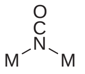
The cyanate ion as a bridging ligand between lanthanide and transition metals. Formation of one-dimensional extended arrays $\{(DMF)_6Ln_2Ni(NCO)_8\}_\infty$ (Ln = Sm, Eu) and monomeric complexes $(DMF)_8Ln_2Ni(NCO)_8$ (Ln = Sm, Eu) with three bridging cyanate ligands

Jianping Liu, Edward A. Meyers, James A. Cowan* and Sheldon G. Shore*

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210, USA. E-mail: shore1@osu.edu

Syntheses and molecular structures of the first cyanate bridged lanthanide-transition metal complexes, $(DMF)_8Ln_2Ni(NCO)_8$ and $\{(DMF)_6Ln_2Ni(NCO)_8\}_\infty$ (Ln = Sm, Eu) with three bridging cyanate ligands are reported; magnetic properties of $(DMF)_8Ln_2Ni(NCO)_8$ (Ln = Sm, Eu) complexes are described.

The cyanate ion[1] $[NCO]^-$ offers features as a bridging ligand that have not yet been adequately exploited by linking metal ions through two types of bonding modes: terminal N-bonding, 1,1-μ-N (**I**)[2–7] and both ends-bonding, 1,3-μ (**II**).[8–10] Complexes that have been reported, with two exceptions, are molecular entities that form a single cyanate or a double cyanate bridge between two metals. Exceptions are a silver cyanate complex, a chain-like array with single cyanate bridges[4] and a copper 2,4-lutidine cyanate complex, a chain-like array with two cyanate bridges.[5]



I

II

Here we report syntheses and molecular structures of the first examples of cyanate bridged complexes with three bridging cyanate ligands between a lanthanide and a transition metal. These are the monomeric complexes $(DMF)_8Ln_2Ni(NCO)_8$ (Ln = Sm **1**, Eu **2**) that can be converted into one-dimensional, extended arrays $\{(DMF)_6Ln_2Ni(NCO)_8\}_\infty$ (Ln = Sm **3**, Eu **4**).

The complexes $(DMF)_xLn_2Ni(NCO)_8$ (x = 6 or 8; Ln = Sm, Eu) were synthesized quantitatively by the reaction of 2 : 1 : 8 molar ratios of $LnCl_3$, $NiCl_2$, and K(NCO) in DMF at ambient temperature over a two day period.† Under slightly different crystallization conditions, two unique types of crystals, monomeric complexes $(DMF)_8Ln_2Ni(NCO)_8$ (Ln = Sm **1**, Eu **2**) and one-dimensional, extended arrays $\{(DMF)_6Ln_2Ni(NCO)_8\}_\infty$ (Ln = Sm **3**, Eu **4**) were obtained.† Both **1** and **2** as well as **3** and **4** are isomorphous. The molecular structures of **2** and **4** are shown in Figs. 1 and 2.‡

In complex **2**, the formula is $[(DMF)_8Eu_2Ni(NCO)_8]$. Since the Ni^{2+} ion is located on the crystallographic inversion center, the formula of the asymmetric unit is one-half the molecular formula. The Eu^{3+} and Ni^{2+} ions are linked together by three bridging cyanate ligands to form a slightly distorted trigonal bipyramidal $Eu(\mu\text{-}N)_3Ni$ unit. Interestingly, the distance between Ni^{2+}–Eu^{3+} [3.256(1) Å] is approximately equal to the sum of their atomic radii (3.20 Å),[11] which is probably a result of the three bridging $[NCO]^-$ groups. The forth cyanate ion is a terminal ligand bonded to an Eu^{3+} center. In addition, four DMF molecules are coordinated to the Eu^{3+} ion through their oxygen atoms. Compound **4** is very similar to compound **2**, except that in complex **2** one DMF molecule around Eu^{3+} is replaced by a cyanate ion thereby resulting in the formation of the extended array complex **4**. In complex **4** two cyanate ions form two cyanate bridges to link another Eu^{3+} and a one-dimensional infinite array is formed. The distance between the two adjacent $Eu(1)^{3+}$ and $Eu(2)^{3+}$ centers is 4.081(1) Å. The distances of Ni^{2+}–$Eu(1)^{3+}$ [3.231(1) Å] and Ni^{2+}–$Eu(2)^{3+}$ [3.235(1) Å] are similar to that observed in complex **2**.

