3D-Coordination Cluster Polymers $[Ln(H_2O)_3Re_6Te_8(CN)_6]\cdot nH_2O$ (Ln = La^{3+}, Nd^{3+}): Direct Structural Analogy with the Mononuclear $LnM(CN)_6\cdot nH_2O$ Family

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Using the hydrothermal method two novel 3D-coordination complexes $[Ln(H_2O)_3Re_6Te_8(CN)_6]\cdot nH_2O$ (Ln = La^{3+}, Nd^{3+}) have been synthesised and structurally characterised. For compound $[La(H_2O)_3Re_6Te_8(CN)_6]\cdot 4H_2O$ (**1**) the unit cell parameters are: Space group $P6_3/m$, a = 9.3060(13), c = 20.528(4) Å, V = 1539.6(4) Å^3, R_f = 0.0597. For compound $[Nd(H_2O)_3Re_6Te_8(CN)_6]\cdot H_2O$ (**2**) the unit cell parameters are: Space group $P6_3$/m, a = 9.3030(10), c = 20.222(4) Å, V = 1515.7(4) Å^3, R_f = 0.0226. The structures of the cluster compounds are topologically analogous to the mononuclear polymeric complex $LaCr(CN)_6\cdot 5H_2O$.

Introduction

Octahedral cluster cyano complexes of transition metals have been intensively studied during the past decade (selected references: $[Re_6Q_8(CN)_6]^{4-}$ [1–3], $[Mo_6Q_8(CN)_6]^{7-}$ [4,5], $[W_6Q_8(CN)_6]^{6-}$ [6], $[Nb_6Cl_{12}(CN)_6]^{4-}$ [7,8] and heterometallic $[Re_{6-x}Mo_xS_8(CN)_6]^{5-}$ [9]). These anions are topological analogues of hexacyanometalate ions $[M(CN)_6]^{n-}$ and the anions can form polymeric arrays based on covalent cyano-bridged interactions with transition metals, for instance $\cdots-Re_6-C\equiv N-M-N\equiv C-Re_6-\cdots$ (selected references: Re:[10–13], W:[14], Nb:[8]). Despite the equivalent disposition of terminal cyano groups in $[M(CN)_6]^{n-}$ and $[M_6Q_8(CN)_6]^{n-}$, it is difficult to expect isotypical structures when $[M(CN)_6]^{n-}$ is changed to $[M_6Q_8(CN)_6]^{n-}$. The reason is the larger size of cluster cyanides compared with mononuclear ones. This increase of linear size leads to a corresponding increase in pore volume, hence the network has a tendency to distort, collapse or to be interpenetrated.

Indeed, from the widely diverse family of cluster cyano-bridged polymers, only three compounds exhibit a direct structural analogy with mononuclear cyanometallates, namely: $Fe_4[Re_6Te_8(CN)_6]_3\cdot 27H_2O$, $Ga_4[Re_6Se_8(CN)_6]_3\cdot 38H_2O$,[15] and $(Me_4N)_2Mn[Nb_6Cl_{12}(CN)_6]$ [16] which crystallises in the highly symmetrical space group $Fm\bar{3}m$ and has an ordinary six-connected network equivalent to the well-known Prussian Blue net.[8] All other reported cluster networks have no examples in the family of mononuclear cyanometallates.

In this paper we report the synthesis and structures of two new coordination compounds based on the cluster complexes $[Re_6Te_8(CN)_6]^{3-}$ and Ln^{3+} (La^{3+}, Nd^{3+}).These compounds demonstrate another example of the direct structural analogy between compounds built from mononuclear $[M(CN)_6]^{n-}$ and cluster expanded $[M_6Q_8(CN)_6]^{n-}$ anions.

