Syntheses and structures of layered compounds based on lanthanides(III) and cubane molybdenum and tungsten telluride cyano complexes

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Eight isostructural polymeric coordination compounds of the general formula $[Ln(DMF)(H_2O)_4][Ln(DMF)_2(H_2O)_4][M_4Te_4(CN)_{12}]\cdot DMF\cdot nH_2O$ (Ln = Er, Ho, Gd, or Sm; M = W or Mo) were prepared for the first time by evaporation in air of aqueous solutions containing the cuboidal telluride anionic complex of tungsten $[W_4Te_4(CN)_{12}]^{6-}$ or molybdenum $[Mo_4Te_4(CN)_{12}]^{7-}$, lanthanide chlorides, and dimethylformamide. The resulting polymeric coordination complexes with layered structures were characterized by X-ray diffraction analysis and IR spectra. The magnetic susceptibilities of the gadolinium complexes were measured.

Key words: tungsten, molybdenum, cluster complexes, telluride complexes, synthesis, X-ray diffraction analysis.

Coordination polymers composed of mononuclear hexacyano- and tetracyanometallate complexes are used for the chemical design of a new generation of sensors, catalysts, and magnetic materials.[1—3] Studies on the synthesis of coordination polymers consisting of transition metal cyanide clusters have been started in recent years. The octahedral $[Re_6Q_8(CN)_6]^{4-}$ (see Refs. 4—10) and tetrahedral $[Re_4Q_4(CN)_{12}]^{4-}$ (see Refs. 11—13) (Q = S, Se, or Te) rhenium clusters were used as building blocks for the construction of compounds containing chains, networks, or three-dimensional frameworks composed of the $\{M_n\}$ clusters, which are linked to each other by the heterometal atoms (M´) through the bridging cyanide ligands: ...M´—NC—$\{M_n\}$—CN—M´—NC...... In our earlier studies, the cuboidal molybdenum and tungsten chalcogenide anions $[M_4Q_4(CN)_{12}]^{n-}$ (M = Mo or W; Q = S, Se, or Te; n = 6, 7, or 8)[14—17] have been used for the preparation of the chain polymeric complex $[Cu(NH_3)_3][Cu(NH_3)_4][Cu(NH_3)_5][W_4Te_4(CN)_{12}]\cdot 5H_2O$ [18] and the unique 3D-polymeric complexes $[M(H_2O)_4]_3[W_4Q_4(CN)_{12}]\cdot nH_2O$ (M = Co, Q = Te;[19] M = Mn, Q = S [20]) containing extremely large pores filled with water molecules.

In the present study, we synthesized the first polymeric coordination complexes **1—8** derived from the $[W_4Te_4(CN)_{12}]^{6-}$ and $[Mo_4Te_4(CN)_{12}]^{7-}$ anionic clusters and Ln^{III} cations (Ln = Er, Gd, Sm, or Ho) and established their structures by X-ray diffraction analysis.

$[Ln(DMF)(H_2O)_4][Ln(DMF)_2(H_2O)_4][W_4Te_4(CN)_{12}]\cdot DMF\cdot nH_2O$

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Ln	Er	Gd	Sm	Ho	Er	Gd	Sm	Ho
n	7	6.5	6.5	7.5	6.5	6	6.5	7.5

Results and Discussion

Compounds **1—8** were prepared by evaporation in air of aqueous solutions containing the cuboidal telluride cluster anions $[W_4Te_4(CN)_{12}]^{6-}$ (Fig. 1) or $[Mo_4Te_4(CN)_{12}]^{7-}$, rare-earth chlorides (Er, Ho, Gd, or Sm), and dimethylformamide. These complexes are unstable in air at room temperature, readily lose water of crystallization, and become X-ray amorphous within several hours.

The syntheses of complexes **5—8** involve one-electron oxidation of the starting paramagnetic anion $[Mo_4Te_4(CN)_{12}]^{7-}$ with atmospheric oxygen to form $[Mo_4Te_4(CN)_{12}]^{6-}$.

