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Polyhedron 26 (2007) 4019-4023



Reassignment of the crystal space group of crystalline $Pr[M(CN)_6] \cdot 5H_2O$ (M = Cr, Fe, Co)

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Received 19 March 2007; accepted 1 May 2007 Available online 10 May 2007

Abstract

Refinement of the X-ray crystal structures of $Pr[M(CN)_6] \cdot 5H_2O$ (M = Cr, Fe, Co) enables their space group to be reassigned to $P6_3/mmc$. Spectral characteristics are reported for M = Cr and the distinction between the pentahydrate and tetrahydrate series is clearly made from assignments of the infrared spectra.

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Keywords: Cyanide bridge; Lanthanide ion; Bimetallic; Crystal structure; Vibrational spectra

1. Introduction

The lanthanide(III) hexacyanometalate(III) hydrates, $Ln^{III}[M^{III}(CN)_6] \cdot nH_2O$ (Ln = lanthanide; M = transition metal; n = 4, 5) are precursors for perovskite-type oxides which have a variety of applications such as chemical sensors and catalysts [1–4]. Their crystal structures consist of alternating cyanide-bridged MC₆ and LnN_6O_y (y = 2, 3) polyhedra in an orthorhombic or hexagonal lattice, depending on the degree of hydration at the lanthanide center [5–7].

In 1973, Bailey et al. [8] determined the crystal structure of La[Fe(CN)₆] \cdot 5H₂O using single crystal X-ray diffraction analysis. They showed that it belongs to the hexagonal space group $P6_3/m$ (no. 176) and that the nine-coordinate lanthanum ion is located at a site of D_{3h} symmetry. This structure was confirmed by Kietaibl and Petter [9]. Bonnet and Paris [10,11] subsequently reported the unit-cell

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parameters of all $\text{Ln}[\text{Fe}(\text{CN})_6] \cdot n\text{H}_2\text{O}$ (n = 4, 5) compounds according to the hexagonal model proposed by Bailey et al. In 1976, the tetrahydrate and the pentahydrate complexes were classified as hexagonal and orthorhombic, respectively, by Hulliger et al. [12,13].

However, there was still a lack of agreement regarding the crystal system of the tetrahydrates. In 1988, Mullica et al. [14,15] reported that $\text{Sm}[\text{Co}(\text{CN})_6] \cdot 4\text{H}_2\text{O}$ belongs to the monoclinic space group $P2_1/m$, just like $\text{Sm}[\text{Fe-}(\text{CN})_6] \cdot 4\text{H}_2\text{O}$. But in 1989, Petter et al. [16] stated that both compounds belong to the orthorhombic space group *Cmcm*. This dispute was settled through a careful reinvestigation on the crystal structures, showing that both compounds belong to the orthorhombic system in space group *Cmcm* [17]. Finally in 1999, Wang et al. [18] studied the properties of a series of lanthanide hexacyanoferrate(III) *n*-hydrates and reported that crystalline Ln[Fe-(CN)_6] $\cdot 4\text{H}_2\text{O}$ (Ln = Sm-Lu) are all orthorhombic with the same space group *Cmcm*.

Previous reports in the literature have assigned the pentahydrate compounds to the hexagonal space group $P6_3/m$ [8–13,18–21]. In 1996, Yukawa et al. [21] reported that

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 $Pr[Co(CN)_6] \cdot 5H_2O$ belongs to $P6_3/m$ just as for other pentahydrates reported before. In the present study, we have reinvestigated the crystal structures of $Pr[M(CN)_6] \cdot 5H_2O$ (M = Cr, Fe, Co) and established a reassignment of the space group to $P6_3/mmc$ (no. 194). The spectral characteristics of these compounds have been interpreted and a clear spectral distinction is made between the tetrahydrate and pentahydrate series.

2. Experimental

 $PrCl_3 \cdot xH_2O$ was prepared from Pr_6O_{11} (Strem, 99.9%) by repeated evaporation with concentrated HCl (AR grade, Reidel-de-Haen). $K_3M(CN)_6$ (M = Cr, Fe, Co) was purchased from Strem Chemicals.