Results and Discussion

Syntheses of 1 and 2: The interaction of $K_4Re_6Te_8(CN)_6$ with $LnCl_3\cdot nH_2O$ under hydrothermal conditions described in the Exp. Sect. gave solid products which consisted of thin dark hexagonal plates of compounds **1** and **2**. X-ray diffraction patterns showed that the bulk samples were single phases with unit cell parameters as follows: **1**: a = 9.316(3), c = 20.521(4); **2**: a = 9.307(3), c = 20.213(4) Å. Chemical analysis (EDAX) of the crystals showed that they contained no potassium. The magnetic susceptibility of **1** is μ_{eff} (298) = 1.81 μ_B which corresponds to one unpaired electron per formula unit $[La(H_2O)_3Re_6Te_8(CN)_6]\cdot 4H_2O$. The magnetic susceptibility of **2** is μ_{eff} (298) = 4.18 μ_B. This value is very close to μ_{eff} = 4.24 μ_B calculated using the equation $\mu^2_{eff} = \mu^2 (Nd^{3+}) + \mu^2([Re_6Te_8(CN)_6]^{3-})$ and corresponds to the presence of two noninteracting paramagnetic centres in the structure, namely Nd^{3+} and $[Re_6Te_8(CN)_6]^{3-}$. Based on magnetic and stoichiometric considerations, we postulate that the cluster complex $[Re_6Te_8(CN)_6]^{4-}$ has undergone one-electron oxidation during the reaction. Redox transformations of $[Re_6Te_8(CN)_6]^{4-}$ have been studied pre-

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viously[17] and it was found that the cluster complex is characterised by an oxidation potential low enough to be oxidised with oxygen dissolved in an aqueous solution. In fact, $[Re_6Te_8(CN)_6]^{4-}$ can lose one electron and the resultant $[Re_6Te_8(CN)_6]^{3-}$ can be isolated as a salt with an organic cation, i.e. $(Et_4N)_2(H)[Re_6Te_8(CN)_6]\cdot 2H_2O$.[18]

Structures of Compounds 1 and 2: Compounds **1** and **2** crystallise in the hexagonal space group *P*6₃/*m* and they have identical coordination networks, i.e. $[Ln(H_2O)_3Re_6Te_8(CN)_6]_{3\infty}$. Structure **1** contains one rhenium atom (Re1), two tellurium atoms (Te1, Te2), one cyano group (C1, N1), Ln1, and O1 (coordinated water) in its asymmetric unit (Figure 1). The centre of the cyanocluster is located in the special position *2a* of the $P6_3/m$ space group and has $\bar{6}$ crystallographic symmetry close to the ideal O_h. Each rhenium atom is coordinated to one cyano group forming an almost linear Re−C−N fragment. Selected bond distances of structures **1**, **2** and other related complexes are listed in Table 1 for comparison. Comparing the bond lengths Re−Re, Re−Te, Re−C and C−N in $[Re_6Te_8(CN)_6]$ we can say that the oxidation does not significantly affect these distances (within the limits of the errors obtained).

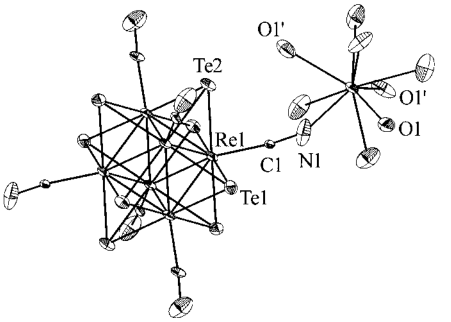

Figure 1. Asymmetric unit of the coordination network of $[Ln(H_2O)_3Re_6Te_8(CN)_6]_{3\infty}$ in the crystal structures of **1** and **2**; the atoms are shown at the 50% probability level

The lanthanide atom Ln1 (La^{3+} as well as Nd^{3+}) is located in the special position *2c* (1/3, 2/3, 1/4) with $\bar{6}$ symmetry. It is coordinated by six nitrogen atoms from the CN groups of different cluster anions and three water molecules. The coordination polyhedron of Ln1 is a regular tricapped trigonal prism (Figure 2) with bond lengths La−O 2.63(3), La−N 2.57(3) Å for **1** and Nd−O 2.645(15), Nd−N 2.537(11) Å for **2**.

