

## Investigation of the crystal structures of new cyano-bridged compounds with $\text{KLaMo}(\text{CN})_8 \cdot 9\text{H}_2\text{O}$ structure type

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The crystal structures of  $\text{KLaW}(\text{CN})_8 \cdot 9\text{H}_2\text{O}$  (I) and  $\text{KNdW}(\text{CN})_8 \cdot 9\text{H}_2\text{O}$  (II), isostructural with  $\text{KLaMo}(\text{CN})_8 \cdot 9\text{H}_2\text{O}$ , have been solved from X-ray single-crystal diffraction data. The compounds crystallize in the monoclinic system, space group  $P2_1/c$  (I:  $a = 8.7692(4)$ ,  $b = 25.2705(11)$ ,  $c = 10.7017(5)$  Å,  $\beta = 117.004(3)^\circ$ ,  $V = 2112.96(17)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 2.302$  g·cm<sup>-3</sup>,  $R1 = 0.0440$  and  $wR2 = 0.1012$  for 3988 independent reflections; II:  $a = 8.7425(4)$ ,  $b = 25.1085(11)$ ,  $c = 10.6210(5)$  Å,  $\beta = 117.218(3)^\circ$ ,  $V = 2073.27(17)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 2.363$  g·cm<sup>-3</sup>,  $R1 = 0.0400$  and  $wR2 = 0.0893$  for 3916 independent reflections). The coordination polyhedra of the tungsten atoms are  $[\text{W}(\text{CN})_8]^{4-}$  square antiprisms, whereas the  $[\text{LnN}_4(\text{H}_2\text{O})_5]^{3+}$  ( $\text{Ln} = \text{La}, \text{Nd}$ ) polyhedra can be described as tricapped trigonal prisms or monocapped square antiprisms; the potassium atoms center distorted monocapped trigonal prisms,  $[\text{KN}_3(\text{OH}_2)_4]$ . The formula of the coordination polymer can be written as  $\{[\text{K}(\text{H}_2\text{O})_2][\text{Ln}(\text{H}_2\text{O})_5][\text{W}(\text{CN})_8]\}_n \cdot 2n\text{H}_2\text{O}$ ,  $\text{Ln} = \text{La}, \text{Nd}$ .

### Potassium / Lanthanum / Neodymium / Octacyanotungstate(IV) / Crystal structure

#### Introduction

Cyano-bridged metal assemblies have been extensively studied. The investigation of octacyanomometallate-based bimetallic systems has been extended to the lanthanide ions. As lanthanide ions often have higher coordination numbers, mixed 4d, 5d - 4f complexes can have very complicated topologies and potential applications as functional materials [1,2].

A better understanding of the property-structure relationship of such materials relies on the synthesis and evaluation of new lanthanide-transition complexes. Synthesis of complexes containing octacyanomometallates and lanthanide ions is challenging, due to the tendency of the rare-earth metal ions to adopt high coordination numbers, and their ability to easily adapt to a given environment [3].

Many authors have been interested in octacyanomometallate complexes of Mo(V) and W(V)

with lanthanide ions. They have reported the existence of the isostructural compounds  $\text{Ln}(\text{H}_2\text{O})_5[\text{M}(\text{CN})_8]$  ( $\text{Ln} = \text{Pr}, \text{Nd}, \text{Eu}, \text{Tb}, \text{Sm}, \text{Gd}; \text{M} = \text{Mo}^{\text{V}}, \text{W}^{\text{V}}$ ) [3-5], and  $\text{Ln}(\text{H}_2\text{O})_4[\text{W}(\text{CN})_8]$  ( $\text{Ln} = \text{Ho}, \text{Er}, \text{Tm}, \text{Lu}$ ) [3], which belong to the space group  $P4/nmm$ , and  $\text{Ln}(\text{H}_2\text{O})_5[\text{W}(\text{CN})_8]$  ( $\text{Ln} = \text{La}$  [3],  $\text{Sm}$  [6]), which belong to the space group  $P4/ncc$ . The crystal structures of all these compounds consist of 2D cyano-bridged corrugated layers.

In a number of our works the crystal structures of heterocationic octacyanomometallate complexes of Mo(IV) and W(IV) with lanthanide and potassium have been investigated:  $\text{KLaMo}(\text{CN})_8 \cdot 9\text{H}_2\text{O}$  [7],  $\text{KSmMo}(\text{CN})_8 \cdot 10\text{H}_2\text{O}$  [8], isostructural  $\text{KLnM}(\text{CN})_8 \cdot 7\text{H}_2\text{O}$ , where  $\text{M} = \text{W}^{\text{IV}}$ ,  $\text{Ln} = \text{Tb}$  [9],  $\text{Dy}$  [10],  $\text{Ho}, \text{Er}$  [11],  $\text{Lu}$  [12] and  $\text{M} = \text{Mo}^{\text{IV}}$ ,  $\text{Ln} = \text{Y}$  [11],  $\text{Gd}$  [12],  $\text{Yb}$  [13].