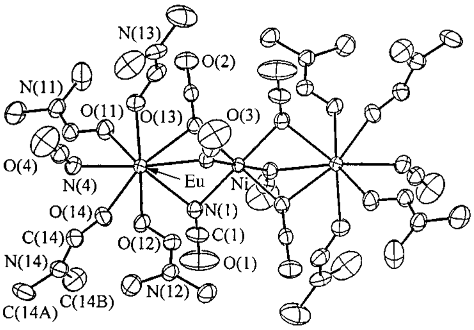


Fig. 1 Molecular structure of $(DMF)_8Eu_2Ni(NCO)_8$ with 50% thermal ellipsoids showing the atomic labelling scheme. DMF hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): Eu–O 2.384(5)–2.435(5), Eu–N 2.422(6)–2.563(6), Ni–N 2.081(6)–2.114(6); N–C 1.14(1)–1.18(1) Å, C–O 1.18(1)–1.20(1); N–Ni–N 84.1(2)–85.4(2), Ni–N–Eu 88.4(2)–89.5(2), C–N–Ni, 127.5(6)–142.3(6), C–N–Eu, 127.4(5)–137.8(6), N–C–O 177(1)–179(1).

In complexes **1**–**4**, only nitrogen atoms in the cyanate ligands are coordinated to the metal centers; oxygen atoms remain free. During the structure refinements assignments for N and O peaks on the difference map were interchanged. Assignments shown in Fig. 1 and 2 gave the lowest wR_2 which provides support that nitrogen and oxygen atoms in the $[NCO]^-$ groups are properly identified. Infrared studies of these complexes in the $\nu_{CN} + \nu_{CO}$, ν_{CN} and δ_{NCO} regions are consistent with those observed in complexes[2,3,12,13] for which only M–NCO bonding is claimed.

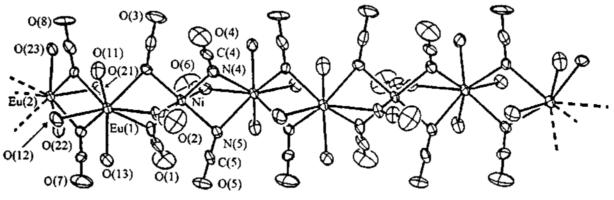


Fig. 2 Molecular structure of $\{(DMF)_6Eu_2Ni(NCO)_8\}_\infty$ with 50% thermal ellipsoids showing the atomic labelling scheme. Only oxygen atoms in DMF were shown for clarity. Selected bond lengths (Å) and angles (°): Eu–O 2.366(9)–2.411(9), Eu–N 2.476(10)–2.517(9), Ni–N 2.096(10)–2.139(9) N–C 1.15(2)–1.20(2) C–O, 1.17(2)–1.21(2); N(7)–Eu–N(8) 69.6(3)–69.8(3), N–Ni–N 178.1(4)–179.2(5), N–Ni–N 82.8(4)–97.4(4), Ni–N–Eu, 88.3(4)–89.5(4), Eu–N–Eu 110.3(4)–110.3(4), C–N–Ni 118.3(8)–129.0(9), C(1,6)–N(1,6)–Eu 142.0(9)–151.4(9), C(7,8)–N(7,8)–Eu 121.0(9)–128.7(9), N–C–O 177(2)–179(2)°.

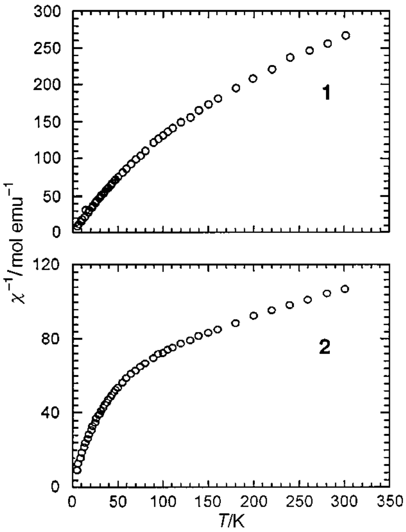


Fig. 3 Plot of $1/\chi$ *vs.* T for complexes $(DMF)_8Sm_2Ni(NCO)_8$ **1** and $(DMF)_8Eu_2Ni(NCO)_8$ **2** at 500 G

