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Communications

Cyanide-Bridged Lanthanide−Transition Metal One-Dimensional Arrays $\{(DMF)_{10}Yb_2[Ni(CN)_4]_3\}_\infty$ and $\{(DMF)_{10}Yb_2[Pt(CN)_4]_3\}_\infty$

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The highly electropositive nature, retracted 4f valence orbitals, and lability of coordinating ligands make the lanthanide metals highly desirable for homogeneous and heterogeneous catalytic studies.[1] Our focus is on synthesizing heterometallic compounds, containing a lanthanide and a transition metal, which might serve as bimetallic catalysts or as precursors to bimetallic particles on oxide surfaces.[2] While direct lanthanide−transition metal bonds are ideal for such purposes, their syntheses can be very challenging. Few such compounds have been structurally characterized.[2b,d,3] Complexes with bridging ligands should be more accessible. Accordingly, we have produced one-dimensional-array complexes where cyanide ions bridge ytterbium and the transition metal nickel or platinum. In addition, array complexes containing cyanide bridges and paramagnetic metal atoms may also serve as molecular magnets.[4] Here we report the syntheses and crystal structures of the novel Yb(III) inorganic arrays $\{(DMF)_{10}Yb_2[Ni(CN)_4]_3\}_\infty$ (**1**) and $\{(DMF)_{10}Yb_2[Pt(CN)_4]_3\}_\infty$ (**2**) (DMF = *N*,*N*-dimethylformamide).

Arrays **1** and **2** were synthesized quantitatively *via* the reaction of a 2:3 ratio of $YbCl_3$ and $K_2M(CN)_4$ (M = Ni, Pt) (eq 1).[5] Single crystals of **1** (yellow) and **2** (colorless) were

$$2YbCl_3 + 3K_2M(CN)_4 \xrightarrow{DMF} \{(DMF)_{10}Yb_2[M(CN)_4]_3\}_\infty + 6KCl \quad (1)$$

$$M = Ni \text{ or } Pt$$

obtained within 48 h after removing DMF under high vacuum until a viscous solution resulted. The structures of **1** and **2** consist of unique nonisostructural one-dimensional arrays (Figures 1 and 2).[6] The structure of **1** consists of two Yb(III) ions bridged by two $Ni(CN)_4{}^{2-}$ anions in a *cis* fashion, generating a "diamond"-shaped Yb_2Ni_2 metal core. These "diamond"-shaped cores are linked by $Ni(CN)_4{}^{2-}$ anions bound to the Yb atoms in a *trans* fashion, creating the one-dimensional array. The repeating molecular unit of **2** is similar to that of **1**; however, **2** consists of two parallel running zigzag chains that are inverted from each other. They are generated by $Pt(CN)_4{}^{2-}$ ions bridging Yb(III) ions in a *cis* fashion. The chains are linked by a series of $Pt(CN)_4{}^{2-}$ ions bridging the Yb atoms in a *trans* fashion. The Yb(III) ions in both structures are bound to three N and five O atoms of the bridging cyanide ions and DMF

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(5) The preparations of **1** and **2** are similar. In a typical synthetic procedure, a 2:3 ratio of $YbCl_3$ and $K_2M(CN)_4$ is allowed to react in DMF (10 mL) at room temperature over several days until all of the $YbCl_3$ dissolves (**1**: 0.358 mmol, 100 mg of $YbCl_3$ and 0.537 mmol, 129 mg of $K_2Ni(CN)_4$. **2**: 0.13 mmol, 37 mg of $YbCl_3$ and 0.20 mmol, 75 mg of $K_2Pt(CN)_4$). **1** and **2** are soluble in DMF, and crystals can be obtained from viscous DMF solutions at room temperature. **1**: IR (Nujol mull; ν_{CN}, cm^{-1}) 2164 (s, sh), 2160 (s), 2150 (s), 2122 (vs), 2110 (m, unresolved); IR (DMF solution; ν_{CN}, cm^{-1}) 2150 (m−s), 2123 (s), 2115 (s), 2113 (s, unresolved); $^{13}C\{^1H\}$ NMR (DMF, 303 K; δ ppm) 129.68 (s). Drying of the crystals for 12−14 h results in the loss of one DMF molecule per empirical unit as determined by elemental analysis. Anal. Calcd for $C_{39}H_{63}N_{21}Ni_3O_9Yb_2$: C, 31.39; H, 4.25; N, 19.71. Found: C, 31.11; H, 3.94; N, 19.41. **2**: IR (Nujol mull; ν_{CN}, cm^{-1}) 2179 (w), 2160 (s), 2134 (s). IR (DMF solution; ν_{CN}, cm^{-1}) 2170 (w), 2144 (w, sh), 2135 (s), 2126 (s), 2122 (s); $^{13}C\{^1H\}$ NMR (DMF, 303 K; δ, ppm) 121.20 (d, $^1J(^{195}PtC) = 1016$ Hz), 121.20 (s); $^{195}Pt\{^1H\}$ NMR (DMF, 303 K; δ (ppm) −4702 (s). Drying of the crystals for 12−14 hours removes one DMF molecule per empirical unit as determined by elemental analysis. Anal. Calcd for $C_{39}H_{63}N_{21}O_9Pt_3Yb_2$ ($x = 9$): C, 24.63; H, 3.33; N, 15.47. Found: C, 24.99; H, 3.12; N, 15.29.

