matsuki, K.; Okimura, Y.; Ohsumi, R.; Nakayama, Y.; Sadaoka, Y. *Chem. Lett.* **1992**, 2145. (c) Traversa, E.; Nunziante, P.; Sakamoto, M.; Watanabe, K.; Sadaoka, Y.; Sakai, Y. *Chem. Lett.* **1995**, 189.

(2) Minh, N. Q. *J. Am. Ceram. Soc.* **1993**, *76*, 563.

(3) Dunbar, K. R.; Heintz, R. A. In *Progress in Inorganic Chemistry*; Karlin, K. D., Ed.; John Wiley & Sons: New York, 1997; Vol. 45, p 283.

(4) (a) Shuk, P.; Vecher, A.; Kharton, V.; Tichonova, L.; Wiemhöfer, H. D.; Guth, U.; Göpel, W. *Sens. Actuators, B* **1993**, *16*, 401. (b) Sadaoka, Y.; Traversa, E.; Sakamoto, M. *J. Mater. Chem.* **1996**, *6(8)*, 1355.

(5) (a) Arakawa, T.; Takada, K. I.; Tsunemine, Y.; Shiokawa, J. *Sens. Actuators* **1988**, *14*, 215. (b) Matuura, Y.; Matsushima, S.; Sakamoto, M.; Sadaoka, Y. *J. Mater. Chem.* **1993**, *3(7)*, 767. (c) Traversa, E.; Matsushima, S.; Okada, G.; Sadaoka, Y.; Sakai, Y.; Watanabe, K. *Sens. Actuators, B* **1995**, *25*, 661.

(6) Sakamoto, M.; Matsuki, K.; Ohsumi, R.; Nakayama, Y.; Matsumoto, A.; Okawa, Y. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 2278.

(7) (a) Mullica, D. F.; Milligan, W. O.; Kouba, W. T. *J. Inorg. Nucl. Chem.* **1979**, *41*, 967. (b) Mullica, D. F.; Milligan, W. O.; Garner, R. L. *Acta Crystallogr., Sect. B* **1980**, *36*, 2561. (c) Mullica, D. F.; Perkins, H. O.; Sappenfield, E. L.; Grossie, D. A. *J. Solid State Chem.* **1988**, *74*, 9. (d) Mullica, D. F.; Perkins, H. O.; Sappenfield, E. L. *J. Solid State Chem.* **1988**, *74*, 419. (e) Mullica, D. F.; Perkins, H. O.; Sappenfield, E. L.; Leschnitzer, D. *Acta Crystallogr., Sect. C* **1989**, *45*, 330. (f) Mullica, D. F.; Sappenfield, E. L. *J. Solid State Chem.* **1989**, *82*, 168. (g) Mullica, D. F.; Sappenfield, E. L. *Acta Crystallogr., Sect. C* **1991**, *47*, 2433. (h) Mullica, D. F.; Sappenfield, E. L. *J. Crystallogr. Spectrosc. Res.* **1991**, *21*, 529. (i) Mullica, D. F.; Alvarez, F. H.; Sappenfield, E. L. *J. Solid State Chem.* **1997**, *129*, 12.

(8) (a) *Extended Linear Chain Compounds*; Miller, J. S., Ed.; Plenum Press: New York, 1982/1983; Vols. I−III. (b) Gliemann, G.; Yersin, H. *Struct. Bonding* **1985**, *62*, 87. (c) *Synthesis and Properties of Low-Dimensional Materials*; Miller, J. S., Epstein, A. J., Eds.; The New York Academy of Sciences: New York, 1978; p 539. (d) Yersin, H. *J. Phys. Chem.* **1978**, *68*, 4707. (e) Yersin, H.; Ammon, W. v.; Stock, M.; Gliemann, G. *J. Lumin.* **1979**, *18/19*, 774.

(9) (a) *Inorganic Semipermeable Membranes*; Research and Development Progress Report No. 723; Milligan, W. O., Ed.; U.S. Department of the Interior, Office of Saline Water: Washington, DC, Oct 1971. (b) *The structure and Morphology of Inorganic Membranes*; Research and Development Progress Report No. 594; Milligan, W. O., Ed.; U.S. Department of the Interior, Office of Saline Water: Washington, DC, Dec 1970.

(10) (a) Amer, I.; Alper, H. *J. Am. Chem. Soc.* **1989**, *111*, 927. (b) Matsubara, S.; Kodama, T.; Utimoto, K. *Tetrahedron Lett.* **1990**, *31*, 6379.

(11) Jain, A. K.; Singh, R. P.; Bala, C. *Analyst* **1982**, *107*, 770.

(12) (a) Knoeppel, D. W.; Shore, S. G. *Inorg. Chem.* **1996**, *35*, 1747. (b) Knoeppel, D. W.; Shore, S. G. *Inorg. Chem.* **1996**, *35*, 5328. (c) Shore, S. G.; Knoeppel, D. W.; Deng, H. B.; Liu, J. P.; White, J. P., III; Chun, S. H. *J. Alloys Compd.* **1997**, *249*, 25. (d) Knoeppel, D. W.; Liu, J. P.; Meyers, E. A.; Shore, S. G. *Inorg. Chem.* **1998**, *37*, 4828. (e) Liu, J. P.; Meyers, E. A.; Shore, S. G. *Inorg. Chem.* **1998**, *37*, 5410.

10.1021/ic000207t CCC: $19.00

lecular magnetic materials.[13] Also, as part of our general interest in cyanide-bridged lanthanide–transition-metal complexes, we are interested in the effects of neutral ligating groups on the coordination geometries of lanthanide metals and, in particular, we wish to know the effects of coordinated water molecules on the formation of network structures, because recent studies in this laboratory[13] show a remarkable difference in magnetic properties between water-free complexes and related complexes that contain water ligands.

Mullica et al.,[7] Hulliger et al.,[14] and others[15–18] reported structure determinations of a series of cyanide-bridged lanthanide–transition-metal hydrates that are extended arrays, whereas we have reported several structures of the H_2O-free cyanide-bridged lanthanide–transition-metal arrays.[12,13c] There are two published results in which multiple H_2O and *N*,*N*-dimethylformamide (DMF) ligands were both present in the lanthanide coordination spheres.[20,21] Unlike the systems in which extended network structures are observed, these complexes exist as oligomers containing two lanthanide and three transition-metal atoms. It appears that the number of ligating water molecules in the lanthanide coordination sphere influences the formation of the network structure, which in turn is critical for achieving long-range magnetic ordering at a finite temperature.[22] We report here the synthesis and X-ray single-crystal structure of $(H_2O)_6(DMF)_6Ho_2[Ni(CN)_4]_3$, **1**. The Ho–$H_2O$ bond is discussed together with direct evidence for the existence of the O–H···NC intermolecular hydrogen bonds in a cyanide-bridged lanthanide–transition-metal oligomeric complex. Because of the similar chemistry among members of the lanthanide series, this compound serves as a model compound for study on the effects of ligating H_2O molecules on the coordination geometry around lanthanide atoms and overall molecular structures.