In this contribution, we report on the structures of the new cyano-bridged octacyanotungstate(IV) complexes  $\text{KLaW}(\text{CN})_8 \cdot 9\text{H}_2\text{O}$  (I) and  $\text{KNdW}(\text{CN})_8 \cdot 9\text{H}_2\text{O}$  (II).

## Experimental

### Synthesis

The compound  $K_4[W(CN)_8] \cdot 2H_2O$  was prepared according to the method described in [14]. The compound  $H_4[W(CN)_8] \cdot 2H_2O$  was prepared by mixing an aqueous solution of 0.1 M  $K_4[W(CN)_8] \cdot 2H_2O$  with a concentrated solution of HCl. The acid solution turned muddy from the potassium ions. Complexes **I** and **II** were prepared by mixing an aqueous acidic solution of  $H_4[W(CN)_8] \cdot 2H_2O$  with  $La_2(CO_3)_3$  or  $Nd_2(CO_3)_3$ ; the reaction was considered to be finished when no more  $CO_2$  was produced. After mixing, the solution was stored in the dark at room temperature. Yellow, well-shaped crystals, suitable for single-crystal diffraction formed after several weeks.

### X-ray diffraction

The single crystals of **I** and **II** selected for the diffraction experiment were approximately  $0.20 \times 0.30 \times 0.40$  mm large. Intensity data were collected at 173 K on a Stoe IPDS 2 [15] diffractometer, using graphite-monochromated Mo  $K\alpha$  radiation (image plate distance 70 mm,  $\phi$  oscillation scans  $0-200^\circ$ , step  $\Delta\phi = 1.0^\circ$ , exposure time 3 min,  $\theta$  range  $1.61-26.11^\circ$ ). The structure was solved by direct methods, using the program package SHELX-97 [16]. The H atoms were located from Fourier difference maps and refined isotropically with restraints on the interatomic distances (O–H bonds:  $0.82(2)$  Å, H...H:  $1.45(2)$  Å) and displacement parameters ( $U_{iso}(H) = 1.5 U_{eq}(O)$ ). The non H atoms were refined

anisotropically, using weighted full-matrix least-squares on  $F^2$ . An empirical absorption correction was applied using the DELREFABS routine in PLATON [17]; transmission factors  $T_{min}/T_{max} = 0.3416/1.000$  (**I**) and  $0.4719/1.000$  (**II**). The structure drawings were prepared with the program DIAMOND [18]. A projection of the structure of **I** and the coordination polyhedra of the W, Ln and K atoms are presented in Fig. 1 and Fig. 2, respectively. Details of the structure refinements for **I** and **II** are given in Table 1 and the final atomic coordinates are listed in Table 2. Selected bond lengths and angles are given in Table 3, hydrogen bonds in Table 4. Fig. 3 shows a projection of the structure of **I** along the direction [100].

## Results

The X-ray diffraction study of the isotopic structures of **I** and **II** reveals that the crystal structure consists of three structural units,  $[LnN_4(OH_2)_5]^{3+}$  ( $Ln = La, Nd$ ),  $[W(CN)_8]^{4-}$  and  $[KN_3(OH_2)_4]^+$  (see Fig. 1). In the  $[LnN_4(OH_2)_5]^{3+}$  unit the Ln atom is nine-fold coordinated by four nitrogen atoms from  $C \equiv N$  groups and five oxygen atoms from  $H_2O$  molecules. The Ln–N bond distances vary slightly, from  $2.620(5)$  to  $2.657(6)$  Å for La ( $Nd-N = 2.564(6)-2.603(5)$  Å), whereas the distances between the Ln atoms and the O atoms of the  $H_2O$  molecules range from  $2.523(5)$  to  $2.611(4)$  Å for La ( $Nd-O = 2.460(5)-2.543(4)$  Å) (see Table 3). The coordination polyhedron of the lanthanide atom can be described as a tricapped trigonal prism, or a monocapped square antiprism with

**Table 1** Experimental details of the structure refinements for  $KLnW(CN)_8 \cdot 9H_2O$  ( $Ln = La, Nd$ ).

Parameter	$KLaW(CN)_8 \cdot 9H_2O$	$KNdW(CN)_8 \cdot 9H_2O$
Empirical formula	$C_8H_{14}KLaN_8O_7W(2H_2O)$	$C_8H_{14}KNdN_8O_7W(2H_2O)$
$M_r$	732.16	737.49
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
$a$ , Å	8.7692(4)	8.7425(4)
$b$ , Å	25.2705(11)	25.1085(11)
$c$ , Å	10.7017(5)	10.6210(5)
$\beta$ , °	117.004(3)	117.218(3)
$V$ , Å <sup>3</sup>	2112.96(17)	2073.27(17)
$Z$	4	4
$D_x$ , g cm <sup>-3</sup>	2.302	2.363
$\mu$ , mm <sup>-1</sup>	7.686	8.277
$\theta$ -range, °	1.61–26.11	1.62–26.10
Number of measured reflections	14516	14174
Number of independent reflections	3988	3916
Number of reflections with $I > 2\sigma(I)$	3675	3553
$R_{int}$	0.0430	0.0377
Number of refined parameters	308	278
$R$ , $wR$ , $S$	0.0440, 0.1012, 1.136	0.0400, 0.0893, 1.104
$R$ , $wR$ ( $I > 2\sigma(I)$ )	0.0401, 0.0992	0.0349, 0.0868
$\rho_{min}/\rho_{max}$ , e Å <sup>-3</sup>	-3.559/2.743	-2.705/2.196

**Table 2** Atomic coordinates and equivalent displacement parameters ( $\text{\AA}^2$ ) for  $\text{KLnW}(\text{CN})_8 \cdot 9\text{H}_2\text{O}$  ( $\text{Ln} = \text{La}, \text{Nd}$ ).

