Europium(III) Tris[dicyanoargentate(I)] Trihydrate, Eu[Ag(CN)$_2$]$_3$.3H$_2$O

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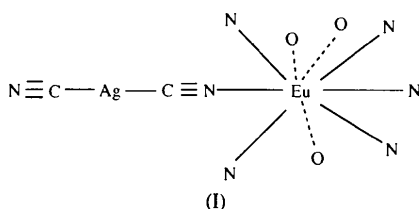*Department of Chemistry, University of Maine, Orono, ME 04469, USA*

Abstract

The structure consists of layers of Ag(CN)$_2^-$ ions arranged in such away that trigonal prisms of N atoms are formed. Each prism is occupied by an Eu^{3+} ion, to which three H$_2$O molecules coordinate and complete the tricapped trigonal geometry.

Comment

The use of lanthanide ions in excited-state studies of low-dimensional compounds is an area currently under extensive investigation. Several recent studies have show that energy transfer enhances the excitation of lanthanide ions much more effectively than direct absorption of light (Bünzli, Froidevaux & Harrowfield, 1993; Bünzli, 1989). Compounds of dicyanoargentates, like the dicyanoaurides, have a layered structure showing weak intermolecular Ag···Ag interactions in the solid state. The counter cation in these compounds usually occupies a hexagonal or a trigonal prismatic hole and interacts with the N atom of the CN$^-$ ligand. The spectroscopic implication of these interactions has been reported recently for the title complex, (I) (Assefa, Shankle, Patterson & Reynolds, 1994). An efficient energy transfer between the Ag(CN)$_2^-$ and Eu^{3+} ions has been observed and it is postulated that it operates through an exchange mechanism (Demas, 1983) that requires an actual overlap between the donor and acceptor wave functions. The title compound was char-

acterized in order to elucidate the correlation between the spectroscopic and structural properties.

Fig. 1 shows the geometry with the atomic labeling scheme. The packing diagram along the c axis is shown in Fig. 2. Surprisingly, the literature contains very few examples of structurally characterized compounds of dicyanoargentates and no example of a rare earth salt with this anion. The Ag(CN)$_2^-$ ions are linear. The Ag—C and C—N distances are in agreement with those found in NaAg(CN)$_2$ (Range, Kühnel & Zabel, 1989) and K$_2$Na[Ag(CN)$_2$]$_3$ (Zabel, Kühnel & Range, 1989). The NC—Ag—CN groups are canted by about 14° with respect to the c axis and the terminal N atoms form a trigonally distorted close-packed layer. The Ag atoms are arranged in layers perpendicular to the c axis. Every Ag atom has four nearest Ag neighbors in a rectangular arrangement with Ag···Ag separations of 3.340 (5) Å (Fig. 3).

The environment of the Eu^{3+} ion consists of six CN$^-$ groups coordinated approximately end-on, resulting in trigonal prismatic geometry. The Eu—N distance of 2.539 (4) Å indicates a strong bonding interaction between the Eu atom and the CN$^-$ ligands. Three H$_2$O molecules complete the tricapped trigonal prism. The
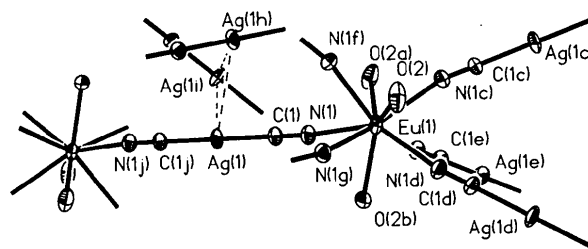

Fig. 1. Drawing (50% probability ellipsoids) of Eu[Ag(CN)$_2$]$_3$.3H$_2$O showing the labeling scheme of the polymer. Labels with letters appended indicate symmetry equivalent positions: (a) $-x + y + 2$, $-x + 1$, z; (b) $-y + 1$, $x - y - 1$, z; (c) $y + 1$, $x - 1$, $1/2 - z$; (d) $-x + 2$, $-x + y + 1$, $1/2 - z$; (e) $x - y$, $-y$, $1/2 - z$; (f) $-y + 1$, $x - y - 1$, z; (g) $-x + y + 2$, $-x + 1$, z; (h) $-x + y + 1$, $-x$, z; (i) $-y$, $x - y - 1$, z; (j) $-x$, $-y - 1$, $-z$.
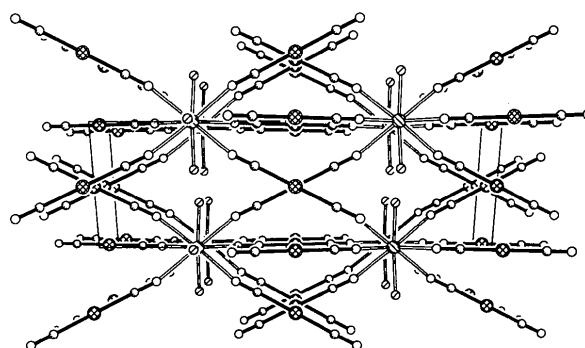
Fig. 2. Packing diagram for Eu[Ag(CN)$_2$]$_3$.3H$_2$O as viewed down the a axis. Large striped circles represent Eu atoms, large hatched circles Ag atoms, small spotted circles N atoms, small striped circles O atoms and small shaded circles C atoms.
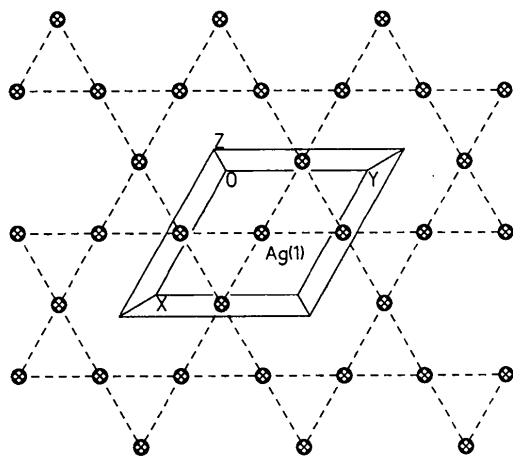

