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Hydrothermal synthesis, structural, Raman, and luminescence studies of Am[M(CN)$_2$]$_3 \cdot$ 3H$_2$O and Nd[M(CN)$_2$]$_3 \cdot$ 3H$_2$O (M = Ag, Au): Bimetallic coordination polymers containing both trans-plutonium and transition metal elements

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Abstract

The polymeric compounds consisting of the man-made element, americium, and gold and silver dicyanides were prepared under mild hydrothermal conditions at 120 °C. It was found that the americium ion and the transition metal ions are interconnected through cyanide bridging in the compounds. Given the similarities in the radii of americium and neodymium, crystals of the latter were also characterized for comparison purposes. The four compounds are isostructural and crystallize in the hexagonal space group, $P6_3/mcm$, with only slight differences in their unit cell parameters. Crystallographic data (Mo$K\alpha$, $\lambda = 0.71073$ Å): Am[Ag(CN)$_2$]$_3 \cdot$ 3H$_2$O (1), $a = 6.7205(10)$ Å, $c = 18.577(3)$ Å, $V = 726.64(19)$, $Z = 2$; Am[Au(CN)$_2$]$_3 \cdot$ 3H$_2$O (2), $a = 6.666(2)$ Å, $c = 18.342(3)$ Å, $V = 705.9(4)$, $Z = 2$; Nd[Ag(CN)$_2$]$_3 \cdot$ 3H$_2$O (3), $a = 6.7042(4)$ Å, $c = 18.6199(14)$ Å, $V = 724.77(8)$, $Z = 2$; and Nd[Au(CN)$_2$]$_3 \cdot$ 3H$_2$O (4), $a = 6.6573(13)$ Å, $c = 18.431(4)$ Å, $V = 707.2(2)$, $Z = 2$. The coordination around the Am and/or Nd consists of six N-bound CN$^-$ groups resulting in a trigonal prismatic arrangement. Three capping oxygen atoms of coordinated water molecules complete the tricapped trigonal prismatic coordination environment, providing a total coordination number of nine for the f-elements. Raman spectroscopy, which compliments the structural analyses, reveals that the four compounds display strong signals in the ν_{CN} stretching region. When compared with KAg(CN)$_2$ or KAu(CN)$_2$, the ν_{CN} stretching frequencies for these compounds blue-shift due to bridging of the dicyanometallate ions with the f-element ions. There is subsequent reduction in electron density at the cyanide center. Compared with the silver systems, the ν_{CN} frequency appears at higher energy in the gold dicyanide complexes. This shift is consistent with the structural data where the carbon–nitrogen bond distance is found to be shorter in the gold dicyanides.

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1. Introduction

The design and synthesis of self-assembling supramolecular systems is of intense interest as a rational route for generating important functional materials. One facet in this crystal engineering approach is the use of relatively weak-bonding interactions, such as hydrogen bonding [1–5].

cyanide-bridged, bimetallic systems prepared by assembling cyanometallates and transition metal and/or lanthanide building blocks exhibit fascinating structural, magnetic, electrochemical, and magneto-optical properties [6–11]. The importance of metal containing polymers for new materials is quite extensive and Au(I)-, Ag(I)-, and Pt(II)-based polymers are of particular importance because of their unique photophysical properties [12–14].

Gold(I) centers are known to form weakly bonding aurophilic interactions which have strengths that are on the same order-of-magnitude as that for hydrogen bonds [15].

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The association usually extends to yield larger oligomers and one- or two-dimensional polymers. In general terms, "aurophilic" bonding of this type is now widely accepted as the most prominent example of a general phenomenon of metallophilicity, and is recognized as a major factor in determining supramolecular structures and properties [16–18]. Hence, the chemistry of Au(I) is satiated with systems that are polymeric by virtue of these Au–Au interactions. In this regard, the linear building block dicyanoaurate, $[Au(CN)_2]^-$, is a convenient unit with which to explore the use of aurophilicity as a supramolecular design element [16–20]. This simple anion has been extensively studied over the years due it its ability to form coordination polymers through cyanide bridging. It can form polymers in a fashion similar to other metal–cyanide anions, where the central Au(I) atom is prone to forming gold–gold bonds both in solution [20–21] and in the solid state [22–26]. Similar structural features are also exhibited in Ag(I) and Pt(II) systems displaying what are known as "argentophilic" and "platinophilic" interactions, respectively.

While a majority of the synthetic procedures of these systems follow conventional solution routes, interest has also been shown in the less-conventional solvothermal techniques. Many homometallic cyanide-bridged copper(I) systems constructed through hydrothermal techniques by using CuCN and aromatic imine ligands as starting materials have been reported recently [27,28]. The first cyanide-bridged bimetallic complex prepared by solvothermal techniques, an Fe(II)–Cu(I) complex, was reported in 2003 by Colacio et al. [29]. Of the vast array of gold complexes reported, an ISI literature search provides $Pb[Au(CN)_2]_2(H_2O)$ as the only compound synthesized recently using a hydrothermal technique [30].