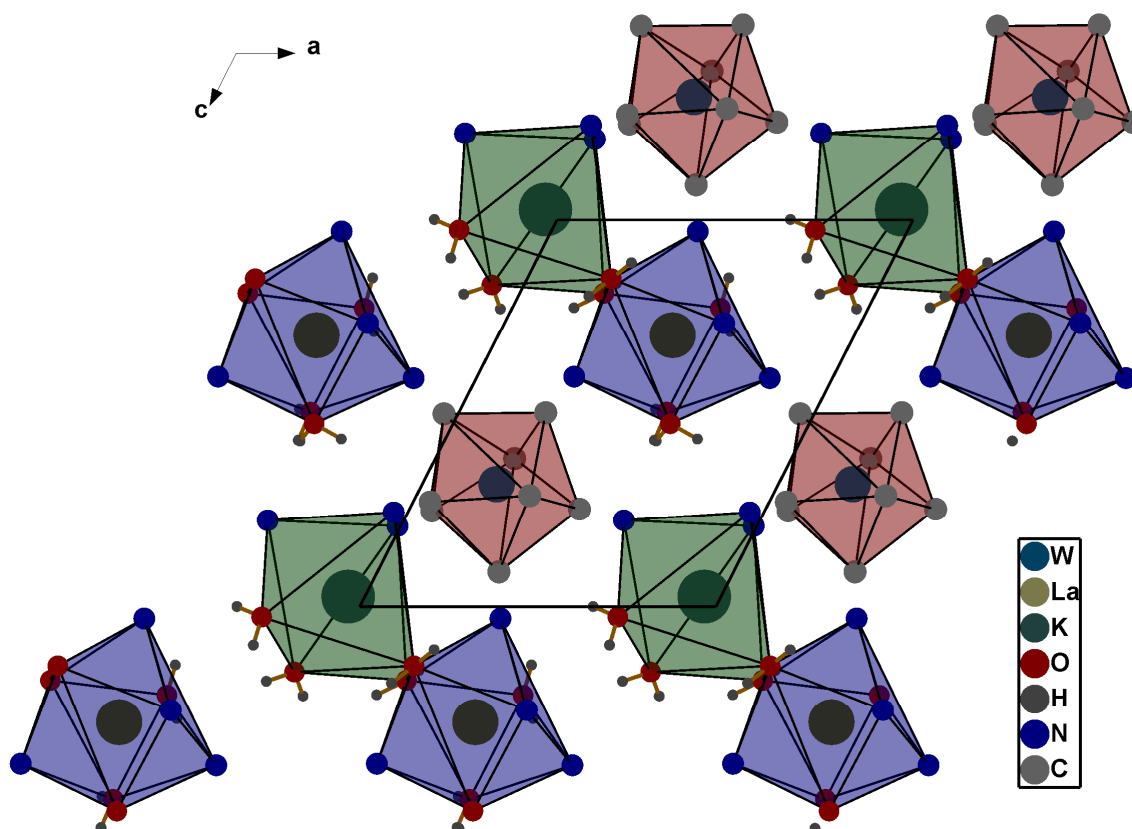
Atom	$\text{KLaW}(\text{CN})_8 \cdot 9\text{H}_2\text{O}$				$\text{KNdW}(\text{CN})_8 \cdot 9\text{H}_2\text{O}$			
	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$
K	0.0470(2)	0.10561(6)	0.02657(2)	0.0308(4)	0.0433(2)	0.10507(6)	0.02535(18)	0.0251(4)
<i>Ln</i>	0.51042(4)	0.39732(2)	0.20271(3)	0.00893(13)	0.50976(4)	0.39769(2)	0.20344(3)	0.00746(12)
W	0.20886(3)	0.60749(2)	0.18269(2)	0.00874(13)	0.20909(3)	0.60716(2)	0.18206(2)	0.00698(11)
C1	0.0396(9)	0.1084(2)	0.4990(7)	0.0165(14)	0.0427(8)	0.1080(2)	0.5021(7)	0.0244(14)
C2	0.0480(8)	0.5543(3)	0.2289(6)	0.0170(13)	0.0465(8)	0.5535(2)	0.2284(7)	0.0134(12)
C3	0.0659(8)	0.6595(3)	0.2524(7)	0.0199(14)	0.0648(8)	0.6597(3)	0.2522(7)	0.0170(13)
C4	0.2228(8)	0.6870(3)	0.1164(6)	0.0184(13)	0.2232(7)	0.6871(2)	0.1155(7)	0.0143(12)
C5	0.3183(7)	0.5290(2)	0.2127(6)	0.0125(12)	0.3209(7)	0.5282(2)	0.2130(6)	0.0237(13)
C6	0.5225(8)	0.1229(3)	0.2524(6)	0.0202(14)	0.5206(7)	0.1228(2)	0.2531(6)	0.0095(5)
C7	0.6589(9)	0.1046(2)	0.0901(7)	0.0137(13)	0.6568(7)	0.1047(2)	0.0889(7)	0.0226(14)
C8	0.7557(8)	0.4061(2)	0.0021(6)	0.0120(12)	0.7536(7)	0.4063(2)	0.0030(6)	0.0095(5)
N1	0.1760(8)	0.3917(2)	0.0912(6)	0.0214(13)	0.1800(8)	0.3927(2)	0.0935(7)	0.0095(5)
N2	0.0397(7)	0.0272(2)	0.2442(6)	0.0199(12)	0.0414(7)	0.0266(3)	0.2451(7)	0.0282(10)
N3	0.0090(8)	0.1867(3)	0.2083(7)	0.0345(15)	0.1120(8)	0.1871(3)	0.2104(8)	0.0318(15)
N4	0.2285(8)	0.7304(2)	0.0839(7)	0.0277(13)	0.2299(8)	0.7304(2)	0.0837(7)	0.0271(14)
N5	0.3831(8)	0.4888(2)	0.2341(6)	0.0215(12)	0.3860(7)	0.4871(2)	0.2333(6)	0.0095(5)
N6	0.3819(9)	0.1294(4)	0.2234(7)	0.045(2)	0.3783(8)	0.1302(3)	0.2214(7)	0.0282(10)
N7	0.5881(8)	0.3984(2)	0.4702(6)	0.0189(12)	0.5861(8)	0.3991(2)	0.4670(6)	0.0095(5)
N8	0.7272(7)	0.4118(2)	0.0951(5)	0.0183(12)	0.7224(7)	0.4108(2)	0.0968(6)	0.0149(11)
O1	0.0902(8)	0.3298(3)	0.3328(8)	0.0567(19)	0.0868(7)	0.3299(3)	0.3302(8)	0.0470(17)