Results and Discussion

Synthesis of $(H_2O)_6(DMF)_6Ho_2[Ni(CN)_4]_3$, 1. The metathesis reaction of $Ho(NO_3)_3{\cdot}6.5H_2O$ with $K_2[Ni(CN)_4]$ in a 2:3 molar ratio in DMF produces $(H_2O)_6(DMF)_6Ho_2[Ni(CN)_4]_3$ quantitatively at room temperature (eq 1). The reaction was complete within 15 min.

Table 1. Crystallographic Data for $(H_2O)_6(DMF)_6Ho_2[Ni(CN)_4]_3$, **1**

$C_{30}H_{54}N_{18}O_{12}Ho_2Ni_3$	$T = -70$ °C
$P2_1/n$ (No. 14)	$\lambda = 0.71073$ Å
$a = 8.907(1)$ Å	$\rho_{calcd} = 1.753$ g cm^{-3}
$b = 25.579(1)$ Å	$\mu = 4.163$ mm^{-1}
$c = 11.761(1)$ Å	$R_{int} = 0.0329$
$\beta = 105.138(1)$°	R1[a] $[I > 2\sigma(I)] = 0.0353$
$V = 2586.32(7)$ Å^3	wR2[b] (all data) $= 0.0766$
$Z = 2$	
fw = 1364.90 amu	

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = \{\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2\}^{1/2}$.

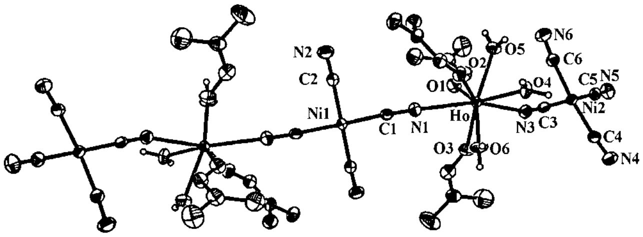

Figure 1. ORTEP drawing (50% thermal ellipsoids) of complex **1**.

$$2Ho(NO_3)_3{\cdot}6.5H_2O + 3K_2[Ni(CN)_4] \rightarrow (H_2O)_6(DMF)_6Ho_2[Ni(CN)_4]_3 + 6KNO_3 + 7H_2O \quad (1)$$

Crystalline KNO_3 precipitated after the volume of the DMF solution was reduced under dynamic vacuum. KNO_3 crystals were removed from the maroon solution by filtration, and the volume of the solution was further reduced. Discrete rectangular single crystals of **1** were obtained when the solution was allowed to stand overnight.

Molecular Structure of Complex $(H_2O)_6(DMF)_6Ho_2[Ni(CN)_4]_3$, 1. X-ray single-crystal analysis revealed **1** to be a complex of formula $(H_2O)_6(DMF)_6Ho_2[Ni(CN)_4]_3$ and monoclinic space group $P2_1/n$, with two molecules of **1** in the unit cell. Crystallographic data for **1** are listed in Table 1. Table 2 contains selected bond distances and angles. The molecular structure of **1** is depicted in Figure 1.

There are two crystallographically independent sites for Ni atoms. The full molecule is generated by a center of symmetry in the crystal at the site of Ni1. The four-coordinated Ni atoms are covalently bonded to CN^- ligands in a slightly distorted square planar geometry.[23] The Ni–C bond distances vary between 1.860(5) and 1.874(5) Å (Table 2). The C–N bond distances range from 1.140(6) to 1.157(6) Å. The Ho–NC interaction is ionic.[7] The two Ho–N–C angles are 157.9(4) and 170.8(4)°. The large deviation is perhaps the result of steric factors. The C–Ni–C bond angles range from 87.9(2) to 92.1(2)°. The Ni–C–N bond angles range from 174.2(5) to 177.5(4)°, consistent with their directional (covalent) bond nature. All the bond distances and angles appear to be normal as compared to those of similar systems.[12,24] The assignment of the carbon and nitrogen of cyanide takes into consideration both the chemical properties of the bridging cyanide ligand and the behavior of the thermal parameters. The present assignment provides more reasonable thermal parameters than reversed

---

(13) (a) Du, B. Ph.D. Dissertation, The Ohio State University, Columbus, OH, 2000. (b) Du, B.; Ebels, U. S.; Wigen, P. E.; Shore, S. G. *Abstracts of the ACS 31st Central Regional Meeting*; American Chemical Society: Washington, DC, 1999; No. 283. (c) Du, B.; Shore, S. G.; Ebels, U. S.; Wigen, P. E. *Abstracts of the 216th ACS National Meeting*; American Chemical Society: Washington, DC, 1998; INOR-596. (d) Du, B.; Knoeppel, D. W.; Meyers, E. A.; Shore, S. G. *Abstracts of the 214th ACS National Meeting*; American Chemical Society: Washington, DC, 1997; INOR-198.

(14) (a) Hulliger, F.; Landolt, M.; Vetsch, H. In *Proceedings of the Tenth Rare Earth Research Conference*, Carefree, AZ, 1973; p 80. (b) Hulliger, F.; Landolt, M.; Vetsch, H. *J. Solid State Chem.* **1976**, *18*, 283, 307. (c) Petter, W.; Gramlich, V.; Hulliger, F. *J. Solid State Chem.* **1989**, *82*, 161. (d) Gramlich, V.; Petter, W.; Hulliger, F. *Acta Crystallogr., Sect. C* **1990**, *46*, 724. (e) Dommann, A.; Vetsch, H.; Hulliger, F. *Acta Crystallogr., Sect. C* **1990**, *46*, 1992, 1994. (f) Xu, X. L.; Emmenegger, R.; Hulliger, F. *Eur. J. Solid State Inorg. Chem.* **1990**, *27*, 537. (g) Hulliger, F.; Vetsch, H.; Xu, X. L. *Eur. J. Solid State Inorg. Chem.* **1995**, *32*, 907.

(15) Bailey, W. E.; Williams, R. J.; Milligan, W. O. *Acta Crystallogr., Sect. B* **1973**, *29*, 1365.

(16) von Kietaibl, H.; Petter, W. *Helv. Phys. Acta* **1974**, *47*, 425.

(17) Klement, U. *Z. Kristallogr.* **1993**, *208*, 285, 288.

(18) Shi, J. M.; Liao, D. Z.; Cheng, P.; Jiang, Z. H.; Wang, G. L.; Yao, X. K.; Wang, H. G. *Acta Chim. Sinica* **1997**, *55*, 467.

(19) Du, B.; Meyers, E. A.; Shore, S. G. Manuscripts in preparation.

(20) Kou, H. Z.; Yang, G. M.; Liao, D. Z.; Cheng, P.; Jiang, Z. H.; Yan, S. P.; Huang, X. Y.; Wang, G. L. *J. Chem. Crystallogr.* **1998**, *28* (4), 303.

(21) Mullica, D. F.; Farmer, J. M.; Cunningham, B. P. *J. Coord. Chem.* **1999**, *48*, 449.