2.1. Syntheses

 $Pr^{III}[M^{III}(CN)_6] \cdot 5H_2O (M = Cr, Fe, Co)$ were prepared by slow evaporation of aqueous solutions of $PrCl_3 \cdot xH_2O$ and $K_3M(CN)_6$ containing stoichiometric amounts of M:Pr. The crystals were dried by tissue and used immediately.

2.2. Spectral measurements

The UV–Visible absorption spectra of aqueous solutions of the complexes were recorded using a HP UV-8453 spectrophotometer to measure the range between 200 and 1100 nm in H₂O at 298 K. Room temperature and 10 K luminescence spectra were excited by the 355 nm line of a Continuum Nd-YAG laser. The emission was dispersed through an Acton 0.5 m monochromator with an 1800 g mm⁻¹ grating blazed at 250 nm and detected by a backilluminated SpectruMM CCD detector. The sample was housed in an Oxford Instruments closed cycle cryostat, with a base temperature of 10 K. The emission from $Pr[Co(CN)_6] \cdot 5H_2O$ was very weak with two broad features at 16257, 16361 cm⁻¹ due to Pr³⁺ emission, and a lower energy band at 14488 cm⁻¹. Infrared absorption spectra were recorded at 295 K using KBr discs. A Perkin-Elmer 2000 FTIR spectrometer was employed with resolution 2 cm^{-1} .

2.3. X-ray crystallography

The X-ray intensity data of the three isomorphous complexes were collected on a Bruker SMART 1000 CCD diffractometer with graphite-monochromatized Mo K α radiation ($\lambda = 0.71073$ Å) at 293 K. In each hkl file, reflections ($hh\bar{2}hl$) with l = 2n + 1 are systematically absent, indicating that the space group is $P6_3/mmc$. In the scenario that such reflections all happen to be too weak to be observed, space group $P6_3/m$ is also possible though unlikely. The structure was solved by direct methods and refined by full-matrix least squares based on F^2 using the SHELXTL program package. All the non-hydrogen atoms were subjected to anisotropic refinement. The aqua ligand O1W and lattice water molecule O2W respectively occupy sites of symmetry m and 3 in space group $P6_3/m$, and mm and 3m in space group $P6_3/mmc$. The hydrogen atoms, which are necessarily disordered when the oxygen atoms occupy the latter three sites, cannot be reliably located in the structure refinement.

3. Results and discussion

3.1. Crystal structures

Table 1 presents experimental and statistical summaries for compounds $Pr[M(CN)_6] \cdot 5H_2O$ (M = Co, Cr, Fe) refined in space groups $P6_3/mand P6_3/mmc$. The structural parameters refined in both space groups show insignificant differences, and consequently the space group of higher symmetry, namely $P6_3/mmc$, should be assigned according to convention. Interestingly, Pretsch et al. [7] reported that when orthorhombic *Cmcm* $Er[Co(CN)_6] \cdot 4H_2O$ loses all its bound and unbound water molecules, it is transformed to hexagonal $Er[Co(CN)_6]$ which belongs to space group $P6_3/mmc$.

The crystal and molecular structure of $Pr[M(CN)_6]$. 5H₂O herein are almost identical to those reported for $La[Co(CN)_6] \cdot 5H_2O$ [19] and $La[Fe(CN)_6] \cdot 5H_2O$ [8]. The structural characteristics of Pr[Cr(CN)₆] · 5H₂O are specified by listing their Wyckoff positions and site symmetries: Pr(1) in 2(c), $\overline{6}m2$; Cr(1) in 2(a), $\overline{3}m$; C(1) in 12(k), m; N(1)in 12(k), m; O(1 W) in 6(h), mm; and O(2 W) in 4(f), 3m (see Fig. 1 for the atom labeling). The Pr^{3+} ion is nine-coordinated in the form of a $PrN_6(H_2O)_3$ group; the Cr^{3+} ion is six-coordinated in the form of an octahedral CrC₆ group; and cyanide linkages between $PrN_6(H_2O)_3$ and CoC_6 groups build an infinite polymeric array (see Fig. 2). Two uncoordinated water molecules occupy zeolitic holes on a 6-fold rotatory-inversion axis above and below the Pr^{3+} ion. The Pr³⁺ ion is coordinated to three aqua ligands in the mirror plane and to the N atoms of six cyanides, with three on each side of the mirror plane. The coordination geometry of Pr^{3+} is thus approximately D_{6h} . The uncoordinated water molecule O(2W) is linked to the coordinated water molecule O(1W) through a weak hydrogen bond, as in $Pr[Co(CN)_6] \cdot 5H_2O$ [21], $La[Co(CN)_6] \cdot 5H_2O$ [19] and $La[Fe(CN)_6] \cdot 5H_2O[8]$.