O2	0.1746(7)	0.2468(2)	0.0755(6)	0.0336(12)	0.1750(7)	0.2473(2)	0.0749(6)	0.0308(12)
O3	0.2364(6)	0.53892(18)	0.6512(5)	0.0180(9)	0.2423(2)	0.5395(2)	0.6544(5)	0.0158(9)
O4	0.2364(6)	0.83329(19)	0.1887(5)	0.0210(10)	0.2408(6)	0.8350(2)	0.1893(5)	0.0175(10)
O5	0.2606(7)	0.4615(2)	0.4741(5)	0.0273(11)	0.2599(6)	0.4612(2)	0.4737(6)	0.0244(11)
O6	0.3900(6)	0.04753(18)	0.4734(5)	0.0185(9)	0.3917(5)	0.0483(2)	0.4770(5)	0.0158(9)
O7	0.4152(7)	0.31207(19)	0.2729(5)	0.0238(11)	0.4162(6)	0.3140(2)	0.2732(5)	0.0221(10)
O8	0.4167(6)	0.33189(18)	0.0034(5)	0.0204(10)	0.4178(6)	0.3333(2)	0.0077(5)	0.0180(10)
O9	0.5610(9)	0.2331(2)	0.0433(6)	0.0428(15)	0.5588(8)	0.2330(2)	0.0434(6)	0.0385(14)
H11	0.032(13)	0.308(4)	0.271(9)	0.085	0.041(12)	0.303(3)	0.284(10)	0.071
H12	0.156(8)	0.345(4)	0.309(11)	0.085	0.143(7)	0.344(4)	0.294(10)	0.071
H21	0.123(10)	0.268(3)	0.013(7)	0.050	0.133(9)	0.262(4)	0.997(5)	0.046
H22	0.133(4)	0.245(4)	0.130(7)	0.050	0.119(4)	0.254(4)	0.117(7)	0.046
H31	0.198(5)	0.522(2)	0.696(7)	0.027	0.204(5)	0.524(2)	0.702(6)	0.024
H32	0.270(5)	0.519(2)	0.610(7)	0.027	0.259(6)	0.519(2)	0.602(6)	0.024
H41	0.173(3)	0.828(3)	0.226(8)	0.032	0.177(3)	0.831(3)	0.226(8)	0.026
H42	0.257(7)	0.8047(16)	0.163(8)	0.032	0.254(7)	0.8068(17)	0.157(8)	0.026
H51	0.244(8)	0.477(3)	0.402(5)	0.041	0.251(8)	0.481(3)	0.410(7)	0.037
H52	0.345(8)	0.058(3)	0.001(7)	0.041	0.332(7)	0.062(2)	0.986(8)	0.037
H61	0.292(8)	0.036(3)	0.434(7)	0.028	0.302(7)	0.032(3)	0.456(7)	0.024
H62	0.405(8)	0.071(2)	0.429(7)	0.028	0.395(6)	0.061(3)	0.407(5)	0.024
H71	0.354(10)	0.292(2)	0.212(5)	0.036	0.344(10)	0.293(2)	0.216(6)	0.033
H72	0.435(9)	0.302(3)	0.351(3)	0.036	0.454(10)	0.302(3)	0.354(3)	0.033
H81	0.411(7)	0.155(2)	0.431(5)	0.031	0.398(8)	0.152(3)	0.433(5)	0.027
H82	0.4520(9)	0.3013(13)	0.011(7)	0.031	0.473(8)	0.3059(18)	0.019(7)	0.027
H91	0.466(8)	0.225(4)	0.037(12)	0.064	0.456(8)	0.225(4)	0.017(9)	0.058
H92	0.629(11)	0.209(3)	0.082(11)	0.064	0.612(11)	0.224(4)	0.129(4)	0.058