(22) (a) van Vleck, J. H. *Rev. Mod. Phys.* **1953**, *25*, 220. (b) Mattis, D. C. *The Theory of Magnetism I*; Springer: Berlin, 1981.

(23) Cotton, F. A.; Wilkenson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley and Sons: New York, 1988.

(24) (a) Moreau-Colin, M. L. *Struct. Bonding* **1972**, *10*, 167. (b) Gliemann, G.; Yersin, H. *Struct. Bonding* **1985**, *62*, 87. (c) Cernak, J.; Dunaj-Jurco, M.; Melnik, M.; Chomic, J.; Skorsepa, J. *Rev. Inorg. Chem.* **1988**, *9*, 259.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $(H_2O)_6(DMF)_6Ho_2[Ni(CN)_4]_3$, **1**[a]

Bond Lengths			
Ho−O(1)	2.341(3)	Ni(2)−C(4)	1.860(5)
Ho−O(2)	2.279(3)	Ni(2)−C(5)	1.865(5)
Ho−O(3)	2.351(3)	Ni(2)−C(6)	1.867(5)
Ho−O(4)	2.422(4)	N(1)−C(1)	1.157(6)
Ho−O(5)	2.342(4)	N(2)−C(2)	1.145(6)
Ho−O(6)	2.309(3)	N(3)−C(3)	1.140(6)
Ho−N(1)	2.477(4)	N(4)−C(4)	1.146(6)
Ho−N(3)	2.431(4)	N(5)−C(5)	1.142(6)
Ni(1)−C(1)	1.870(5)	N(6)−C(6)	1.144(6)
Ni(1)−C(2)	1.874(5)		
Ni(2)−C(3)	1.872(5)		

Angles			
O(2)−Ho−O(6)	82.01(13)	O(3)−Ho−O(4)	126.58(13)
O(2)−Ho−O(1)	117.69(12)	O(2)−Ho−N(3)	140.41(12)
O(6)−Ho−O(1)	142.96(12)	O(6)−Ho−N(3)	100.83(13)
O(2)−Ho−O(5)	79.02(13)	O(1)−Ho−N(3)	83.57(12)
O(6)−Ho−O(5)	146.99(14)	O(5)−Ho−N(3)	78.02(13)
O(1)−Ho−O(5)	70.04(13)	O(3)−Ho−N(3)	73.26(13)
O(2)−Ho−O(3)	141.78(12)	O(4)−Ho−N(3)	73.01(14)
O(6)−Ho−O(3)	71.68(13)	O(2)−Ho−N(1)	72.48(12)
O(1)−Ho−O(3)	74.63(12)	O(6)−Ho−N(1)	83.46(13)
O(5)−Ho−O(3)	136.34(13)	O(1)−Ho−N(1)	74.49(12)
O(2)−Ho−O(4)	69.56(13)	O(5)−Ho−N(1)	115.60(13)
O(6)−Ho−O(4)	75.49(13)	O(3)−Ho−N(1)	77.32(12)
O(1)−Ho−O(4)	139.20(12)	O(4)−Ho−N(1)	138.55(14)
O(5)−Ho−O(4)	72.66(14)	N(3)−Ho−N(1)	147.03(13)
C(1)−Ni(1)−C(2)	92.11(19)	N(5)−C(5)−Ni(2)	176.5(4)
C(1)−Ni(1)−C(2)#1	87.89(19)	N(6)−C(6)−Ni(2)	174.2(5)
C(4)−Ni(2)−C(5)	89.8(2)	Ho−O(4)−H(41)	138(3)
C(4)−Ni(2)−C(6)	173.7(2)	Ho−O(4)−H(42)	116(5)
C(5)−Ni(2)−C(6)	89.6(2)	H(41)−O(4)−H(42)	105(6)
C(4)−Ni(2)−C(3)	90.67(19)	Ho−O(5)−H(51)	119(3)
C(5)−Ni(2)−C(3)	175.0(2)	Ho−O(5)−H(52)	128(3)
C(6)−Ni(2)−C(3)	90.51(19)	H(51)−O(5)−H(52)	109(5)
C(1)−N(1)−Ho	170.8(4)	Ho−O(6)−H(61)	124(4)
C(3)−N(3)−Ho	157.9(4)	Ho−O(6)−H(62)	124(4)
N(1)−C(1)−Ni(1)	177.3(4)	H(61)−O(6)−H(62)	111(5)
N(2)−C(2)−Ni(1)	177.5(4)		
N(3)−C(3)−Ni(2)	176.9(4)		
N(4)−C(4)−Ni(2)	174.9(5)		

[a] Symmetry transformations used to generate equivalent atoms: #1, $-x + 2, -y + 1, -z$.

C−N assignments and is consistent with known structural information on cyanide-bridged complexes.[7,12,24]

Holmium is eight-coordinated, a coordination geometry best described as a distorted bicapped (square face) trigonal prism (Figure 2A). It is the least common coordination geometry among three possible choices for eight-coordinated lanthanide complexes: dodecahedron (D), square antiprism (A), and bicapped (square face) trigonal prism (T).[25] The geometric assignment here is based on a set of criteria proposed by Porai-Koshits and Aslanov.[26] The first criterion used is the four dihedral angles (δ) for the four pairs of the faces of a convex dodecahedron that share the edges formed between adjacent vertexes with five connections (Figure 2B).[26] The δ values for complex **1** clearly support the bicapped trigonal prismatic assignment when compared with the values for the three ideal models (Table 3). In particular, O1−N1−O2−O5 defines a slightly distorted square plane as indicated by its small δ value of 4.8(2)°. No other square plane is found in the polyhedron. The second criterion is the degree of nonplanarity (ϕ) of the two body-diagonal trapezoids, defined as O1−O5−O4−O6 and O2−N1−O3−N3 for complex **1** (Figure 2C).[26] The two ϕ values are 20.5(2) and 15.1(2)°, respectively. They are consistent with the bicapped trigonal prismatic assignment (Table 3). Lippard proposed a different criterion to classify eight-coordinated geometry, namely, the dihedral angle ω between the two trapezoids.[27c] The ω angle is 84.9(1)° for complex **1**. It is midway between the angles for an ideal dodecahedron and an ideal square antiprism (Table 3),[27c] which was shown by Porai-Koshits and Aslanov to be consistent with an ideal bicapped (square face) trigonal prism.[26] The low symmetry of T enables holmium to provide a variety of coordination sites to accommodate different ligating groups.[27d] Through an adaptation of T, it also allows **1** to achieve the maximum separation for the two charged $[Ni(CN)_4]^{2-}$ groups with the N1−Ho−N3 angle at 147.0(1)°.[27,28]