Six $[NCO]^-$ groups coordinate to a Ni^{2+} ion through the nitrogen atoms to form an approximately octahedral geometry around Ni^{2+} in both **2** and **4**. The coordination geometry around the Eu^{3+} center is a slightly distorted square antiprism in both **2** and **4**. In **2**, four nitrogen atoms from the $[NCO]^-$ groups and four oxygen atoms from the DMF molecules are coordinated to Eu^{3+}. In **4**, five nitrogen atoms from the $[NCO]^-$ groups and three oxygen atoms from the DMF molecules are coordinated to Eu^{3+}. Bridging $[NCO]^-$ groups between $Eu(1)^{3+}$ and $Eu(2)^{3+}$ ions share an edge of one antiprism base which is the cornerstone for the formation of the one-dimensional infinite chain.

Magnetic properties of **1** and **2** were studied.§ The complexity of the magnetic systems precludes a detailed theoretical analysis at this time, however, several significant observations were made. Both complexes show approximately Curie behavior below 30 K, and deviations at higher temperatures that are manifest as increased susceptibilities (Fig. 3). The deviations normally expected from Curie behavior at low temperature are small relative to the deviations shown at higher temperature for these compounds. Therefore it is the larger effect at higher temperature on which we focus our attention. Ground terms of $^6H_{5/2}$ and $^3F_4$ are assumed for the Sm^{3+} and Ni^{2+} centers in complex **1**, respectively.[14] For Sm^{3+} the first electronic excited state is typically too high in energy to contribute to the magnetic behavior, and so the magnetic properties may arise from antiferromagnetic coupling of the Ln^{3+} and Ni^{2+} ions with population of higher magnetic states at elevated temperature. For Eu^{3+} in complex **2**, a ground state term of $^7F_0$ is assumed. Since the ground state of Eu^{3+} is diamagnetic, the deviation from Curie behavior above 30 K requires a significant contribution from antiferromagnetic coupling of the low lying first excited electronic state of Eu^{3+} to be considered, although the coupling phenomenon may be more complex than the case of Sm^{3+}. Consistent with such a scheme, the low temperature magnetic moment of the europium complex **2** is approximately that of the free Ni^{2+} ion.

We thank the National Science Foundation to support this work through Grant CHE94-09123 and CHE97-00394. We thank Professor Susan M. Kauzlarich and Julia Y. Chan of the University of California at Davis for collecting SQUID data and Professor Samaresh Mitra for helpful comments.

Notes and References

† Preparation of **2** and **4** are described here. Complexes **1** and **3** were prepared in a similar manner. In a dry box, $EuCl_3$ (258.3 mg, 1.0 mmol), $NiCl_2$ (64.8 mg, 0.50 mmol), K(NCO) (324.5 mg, 4.0 mmol), and DMF (*ca.* 15 ml) were placed in a flask and the mixture was stirred for 2 days at ambient temperature under N_2. Filtration separated the KCl precipitate from the deep blue solution. DMF was removed from the filtrate under dynamic vacuum. After 12 h, colorless crystals of $(DMF)_8Eu_2Ni(NCO)_8$ were collected. Yield: nearly quantitative. IR (KBr pellet, cm^{-1}): $\nu_{CN} + \nu_{CO}$: 3518w, 3487w, 3463w, 3397w, 3391w; ν_{CN}: 2188vs, 2180vs, sh, 2122m, (unresolved), δ_{NCO}: 679s, 645w, 631m, 625m, sh, 621m; the remainder of absorption bands belong to DMF: 2940w, 2813vw, 1649s, 1500w, 1440m, 1420w, sh, 1376m, 1251w, 1115m, 1066w, 1015vw, 866vw, 661m. IR (DMF solution, cm^{-1}): $\nu_{CN} + \nu_{CO}$: 3516w, 3491w, 3369w, ν_{CN}: 2194s, sh, 2177vs, ν_{CO}: 1326w, 1260w, δ_{NCO}: 677s, 632m, 619m. Anal: Calc. for $C_{32}H_{56}N_{16}O_8Eu_2Ni$: C, 29.94; H, 4.40; N, 17.46. Found: C, 29.93; H, 4.30; N, 17.50%.

When the filtrate was pumped on for a longer period of time, a viscous oil was formed. After 12 h, colorless crystals consisting of both $(DMF)_8Eu_2Ni(NCO)_8$ and $\{(DMF)_6Eu_2Ni(NCO)_8\}_\infty$ were collected.