The IR spectra of complexes **1—8** (Table 1) have either one broadened or two C≡N stretching vibration bands in the range of 2105—2150 cm^{-1}, which is consistent with the results of X-ray diffraction analysis (see below) and

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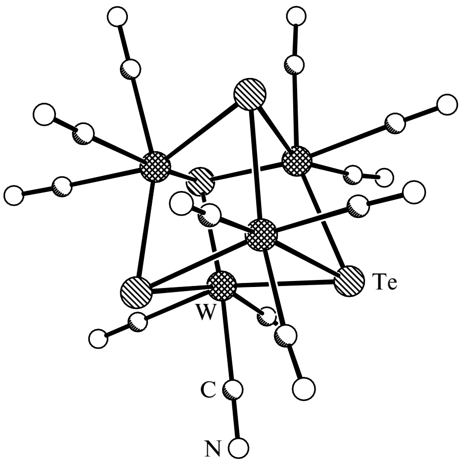

Fig. 1. Structure of the $[W_4Te_4(CN)_{12}]^{6-}$ anionic complex.

provides evidence for the presence of two types of cyanide ligands. The lower-frequency bands correspond to stretching vibrations of the terminal CN groups, and the higher frequencies ν_{CN} belong to vibrations of the bridging CN groups.

The structures of compounds **1**—**3** and **5**—**7** were established by X-ray diffraction analysis. Since the crystals of complexes **4** and **8** were of poor quality, only their unit cell parameters were determined. All compounds are isostructural and crystallize in the monoclinic system (space group $P2_1$, $Z = 2$).

According to the results of X-ray diffraction analysis, the complexes have polymeric layered structures. The layers are composed of the $\{M_4Te_4(CN)_{12}\}$ cluster fragments linked to each other by the lanthanide atoms (Ln = Er, Ho, Gd, or Sm). The Ln atoms are coordinated by the nitrogen atoms of the CN ligands. The projections of the layers onto the *ab* and *bc* planes are shown in Figs. 2 and 3, respectively. The compounds contain two types of lanthanide atoms, *viz*., Ln(1) and Ln(2), which have the same coordination number (8) but differ in the coordination environment (3 N(CN) + O(DMF) + 4 H_2O for Ln(1) and 2 N(CN) + 2 O(DMF) + 4 H_2O for Ln(2)). The coordination environments of lanthanides are illustrated in Fig. 4 by the example of gadolinium. In complexes **1**—**8**, each $\{M_4Te_4(CN)_{12}\}$ cluster fragment is linked to three Ln(1) atoms and two Ln(2) atoms through the bridging CN ligands to form the crimped electroneutral layer $^{2}_{\infty}\{[Ln(DMF)(H_2O)_4][Ln(DMF)_2(H_2O)_4][M_4Te_4(CN)_{12}]\}$. The environment of the cluster complex in the layer is shown in Fig. 5. The space between the layers is occupied by the uncoordinated water and DMF molecules.

In the compounds under consideration, the cuboidal M_4Te_4 cluster cores are distorted from the ideal symme-

Table 1. Yields, elemental analysis data, and positions of the ν_{CN} bands in the IR spectra of complexes **1**—**4** and **6**—**8**

Complex	Yield (%)	Found/Calculated (%)			IR, ν_{CN}/cm^{-1}
		C	N	H	
1	98	11.65 11.70	9.13 9.09	2.49 2.41	2105, 2125
2	98	11.81 11.79	9.10 9.17	2.33 2.43	2120
3	96	11.80 11.86	9.30 9.22	2.39 2.45	2115
4	97	11.70 11.72	9.17 9.11	2.35 2.42	2115
6	86	13.71 13.65	10.70 10.61	2.73 2.82	2120, 2150
7	88	13.62 13.78	10.65 10.71	2.77 2.84	2125
8	90	13.75 13.68	10.70 10.63	2.73 2.82	2105, 2120