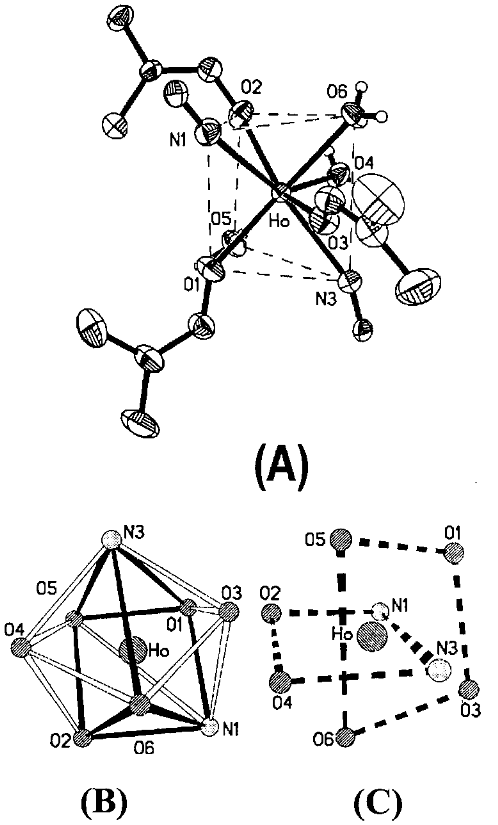

Figure 2. The ORTEP drawing (50% thermal ellipsoids) of (A) the bicapped (square face) trigonal prismatic coordination geometry around Ho(III) in complex **1**, (B) the convex polyhedron around Ho(III), and (C) the two body-diagonal trapezoids.

There is one DMF, one H_2O, and one $[Ni(CN)_4]^{2-}$ group for each of the two triangular faces of the trigonal prism (Figure 2B). Two of the square faces are capped by one H_2O and one DMF. The average of the N−Ho−O(H_2O) angles is 98°, larger than the average of 87° for the N−Ho−O(DMF) angles. From a steric point of view, one would expect the opposite to be true because a DMF molecule is a much more bulky ligand than an H_2O molecule. However, because H_2O is more polar than DMF, the electrostatic repulsive force between H_2O and $[Ni(CN)_4]^{2-}$

---

(25) (a) Lippard, S. J. In *Progress in Inorganic Chemistry*; Cotton, F. A., Ed.; John Wiley & Sons: New York, 1967; Vol. 8, p 109. (b) Muetterties, E. L.; Wright, C. M. *Q. Rev., Chem. Soc.* **1967**, *21*, 109. (c) Sinha, S. P. *Struct. Bonding* **1976**, *25*, 69. (d) Kepert, D. L. In *Progress in Inorganic Chemistry*; Lippard, S. J., Ed.; John Wiley & Sons: New York, 1978; Vol. 24, p 179. (e) King, R. B. *Polyhedron* **1994**, *13*, 2005.

(26) Porai-Koshits, M. A.; Aslanov, L. A. *Zh. Strukt. Khim.* **1972**, *13*, 266.

(27) (a) Hoard, J. L.; Silverton, J. V. *Inorg. Chem.* **1963**, *2*, 235. (b) Kepert, D. L. *J. Chem. Soc.* **1965**, 4736. (c) Lippard, S. J.; Russ, B. J. *Inorg. Chem.* **1968**, *7*, 1686. (d) Muetterties, E. L. *Inorg. Chem.* **1973**, *12*, 1963.

(28) King, R. B. *Polyhedron* **1994**, *13*, 2005.

Table 3. δ, ϕ, and ω Angles (deg) for Ideal Dodecahedron, Bicapped (Square Face) Trigonal Prism, Square Antiprism, and the Polyhedron around Ho(III) in $(H_2O)_6(DMF)_6Ho_2[Ni(CN)_4]_3$, **1**

	δ^a				ϕ^a	ω^b
dodecahedron	29.5	29.5	29.5	29.5	0	90
bicapped trigonal prism	0	21.7	48.2	48.2	16.1	83.7
square antiprism	0	0	52.5	52.5	24.5	77.4
$Ho(CN)_2(DMF)_3(H_2O)_3$ (**1**)	4.8(2)	23.1(1)	50.5(2)	50.5(2)	15.1(2)/20.5(2)	84.9(1)

[a] See ref 26. [b] See ref 27c.

Table 4. Comparison of the Average Ln−O and Ln−N Distances for Complex **1** and Some Complexes with Reported Structures

	average bond length (Å)				
complex formula	Ho−O(H_2O)	Ho−O(DMF)	Ho−N (t)^a	Ho−N (b)^a	CN
$\{(H_2O)_6(DMF)_6Ho_2[Ni(CN)_4]_3\}_\infty$, **1**	2.358(4)	2.324(3)	2.431(4)	2.477(4)	8

	average bond length (Å)				
complex formula	Ln−O	Ho−O (calcd)	Ln−N	Ho−N (calcd)	CN
$\{(DMF)_{10}Sm_2[Ni(CN)_4]_3\}_\infty{}^b$	2.383(4)	2.319	2.522(5)	2.458	8
$\{K(DMF)_7Eu[Ni(CN)_4]_2\}_\infty{}^c$	2.387(5)	2.336	2.525(6)	2.474	8
$\{(DMF)_{10}Eu_2[Ni(CN)_4]_3\}_\infty{}^b$	2.361(4)	2.310	2.523(5)	2.472	8
$\{(DMF)_{10}Er_2[Ni(CN)_4]_3\}_\infty{}^b$	2.315(5)	2.326	2.443(5)	2.454	8
$\{(DMF)_{10}Yb_2[Ni(CN)_4]_3\}_\infty{}^d$	2.294(5)	2.324	2.427(6)	2.457	8

[a] t = terminal $[Ni(CN)_4]^{2-}$ group, b = bridging $[Ni(CN)_4]^{2-}$ group. [b] See ref 12d. [c] See ref 19. [d] See ref 12a.

is stronger than that between DMF and $[Ni(CN)_4]^{2-}$. In many cases, the repulsive force between H_2O molecules and metallocyanides appears to be strong enough to override other factors. For example, in complexes $(H_2O)_3Ln[M(CN)_6]\cdot nH_2O$ and $K(H_2O)_2Ln[M(CN)_6]\cdot nH_2O$ (Ln = Sm, Lu; M = Cr, Fe, Co), the six bulky $[M(CN)_6]^{3-}$ groups in the Ln coordination spheres are in close proximity to each other, whereas the smaller neutral H_2O molecules are in the equatorial (capped) positions of capped trigonal prisms.[7,14]

These observations may help to explain why only oligomeric products were obtained in complexes with three or more water molecules and DMF molecules in the Ln coordination spheres. Complexes with two water molecules and DMF in the Ln coordination spheres have not yet been reported to our knowledge. In complexes with DMF molecules as the only space-filling ligating groups, the arrangement of ligands accommodates both bulky but neutral DMF molecules and electrorepulsive $[M(CN)_x]^{n-}$ groups.[12] However, the small but polar H_2O molecule introduces an important electrostatic component in the packing in complexes with H_2O molecules as the only space-filling groups.[7,14] We observed in several complexes that replacement of a single DMF by H_2O seemed sufficient to disrupt these delicate balances.[19] Even though the extended cyanide-bridged structures were preserved in all the cases, the charged $[M(CN)_4]^{2-}$ (M = Ni, Pt) groups are forced into each other to form the triangular faces opposite to the H_2O sites. Addition of more H_2O molecules in the presence of bulky DMF molecules, as in the case of complex **1**, appears to disrupt the balances between the sterically bulky DMF molecules and the charged $[M(CN)_4]^{2-}$ groups as well as those between the small polar H_2O molecules and the charged $[M(CN)_4]^{2-}$ groups. This makes it difficult to introduce a third charged $[M(CN)_4]^{2-}$ group into the lanthanide coordination sphere; hence discrete small oligomeric molecules are formed.