(6) Diffraction data (Enraf-Nonius CAD4, Mo Kα) were corrected for Lorentz and polarization and absorption (empirical) effects. Structure solution involved a combination of MULTAN 11/82 and difference Fourier syntheses. Crystal data for $\{(DMF)_{10}Yb_2[Ni(CN)_4]_3\}_\infty$ (−60 °C): space group $P\bar{1}$ (No. 2), $a = 10.257(4)$ Å, $b = 10.973(2)$ Å, $c = 15.1095(4)$ Å, $\alpha = 73.65(2)°$, $\beta = 84.35(3)°$, $\gamma = 83.91(2)°$, $V = 1618.4(8)$ Å^3, fw = 1565.38, ρ(calcd) = 1.667 g/cm^3, $Z = 2$, $\mu = 40.7$ cm^{-1}; $R_F = 0.029$, $R_{wF} = 0.034$, GOF = 2.167 (539 variable parameters refined) for 3773 $I \geq 3.0\sigma(I)$ refined of 4502 independent reflections (4° $\leq 2\theta \leq$ 45°). Crystal data for $\{(DMF)_{10}Yb_2[Pt(CN)_4]_3\}_\infty$ (25 °C): space group $P\bar{1}$ (No. 2), $a = 9.169(2)$ Å, $b = 11.736(3)$ Å, $c = 16.204(4)$ Å, $\alpha = 79.81(2)°$, $\beta = 75.10(2)°$, $\gamma = 80.88(2)°$, $V = 1646.8(8)$ Å^3, fw = 1974.52, ρ(calcd) = 2.187 g/cm^3, $Z = 2$, $\mu = 92.8$ cm^{-1}; $R_F = 0.026$, $R_{wF} = 0.030$, GOF = 2.834 (539 variable parameters refined) for 3857 $I \geq 3.0\sigma(I)$ refined on 4502 independent reflections (4° $\leq 2\theta \leq$ 45°).

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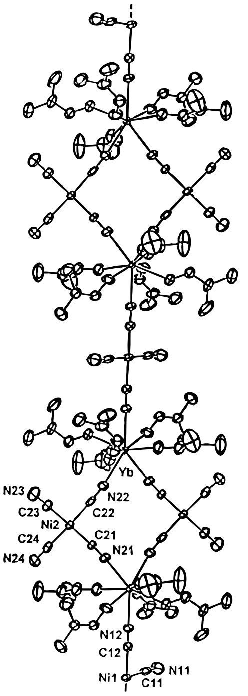


Figure 1. ORTEP drawing (50% probability ellipsoids) of a portion of $\{(DMF)_{10}Yb_2[Ni(CN)_4]_3\}_\infty$ (**1**) showing the atomic labeling scheme. DMF hydrogens are omitted. Selected bond distances (Å): Yb−O, 2.265(5)−2.336(5); Yb−N, 2.401(6)−2.445(6); Ni−C, 1.858(6)−1.871(9); C≡N, 1.134(8)−1.151(9). Selected bond angles (deg): Yb−N12−C12, 178.1(6); Yb−N21−C21, 174.7(5); Yb−N22−C22, 169.6(6); C−Ni−C, 88.8(3)−91.3(3); Ni−C−N, 173.1(7)−178.0(6).

molecules, respectively, resulting in slightly distorted square antiprisms. Differences in coordination of the ligands to the Yb(III) ions result in the two different structural types (Chart 1). In light of this information and the fact that both structures contain similar repeating molecular units, it is conceivable that a two-dimensional sheet might be obtained which contains the two different Yb(III) coordination geometries. Such an occurrence is not unprecedented.[2d]