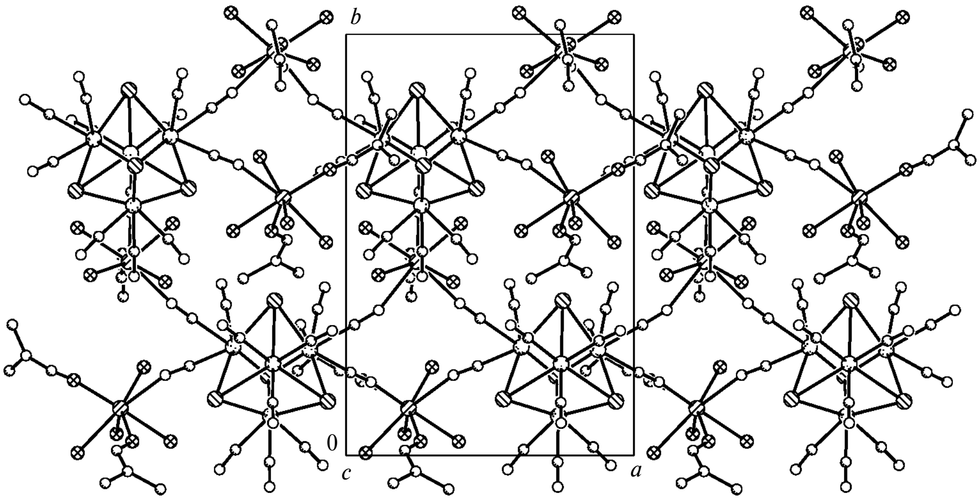

Fig. 2. Unit cell of coordination polymer **2** projected onto the *ab* plane. The uncoordinated H_2O and DMF molecules are omitted.

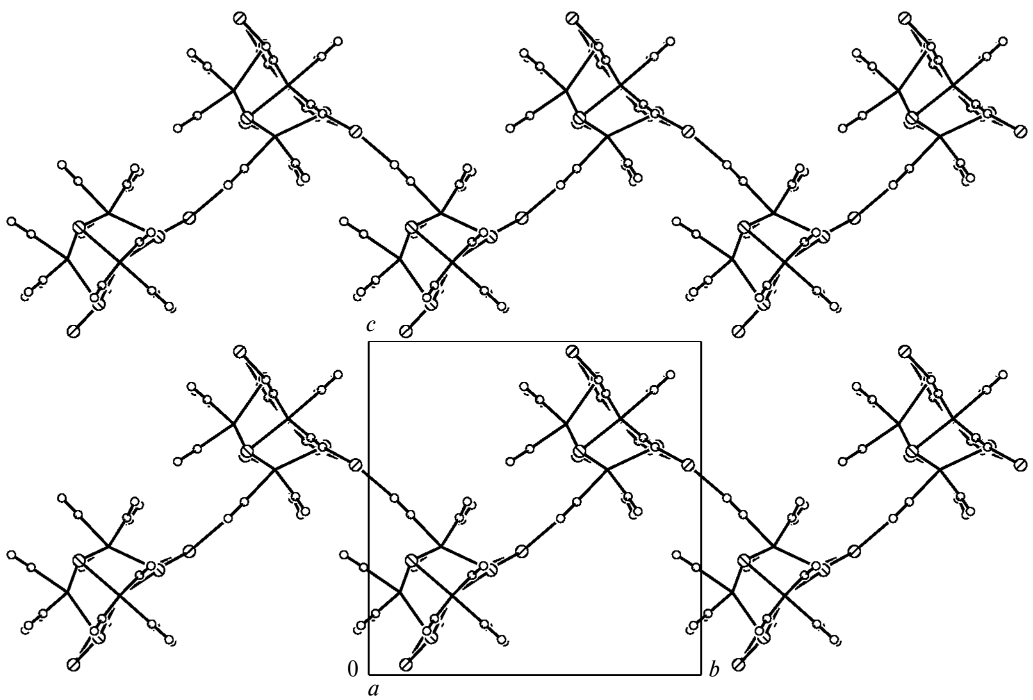

Fig. 3. Unit cell of coordination polymer **2** projected onto the *bc* plane. The uncoordinated H_2O and DMF molecules are omitted.