The Ho−O(DMF) bond distances range from 2.279(3) to 2.351(3) Å, whereas the Ho−O(H_2O) bond distances range from 2.309(3) to 2.422(4) Å for complex **1** (Table 4). They are in agreement with the Ho−O($CH_3CO_2^-$) and Ho−O(H_2O) bond distances reported for $Ho(AcO)_3(H_2O)_2$, also an eight-coordinated complex.[29] The two Ho−N bond distances in complex **1** are 2.431(4) and 2.477(4) Å, respectively. These Ho−O and Ho−N bond distances are shorter than those reported for $Na[Ho(EDTA)(H_2O)_3]$, a nine-coordinated complex.[30] The effect of the coordination number is evident for Ho−O bond distances between the two complexes. The longer of the two Ho−N bonds corresponds to the isocyanide linkage Ho−N1−C1 of the bridging $[Ni(CN)_4]^{2-}$ unit. This reflects the steric effect experienced by the bridging unit. Some interesting observations were gained when comparing the average bond distances of complex **1** with those of other lanthanide complexes of the series (Table 4). The average Ho−O(DMF) bond distance is very close to the expected value based on other lanthanide complexes. The Ho−N bond distances in Table 4 also correlate well with the Ho−N1 bond distance. Not coincidentally, all of the cited lanthanide complexes contain only bidentate bridging $[Ni(CN)_4]^{2-}$ units.[12a,d,19] The difference between the average Ho−O and Ho−N bond distances is 0.113(4) Å, as compared to the expected difference of 0.11 Å.[31] All bonds and angles within DMF molecules are normal.

Evidence for Intermolecular O−H···NC Hydrogen Bonding. An interesting structural aspect of complex **1** is revealed by the positions of the hydrogen atoms of the ligating H_2O molecules. It was suggested that there exist intermolecular hydrogen bonds between the ligating H_2O molecules and the terminal CN^- ligands and/or zeolitic H_2O molecules in several cyanide-bridged lanthanide−transition-metal complexes.[7,19,20] Those claims were, however, based on the O···O and O···N distances and in some cases were also implied by spectroscopic data.[7,19] However, these short distances may result simply from the crystal packing in the solid state.[32c] The location of hydrogen positions can provide a conclusive answer to the existence of such hydrogen bonds.[32]

Although the neutron diffraction method provides the most definitive evidence for the existence of hydrogen bonds, the

---

(29) Aslanov, L. A.; Korytnyi, E. F.; Porai-Koshits, M. A. *Zh. Strukt. Khim.* **1971**, *12*, 661.

(30) Templeton, L. K.; Templeton, D. H.; Zalkin, A. *Acta Crystallogr., Sect. C* **1985**, *41*, 355.

(31) Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *32*, 751.

(32) (a) Hamilton, W. C.; Ibers, J. A. *Hydrogen Bonding in Solids*; Benjamin, Inc.: New York, 1968. (b) Jeffrey, G. A. *An introduction to Hydrogen Bonding*; Oxford University Press: New York, 1997. (c) Steiner, T.; Saenger, W. *Carbohydr. Res.* **1994**, *259*, 1.

Table 5. Hydrogen Bond Distances (Å) and D−H···A Bond Angles (deg, D = Donor, A = Acceptor) in Complex $(H_2O)_6(DMF)_6Ho_2[Ni(CN)_4]_3$, **1**[a,b]

O(5)−H(52)	0.92(7)	H(52)···N(4)#1	1.83(7)	O(5)···N(4)#1	2.747(6)	O(5)−H(52)···N(4)#1	172(7)
O(6)−H(62)	0.76(5)	H(62)···N(5)#2	2.02(6)	O(6)···N(5)#2	2.774(6)	O(6)−H(62)···N(5)#2	172(5)
O(4)−H(41)	0.87(6)	H(41)···N(6)#4	2.01(6)	O(4)···N(6)#4	2.868(6)	O(4)−H(41)···N(6)#4	169(5)
O(6)−H(61)	0.83(6)	H(61)···N(2)#3	2.00(6)	O(6)···N(2)#3	2.823(6)	O(6)−H(61)···N(2)#3	172(6)
O(5)−H(51)	0.71(5)	H(51)···N(5)#5	2.29(5)	O(5)···N(5)#5	2.941(6)	O(5)−H(51)···N(5)#5	153(5)
O(4)−H(42)	0.70(7)	H(42)···N(4)#5	2.53(7)	O(4)···N(4)#5	3.192(6)	O(4)−H(42)···N(4)#5	158(8)

H···N (calcd)[c]	H···N (obs)[c]	O···N (calcd)[c]	O···N (obs)[c]
2.7	1.9	2.9	2.8

[a] See ref 33. [b] Symmetrical operations: #1, $1 + x, y, z$; #2, $x, y, -1 + z$; #3, $-1 + x, y, z$; #4, $-{}^1/_2 + x, {}^2/_3 - y, {}^1/_2 + z$; #5, ${}^1/_2 + x, {}^2/_3 - y, -{}^1/_2 + z$. [c] See ref 32a.

high operational expense of the technique prevents it from becoming a routine analytical tool. Furthermore, its application on lanthanide complexes is also limited because, generally, they have large neutron-capture cross sections. Although it is difficult to locate hydrogen atoms by X-ray diffraction because of their small contributions to the reflection intensities,[32] with the aid of a charge-coupled device (CCD) area detector we were able to obtain a large reflection data set of high quality and great redundancy for complex **1**, with accurate measurements of the intensities for the reflections at relatively small scattering angles. The hydrogen atoms of the ligating H_2O molecules were located and refined isotropically, and some of their significant bond distances and angles for complex **1** are given in Table 5.