**Table 3** Selected bond distances and angles in  $KLnW(CN)_8 \cdot 9H_2O$  ( $Ln = La, Nd$ ).

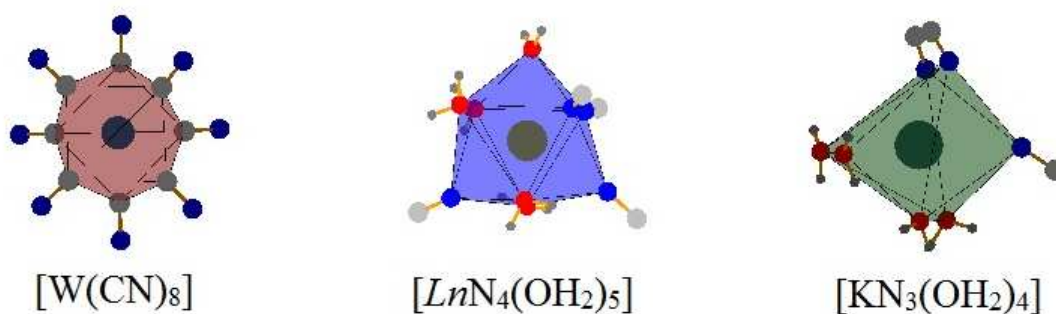
KLaW(CN) <sub>8</sub> ·9H <sub>2</sub> O				KNdW(CN) <sub>8</sub> ·9H <sub>2</sub> O			
Atoms	$\delta, \text{\AA}$	Atoms	$\omega, ^\circ$	Atoms	$\delta, \text{\AA}$	Atoms	$\omega, ^\circ$
W–C(1)	2.163(6)	C(1)–W–C(2)	73.5(2)	W–C(1)	2.176(7)	C(1)–W–C(2)	73.2(2)
W–C(2)	2.162(7)	C(1)–W–C(3)	78.4(3)	W–C(2)	2.171(6)	C(1)–W–C(3)	78.2(2)
W–C(3)	2.169(7)	C(1)–W–C(4)	83.0(2)	W–C(3)	2.178(7)	C(1)–W–C(4)	83.2(2)
W–C(4)	2.153(7)	C(1)–W–C(5)	109.9(2)	W–C(4)	2.150(6)	C(1)–W–C(5)	110.2(2)
W–C(5)	2.163(6)	C(1)–W–C(6)	142.2(3)	W–C(5)	2.168(6)	C(1)–W–C(6)	142.2(2)
W–C(6)	2.167(6)	C(1)–W–C(7)	144.7(3)	W–C(6)	2.174(5)	C(1)–W–C(7)	144.7(2)
W–C(7)	2.169(6)	C(1)–W–C(8)	71.6(2)	W–C(7)	2.165(7)	C(1)–W–C(8)	72.3(2)
W–C(8)	2.164(7)	C(2)–W–C(3)	76.1(3)	W–C(8)	2.161(6)	C(2)–W–C(3)	75.9(2)
C(1)–N(1)	1.155(8)	C(2)–W–C(4)	142.8(2)	C(1)–N(1)	1.147(9)	C(2)–W–C(4)	142.7(2)
C(2)–N(2)	1.159(9)	C(2)–W–C(5)	71.8(2)	C(2)–N(2)	1.151(9)	C(2)–W–C(5)	72.2(2)
C(3)–N(3)	1.154(9)	C(2)–W–C(6)	139.9(2)	C(3)–N(3)	1.147(9)	C(2)–W–C(6)	140.3(2)
C(4)–N(4)	1.159(9)	C(2)–W–C(7)	78.2(2)	C(4)–N(4)	1.149(9)	C(2)–W–C(7)	78.6(2)
C(5)–N(5)	1.136(8)	C(2)–W–C(8)	119.3(2)	C(5)–N(5)	1.150(8)	C(2)–W–C(8)	119.7(2)
C(6)–N(6)	1.139(9)	C(3)–W–C(4)	71.1(3)	C(6)–N(6)	1.145(8)	C(3)–W–C(4)	71.1(2)
C(7)–N(7)	1.146(9)	C(3)–W–C(5)	142.3(2)	C(7)–N(7)	1.155(9)	C(3)–W–C(5)	142.5(2)
C(8)–N(8)	1.140(9)	C(3)–W–C(6)	119.7(3)	C(8)–N(8)	1.152(8)	C(3)–W–C(6)	119.9(2)
K(1)–O(5)	2.768(6)	C(3)–W–C(7)	74.5(2)	K(1)–O(5)	2.758(5)	C(3)–W–C(7)	74.6(2)
K(1)–O(1)	2.797(8)	C(3)–W–C(8)	139.1(2)	K(1)–O(1)	2.797(7)	C(3)–W–C(8)	139.2(2)
K(1)–O(3)	2.888(5)	C(4)–W–C(5)	144.8(2)	K(1)–O(3)	2.869(5)	C(4)–W–C(5)	144.5(2)
K(1)–O(4)	2.945(5)	C(4)–W–C(6)	73.9(2)	K(1)–O(4)	2.909(5)	C(4)–W–C(6)	73.6(2)
K(1)–N(5)	2.794(6)	C(4)–W–C(7)	108.7(2)	K(1)–N(5)	2.781(6)	C(4)–W–C(7)	108.3(2)
K(1)–N(1)	2.947(7)	C(4)–W–C(8)	78.1(2)	K(1)–N(1)	2.949(7)	C(4)–W–C(8)	78.0(2)
K(1)–N(2)	3.080(6)	C(5)–W–C(6)	76.8(2)	K(1)–N(2)	3.061(7)	C(5)–W–C(6)	76.6(2)
La(1)–O(8)	2.523(5)	C(5)–W–C(7)	80.0(2)	Nd(1)–O(8)	2.460(5)	C(5)–W–C(7)	80.1(2)
La(1)–O(7)	2.544(5)	C(5)–W–C(8)	75.6(2)	Nd(1)–O(7)	2.489(5)	C(5)–W–C(8)	75.5(2)
La(1)–O(4)	2.560(4)	C(6)–W–C(7)	72.3(2)	Nd(1)–O(4)	2.502(4)	C(6)–W–C(7)	72.4(2)
La(1)–O(6)	2.593(4)	C(6)–W–C(8)	74.6(2)	Nd(1)–O(6)	2.533(4)	C(6)–W–C(8)	73.9(2)
La(1)–O(3)	2.611(4)	C(7)–W–C(8)	142.5(2)	Nd(1)–O(3)	2.545(4)	C(7)–W–C(8)	142.0(2)
La(1)–N(3)	2.620(5)			Nd(1)–N(3)	2.571(5)		
La(1)–N(7)	2.624(6)			Nd(1)–N(7)	2.564(6)		
La(1)–N(6)	2.654(6)			Nd(1)–N(6)	2.575(6)		
La(1)–N(8)	2.657(6)			Nd(1)–N(8)	2.603(5)		