try T_d to C_1. The principal bond lengths in the complexes are given in Table 2. The average W—W and W—Te bond lengths in complexes **1**, **2**, and **3** (2.97 and 2.69 Å, respectively) are equal to the corresponding bond lengths in the $K_6[W_4Te_4(CN)_{12}] \cdot 5H_2O$,[14,15] $[Cd(NH_3)_4]_3[W_4Te_4(CN)_{12}]$,[21] and $[Cu(NH_3)_3][Cu(NH_3)_4][Cu(NH_3)_5][W_4Te_4(CN)_{12}] \cdot 5H_2O$ [18] complexes. The W—W bond lengths in different compounds vary only slightly (~0.1 Å).

The average Mo—Mo bond lengths in complexes **5** (2.967 Å), **6** (2.915 Å), and **7** (2.965 Å) (see Table 1) differ substantially both from each other and from the corresponding distances in the $K_7[Mo_4Te_4(CN)_{12}] \cdot 12H_2O$ [14] (2.992 Å) and $Cs_6[Mo_4Te_4(CN)_{12}] \cdot 2H_2O$ [14—15] (2.966 Å)

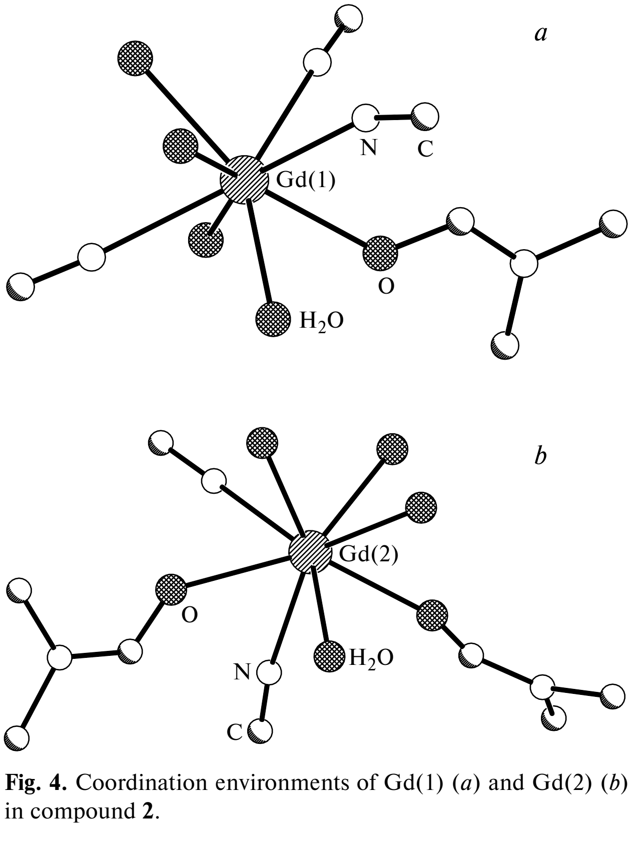

Fig. 4. Coordination environments of Gd(1) (*a*) and Gd(2) (*b*) in compound **2**.

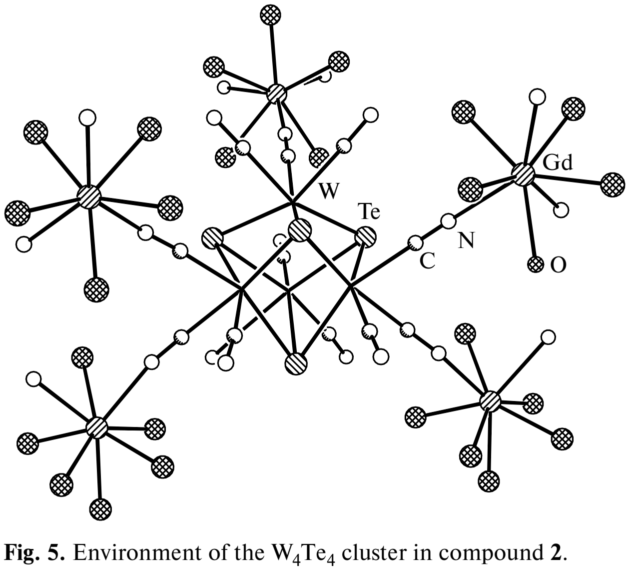

Fig. 5. Environment of the W_4Te_4 cluster in compound **2**.