The synthesis of trans-plutonium compounds, especially as single crystals, is complicated by the limited availability of the materials and restriction on the experimental procedures that can be adapted due to their high radiotoxicity. Single-crystal X-ray studies in most cases are not possible given the radioactive nature that restricts handling and reduces the stability of the crystals. As a result, most of the potential compounds of these are unexplored due to the special equipment and facilities needed to deal with such materials, as well as crystal deterioration that arises due to self-irradiation.

In this paper, we report an example of a trans-plutonium element linked to a transition metal through cyanide bridging to form a three-dimensional coordination polymeric structure. Only a handful of coordination polymeric compounds have been described involving the trans-uranium element, neptunium [31,32]. To the best of our knowledge, prior examples of coordination polymers involving the trans-plutonium elements do not exist.

The polymeric compounds between the man-made element, americium, and gold and silver dicyanides were prepared using the less-conventional hydrothermal synthetic procedure. When compared to the more traditional,

slow evaporation technique, the hydrothermal synthetic procedure is especially useful for more-rapid single-crystal growth, which helps counter the internal, radioactive-induced crystal deterioration. The neodymium system is reported for structural comparison, since Nd^{3+} has a similar ionic size to that of Am^{3+}.

2. Experimental Section

2.1. Materials and methods

The americium used in these studies was made available through the US Department of Energy. Nd_2O_3 (Research Chemicals, 99.9%), $NdCl_3$ (Strem Chemicals, 99.9%), $KAg(CN)_2$ (Alfa-Aesar, 99.9%), and $KAu(CN)_2$ (Alfa-Aesar, 99.99%) were used as received. Triply distilled water was used in all reactions. An aqueous $AmCl_3$ solution was prepared by dissolving Am metal in 1 M HCl, evaporating the resulting solution to dryness, and then dissolving the solid product in H_2O. An aqueous solution of $Nd(NO_3)_3$ was prepared by dissolving Nd_2O_3 in concentrated HNO_3, evaporating the solution to dryness, and then dissolving the resultant solid in H_2O. The isotopic purity of the americium was determined to be >99.9% ^{243}Am by mass spectrometric analysis. *It should be noted that special training and experimental facilities are required in order to perform work with highly radioactive transuranium materials, such as americium.* Preparations of the $Am[M(CN)_2]_3 \cdot 3H_2O$ (M = Ag, Au) were conducted in glove boxes in accordance with the established policies for handling radioactive materials at the Oak Ridge National Laboratory. To decrease the likelihood of radioactive contamination, the established policies required that americium samples selected for X-ray and spectroscopic analyses be doubly contained.

2.2. Syntheses of $Am[M(CN)_2]_3 \cdot 3H_2O$ (M=Ag, **1**; Au, **2**)

The synthesis of $Am[Ag(CN)_2]_3 \cdot 3H_2O$, (**1**), proceeded by adding $AmCl_3$ (40 µL, 0.095 M) to a quartz reaction vessel that had been loaded with solid $KAg(CN)_2$ (2.269 mg, 11.4 µmol). The reaction vessel was flame sealed and heated to 120 °C, where the reaction/crystallization occurred under autogenously generated pressure. After 67 h, the sample vessel was allowed to self-cool to room temperature. The product consisted of yellow crystals of **1** in the form of hexagonal plates. The synthesis of $Am[Au(CN)_2]_3 \cdot 3H_2O$ (**2**) was similar to the synthesis of compound **1**, except that $KAu(CN)_2$ (3.212 mg, 11.1 µmol) was used. Crystals of **2** were pink and also consisted of hexagonal plates.

2.3. Syntheses of $Nd[M(CN)_2]_3 \cdot 3H_2O$ (M=Ag, **3**; Au, **4**)

The syntheses of compounds **3** and **4** were performed in a manner similar to that described for the americium compounds above. For compound **3**, $Nd(NO_3)_3$ (85.3 µL,

0.233 M) and $KAg(CN)_2$ (11.865 mg, 59.6 μmol) were reacted, while $NdCl_3$ (91.4 μL, 0.225 M) and $KAu(CN)_2$ (17.769 mg, 61.7 μmol) were used in the synthesis of **4**. Crystals in the form of purple hexagonal plates for **3** and **4** were recovered from the reactions as the major solid products. Powder X-ray diffraction experiments revealed the presence of several minor unindexed lines that were not consistent with either the desired products or starting materials. The purity of **3** and **4** was estimated to be ∼95% based on these studies. However, X-ray and spectro-scopical studies were conducted on single crystals which provided reproducible results. Average yields for **3** and **4** based on a number of reactions are 55%.