the square faces formed by two N atoms and two O atoms, which are *trans* in one square face and *cis* in the other. The W atoms are eight-fold coordinated by C≡N, forming  $[W(CN)_8]^{4-}$  square antiprisms, which are linked to the  $[LnN_4(OH_2)_5]^{3+}$  groups by cyanide bridging (see Fig. 2). Consequently, for each  $[W(CN)_8]^{4-}$  unit, there are four cyano ligands acting as bridging units, and four terminal units. The W–C distances in both compounds range from 2.150(6) to 2.178(7) Å, and the C≡N distances from 1.136(8) to 1.155(9) Å. The W–C–N bond angles take values between 177.0(5) and 178.8(6)° and do thus not deviate significantly from 180°. The K ions are surrounded by three N atoms from C≡N groups and four O atoms from H<sub>2</sub>O molecules, which together form deformed monocapped trigonal prisms

$[KN_3(OH_2)_4]^+$ . Each  $[W(CN)_8]^{4-}$  anion is N-linked by three bridging cyano ligands with *Ln* cations in one layer, and by one cyano ligand with a *Ln* cation in an adjacent layer, to form double layers. Three other CN groups are coordinated by two K ions. Only one cyano group in the anion  $[W(CN)_8]^{4-}$  acts as terminal ligand. Consequently, the structures of **I** and **II** consist of double layers of  $[W(CN)_8]^{4-}$ ,  $[LnN_4(OH_2)_5]^{3+}$ , and  $[KN_3(OH_2)_4]^+$  polyhedra. The uncoordinated water molecules are sandwiched between the layers (see Fig. 3). This leads to the formation of a two-dimensional structure. The formula of the coordination polymer can be written as  $\{[K(H_2O)_2][Ln(H_2O)_5][W(CN)_8]\}_n \cdot 2nH_2O$ . Several types of hydrogen bonding are observed in the structure. They involve the coordinated and



**Fig. 1** Projection of the structure of  $\{[K(H_2O)_2][La(H_2O)_5][W(CN)_8]\}_n \cdot 2nH_2O$  along the direction  $[010]$ .