The bond lengths and angles in $Pr[M(CN)_6] \cdot 5H_2O$ are reported in Table 2. The C=N bond distances do not differ from standard values [22]. The M–C bond distance is 8.5% shorter for the low-spin 3d⁶ ion compared with low-spin 3d³, and the trend with atomic number exhibits the linear relation shown in Fig. 3. A similar linear regression, but with a 7% more negative slope, is found for the M–C bond distances in K₃M(CN)₆ (M = Cr, Mn, Fe, Co [22]) where there is no cyanide bridging. The involvement of covalency in the M–C bond in Pr[M(CN)₆] \cdot 5H₂O is exhibited by its strict directional character with the angle N–C–M being linear.

Table 1 Experimental and statistical summaries for Pr[M(CN)₆] · 5H₂O

	$Pr[Co(CN)_6] \cdot 5H_2O$		$Pr[Cr(CN)_6] \cdot 5H_2O$		$Pr[Fe(CN)_6] \cdot 5H_2O$	
	<i>P</i> 6 ₃ / <i>m</i>	P6 ₃ /mmc	$P6_3/m$	P6 ₃ /mmc	P6 ₃ /m	P6 ₃ /mmc
Empirical formula Formula weight	C ₆ H ₁₀ CoN ₆ O ₅ Pr 446.04	C ₆ H ₁₀ CoN ₆ O ₅ Pr 446.04	C ₆ H ₁₀ CrN ₆ O ₅ Pr 439.11	C ₆ H ₁₀ CrN ₆ O ₅ Pr 439.11	C ₆ H ₁₀ FeN ₆ O ₅ Pr 442.96	C ₆ H ₁₀ FeN ₆ O ₅ Pr 442.96
Crystal system	hexagonal	hexagonal	hexagonal	hexagonal	hexagonal	hexagonal
Space group $a(Å)$	$P6_3/m$ (no.176) 7.4748 (6)	<i>P</i> 6 ₃ / <i>mmc</i> (no.194) 7.4748 (6)	$P6_3/m$ (no.176) 7.6734(5)	<i>P</i> 6 ₃ / <i>mmc</i> (no.194) 7.6734(5)	$P6_3/m$ (no.176) 7.524(1)	<i>P</i> 6 ₃ / <i>mmc</i> (no.194) 7.524(1)
b (Å)	7.4748(6)	7.4748(6)	7.6734(5)	7.6734(5)	7.524(1)	7.524(1)
c (Å)	14.220(3)	14.220(3)	14.674(2)	14.674(2)	14.351(3)	14.351(3)
α (°)	90	90	90	90	90	90
β (°)	90	90	90	90	90	90
γ (°)	120	120	120	120	120	120
$V(\text{\AA}^3)$	688.1(1)	688.1(1)	748.2(1)	748.2(1)	703.5(2)	703.5(2)
Ζ	2	2	2	2	2	2
$T(\mathbf{K})$	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)
$D ({\rm mg}{\rm m}^{-3})$	2.153	2.153	1.949	1.949	2.091	2.091
$\mu (\mathrm{mm}^{-1})$	4.728	4.728	3.965	3.965	4.476	4.476
Total data	1953	1849	2018	1900	2298	272
Unique data	699	425	759	458	242	240
Goodness-of-fit	1.083	1.104	1.134	1.173	1.102	1.061
$R_1 \left[I \ge 2\sigma(I)\right]^{\rm a}$	0.0244	0.0234	0.0212	0.0183	0.0352	0.0419
$wR_2 [I \ge 2\sigma(I)]^{b}$	0.0619	0.0618	0.0528	0.0445	0.0972	0.1178
R_1 (all data)	0.0276	0.0241	0.0293	0.0213	0.0465	0.0492
wR_2 (all data)	0.0634	0.0620	0.0557	0.0456	0.1042	0.1235