2.4. Single-crystal X-ray diffraction

Single crystals of compounds **1**–**4** were selected for the X-ray diffraction studies. The crystals of $Am[Ag(CN)_2]_3 \cdot 3H_2O$ (**1**) and $Am[Au(CN)_2]_3 \cdot 3H_2O$ (**2**) were sealed in quartz capillaries and then placed inside polyethylene tubes used for secondary containment. The crystals of $Nd[Ag(CN)_2]_3 \cdot 3H_2O$ (**3**) and $Nd[Au(CN)_2]_3 \cdot 3H_2O$ (**4**) were mounted on the tips of quartz fibers. The crystals were aligned on a Bruker SMART APEX CCD X-ray diffractometer with a digital camera. Intensity measure-ments were performed using graphite monochromated, $MoK\alpha$ radiation from a sealed X-ray tube equipped with a monocapillary collimator. The intensities of reflections of a sphere were collected by a combination of three sets of exposure frames. Each set had a different ϕ angle for the crystal, and each exposure covered a range of $0.3°$ in ω. A total of 1800 frames were collected with exposure times per frame of 15 s for **1**, 20 s for **2**, and 30 s for compounds **3** and **4**.

The determination of integrated intensities and a global-cell refinement were performed with the Bruker SAINT (v 6.02) software package using a narrow-frame, integra-tion algorithm. A semi-empirical absorption correction was applied using SADABS [33]. The program suite SHELXTL (v 5.1) was used for space group determination (XPREP), structure solution (XS), and least-squares refinement (XL) [34]. A Patterson function was used to locate the heavy atom positions. The C, N, and O atomic positions were located in difference maps. The hydrogen atoms of the water molecules were not located or calculated. The scattering factor, real and imaginary dispersion terms, and the linear absorption coefficient for americium [35] were manually inputted into the SHELXTL instruction files. The final refinements for **1**, **3**, and **4** included anisotropic displacement parameters for all atoms and a secondary extinction parameter; for **2**, only the americium and gold atoms were refined anisotropically. Experimental challenges included very small crystals coupled with the double containment required for the X-ray experiments, which resulted in a lower quality X-ray structure for **2**. Crystallographic details for compounds **1**–**4** are listed in Table 1. Further details of the crystal structure investiga-tions may be obtained from the Fachinformationzentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (Fax: (+49)7247-808-666; Email: crysdata@fiz-karlsruhe. de) on quoting the depository numbers CSD-417896 for **1**, CSD-417897 for **2**, CSD-417898 for **3**, and CSD-417899 for **4**.

2.5. Raman spectroscopy

Raman spectroscopy was performed using an argon-ion laser (Coherent, model 306) and a double-meter spectro-meter (Jobin-Yvon Ramanor model HG.2S). The resolution

Table 1
Crystallographic data for $Am[Ag(CN)_2]_3 \cdot 3H_2O$ (**1**), $Am[Au(CN)_2]_3 \cdot 3H_2O$ (**2**), $Nd[Ag(CN)_2]_3 \cdot 3H_2O$ (**3**), and $Nd[Au(CN)_2]_3 \cdot 3H_2O$ (**4**)

Formula	$Am[Ag(CN)_2]_3 \cdot 3H_2O$	$Am[Au(CN)_2]_3 \cdot 3H_2O$	$Nd[Ag(CN)_2]_3 \cdot 3H_2O$	$Nd[Au(CN)_2]_3 \cdot 3H_2O$
Formula mass	776.84	1044.13	678.02	945.31
Color and habit	Yellow, hexagonal plate	Pink, hexagonal plate	Purple, hexagonal plate	Purple, hexagonal plate
Crystal system	*Hexagonal*	Hexagonal	Hexagonal	Hexagonal
Space group	$P6_3/mcm$ (No. 193)	$P6_3/mcm$ (No. 193)	$P6_3/mcm$ (No. 193)	$P6_3/mcm$ (No. 193)
a (Å)	6.7205(10)	6.666(2)	6.7042(4)	6.6573(13)
c (Å)	18.577(3)	18.342(6)	18.620(1)	18.431(4)
V (Å^3)	726.64(19)	705.9(4)	724.77(8)	707.2(2)
Z	2	2	2	2
T (°C)	21	21	21	21
λ (Å)	0.71073	0.71073	0.71073	0.71073
$2\theta_{max}$	56.58	50.36	56.54	56.54
ρ_{calcd} (g cm^{-3})	3.551	4.913	3.107	4.440
μ($MoK\alpha$) (mm^{-1})	9.212	36.463	7.525	34.643
Reflections collected	6567	4793	6464	6247
Independent reflections	360 [$R(int) = 0.0406$]	254 [$R(int) = 0.3069$]	360 [$R(int) = 0.0266$]	350 [$R(int) = 0.0520$]
Data/restraints/parameters	360/0/24	254/0/15	360/0/24	350/0/24
$R(F)$[a] for $F_o^2 > 2\sigma(F_o^2)$[a]	0.0149	0.0404	0.0141	0.0304
$R_w(F_o^2)$[b]	0.0371	0.0881	0.0505	0.0677

[a] $R(F) = \sum ||F_o| - |F_c|| / \sum |F_o|$.