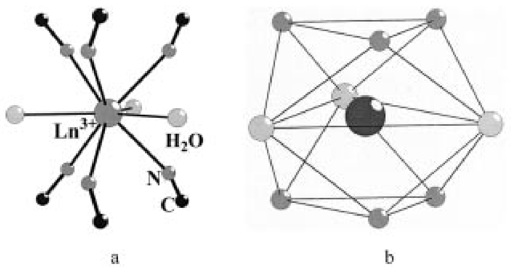

Figure 2. Coordination environments of Ln^{3+} in the crystal structures of **1** and **2** (a); coordination polyhedron around the Ln^{3+} cations (b)

The cluster complex $[Re_6Te_8(CN)_6]^{3-}$ is linked via lanthanide cations to produce a 3D-coordination network $[Ln(H_2O)_3Re_6Te_8(CN)_6]_{3\infty}$. Cluster complexes form six bridging cyano groups with Ln^{3+}. Six nitrogen atoms and three water molecules constitute the coordination sphere of the lanthanide cations as shown in Figure 2. In the network, the cluster complexes and Ln^{3+} cations are arranged in layers (Figure 3, *a*) parallel to the crystallographic *ab* plane and their packing can be presented as a sequence ···ABAC··· (A = cluster complex; B and C = lanthanide cations). For polymeric compounds based on octahedral cluster complexes, this kind of network has a sufficiently high packing coefficient of 69% (i.e. the coordination network occupies 69% of the cell volume).[19]

The connectivity of the network can be described as a (6,6)-connected net according to the nomenclature detailed in a review.[20] The nodes are Ln^{3+} lanthanide cations in a regular triangular prismatic environment of six nitrogen atoms belonging to the cluster complexes, the cluster complexes being coordinated to Ln^{3+} cations via six octahedrally arranged cyano groups. Rare earth cations have larger ionic radii than *3d* transition metals which drives the formation of the new type of network of octahedral cluster cyanometallates.

In compounds **1** and **2**, the coordination networks are isostructural while the total amount and locations of solvent water molecules in **1** and **2** are different. In the final difference electron density map of **1**, two peaks were found. One of them, assigned to O(1 W), is located on a mirror plane (position *6h*). In the unit cell, these atoms form an equilateral triangle with O···O distances of 3.02 Å around a special point of $\bar{6}$. The U_{eq} parameter is quite high (0.21

Table 1. Bond lengths in the cluster complexes $[Re_6Te_8(CN)_6]^{4-}$, $[Re_6Te_8(CN)_6]^{3-}$ and other selected compounds

Formula	Re−Re	Re−Te	Re−C	C−N
$[La(H_2O)_3Re_6Te_8(CN)_6]\cdot 4H_2O$ (**1**)	2.6780(19), 2.6814(18), av. 2.6797	2.683(3)−2.704(2), av. 2.694	2.05(3)	1.24(4)
$[Nd(H_2O)_3Re_6Te_8(CN)_6]\cdot H_2O$ (**2**)	2.6813(10), 2.6834(9), av. 2.6824	2.6749(16)−2.7065(11), av. 2.6915	2.095(15)	1.149(18)
$(Et_4N)_2(H)[Re_6Te_8(CN)_6]\cdot 2H_2O$[18]	2.676(1), 2.677(2)	2.682(2)−2.708(2); av. 2.691	2.09(5)	1.15(3), 1.19(5); av. 1.16
$Cs_4[Re_6Te_8(CN)_6]\cdot 2H_2O$[3]	2,674(1)−2.698(1); av. 2.684	2.691(1)−2.708(1); av. 2.698	2.09(2)−2.10(2); av. 2.10	1.12(2) − 1.17(2); av. 1.14
$Ba_2[Re_6Te_8(CN)_6]\cdot 12H_2O$[3]	2.671(2)−2.691(2); av. 2.681	2.695(2)−2.713(2); av. 2.702	2.09(2)−2.10(2); av. 2.10	1.14(3)−1.16(3); av. 1.15