Intermolecular hydrogen bond interaction is shown in Figure 3, which shows the stacking of oligomers. The O−H bond lengths in complex **1** range from 0.76(5) to 0.92(7) Å, compared to an expected value of 0.96 Å.[32] In general, distances measured by X-ray methods for bonds that involve H are systematically shorter than their expected values.[32a] The H···N interatomic distances range from 1.83(7) to 2.53(7) Å, and the O−H···N angles range from 153(5) to 172(6)°. If the O−H bond lengths are corrected to their expected values,[34] these values become 1.81−2.31 Å and 131−172°. Hydrogen bonding is generally accepted to be present if H···N distances are appreciably shorter than the van der Waals contact distance between H and N (2.55 Å) and if the appropriate angles are appreciably greater than 90°.[32b,34a] On the basis of these criteria, all of the close H···N contacts in complex **1** should be considered as hydrogen bonds. However, their strengths vary greatly. The first four hydrogen bonds of Table 5 should be considered strong, the fifth moderate, and the sixth weak. To further explore these distinctions, difference maps were generated to inspect the electron density distribution along the expected hydrogen bond directions.[35] In each map, the respective H_2O molecule and the corresponding N atoms of the CN ligands involved in the hydrogen bonding interactions were removed from the final refinement result. The structure factors were then recalculated without carrying out the least-squares refinement (L.S. set to 0). High angle refinement was performed with a modified weighting scheme in order to avoid bias introduced by the “missing” electron density. Figure 4 shows the difference maps at the level defined by the least-squares planes for each coordinated water molecule. In the cases of O4···N6, O5···N4, O6···N2, and O6···N5, the hydrogen electron density contours (corresponding to H41, H52, H61, and H62, respectively) clearly protrude toward the corresponding nitrogen atoms along the directions of expected hydrogen bonds. In contrast, the electron density contours of H42 and H51 (between O4···N4 and O5···N5, respectively) actually displayed hollowed faces along the directions of potential hydrogen bonds. This demonstrates the weakness of using solely the D−A (donor−acceptor) distance to infer the existence and the strength of a hydrogen bond, because O5···N5 has a distance of 2.941(6) Å and would have been considered as a moderately strong hydrogen bond if solely based on this standard. Using neutron diffraction data, Steiner and Saenger studied the correlation between the O···O diatomic distances and the probability for correct hydrogen bond assignment.[32c] The diatomic distances, first suggested by Hamilton and Ibers, are sufficient for the assignment of strong hydrogen bonds and are generally correct for moderate hydrogen bonds.[32a] There is, however, a significant drop-off in the probability for the correct assignment of weak hydrogen bonds.[32c] In the case of complex **1**, the short O4···N4 and O5···N5 distances appear to be due in part to the crystal packing forces. The strength of a hydrogen bond can sometimes be inferred by examining the D···A−Y angle if the exact locations of the hydrogen atoms are not readily available. For example, the lone pair on the nitrogen end of a cyano group is in an sp hybridized orbital. A strong hydrogen bond requires the O···N−C angle to be close to 180°. Any significant deviation will therefore serve as an indication of a weak hydrogen bond. It is clear from Figure 4 that the lone pairs of the prospective cyano ligands C4−N4 and C5−N5 are not in positions for effective overlap with the orbitals of H42 and H51, respectively.

The coordination geometries of the oxygen atoms in the H_2O−Ho bonds are of interest. All three H_2O−Ho entities have nearly perfect trigonal planar arrangements. The sums of the three angles around the oxygen atoms are 360(6)° for O4, 358(4)° for O5, and 358(4)° for O6. The oxygen atoms are only ±0.05(4) Å from the least-squares planes defined by the Ho atom and two hydrogen atoms. This observed trigonal planar geometry rather than the expected trigonal pyramidal coordination is intriguing in that it suggests the possibility of sp^2 hybridization for the oxygen. It should be noted that Ho−O distances for the carbonyl oxygens of the DMF molecules are comparable to the Ho−O distances of the water molecules, which is significant because the DMF oxygens are sp^2 hybridized.

Infrared Spectra of Complex $(H_2O)_6(DMF)_6Ho_2[Ni(CN)_4]_3$, 1. Figures showing the Fourier transform infrared (FT-IR) spectra of complex **1** and its D_2O substituted product are provided in the Supporting Information. A broad absorption band at 3560−3050 cm^{-1} was observed in the KBr pellet FT-IR spectrum of complex **1**. This supports the presence of O−H···N hydrogen bonds. An “isolated” water molecule would

---

(33) The data in Table 5 were generated by the PLATON package. Spek, A. L. *PLATON*; Utrecht University: Utrecht, The Netherlands, 1980−1999.

(34) (a) Taylor, R.; Kennard, O. *Acta Crystallogr., Sect. B* **1983**, *39*, 133. (b) Jeffrey, G. A.; Lewis, L. *Carbohydr. Res.* **1978**, *60*, 179. (c) Jeffrey, G. A.; Takagi, S. *Acc. Chem. Res.* **1978**, *11*, 264.

(35) The difference maps were generated using the SHELXTL-97 program; see ref 44.

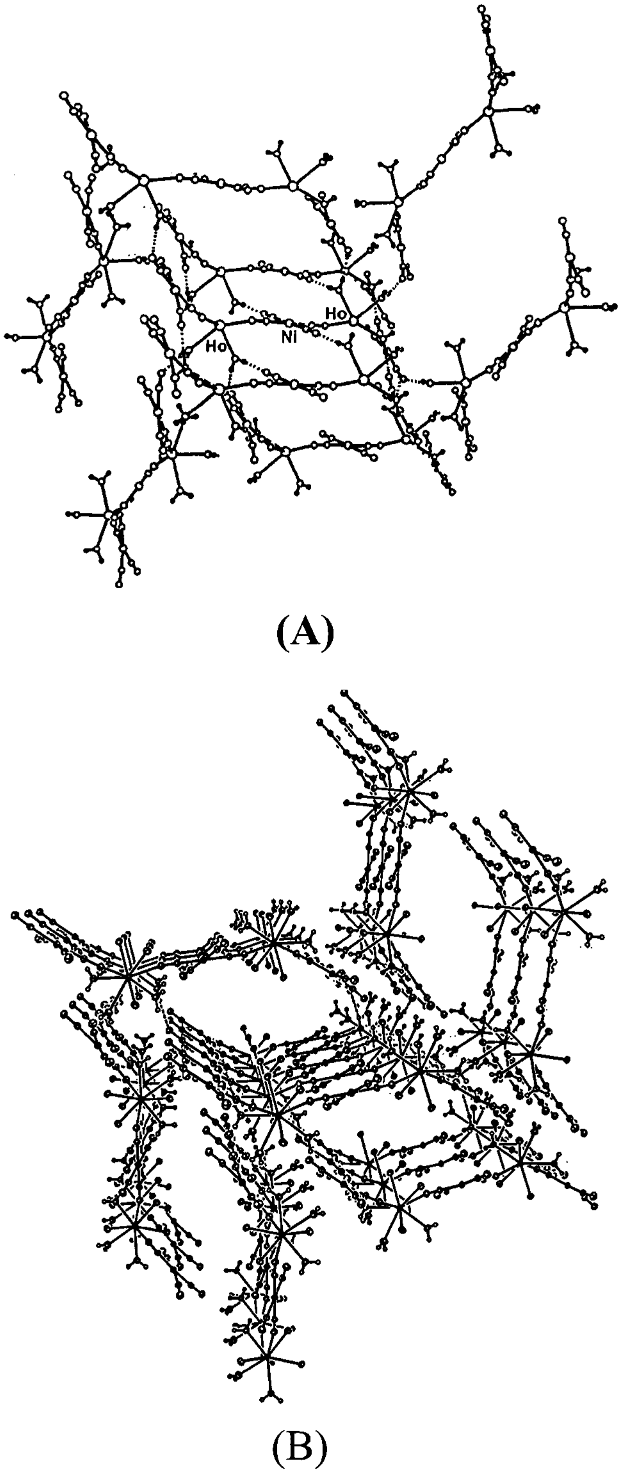

Figure 3. (A) Stacking of complex **1** to show hydrogen bonding between the oligomers. Hydrogen bonds are represented by dashed lines. For the purpose of clarity, some atoms nonessential to this representation have been deleted. (B) An extended view of the stacking of oligomers.