[b] $R_w(F_o^2) = \left[\sum \left[w(F_o^2 - F_c^2)^2 \right] / \sum w F_o^4 \right]^{1/2}$.

of the monochromator at 514.5 nm is 0.5 cm^{-1}. The monochromator is interfaced with a personal computer; scanning and data collections are controlled by LabSpec (version 3.04) software. Signal detection is acquired with a water-cooled photo-multiplier tube (Hamamatsu R636). The 528 nm wavelength was the principal argon laser line used for excitation in these experiments. The reported spectra are uncorrected for instrumental responses, but the monochromator positions and wavenumber accuracies were calibrated daily using the Hg line at 18312.7 cm^{-1} (546.1 nm) from an external source. Additional calibration was conducted using the tri-azaphospha-adamantane ligand (TPA), which exhibits several sharp and intense Raman bands in the region of interest.

2.6. Emission spectroscopy

The 514.5 nm line was used for the excitation of the americium complexes. The luminescence spectra were collected using an Instrument SA optical system consisting of a monochromator (model 1000 M) attached to CCD, PMT, and IR detectors. Additional spectra of higher resolution were collected using a HG2.S monochromator. Data analyses were performed with Grams/32 software (Galactic, version 5.1).

3. Results and discussion

3.1. Material syntheses

Given the limited quantities of americium available, the reaction conditions were first optimized by formation of Nd[M(CN)$_2$]$_3 \cdot$ 3H$_2$O (M = Ag(**3**), Au(**4**)) before the syntheses of Am[M(CN)$_2$]$_3 \cdot$ 3H$_2$O (M = Ag (**1**), Au (**2**)) were attempted. These conditions are given in the experimental section. Initial hydrothermal reactions between Nd(NO$_3$)$_3$ and KAg(CN)$_2$ were attempted at 170 °C, but under these conditions the dicyanoargentate anions decompose, resulting in the reduction of Ag$^+$ and formation of silver metal. As determined by single-crystal X-ray characterization, Nd(CO$_3$)(OH) [36] was also isolated under the above conditions. However, high-quality crystals of compounds **3** or **4** are isolated as the sole crystalline products when NdCl$_3$ is reacted with KAg(CN)$_2$ or KAu(CN)$_2$ in a 1:3 ratio at 120 °C. When Nd(NO$_3$)$_3$ is reacted with KAu(CN)$_2$ at 120 °C, Nd[Au(CN)$_2$]$_3 \cdot$ 3H$_2$O is formed as well as an unidentified yellow microcrystalline powder. Reaction times from 16 h to 3 days have been tried and this period was found adequate for the syntheses. Once the synthetic procedures were optimized on the neodymium systems, compounds **1** and **2** were prepared under similar reaction conditions.

Previous reports have outlined the syntheses of similar tris-(dicyanoargentate) lanthanide trihydrates or tris-(dicyanoaurate) lanthanide trihydrates either by slow evaporation [18,26,37] or by gel growth [38] methods. Our synthetic approach for compounds **1–4** was to use the hydrothermal technique, a method that has also been used recently in the preparation of other transition metal cyanides [39–40]. This method is particularly attractive for the americium systems, and single crystals of Am[M(CN)$_2$]$_3 \cdot$ 3H$_2$O (M = Ag(**1**), Au(**2**)) can be grown with small quantities of reactants (e.g., 0.92 mg Am) in sealed reaction tubes.

3.2. Crystal structures

Compounds **1–4** all exhibit the same structure, crystallizing in the hexagonal space group, $P6_3/mcm$, and are isostructural to the previously reported Eu[Ag(CN)$_2$]$_3 \cdot$ 3H$_2$O [26]. This structural type has also been reported for several additional tris(dicyanoargentate)lanthanide trihydrates or tris(dicyanoaurate)lanthanide trihydrates [38,41–42]. Due to the structural similarities of the 1-4 compounds reported here, for brevity, only the structure of Am[Ag(CN)$_2$]$_3 \cdot$ 3H$_2$O (**1**) will be discussed in detail; some important comparisons with the other structures will be addressed. Table 1 contains the crystallographic data for these four compounds, and selected bond lengths for compounds **1–4** are given in Tables 2 and 3.