**Fig. 2** Coordination polyhedra in the structure of  $\{[K(H_2O)_2][Ln(H_2O)_5][W(CN)_8]\}_n \cdot 2nH_2O$ .

uncoordinated water molecules and both bridging and terminal  $C\equiv N$  nitrogen atoms. A list of hydrogen bonds with donor...acceptor distances  $\leq 3.5 \text{ \AA}$  is given in [Table 4](#).

## Discussion

The compounds **I** and **II** have similar structures and are isostructural to  $KLaMo(CN)_8 \cdot 9H_2O$  [7], but differ substantially from the structures of other octacyano

complexes of molybdenum and tungsten(V,IV) [3-13], which have different connections and belong to different space groups. The complexes  $Ln(H_2O)_5[M(CN)_8]$  ( $Ln = Pr, Nd, Eu, Tb, Sm, Gd$ ;  $M = Mo^V, W^V$ ) and  $Ln(H_2O)_4[W(CN)_8]$  ( $Ln = Ho, Er, Tm, Lu$ ) [3-5] are isostructural, have tetragonal symmetry and crystallize in the space group  $P4/nmm$ , except  $Ln(H_2O)_5[W(CN)_8]$  ( $Ln = La$  [3],  $Sm$  [6]), which belong to the space group  $P4/ncc$ . The water molecules in all these compounds are included in the coordination sphere of the lanthanide ions. It is

**Table 4** Hydrogen bonds in KLaW(CN)<sub>8</sub>·9H<sub>2</sub>O (D...A distances ≤ 3.3 Å) and KNdW(CN)<sub>8</sub>·9H<sub>2</sub>O (D...A distances ≤ 3.5 Å).

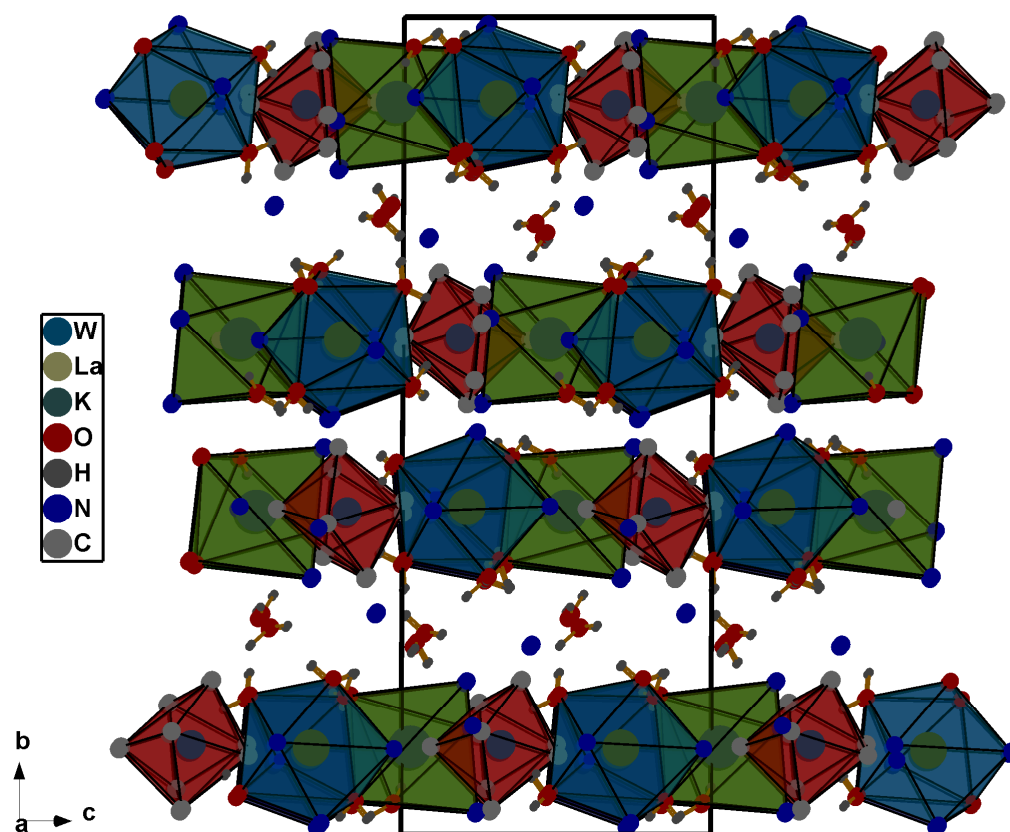
KLaW(CN) <sub>8</sub> ·9H <sub>2</sub> O				
D–H...A	D–H, Å	H...A, Å	D...A, Å	D–H...A, °
O3–H31...N2	0.82(2)	2.09(3)	2.884(7)	161(7)
O3–H32...O5	0.82(2)	2.02(3)	2.798(7)	159(7)
O7–H72...O9	0.81(2)	2.05(4)	2.820(8)	159(9)
O7–H71...O2	0.82(2)	1.95(3)	2.754(7)	170(9)
O6–H61...N2	0.82(2)	2.24(4)	2.979(6)	152(6)
O6–H62...O8	0.81(2)	2.56(7)	3.062(7)	121(7)
O6–H62...N6	0.81(2)	2.58(3)	3.358(10)	162(6)
O8–H82...O9	0.82(2)	1.92(2)	2.743(7)	173(8)
O8–H81...N6	0.82(2)	2.21(2)	3.033(8)	173(7)
O4–H42...N4	0.82(2)	2.03(3)	2.819(8)	161(7)
O5–H51...N5	0.82(2)	2.61(5)	3.275(8)	140(6)
O2–H21...N4	0.82(2)	2.78(8)	3.203(8)	114(7)
O2–H22...N3	0.82(2)	2.21(7)	2.883(9)	140(9)