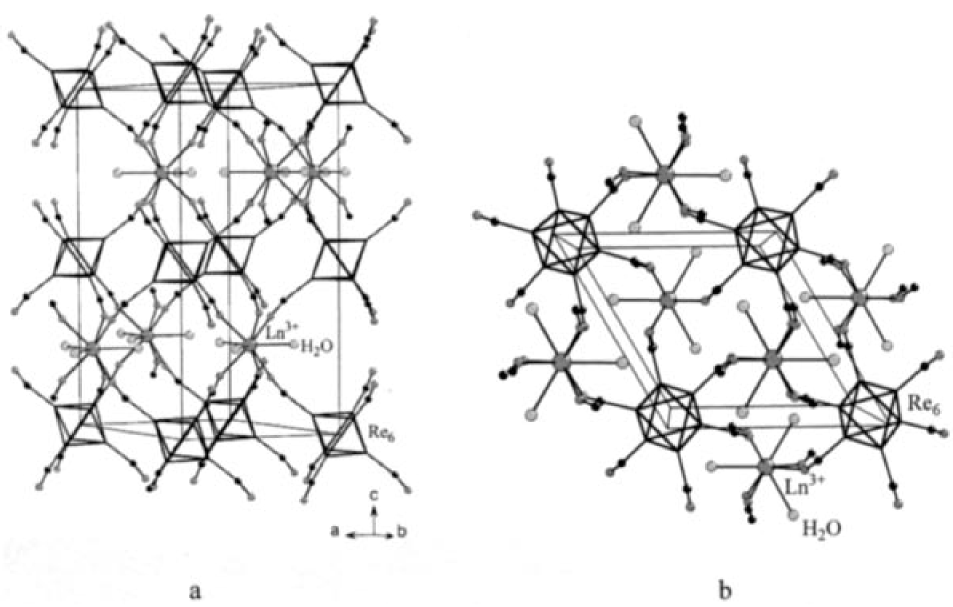

Figure 3. Coordination networks in the structures of **1** and **2** showing the layers of the cluster cores of $\{Re_6Te_8\}$ and the Ln^{3+} cations (a); view along the *c* direction (b)

$Å^{-2}$) but our attempt to refine the site occupancy factor (s. o. f.) did not give any improvement in the residuals. The second peak, assigned to O(2 W), was found in a *4f* special position (1/3, 2/3, *z*). This atom is located between three nitrogen atoms of the CN groups with O···N distances equal to 2.60 Å. The refinement of its s. o. f. resulted in a value of 0.5 with $U_{eq} = 0.085$ $Å^{-2}$.

In **2**, the final difference electron density map contained only one suitable peak which was assigned to an oxygen atom disordered over three positions around the special point of a $\bar{6}$ axis forming a triangle on a mirror plane. The O···O distances in the triangle of 1.34 Å are short, indicating that only one of three symmetrically related positions is actually occupied. Therefore, the s. o. f. was set to 33%. The resultant $U_{eq} = 0.079$ $Å^{-2}$ is as expected for solvent water molecules.

Structural Analogy with Mononuclear Compounds: Compounds **1** and **2** possess symmetry and a packing motif equivalent to mononuclear complexes with the general formula $LnM(CN)_6{\cdot}nH_2O$ or $ALnM(CN)_6{\cdot}nH_2O$. Indeed, compounds **1**, **2**, $[La(H_2O)_3Cr(CN)_6]{\cdot}2H_2O$[21], $[La(H_2O)_2Fe(CN)_6]{\cdot}2H_2O$[22] and $Cs[Ce(H_2O)_3Fe(CN)_6]{\cdot}H_2O$[23] crystallise in the space group $P6_3/m$. The cell parameters as well as the bond distances $Ln-O(H_2O)$ and $Ln-N(CN)$ are listed in Table 2. The packing of the cluster cores in **1** and **2** mimics the packing of the cations Cr^{3+}, Fe^{3+} and Fe^{2+} (Figure 4), as well as the packing motives of the lanthanide cations La^{3+}, Ce^{3+} and Nd^{3+}. A comparison of the angles in the coordination networks of **1**, **2** and $[La(H_2O)_3Cr(CN)_6]{\cdot}2H_2O$ revealed a moderate variation.

In these five structures, the coordination sphere of the lanthanide cation is tricapped trigonal prismatic containing six nitrogen atoms and three water molecules (Figure 2), except for $[La(H_2O)_2Fe(CN)_6]{\cdot}2H_2O$ in which one water molecule is absent and a two-capped trigonal prism (hendecahedron) is formed. Other known $Ln-[M(CN)_6]$ compounds crystallising in the orthorhombic system include[23−27] ($TlTmRu(CN)_6{\cdot}3H_2O$, $ErFe(CN)_6{\cdot}4H_2O$, $NdCo(CN)_6{\cdot}4H_2O$, $GdKFe(CN)_6{\cdot}3H_2O$, $YbKFe(CN)_6{\cdot}3.5H_2O$) and examples in the monoclinic system include[23,28−30] $CsLnFe(CN)_6{\cdot}5H_2O$ (Ln = Ce, Pr, Nd), $SmFe(CN)_6{\cdot}4H_2O$, $SmKFe(CN)_6{\cdot}3H_2O$ and $SmCo(CN)_6{\cdot}4H_2O$. However, their crystal structures exhibit similar packings of the building blocks and motives to those seen in coordination networks.[31]