(I)

Fig. 3. Drawing showing the Ag···Ag interactions [3.344 (1) Å].

three O atoms of the water molecules are coplanar with the Eu atom, by symmetry. The Eu—O distance is short [2.452 (6) Å] and, thus, the total coordination number of the Eu^{3+} ion is nine. While there exists a mirror plane along the plane that contains the three O atoms and the Eu atom, no perpendicular plane is evident as the O atoms are situated approximately 6.5° away from the N—Eu—N plane [N(1)—Eu—O(1) = 133.41 (9) *versus* N(1)—Eu—N(1c) = 139.81 (7)°]. Thus, the Eu atom has essentially C_3 symmetry, as predicted from the splitting of the $^5D_0$–$^7F_1$ transition observed in the photoluminescence study of the title compound.

Experimental

Addition of a stoichiometric amount of Eu(NO$_3$)$_3$.6H$_2$O to an aqueous solution of KAg(CN)$_2$ and slow evaporation provided crystals of the title complex.

Crystal data

Eu[Ag(CN)$_2$]$_3$.3H$_2$O	Mo $K\alpha$ radiation
M_r = 1371.4	λ = 0.71073 Å
Hexagonal	Cell parameters from 25
$P6_3/mcm$	reflections
a = 6.688 (1) Å	θ = 10–15°
c = 18.479 (7) Å	μ = 16.699 mm^{-1}
V = 715.8 (4) Å^3	T = 293 (2) K
Z = 2	Block
D_x = 6.363 Mg m^{-3}	0.3 × 0.25 × 0.1 mm
	Colorless

Data collection

Siemens $R3m/E$ diffractom-	R_{int} = 0.052
eter	θ_{max} = 25°
ω (Wyckoff) scans	h = −4 → 0
Absorption correction:	k = 0 → 8
ψ scans (see below)	l = 0 → 22
1442 measured reflections	3 standard reflections
332 independent reflections	monitored every 97
306 observed reflections	reflections
[$I > 2\sigma(I)$]	intensity decay: 0.5%

Refinement

Refinement on F^2	$\Delta\rho_{max}$ = 2.42 e Å^{-3}
$R(F)$ = 0.0351	$\Delta\rho_{min}$ = −1.88 e Å^{-3}
$wR(F^2)$ = 0.0899	Extinction correction:
S = 1.15	SHELXL93 (Sheldrick,
332 reflections	1993)
28 parameters	Extinction coefficient:
H atoms riding	0.0351 (27)
$w = 1/[\sigma^2(F_o^2) + (0.0575P)^2$	Atomic scattering factors
+ 1.1295P]	from *International Tables*
where $P = (F_o^2 + 2F_c^2)/3$	*for Crystallography* (1992,
$(\Delta/\sigma)_{max}$ = 0.001	Vol. C, Tables 4.2.6.8 and
	6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Eu1	1	0	1/4	0.0136 (4)
Ag1	1/2	0	0	0.0366 (4)
N1	0.7391 (6)	0	0.1502 (2)	0.0311 (10)
C1	0.6539 (8)	0	0.0965 (2)	0.0294 (11)
O1	1.3666 (9)	0	1/4	0.046 (2)

Table 2. *Selected geometric parameters (Å, °)*

Eu1—O1	2.452 (6)	Ag1···Ag1^i	3.3440 (5)
Eu1—N1	2.539 (4)	N1—C1	1.144 (6)
Ag1—C1	2.059 (5)		
O1^{ii}—Eu1—O1	120.0	Ag1^i···Ag1···Ag1^{iv}	180.0
O1—Eu1—N1	133.41 (9)	C1—N1—Eu1	166.5 (4)
N1—Eu1—N1^{iii}	139.81 (7)	N1—C1—Ag1	179.9 (4)

Symmetry codes: (i) $-y, x - y - 1, z$; (ii) $2 - x + y, 1 - x, z$; (iii) $2 - x + y, 1 - x, \frac{1}{2} - z$; (iv) $1 - y, x - y, z$.