Fig. 1 shows the coordination geometry around the americium atom with the atomic labeling schemes. The environment for the Am^{3+} ion in **1** consists of six N-bound CN$^-$ groups coordinated approximately end-on in a trigonal prismatic arrangement. In addition, three water molecules cap the rectangular faces of the prism. The resultant tricapped trigonal prismatic coordination environment of the Am site is shown in Fig. 1. The overall cyanide coordination is also shown at one site, but the three-dimensional interaction is clearly evident in the packing diagram shown in Fig. 2. The tricapped trigonal prismatic coordination geometry around the Am^{3+} is a D_{3h}

Table 2
Selected bond distances (Å) for Am[Ag(CN)$_2$]$_3 \cdot$ 3H$_2$O (**1**), and Nd[Ag(CN)$_2$]$_3 \cdot$ 3H$_2$O (**3**)

Am[Ag(CN)$_2$]$_3 \cdot$ 3H$_2$O		Nd[Ag(CN)$_2$]$_3 \cdot$ 3H$_2$O	
Am(1)–N(1) × 6	2.570(5)	Nd(1)–N(1) x 6	2.585(2)
Am(1)–O(1) × 3	2.496(7)	Nd(1)–O(1) x 3	2.478(3)
C(1)–N(1)	1.132(7)	C(1)–N(1)	1.134(3)
Ag(1)–C(1) × 2	2.072(6)	Ag(1)–C(1) x 2	2.059(3)
Ag(1)···Ag(1)'	3.3603(5)	Ag(1)···Ag(1)'	3.3521(2)

Table 3
Selected bond distances (Å) for Am[Au(CN)$_2$]$_3 \cdot$ 3H$_2$O (**2**) and Nd[Au(CN)$_2$]$_3 \cdot$ 3H$_2$O (**4**)

Am[Au(CN)$_2$]$_3 \cdot$ 3H$_2$O		Nd[Au(CN)$_2$]$_3 \cdot$ 3H$_2$O	
Am(1)–N(1) × 6	2.60(3)	Nd(1)–N(1) × 6	2.598(7)
Am(1)–O(1) × 3	2.51(4)	Nd(1)–O(1) × 3	2.479(12)
Au(1)–C(1) × 2	2.06(4)	Au(1)–C(1) × 2	1.984(10)
C(1)–N(1)	1.07(5)	C(1)–N(1)	1.14(1)
Au(1)···Au(1)'	3.3330(11)	Au(1)···Au(1)'	3.3287(6)

Fig. 1. An illustration of the tricapped trigonal prismatic coordination environment around the Am^{3+} centers in $Am[Ag(CN)_2]_3 \cdot H_2O$ (1). 50% displacement ellipsoids are shown.

Fig. 2. The packing diagram for $Am[Ag(CN)_2]_3 \cdot 3H_2O$ (1) as viewed down the a-axis. Green Am, red = O and blue = nitrogen atoms of the cyanide ligand.

site symmetry. The three O atoms of the water molecules are coplanar with the Am atom, by symmetry. The Am–O distance of 2.496(7) Å is shorter than the Am–N distance of 2.570 Å. The average bond length between the Am atom and the coordinated water molecules is comparable to the Am–O distance of 2.434(16) found for the coordinated water molecule in $(C_7H_5O_3)_3Am \cdot H_2O$ [43]. Our structure consists of one unique Am–N distance of 2.570(5) Å, which is within the range of Am–N distances found in other compounds. For comparison, an Am–N distance of 2.50 Å is reported for AmN (americium nitride) [44], while longer Am–N bond distances of 2.617(2) and 2.626(2) are found in $(C_{10}N_2H_8)(C_5NS_2H_{10})_3Am$ [45]. Each silver atom in compound 1 is coordinated to the carbon atoms of two cyanide anions, resulting in nearly linear $Ag(CN)_2^-$ units, as

found in other dicyanoargentates [26,41]. This arrangement is shown clearly in the packing diagram of Fig. 2.

In the structure of 1, the $[AmN_6O_3]$ polyhedra are arranged in layers found in the crystallographic (ab) plane. As shown in Fig. 2, these alternating layers of Ag atoms and Am polyhedra are bridged with cyanide linkages resulting in an overall three-dimensional framework for $Am[Ag(CN)_2]_3 \cdot 3H_2O$ (1). The silver atoms in 1 form a Kagomé lattice, also found in the ab plane that separates the layers of americium polyhedra. As shown in Fig. 3, every Ag atom has four nearest Ag neighbors, with uniform Ag⋯Ag separations of 3.3603(5) Å.