‡ Diffraction data were collected with an Enraf-Nonius CAD4 diffractometer using Mo-Kα radiation. All data were corrected for Lorentz and polarization and empirical absorption effects. Crystallographic computations were carried out using SHELXTL program,[15] with trial structures obtained by direct method.

Crystal data: $(DMF)_8Eu_2Ni(NCO)_8$ **2** (-60 °C), monoclinic, space group $P2_1/c$, $a = 11.199(2)$, $b = 17.581(7)$, $c = 13.492(6)$ Å, $\beta = 110.34(2)°$, $V = 2490.6$ Å^3, $M = 1283.56$, $Z = 4$, $D_c = 1.712$ g cm^{-3}, $\mu = 2.940$ mm^{-1}, $F(000) = 1284.0$, R_1 [3569 independent reflections with $I > 2\sigma(I)$] = 0.0484 ($R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$), wR_2 (4684 reflections measured) = 0.1496 [$wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$). $\{(DMF)_6Eu_2Ni(NCO)_8\}_\infty$ **3** (-60 °C), monoclinic, space group $P2_1$, $a = 9.404(2)$, $b = 21.060(8)$, $c = 10.915(5)$ Å, $\beta = 96.41(3)°$, $V = 2148.1(3)$ Å^3, $M = 1137.37$, $Z = 2$, $D_c = 1.758$ g cm^{-3}, $\mu = 3.391$ mm^{-1}, $F(000) = 1124.0$, R_1 [3486 independent reflections with $I > 2\sigma(I)$] = 0.0340 ($R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$), wR_2, (4209 reflections measured) = 0.0886 [$wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$). CCDC 979.

§ DC magnetization data were obtained with Quantum Design MPMS Superconducting Quantum Interference Device (SQUID) magnetometer with a 5.5 Tesla superconducting magnet. Data were collected and analyzed with the Magnetic Property Measurement System (MPMS) software supplied by Quantum Design. All samples were measured in zero field and then field cooled. Temperature dependent magnetization data were obtained by first measuring the zero field cooled (ZFC) magnetization in the field while warming from 5 to 300 K, then measuring magnetization while cooling back to 5 K with the field applied to obtain the field cooled (FC) data.

1 A. M. Golub, H. Köhler and V. V. Skopenko, *Chemistry of Pseudohalides*, Elsevier, Amsterdam, 1986, ch. 4, p. 186.
2 D. J. Brauer, H. Bürger, G. Pawelke, K. H. Flegler and A. Hass, *J. Organomet. Chem.*, 1978, **160**, 389.
3 J. Nelson and S. M. Nelson, *J. Chem. Soc. A*, 1969, 1597.
4 D. Britton and J. D. Dunitz, *Acta Crystallogr.*, 1965, **18**, 424.
5 F. Valach, M. Dunaj-Jurčo, J. Garaj and M. Havstijova, *Collect. Czech. Chem. Commun.*, 1974, **39**, 380.
6 W. Beck and K. Werner, *Chem. Ber.*, 1971, **104**, 2901.
7 A. Yu. Tsivadze, G. V. Tsintsadze, Yu. Ya. Kharitonov, A. M. Golub and A. M. Mamulashvili, *Russ. J. Inorg. Chem.*, 1970, **15**, 934.
8 D. M. Duggan and D. N. Hendrickson, *J. Chem. Soc., Chem. Commun.*, 1973, 411.
9 D. M. Duggan and D. N. Hendrickson, *Inorg. Chem.*, 1974, **13**, 2056.
10 T. Schönherr, *Inorg. Chem.*, 1986, **25**, 171.
11 J. C. Slater, *J. Chem. Phys.*, 1964, **41**, 3199.
12 R. A. Bailey, S. L. Kozak, T. W. Michelsen and W. N. Mills, *Coord. Chem. Rev.*, 1971, **6**, 407 and references therein.
13 A. H. Norbury, *Adv. Inorg. Chem. Radiochem.*, 1975, **17**, 231 and references therein.
14 R. S. Drago, *Physical Methods for Chemists*, Saunders, New York, 2nd Edn., 1992, p. 469.
15 SHELXTL (version 5), used to solve and refine crystal structures from diffraction data. Siemens Energy and Automation, Inc. 1994.

Received in Bloomington, IN, USA, 8th June 1998; 8/04348E