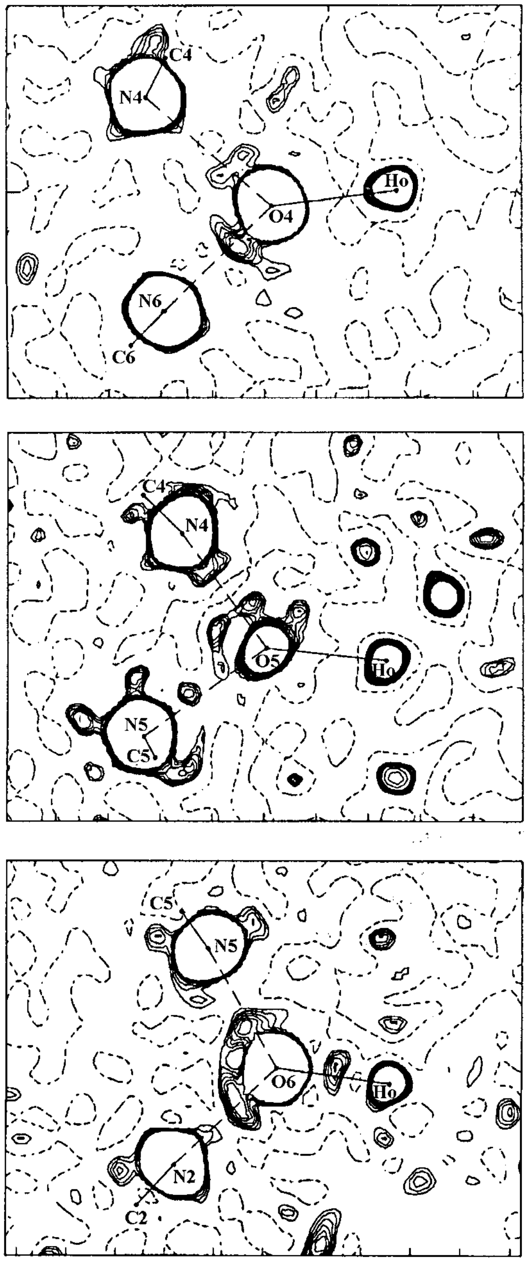

Figure 4. Experimental difference electron density maps showing the three coordinated water molecules and the hydrogen bonds to the nitrogen atoms of the cyano groups. Contours are drawn at intervals of 0.05 e Å^{-3}. Negative contours are dashed lines.

have a sharp absorption around 3650–3600 cm^{-1} for the "free" O–H stretching.[36] By use of the empirical rules proposed by Nakamoto et al.,[37] the O(H)···N distances were predicted to be 2.60, 2.77, and 3.28 Å, corresponding to the three maxima of the broad O–H stretching band at 3068, 3148, and 3301 cm^{-1}, respectively. These values are reasonably close to the experimentally determined O(H)···N distances of complex **1** (Table 5). The O–H stretching band shifted to the 2600–2300 cm^{-1} region with maxima at 2322, 2396, and 2507 cm^{-1} when the ligating H_2O was replaced by D_2O. The rocking and wagging vibrations of the coordinated water molecules were observed as sharp bands at 866 and 722 cm^{-1}.[38] Two sharp bands at 540 and 492 cm^{-1} are assigned to Ni–C stretching and Ni–C–N deformation vibrations, respectively.[38]

The Nujol mull FT-IR spectrum of complex **1** (provided in the Supporting Information) displayed a strong absorption band at 2121 cm^{-1}, with an unresolved shoulder at 2126 cm^{-1}. This

---

(36) Sorrell, T. N. *Interpreting Spectra of Organic Molecules*; University Science Books: Mill Valley, CA, 1988; pp 16, 33.

(37) Nakamoto, K.; Margoshes, M.; Rundle, R. E. *J. Am. Chem. Soc.* **1955**, *77*, 6480.

(38) (a) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; John Wiley & Sons: New York, 1986; p 278. (b) Adams, D. M. *Metal–Ligand and Related Vibrations*; Edward Arnold: London, 1967.

band is assigned to the CN stretching vibration of the nonbridging cyano groups of the $[Ni(CN)_4]^{2-}$ units in complex **1**. This absorption band is comparable to that of the nonbridging cyano groups in $K_2[Ni(CN)_4]$. The shoulder band at 2126 cm^{-1} is due to the small perturbation of the lattice interactions in the solid state.[39] The strong absorption band at 2145 cm^{-1} and the medium-strong band at 2160 cm^{-1} are assigned to the bridging cyano groups from the trans-bridging $[Ni(CN)_4]^{2-}$ units (Ni1). Similar absorption patterns were observed for other complexes containing bridging cyano groups.[12,38] The weak absorption band at 2135 cm^{-1}, which was not present for complexes with double-bridged $[Ni(CN)_4]^{2-}$ units, is assigned to the lone bridging cyano groups of the single-bridged terminal $[Ni(CN)_4]^{2-}$ units (Ni2). The CN stretching band is expected to shift to a higher wavenumber when a cyano group is bridged to a second metal.[40]

Experimental Section

General Data. All manipulations were carried out on a standard high vacuum line or in a drybox under an atmosphere of dry, 99.99%-pure N_2. Molecular sieves (4 Å, Linde) were heated to 150 °C under dynamic high vacuum ($10^{-4}-10^{-5}$ mmHg) overnight prior to use. DMF (Baker) was stirred over pretreated 4-Å molecular sieves for 1 week in a Pyrex flask, degassed under vacuum, and distilled at 70−80 °C into a Pyrex flask kept at −78 °C by a 2-propanol−Dry Ice bath. DMF was stored in a drybox. Deuterium oxide (MSD Isotopes) and $Ho(NO_3)_3 \cdot 6.5H_2O$ (Aldrich) were used as received. $K_2[Ni(CN)_4] \cdot H_2O$ (Strem) and KBr (Aldrich) were dried at 150 °C under dynamic vacuum for 16 and 24 h, respectively, and stored in a drybox.

FT-IR spectra were recorded on a Mattson Polaris spectrometer with 2 cm^{-1} resolution. Nujol mull samples were prepared by grinding ca. 5 mg of the samples with a drop of mineral oil in an agate mortar and analyzed as thin films placed between KBr plates in an airtight sample holder. KBr pellets were prepared by first grinding 5 mg of the samples and ca. 95 mg of dry KBr together in an agate mortar and then compressing them into thin pellets in a metal cell. Elemental analysis was performed by Galbraith Laboratories, Inc. (Knoxville, TN).