Table 2. Principal interatomic distances in complexes **1**—**3** and **5**—**7**

Complex	M—M/Å	Δ(M—M)/Å	V(M$_4$)/Å^3	M—Te/Å	Δ(M—Te)/Å
1	2.918—3.009, aver. 2.970	0.090	3.086	2.679—2.704, aver. 2.690	0.025
2	2.899—3.019, aver. 2.968	0.120	3.078	2.676—2.708, aver. 2.691	0.032
3	2.905—3.022, aver. 2.967	0.117	3.073	2.676—2.706, aver. 2.690	0.030
5	2.882—3.014, aver. 2.967	0.133	3.090	2.667—2.698, aver. 2.681	0.031
6	2.874—3.019, aver. 2.915	0.145	3.031	2.646—2.683, aver. 2.667	0.037
7	2.881—3.034, aver. 2.965	0.153	3.066	2.665—2.699, aver. 2.679	0.034

complexes. The average Mo—Te bond lengths in complexes **5** and **7** have virtually identical values and are equal to the corresponding bond lengths in the $Cs_6[Mo_4Te_4(CN)_{12}] \cdot 2H_2O$ complex (2.678 Å).

Analysis of the environment about the rare-earth cations showed that the nature of the cluster anion (whether it be the Mo_4 or W_4 core) has no noticeable effect on the Ln—NC distances. It should be noted that the characteristic shortening of the Ln—O and Ln—N distances ("lanthanide contraction") is observed in the Sm—Gd—Er series. The distances of the same type (for example, Ln—OH_2) vary over broad ranges, which is also rather typical of lanthanides. For example, according to the data from the Cambridge Structural Database,[22] the Ln—O distances in the $[Ln(H_2O)_9]^{3+}$ aqua ions are in the ranges of 2.42—2.55 Å (Ln = Sm, BUVWUK01), 2.40—2.54 Å (Ln = Gd, BUVVOD), and 2.17—2.64 Å (Ln = Er, AERETS02).

The measured effective magnetic moments of complexes **2** and **6** (7.96 and 7.91 μB for **2** and **6**, respectively, per Gd atom) are in good agreement with the published data[23] for the Gd^{III} complexes in which there is no exchange coupling between the paramagnetic centers.

Experimental

The reagents of analytical grade were used. The starting $K_6[W_4Te_4(CN)_{12}] \cdot 5H_2O$ and $K_7[Mo_4Te_4(CN)_{12}] \cdot 12H_2O$ compounds were prepared according to procedures described previously[1,2] from a mixture of polymeric tungsten ditelluride or the triangular molybdenum telluride complex $Mo_3Te_7I_4$ and KCN. The IR spectra were recorded on a Bruker IFS-85 Fourier spectrometer in KBr pellets. The magnetic measurements were carried out at room temperature by the Faraday method.

Synthesis of n-crystal hydrates of [tetraaquadimethylformamidelanthanide(III)][tetraaquabis(dimethylformamide)lanthanide(III)][(dodecacyanotetra-μ$_3$-tellurotetratungstanate(W—W)] dimethylformamide solvate $[Ln(DMF)(H_2O)_4][Ln(DMF)_2(H_2O)_4][W_4Te_4(CN)_{12}] \cdot DMF \cdot nH_2O$ (Ln = Er, Gd, Sm, Ho) (general procedure). A 5% aqueous solution of Ln chlorides (Ln = Sm, Gd, Ho, or Er) (1 mL) and 3—4 drops of dimethylformamide were added to an aqueous solution (1 mL) containing the $K_6[W_4Te_4(CN)_{12}] \cdot 5H_2O$ complex (20 mg). After 3 days, black bulk crystals precipitated from the solution. The crystalline compound was filtered through a paper filter, washed with a 70% aqueous solution of ethanol, and dried in air for 1 h. The results of elemental analysis, yields, and IR spectroscopic data are given in Table 2.