Upon replacing silver by gold, and/or Am^{3+} by Nd^{3+} the overall structural features remain unchanged. However, subtle differences are evident that could affect some of the

Fig. 3. Drawing showing the Kagomé lattice contained in the structure of compounds **1–4**. Au···Au or Ag···Ag interactions are indicated by the dashed lines. Every Ag or Au atom is surrounded by four other silver or gold atoms placed in a rectangular arrangement.

Fig. 4. Raman spectrum of: (a) $KAg(CN)_2$; (b) $Nd[Ag(CN)_2]_3 \cdot 3H_2O$; and (c) $Am[Ag(CN)_2]_3 \cdot 3H_2O$.

Table 4
Assignment of Raman bands (cm^{-1})

$Am[Au(CN)_2]_3$	$Nd[Au(CN)_2]_3$	$Nd[Ag(CN)_2]_3$	Assignment
2176	2166	2160	$v(CN)$
	2158		$vCN)$
	491		$v(AuC)$
	474		$v(AuC)$
		412	$v(AgC)$
		384	$v(AgC)$
	347		
	330		$\delta(AuCN)$
		308 (sh)	
		289	$\delta(AgCN)$
		274 (sh)	
	226		Lattice modes
	183		Lattice modes
	152		Lattice modes
	120		Lattice modes
	79		$v(Au–Au)$

The small size of the americium samples precluded the collection of a reliable data in the low-frequency region.

spectroscopic properties of the complexes. In **2**, the Au···Au separation is slightly smaller (3.3330(11) Å) than the Ag···Ag separation in **1**. When compared with the Am compounds, the $M \cdots M$ ($M = $ Ag, Au) distances are smaller for the corresponding neodymium compounds. For example, the Ag···Ag and Au···Au distances are 3.3521(2) and 3.3287(6) Å in the Nd compounds **3** and **4**, respectively. This contributes to the smaller unit cell volumes observed in the gold compounds ($\sim$2.6%) as compared with the silver compounds with the same f-element species (i.e. Am or Nd). Although gold has a higher Z than silver, the reduction in molecular volume can be traced to the smaller covalent radii arising from the larger "relativistic contraction" for gold [46,47]. Thus, the bonding interactions reflect that, gold is more prone for covalent interaction than silver [48].

3.3. Raman studies

The Raman spectra for the silver dicyanide complexes are shown in Fig. 4 in the v_{CN} stretching region; the band assignments are given in Table 4. As shown in Fig. 4a, the CN symmetric stretch for $KAg(CN)_2$ is observed at 2145 cm^{-1}, consistent with the previously reported value for this compound [49]. Upon coordination with Nd^{3+}, the v_{CN} band blue-shifts by $\sim$15 cm^{-1} and a single strong band appears at 2160 cm^{-1}. No significant change is observed on the v_{CN} symmetric stretching band when neodymium is replaced by the actinide, americium, due to their very

similar ionic radii. However, the small size of the $Am[Ag(CN)_2]_3 \cdot 3H_2O$ crystals results in a weak Raman signal and required a large number of data collection to counter the background noise. The shift of the v_{CN} to higher energy for compound 3 is consistent with data reported for most cyanometalates that show a blue-shifting upon nitrile binding. This shift can be rationalized as due to a substantial electron density withdrawal from the antibonding N lone pair upon bridging with f-element ions. Only metals such as Tl and Pb, that participate in back-bonding to the CN group, are known to exhibit red-shifted v_{CN} symmetric stretching bands [50].

The Raman spectra of the gold dicyanide complexes are shown in Fig. 5 and cover the v_{CN} stretching region. The spectrum of $KAu(CN)_2$ shown in Fig. 5a has a single band at 2162 cm^{-1}. In the neodymium complex the band splits into two: a strong band at 2166 cm^{-1} and a much weaker one at $\sim$2158 cm^{-1} in a ratio of 1:20, respectively. The
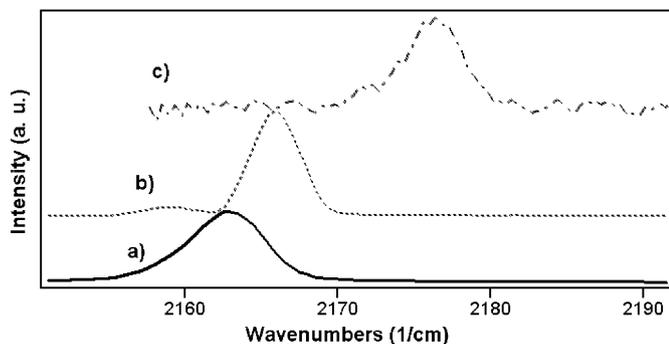
Fig. 5. Raman spectrum of: (a) $KAu(CN)_2$; (b) $Nd[Au(CN)_2]_3 \cdot 3H_2O$; and (c) $Am[Au(CN)_2]_3 \cdot 3H_2O$.