In conclusion, we have prepared two new coordination compounds based on the cluster complexes $[Re_6Te_8(CN)_6]^{3-}$ and Ln^{3+} (La^{3+}, Nd^{3+}). These com-

Table 2. Selected bond lengths and cell parameters in compounds **1**, **2** and some mononuclear cyanometallates

Formula	$Ln-O(H_2O)$ (Å)	$Ln-N(CN)$ (Å)	Cell parameters (Å)
$[La(H_2O)_3Re_6Te_8(CN)_6]{\cdot}4H_2O$ (**1**)	2.63(3)	2.57(3)	*a* = 9.3060(13), *c* = 20.528(4)
$[Nd(H_2O)_3Re_6Te_8(CN)_6]{\cdot}H_2O$ (**2**)	2.645(15)	2.537(11)	*a* = 9.303(10), *c* = 20.222(4)
$[La(H_2O)_3Cr(CN)_6]{\cdot}2H_2O$[21]	2.591(5)	2.619(5)	*a* = 7.7053(4), *c* = 14.8155(9)
$[La(H_2O)_2Fe(CN)_6]{\cdot}2H_2O$[22]	2.50(6)	2.56(3)	*a* = 7.541(3), *c* = 13.955(9)
$Cs[Ce(H_2O)_3Fe(CN)_6]{\cdot}H_2O$[23]	2.682(4)	2.575(3)	*a* = 7.4415(5), *c* = 14.129(1)

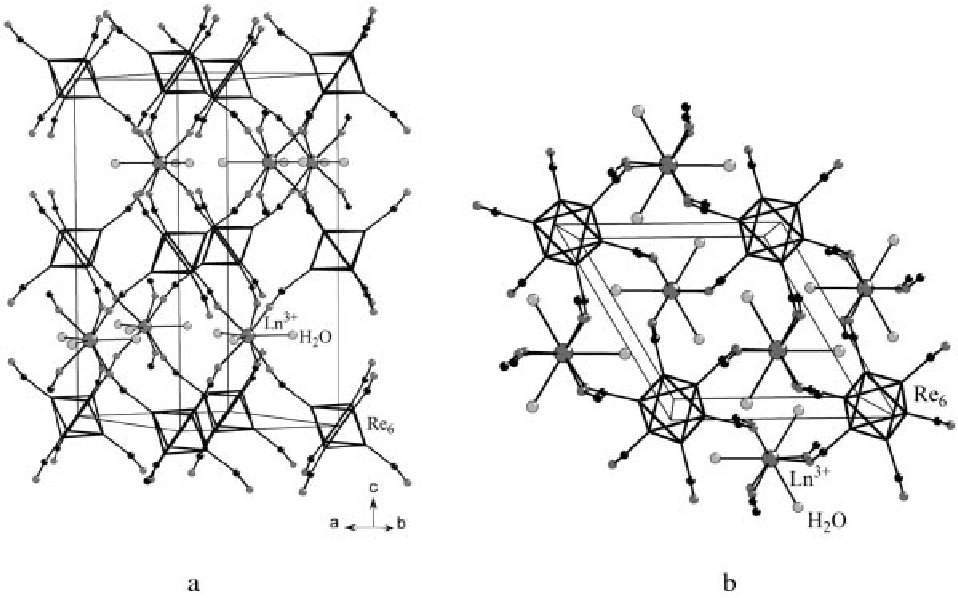

Figure 4. Coordination network in $[La(H_2O)_3Cr(CN)_6]\cdot 2H_2O$ showing layers of Cr^{3+} and La^{3+} cations (a); view along the *c* direction (b)

pounds exhibit a direct structural analogy with the $LnM(CN)_6\cdot nH_2O$ family.

Experimental Section

General: $K_4[Re_6Te_8(CN)_6]$[3] was prepared from polymeric Re_6Te_{15}.[32] All other reagents were used as purchased. Infrared spectra were measured in KBr disks with a Bruker IFS-85 spectrometer. X-ray powder diffraction data (XPD) were obtained with a Philips APD 1700 powder diffractometer using Cu-K_α radiation. Magnetic measurements were performed with a Quantum Design SQUID magnetometer, field 5 kOe.