Preparation of $(H_2O)_6(DMF)_6Ho_2[Ni(CN)_4]_3$, 1. In a drybox, 188 mg (0.4 mmol) of $Ho(NO_3)_3 \cdot 6.5H_2O$ and 145 mg (0.6 mmol) of $K_2[Ni(CN)_4]$ were added to 20 mL of dry DMF in a 50-mL flask equipped with a Kontes Teflon stopcock and a magnetic stirring bar. After all reactants were dissolved in DMF, the reaction mixture was stirred for another 15 min at room temperature. The maroon solution was degassed, and the extra DMF was removed under dynamic vacuum. During the process, KNO_3 precipitated as colorless crystals that were cubic in shape, which was confirmed by X-ray diffraction. The volume of the solution was reduced to about 2 mL; then crystalline KNO_3 was removed in a drybox by filtration through a pipet stuffed with a small piece of tissue paper. The solution was degassed again and further reduced to about 0.5 mL. The oily supersaturated solution was allowed to stand overnight. X-ray quality orange rectangular single crystals of complex **1** were obtained. Yield: 261 mg (95.6%; calcd, 273 mg). Drying of the crystals under vacuum for 12−14 h resulted in the loss of one DMF molecule per empirical unit as determined by elemental analysis. Anal. Calcd for $C_{27}H_{47}N_{17}O_{11}Ho_2Ni_3$: C, 25.10; H, 3.67; N, 18.44. Found: C, 25.04; H, 3.74; N, 18.27. IR (Nujol mull, ν_{CN}, cm^{-1}): 2160 (m), 2145 (vs), 2135 (w), 2126 (s, sh), 2121 (s). IR (KBr, cm^{-1}): 3560−3050 (m, br, ν_{OH}), 2936 (s, br, ν_{CH}), 2815 (m, $\nu_{C(O)H}$), 2150 (vs, br, ν_{CN}), 2148 (s, sh, ν_{CN}), 2135 (m, sh, ν_{CN}), 2123 (vs, ν_{CN}), 1673 (s, br, ν_{CO}), 866 (s, δ_{H-O-H}), 722 (m, δ_{H-O-H}), 540 (m, ν_{Ni-C}), 492 (m, δ_{Ni-C-N}).

Preparation of $(D_2O)_6(DMF)_6Ho_2[Ni(CN)_4]_3$. $Ho(NO_3)_3 \cdot 6.5H_2O$ (94 mg, 0.2 mmol) was dissolved into 5 mL of D_2O in a 25-mL round-bottom flask. The maroon solution was stirred for 24 h at room temperature. After removal of H_2O and unreacted D_2O, the solid product was redissolved in 10 mL of dry DMF. To the solution was added 73 mg (0.3 mmol) of $K_2[Ni(CN)_4]$. $(D_2O)_6(DMF)_6Ho_2[Ni(CN)_4]_3$ was obtained following the previous procedure. Yield: 114 mg (83.2%; calcd, 137 mg). IR (KBr, cm^{-1}): 2934 (s, br, ν_{CH}), 2815 (m, $\nu_{C(O)H}$), 2600−2300 (m, br, ν_{OH}), 2150 (vs, br, ν_{CN}), 2148 (s, sh, ν_{CN}), 2135 (m, sh, ν_{CN}), 2123 (vs, ν_{CN}), 1673 (s, br, ν_{CO}).

X-ray Structure Determination. Single crystals were transferred into a drop of paratone oil on a glass slide under a nitrogen atmosphere in a drybox. A suitable single crystal was selected under a microscope and mounted at the tip of a quartz fiber with a thin layer of Apiezon grease. The sample was glued to a brass pin and placed on the goniometer under a nitrogen stream of −70 °C maintained by an Oxford Cryosystems cryostream cooler. Single-crystal X-ray diffraction data were collected on a Nonius Kappa CCD diffractometer using graphite monochromated Mo Kα radiation (0.710 73 Å). Ten frames were obtained through the ϕ scan routine (from −180 to −170°) with detector distance at 40 mm, frame width at 1°/frame, and scan time of 2 × 10 s/frame. Unit cell parameters were obtained based on these 10 frames using the automatic peak searching and indexing programs of the Denzo-SMN package (Nonius BV, 1999).[41] Optimum data collection conditions were then set with detector distance at 40 mm, frame width at 1°/frame, and scan time of 2 × 20 s/frame. Data collection was carried out by performing an ω scan with data completeness of 99.5% for the whole sphere of the reciprocal space $4° \leq 2\theta \leq 55°$. A total of 1268 frames were collected. Data integration was carried out using the Denzo-SMN package. Absorption correction was applied using the SORTAV program[42] provided by the MaXus software (version 3.0, Nonius BV, 1999).[43] Data merging was performed using the data preparation program supplied by the SHELXTL-97 program (version 97-2, Bruker AXS, 1998).[44]

The structure was solved using the SHELXTL-97 structure solution package. The Patterson method was employed to locate Ho and Ni atoms. The positions of other non-hydrogen atoms were obtained from difference Fouriers and refined on F^2 through full-matrix least-squares refinement procedures. After all non-hydrogen atoms were located and refined anisotropically, the hydrogen atoms of the coordinated water molecules were located and refined isotropically. The hydrogen atoms of DMF molecules were calculated assuming standard $-CH$ and $-CH_3$ geometries.

Acknowledgment. This work was supported by the National Science Foundation through Grants CHE97-00394 and CHE99-01115.

Supporting Information Available: Figures showing the FT-IR spectra of $(H_2O)_6(DMF)_6Ho_2[Ni(CN)_4]_3$, its D_2O substituted product, and a unit cell packing diagram and an X-ray crystallographic data for the structure determination of $(H_2O)_6(DMF)_6Ho_2[Ni(CN)_4]_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

IC000207T

---

(39) Kubas, G. J.; Jones, L. H. *Inorg. Chem.* **1974**, *13*, 2816.

(40) Swanson, B. I.; Rafalko, J. J. *Inorg. Chem.* **1976**, *15*, 249.

(41) Otwinowski, Z.; Minor, W. In *Methods in Enzymology*; Carter, C. W., Jr., Sweet, R. M., Eds.; Academic Press: New York, 1997; Vol. 276(A), p 307.

(42) (a) Blessing, R. H. *Acta Crystallogr., Sect. A* **1995**, *51*, 33. (b) Blessing, R. H. *J. Appl. Crystallogr.* **1997**, *30*, 421.

(43) Mackay, S.; Gilmore, C. J.; Edwards, C.; Tremayne, M.; Stuart, N.; Shankland, K. *MaXus*: *a computer program for the solution and refinement of crystal structures from diffraction data*; University of Glasgow: Scotland, Nonius BV: Delft, The Netherlands, and Mac-Science Co. Ltd.: Yokohama, Japan, 1998.

(44) Sheldrick, G. M. *SHELXTL-97*: *A Structure Solution and Refinement Program*; University of Göttingen: Germany, 1998.