 $\overset{a}{\xrightarrow{}} R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \\ wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]^{1/2}.$



Fig. 1. Coordination environment of the metal atoms in Pr[Cr(CN)₆] · 5H₂O (50% thermal ellipsoids) with atom labeling.

In contrast, the C-N-Pr angle is bent, and the Pr-O distance is longer whereas the Pr-N distance is shorter for M = Cr than for M = Co. However, these changes are minor (<1.5%) and of similar magnitudes to measurement errors. The La-O and La-N bond distances in $La[M(CN)_6] \cdot 5H_2O$ (M = Fe, Co) [8,19]; refined in space group $P6_3/m$) are slightly longer (~2-3%) than those in the corresponding $Pr[M(CN)_6] \cdot 5H_2O$ compounds.

3.2. Infrared spectra

The vibrational mode of predominantly CN stretching character in octahedral $M(CN)_6{}^{3-}$ ions in the solid state



Fig. 2. Three-dimensional coordination network of Pr[Cr(CN)₆] · 5H₂O bridged by cyanide groups viewed along the a-axis. Uncoordinated water molecules are omitted for clarity.

Table	2				
Bond	lengths (Å)	and angles	(°) for	$Pr[M(CN)_6]$:	5H ₂ O

	M = Cr	M = Fe	M = Co
Pr(1)–O(1W)	2.563(4)	2.54 (1)	2.536(6)
Pr(1)–N(1)	2.563(3)	2.58 (1)	2.577(4)
M(1)-C(1)	2.061(3)	1.96(1)	1.889(4)
C(1)–N(1)	1.144(4)	1.12 (2)	1.145(6)
O(1W)–Pr(1)–N(1)	69.13(3)	69.1 (1)	69.13(4)
N(1)-C(1)-M(1)	179.1(3)	179(1)	180.0(5)
C(1)–N(1)–Pr(1)	171.7(3)	171(1)	170.6(4)



Fig. 3. Plot of M–C bond distance versus atomic number of M for $Pr[M(CN)_6] \cdot 5H_2O$.

is observed at 2142 cm^{-1} (M = Co) and at 2138 cm^{-1} (M = Cr) [22]. For Ln[M(CN)₆] · *n*H₂O, members of the n = 5 series easily transform at room temperature into n = 4, but the two series are readily distinguished by the characteristic water and CN stretching peaks in the IR spectra, as shown for Pr[Cr(CN)₆] · 5H₂O and Pr[Fe- $(CN)_6$]·4H₂O in Fig. 4, where the appropriate structures are also drawn. The inset in the figure shows the spectral region of $Pr[Cr(CN)_6] \cdot 5H_2O$ between 2100 and 2200 cm^{-1} in detail. Note that only one strong CN stretch band is observed (corresponding to ${}^{12}C^{14}N$ at 2156 cm⁻¹) for the pentahydrate. From their positions and relative intensities, the weak features at 2112, 2125 cm^{-1} in the inset correspond to ¹³C¹⁴N and ¹²C¹⁵N stretching bands, respectively. By contrast, two prominent CN stretching bands are observed for the tetrahydrate system Pr[Fe- $(CN)_{6}$ · 4H₂O. Furthermore, the water bending mode region ($\sim 1610 \text{ cm}^{-1}$) shows one broad band for the pentahydrate but two prominent sharper bands for the tetrahydrate. The large breadth of this band in $Pr[Cr(CN)_6] \cdot 5H_2O$ (Fig. 4) illustrates the large thermal amplitude of the coordinated aquo ligand. The water stretching region (3000–3610 cm⁻¹) is complex for both the tetrahydrate and pentahydrate systems because bands due to both coordinated and hydrogen-bonded water appear together with vibrational overtones. The lowest energy band in Fig. 4 for the spectrum of $Pr[Cr(CN)_6] \cdot 5H_2O$ is the Cr–C stretch at 435 cm⁻¹.