Fig. 6. Raman spectra of the compounds covering the low-energy (50–550 cm^{-1}) vibrational region: (a) $KAg(CN)_2$; (b) $Nd[Ag(CN)_2]_3 \cdot 3H_2O$; (c) $KAu(CN)_2$; and (d) $Nd[Au(CN)_2]_3 \cdot 3H_2O$.

Fig. 7. Emission spectrum of $Am[Ag(CN)_2]_3 \cdot 3H_2O$ (1) obtained, using the 514.5 nm argon-ion laser line as an excitation source.

spectrum shown in Fig. 5c corresponds to the $Am[Au(CN)_2]_3 \cdot 3H_2O$ system, where the ν_{CN} symmetrical stretching band is significantly blue-shifted as compared to either $KAu(CN)_2$ or $Nd[Au(CN)_2]_3 \cdot 3H_2O$. This band appears at 2176 cm^{-1}. The blue shift in the ν_{CN} stretch indicates bridging of gold and americium, which results in a substantial electron density removal from the cyanide group. When compared with the silver systems, the ν_{CN} frequency appears at a higher energy for the gold dicyanide complexes. The shift to higher frequency is consistent with the structural data where the carbon–nitrogen bond distance is shorter in the gold dicyanide systems. In the Nd–Ag compound the CN bond distance is 1.134(3) Å, with error of the C–N distance of 1.14(1) found in the Nd–Au system. However, the CN bond distance is reduced from 1.132 to 1.07 Å on going from the Am–Ag to the Am–Au system, indicating bond strengthening in the latter system.

In the low-energy region, the neodymium compounds provide detailed and well-defined spectral profiles. Although not clearly defined in the $KAg(CN)_2$ spectrum (Fig. 6a), the $Nd[Ag(CN)_2]_3 \cdot 3H_2O$ system has a well-resolved doublet (Fig. 6b) at 412 and 384 cm^{-1}, which is assignable to the ν_{Ag-C} stretch. A broad band centering at 289 cm^{-1} is also observed with shoulders at 308 and 274 cm^{-1}, which is blue-shifted compared with that for $KAg(CN)_2$ system, (observed at 249 cm^{-1}). These bands are assigned to the Ag–CN bending modes. In the $Nd[Au(CN)_2]_3 \cdot 3H_2O$ system, the Au–C stretching appears (Fig. 6d) as a doublet at blue-shifted positions of 474 and 491 cm^{-1}, when compared with the silver compounds. The blue shift is consistent with a stronger Au–C bond inferred from the M–C distances (2.001 vs. 2.063 Å in Au–C vs. Ag–C, respectively). The Au–CN bending mode in $Nd[Au(CN)_2]_3 \cdot 3H_2O$ is also blue-shifted to 347 and 330 cm^{-1} compared with the values for the Ag–CN modes (Fig. 6b), and the Au–CN bend in $KAu(CN)_2$ (Fig. 6c). Additional Raman bands are observed in the lower-energy region at 226, 183, 152, and 120 cm^{-1}; all bands are assigned to lattice modes. The much stronger band at 79 cm^{-1} is assignable to the Au–Au stretching [51].

Although, it would be desirable to compare the lanthanide Raman data with those for the actinide complexes, the sample sizes available for analysis combined with the reduced signal intensity in the low-frequency vibrational region limited our ability to collect as suitable Raman data on the americium compounds. However, the structural comparisons indicate that the M–C (M = Ag, Au) distances in the americium complexes are longer than those of the neodymium systems and a red shift would be anticipated in the ν_{MC} vibrational modes for the Am compounds.
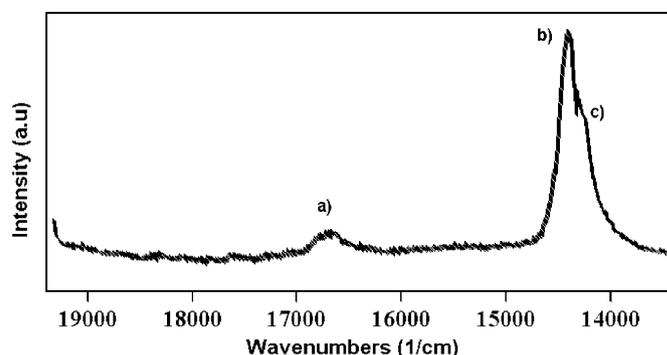
3.4. Photoluminescence studies

The photoluminescence spectrum of crystalline $Am[Ag(CN)_2]_3 \cdot 3H_2O$ is shown in Fig. 7. The 514.5 nm laser line, which is essentially in resonance with the $^5L_{6'}$ level, was used to excite the sample. As is evident from the absorption spectrum shown in Fig. 8, the $^5L_{6'}$ has the largest absorbance of the f–f transitions within the americium excited levels. Excitation to this level with the 514.5 nm laser line produces emission bands originating from two different excited states. The broad weak band centering at $\sim$16700 cm^{-1} corresponds to the $^5L_{6'} \rightarrow {}^7F_{1'}$ transition [52,53].