The solid state structures of **1** and **2** differ from their solution structures as observed by DMF solution infrared spectra[5] which suggest that ion-paired species exist. If nonfluctional structures exist in solution, the $^{13}C\{^1H\}$ NMR spectra of **1** and **2** should display multiple resonances owing to both terminal and bridging cyanide ligands. However, the $^{13}C\{^1H\}$ NMR spectrum of **1** in DMF at room temperature shows only one resonance at 129.68 ppm. This resonance is shifted 2.4 ppm upfield from $K_2Ni(CN)_4$ in DMF. Consistent with the spectrum of **1**, the $^{13}C\{^1H\}$ NMR spectrum of **2** in DMF displays a three-line resonance pattern due to coupling to ^{195}Pt at 121.20 ppm ($^1J(^{195}PtC) = 1016$ Hz). This resonance is shifted slightly upfield from the $^{13}C\{^1H\}$ signal of $K_2Pt(CN)_4$ in DMF at 122.49 ppm ($^1J(^{195}PtC) = 1008$ Hz). The ^{195}Pt NMR spectrum of **2** in DMF shows one resonance at −4702 ppm, which is comparable to those spectra of $K_2Pt(CN)_4$ in DMF (−4672 ppm).

The solution NMR data clearly show that the $M(CN)_4^{2-}$ ions in **1** and **2** are equivalent on the NMR time scale, suggesting that ionization occurs. Electrical conductance measurements in DMF were used to confirm this. Molar conductivities, Λ_M, of 1 mM DMF solutions of **1** and **2** are 102 and 108 cm^2 Ω^{-1} mol^{-1}, respectively. These values are intermediate between those expected for 1:1 and 2:1 electrolytes.[7] These results are consistent with the arrays dissociating to the eight-coordinate[8] complex ions $\{(DMF)_6Yb[M(CN)_4]_2\}^-$ and $\{(DMF)_7Yb[M(CN)_4]\}^+$ followed by one DMF molecule displacing one $M(CN)_4^{2-}$ anion from $\{(DMF)_6Yb[M(CN)_4]_2\}^-$ to produce a system intermediate between a 1:1 and 2:1 electrolyte (eq 2).

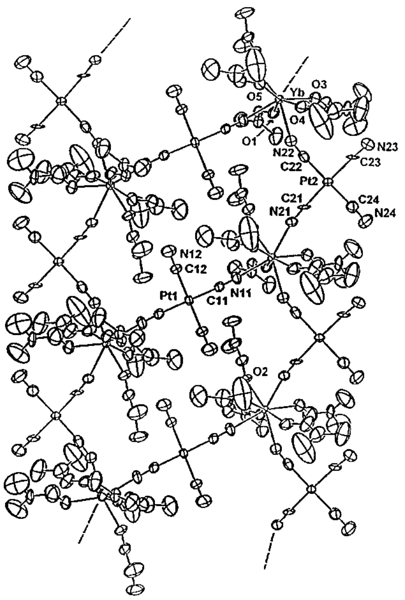
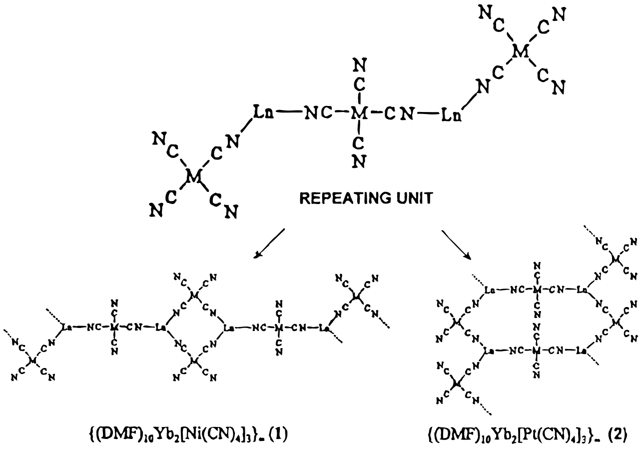


Figure 2. ORTEP drawing (50% probability ellipsoids) of a portion of $\{(DMF)_{10}Yb_2[Pt(CN)_4]_3\}_\infty$ (**2**) showing the atomic labeling scheme. DMF hydrogens are omitted. Selected bond distances (Å): Yb−O, 2.271(6)−2.337(6); Yb−N, 2.411(8)−2.467(8); Pt−C, 1.97(1)−1.99(1); C≡N, 1.12(1)−1.17(1). Selected bond angles (deg): Yb−N11−C11, 166.9(8); Yb−N21−C21, 168.8(7); Yb−N22−C22, 156.3(7); C−Pt−C, 88.3(4)−93.1(4); Pt−C−N, 174.3(9)−179(1).

Chart 1



$$\{(DMF)_6Yb[M(CN)_4]_2\}^- + \{(DMF)_7Yb[M(CN)_4]\}^+ \underset{-DMF}{\overset{+DMF}{\rightleftharpoons}} 2\{(DMF)_7Yb[M(CN)_4]\}^+ + M(CN)_4^{2-} \quad (2)$$

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Supporting Information Available: Listings of crystallographic data, positional parameters, and anisotropic thermal parameters for **1** and **2** (13 pages). Ordering information is given on any current masthead page.

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