3.3. UV–Vis spectra of aqueous solutions of $Pr[M(CN)_6]$

The UV-Vis absorption spectra of aqueous solutions of $Pr[M(CN)_6] \cdot 5H_2O$ are compared with $K_3[Co(CN)_6](aq)$ in Fig. 5 and serve to show the presence of free $M(CN)_6^{3-1}$ ions in solution. The sharp, weak features between 443 nm and 485 nm are due to $4f^2-f^2$ intra-configurational transitions of Pr³⁺. Although the lowest energy band (485 nm) clearly corresponds to the ${}^{3}P_{0} \leftarrow {}^{3}H_{4}$ transition, the higher energy features are not clearly resolved and too broad to permit specific assignments. The bands at 306, 379 nm for M = Cr occur at similar wavelengths (308, 375 nm) to corresponding features in the room temperature absorption spectrum of crystalline Cs₂KCr(CN)₆ [23]. These features have been assigned to spin-allowed ligand field transitions corresponding to ${}^{4}T_{1g}$, ${}^{4}T_{2g} \leftarrow {}^{4}A_{2g}$, respectively [23]. The much stronger bands at 262 and \sim 200–220 nm correspond to charge-transfer transitions. The features at \sim 257 and 307 nm in the spectrum of aqueous $Pr[Co(CN)_6]$ are at similar wavelengths to the spectrum of aqueous $K_3Co(CN)_6$ and correspond to ${}^1T_{2g}$, ${}^1T_{1g} \leftarrow {}^1A_{1g}$ transitions, respectively [22]. The sharp increase in absorbance at ~ 200 nm corresponds to a charge transfer transition. This band is at higher energy than in $Cr(CN)_6^{3-}$ due to the greater cation polarizing power and shorter M-C bond distance.



Fig. 4. FTIR spectra of $Pr[Fe(CN)_6] \cdot 4H_2O$ and $Pr[Cr(CN)_6] \cdot 5H_2O$. The inset shows the expanded CN stretch region of the latter.



Fig. 5. UV–visible absorption spectra between 200 and 600 nm of aqueous solutions of $Pr[M(CN)_6]$ (M = Cr, Co) and comparison with $K_3Co(CN)_6(aq)$. The scale expansion is shown in the top figure.

4. Conclusions

The space group $P6_3/m$ previously reported for the crystal structure of $Pr[Co(CN)_6] \cdot 5H_2O$ [21] has been revised herein to $P6_3/mmc$, which also holds for the isomorphous Cr and Fe compounds. The distinction between the $Ln[M(CN)_6] \cdot nH_2O$ tetrahydrate (n = 4) and pentahydrate (n = 5) series has been demonstrated on the basis of IR spectral assignments. Our spectra for the pentahydrates are in essential agreement with that reported for La[Co- $(CN)_6] \cdot 5H_2O$ [19], but show differences from the spectra reported for Ln[Fe(CN)_6] $\cdot 5H_2O$ (Ln = La, Pr, Nd) where some decomposition to the tetrahydrates may have occurred [18]. Our IR spectrum of $Pr[Fe(CN)_6] \cdot 4H_2O$ is similar to that reported for Nd[Fe(CN)_6] $\cdot 4H_2O$ [24].

Acknowledgements

We thank Dr. S.K. Mak for technical help in the early part of this study and the Hong Kong University Grants Council for support under CERG Grant CityU 1115/02P.

Appendix A. Supplementary material

CCDC 637207, 637208 and 645301 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam. ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10. 1016/j.poly.2007.05.002.

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