The most intense band appears at 14,350 with a broad shoulder 14,250 cm^{-1}. In this region, americium
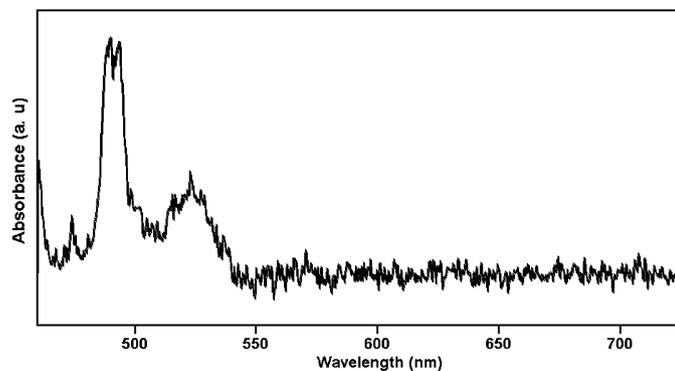
Fig. 8. Solid-state absorption spectrum of a Am[Ag(CN)$_2$]$_3 \cdot$ 3H$_2$O single crystal. [Absorbance is in arbitrary units.]

luminescence spectar are known of overlapping emissions originating from two different excited levels [52–59]. Based on the established assignments, the higher energy of the emission (with a maximum at 14350 cm^{-1}) corresponds to the $^5D_{1'} \rightarrow ^7F_{1'}$ transitions [54–59], while the lower-energy side mainly corresponds to contributions from the $^5L_{6'} \rightarrow ^7F_{2'}$ transitions. When compared with the americium iodates and borosilicate matrices reported earlier [60–61], the most intense band for the americium emission in the Am[Ag(CN)$_2$]$_3 \cdot$ 3H$_2$O system is red-shifted by 250 cm^{-1}. The relative intensities of the emissions from the two excited states are temperature dependent. In the spectrum collected at liquid nitrogen temperature, the lower-energy emission originating from the $^5L_{6'}$ state has comparable intensity to that of the higher-energy band corresponding to the $^5D_{1'} \rightarrow ^7F_{1'}$ transition. The lower-energy band also shows a well-resolved shoulder at ~14,000 cm^{-1}. The relative decrease of the emission intensity originating from the lower excited state ($^5D_{1'}$) is indicative of the reduced thermal deactivation from the upper $^5L_{6'}$ level. The presence of water molecules in the coordination sphere of the Am ion is expected to bridge the gap and facilitate cascading of the excitation to the lower excited level. Radiative transitions from this emitting level to the various ground levels enhances the emission originating from this state.

Several attempts to observe emission from the Am[Au(CN)$_2$]$_3 \cdot$ 3H$_2$O were not successful, although Am^{3+} is one of the strong, spectral-emitting actinide ions. The americium emission in the gold complex is quenched, even at liquid nitrogen temperature, indicating the presence of an intense, non-radiative mechanism responsible for the dissipation of the excitation energy.

4. Summary

The polymeric compounds between americium and gold and silver dicyanides were prepared using a hydrothermal synthetic procedure. Single crystals of Am[M(CN)$_2$]$_3 \cdot$ 3H$_2$O ($M =$ Ag, Au) were obtained from the reaction of AmCl$_3$ and M(CN)$_2^-$ ($M =$ Ag, Au) under mild hydrothermal conditions of 120 °C. The americium ion and the

transition metals are interconnected through cyanide bridging.

The isostructural neodymium compounds were prepared for comparison with the americium compounds. All four of these compounds studied crystallize in the same hexagonal space group with only slight differences occurring in their unit cell parameters. The coordination around the Am or Nd consists of six CN$^-$ groups coordinated through the N atoms resulting in a trigonal prismatic environment. Three oxygen atoms of coordinated water molecules complete the tricapped trigonal prismatic coordination environment for Am^{3+} providing a total coordination number of nine. Raman spectroscopy, which compliments the structural work, reveals that all of the compounds display strong signals in the ν_{CN} stretching region. When compared with KAg(CN)$_2$ or KAu(CN)$_2$, the ν_{CN} stretching frequency in all the compounds blue-shift due to bridging and substantial electron density removal from the cyanide center. When compared with the silver systems, the ν_{CN} stretching frequency appears at higher energy in the gold dicyanide complexes. The shift to higher frequency is consistent with the structural data where the carbon–nitrogen bond distance decreases in the gold dicyanide systems when compared with the silver system.

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