A suitable crystal was chosen and mounted on a glass fiber at room temperature with epoxy cement. Inspection of axial photographs about each of the three axes confirmed the axis length and Laue symmetry. ω scans of several intense reflections indicated acceptable crystal quality. Background measurements were recorded by the stationary crystal and stationary counter technique at the beginning and end of each reflection for half the total scan time. O-bound H atoms were located in a difference Fourier map and then fixed at O—H = 0.85 Å. H-atom parameters were not refined. The large residual electron-density peaks and holes lie 0.87 Å from the Eu atom. The absorption correction was based on ψ scans and the large residuals and large transmission values suggest that the correction is possibly poor.

Data collection: *P3 Software* (Nicolet, 1982a). Data reduction: *XTAPE* (Nicolet, 1982b). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Software used to prepare material for publication: *CIFGEN* (Reibenspies, 1994).

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Distant Copper–Copper Interactions in a Metal-Organic Compound in the Solid State: Hexakis[(μ3-4,6-dimethylpyrimidine-2-thiolato-N:S:S)copper(I)] Dihydrate

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Abstract

In the hexameric complex of the title compound, $[Cu(C_6H_7N_2S)]_6.2H_2O$, each of the six Cu^I atoms exhibits highly distorted square-pyramidal coordination geometry with two adjacent Cu^I atoms and two thiolate S atoms occupying the basal positions, and an azomethine N atom at the apex. The molecule consists of two centrosymmetrically related distorted tricapped trigonal prisms, formed by three Cu^I and three thiolate S atoms. The three planar tridentate $C_6H_7N_2S$ ligands

are almost normal to their corresponding basal planes. Each thiolate S atom bridges two Cu^I atoms, the ligand thus coordinating to form two five-membered open envelopes. In the hexamer, the six Cu^I atoms are in a perfect chair conformation and this hints at a distant $Cu^I \cdots Cu^I$ interaction.

Comment

The discovery of the antibacterial, antiviral and antimicrobial properties (Rosenfield, Mascharak & Arora, 1987) of 4,6-dimethylpyrimidine-2-thiol (4,6Me₂Pm-2SH) and its metal complexes, and the use of copper–sulfur compounds (Krebs & Henkel, 1991) as models for copper–cysteine centres in metalloproteins like plastocyanin and azurin (Freeman, 1980), prompted the synthesis and structural investigation of the title complex. The crystal structure of $[Cu(4,6Me_2Pm2S)]_6.2H_2O$, (IV), is presented here and the metal coordination and nature of the bonding are discussed.

(IV)
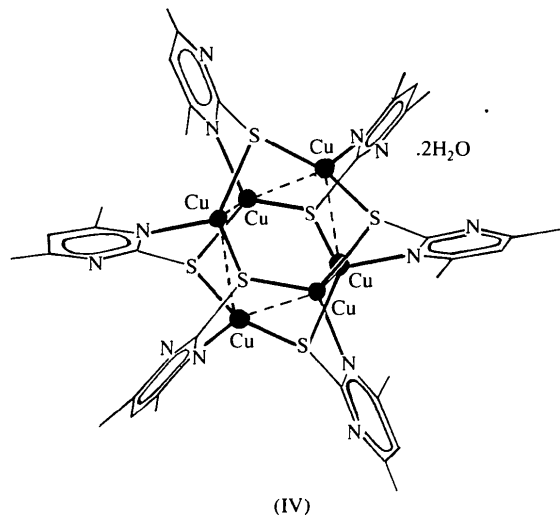
The structure (Fig. 1) consists of discrete centrosymmetric hexamers of (4,6-dimethylpyrimidine-2-thiolato)copper(I) and water of crystallization. The coordination geometry of the molecule (Table 2) is best described in terms of two centrosymmetrically related distorted tricapped trigonal prisms with bases $Cu(1) \cdots Cu(2^i) \cdots Cu(3)$ and $S(1) \cdots S(2^i) \cdots S(3)$. Each Cu^I atom, near the centre of the rectangular faces of the prism, exhibits highly distorted square-pyramidal coordination geometry with two adjacent Cu^I and two thiolato S atoms occupying the basal positions, and an azomethine N atom at the top of the pyramid. Each basal plane is planar to within ±0.018 (2) Å and the Cu^I atoms deviate above the plane by 0.836 (1), 0.733 (1) and 0.814 (1) Å. The Cu^I—N [2.021 (5)–2.044 (5) Å] and $Cu(1)$—S [2.239 (2)–2.264 (2) Å] distances are within normal ranges.