KNdW(CN) <sub>8</sub> ·9H <sub>2</sub> O				
D–H...A	D–H, Å	H...A, Å	D...A, Å	D–H...A, °
O3–H31...N2	0.82(2)	2.11(4)	2.883(7)	158(7)
O3–H32...O5	0.82(2)	1.99(3)	2.800(7)	169(7)
O7–H72...O9	0.82(2)	2.00(2)	2.813(8)	174(9)
O7–H71...O2	0.83(2)	1.94(2)	2.761(7)	177(7)
O6–H61...N2	0.82(2)	2.35(5)	2.974(7)	133(5)
O6–H62...N6	0.81(2)	2.58(3)	3.364(9)	160(7)
O8–H82...O9	0.82(2)	1.95(3)	2.752(7)	167(8)
O8–H81...N6	0.82(2)	2.24(3)	3.041(8)	166(6)
O4–H42...N4	0.82(2)	2.04(3)	2.838(8)	164(4)
O5–H51...N2	0.82(2)	2.58(6)	3.072(8)	120(6)
O5–H21...N5	0.82(2)	2.71(3)	3.483(8)	160(6)
O1–H12...O7	0.83(3)	2.61(9)	3.228(7)	132(10)
O2–H22...N3	0.82(2)	2.36(8)	2.880(8)	123(8)

interesting to note that in the complexes formed by elements of the cerium subgroup, the coordination polyhedron of the *Ln* atom consists of nine atoms, [*Ln*N<sub>4</sub>O<sub>5</sub>], and can be described as a slightly deformed monocapped square antiprism, whereas in the complexes of rare-earths of the yttrium subgroup the coordination polyhedron of *Ln* atoms is an eight-vertex [*Ln*N<sub>4</sub>O<sub>4</sub>] slightly distorted square antiprism [3]. Crystallization water molecules are absent in this complexes. The complexes **I**, **II** and KLaMo(CN)<sub>8</sub>·9H<sub>2</sub>O differ from other cyano complexes of Mo(IV), W(IV) by the higher number of water molecules, which results in a considerably different structure [8–13]. In these compounds, the coordination polyhedra of the Mo and W atoms are slightly different. In the *Ln*-W<sup>V</sup> complexes the [W(CN)<sub>8</sub>]<sup>3-</sup> units either exhibit slightly distorted dodecahedral geometry [3] or can be described as square antiprisms [6]. The coordination polyhedra

[*M*(CN)<sub>8</sub>]<sup>4-</sup> (*M* = Mo<sup>IV</sup>, W<sup>IV</sup>) are square antiprisms. The lanthanide atoms also have different coordination geometries. Nitrogen atoms and water molecules form a monocapped square antiprism of composition [*Ln*N<sub>4</sub>(OH<sub>2</sub>)<sub>5</sub>] around the *Ln* atom the studied compounds, whereas the Tb atoms in KTbW(CN)<sub>8</sub>·7H<sub>2</sub>O center square antiprisms, [TbN<sub>4</sub>(OH<sub>2</sub>)<sub>4</sub>] [9], and the Sm atoms in KSmMo(CN)<sub>8</sub>·10H<sub>2</sub>O tricapped trigonal prisms, [SmN<sub>4</sub>(OH<sub>2</sub>)<sub>5</sub>] [8]. The coordination polyhedra of the potassium atoms in **I**, **II**, and KLaMo(CN)<sub>8</sub>·9H<sub>2</sub>O are [KN<sub>3</sub>(OH<sub>2</sub>)<sub>4</sub>] deformed monocapped trigonal prisms, which differ from the [KN<sub>4</sub>(OH<sub>2</sub>)<sub>3</sub>] polyhedra in KSmMo(CN)<sub>8</sub>·10H<sub>2</sub>O [8] and the [KN<sub>5</sub>(OH<sub>2</sub>)<sub>2</sub>] polyhedra in KTbW(CN)<sub>8</sub>·7H<sub>2</sub>O [9]. A comparison of the shortest W–C, Mo–C and C≡N distances in **I**, **II**, and the KLaMo(CN)<sub>8</sub>·9H<sub>2</sub>O compound shows that the W–C distances are shorter than their Mo–C analogues and the W–C≡N angles larger than the Mo–C≡N angles.



**Fig. 3** Projection of the structure  $\{[K(H_2O)_2][La(H_2O)_5][W(CN)_8]\}_n \cdot 2nH_2O$  along the direction  $[100]$ .

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