X-ray Structural Studies: The diffraction measurements were performed by standard techniques at 298(2) K with an Enraf−Nonius CAD4 diffractometer (graphite-monochromated Mo-K_α radiation). Face-indexed absorption corrections were applied. The crystal structures were solved by direct methods and refined by full-matrix least-squares methods using SHELX-97.[33] Hydrogen atoms of the water molecules were not located. Dark hexagonal plates of **1** and **2** were selected from the reaction products.

Crystallographic Data for 1: $C_6H_{14}La_1N_6O_7Re_6Te_8$, *FW* = 2559.16, hexagonal crystal system, space group $P6_3/m$, $a = 9.3060(13)$, $c = 20.528(4)$ Å, $V = 1539.6(4)$ Å^3, $Z = 2$, $D_{calcd.} = 5.443$ g·cm^{-3}, $\mu = 32.299$ mm^{-1}. Total 2416 reflections were collected up to $\theta_{max.} = 24.97°$, of which 939 independent ($R_{int} = 0.1394$). Final residuals are: $R1 = 0.0597$, $wR2 = 0.1339$ for 493 $F_{hkl}(4\sigma)$, $R1 = 0.0941$, $wR2 = 0.1578$ for all unique reflections.

Crystallographic Data for 2: $C_6H_8N_6NdO_4Re_6Te_8$, *FW* = 2510.45, crystal system is hexagonal, space group $P6_3/m$, $a = 9.3030(10)$, $c = 20.222(4)$ Å, $V = 1515.7(4)$ Å^3, $Z = 2$, $D_{calcd.} = 5.501$ g·cm^{-3}, $\mu = 33.108$ mm^{-1}. Total 3537 reflections were collected up to $\theta_{max.} = 27.46°$, of which 1196 independent ($R_{int} = 0.0633$). Final residuals are: $R1 = 0.0226$, $wR2 = 0.0441$ for 616 $F_{hkl}(4\sigma)$, $R1 = 0.0606$, $wR2 = 0.0585$ for all unique reflections.

Further details of the crystal-structure investigation(s) may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number(s) CSD-413628 (for **1**) and CSD-413629 (for **2**). X-ray powder patterns of samples **1** and **2** are also included.

Preparation of $[La(H_2O)_3Re_6Te_8(CN)_6]\cdot 4H_2O$ (1): A mixture of $LaCl_3\cdot 7H_2O$ (0.033 g, 0.09 mmol) and $K_4Re_6Te_8(CN)_6$ (0.050 g, 0.02 mmol) was placed in a glass ampoule (15 mL) and an aqueous solution of ammonia was added to the mixture to adjust the pH to 9. The ampoule was sealed and heated at 140 °C for two days. The ampoule was then gradually cooled. The product consisted of dark hexagonal plates and a thin light precipitate as well as a reasonable quantity of a dark crystalline powder. The dark plates were selected, washed with water and dried in air. Yield ca. 0.020 g (39%). In our opinion, the presence of ammonia in the reaction solution results in better crystallisation. IR: ν_{CN} 2098−2085 (broad), ν_{OH} 1610; δ_{HOH} 3572 (broad); ν_{Re-C} 453 cm^{-1}. μ_{eff} (298 K) = 1.81 μ_B.

Preparation of $[Nd(H_2O)_3Re_6Te_8(CN)_6]\cdot H_2O$ (2): The same method was used to prepare **2**, $NdCl_3\cdot 6H_2O$ (0.040 g, 0.10 mmol) being the source of Nd^{3+}. Yield ca. 0.015 g (30%). IR: δ_{HOH} 3559, 3521; ν_{CN} 2081; ν_{OH} 1566; ν_{Re-C} 454 cm^{-1}. μ_{eff} (298 K) = 4.18 μ_B.

Acknowledgments

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[31] Vector equations between monoclinic and hexagonal cells are: $a_{hex} \approx a_{monocl}$, $b_{hex} \approx c_{monocl}$, $c_{hex} \approx -b_{monocl}$, $\beta_{monocl} \approx 120°$. Vector Equations between orthorhombic (*C*-centered, *Cmcm*, primitive, *Pnma)* and hexagonal unit cell: $a_{hex} \approx (a_{orth} + b_{orth})/2$, $b_{hex} \approx -a_{orth}$, $c_{hex} \approx c_{orth.}$

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