Table 3. Crystallographic characteristics and details of X-ray diffraction studies of compounds **1**—**3**

Parameter	**1**	**2**	**3**
Composition	$C_{24}H_{58}Er_2N_{16}O_{19}Te_4W_4$	$C_{24}H_{57}Gd_2N_{16}O_{18.5}Te_4W_4$	$C_{24}H_{57}N_{16}O_{18.5}Sm_2Te_4W_4$
Molecular weight	2455.18	2426.16	2412.36
a/Å	11.037(4)	11.1574(4)	11.166(3)
b/Å	16.180(7)	16.2370(9)	16.248(4)
c/Å	16.306(9)	16.3264(12)	16.344(6)
β/deg	94.17(7)	94.535(12)	94.34(2)
V/A^3	2904(2)	2948.5(3)	2956.8(15)
ρ_{calc}/g cm^{-3}	2.808	2.733	2.710
μ/mm^{-1}	12.787	11.997	11.706
Crystal dimensions/mm	0.28×0.20×0.14	0.44×0.30×0.03	0.50×0.38×0.15
2θ$_{max}$/deg	50	50	55
Measured/independent reflections	5455/5268	5609/5410	7386/7036
Observed reflections, $F_o > 4\sigma(F_o)$	5007	5146	6808
R_{int}	0.0369	0.0423	0.0165
R_1 for $F_o > 4\sigma(F_o)$	0.0332,	0.0317	0.0251
wR_2 for all reflections	0.0885	0.0776	0.0608
GOOF for all reflections	1.059	1.056	1.062

Table 4. Crystallographic characteristics and details of X-ray diffraction studies of compounds **5—7**

Parameter	**5**	**6**	**7**
Composition	$C_{24}H_{57}Er_2Mo_4N_{16}O_{18.5}Te_4$	$C_{24}H_{56}Gd_2Mo_4N_{16}O_{18}Te_4$	$C_{24}H_{57}Sm_2Mo_4N_{16}O_{18.5}Te_4$
Molecular weight	2094.54	2065.51	2060.72
a/Å	11.0778(17)	11.037(4)	11.1742(15)
b/Å	16.175(2)	16.180(7)	16.2622(18)
c/Å	16.279(3)	16.306(9)	16.357(4)
β/deg	94.17(2)	94.17(7)	94.49(4)
V/Å^3	2909.2(8)	2904(2)	2963.3(9)
ρ_{calc}/g cm^{-3}	2.391	2.362	2.310
μ/mm^{-1}	5.724	5.127	4.769
Crystal dimensions/mm	0.74×0.32×0.18	0.80×0.30×0.13	0.40×0.16×0.12
$2\theta_{max}$/deg	50	56	56
Measured/independent reflections	5621/5328	7619/7363	7702/7364
Observed reflections, $F_o > 4\sigma(F_o)$	4631	7310	7150
R_{int}	0.0441	0.0104	0.0687
R_1 for $F_o > 4\sigma(F_o)$	0.0601	0.0224	0.0245
wR_2 for all reflections	0.1504	0.0571	0.0610
GOOF for all reflections	1.165	1.160	1.072

Synthesis of n-crystal hydrates [tetraaquadimethylformamidelanthanide(III)][tetraaquabis(dimethylformamide)lanthanide(III)][(dodecacyanotetra-μ$_3$-tellurotetramolybdate(Mo—Mo)] dimethylformamide solvate, $[Ln(DMF)(H_2O)_4][Ln(DMF)_2(H_2O)_4][Mo_4Te_4(CN)_{12}] \cdot DMF \cdot nH_2O$ (Ln = Er, Gd, Sm, or Ho) (general procedure). A 5% aqueous solution of Ln chlorides (Ln = Sm, Gd, Ho, or Er) (1 mL) and 3—4 drops of dimethylformamide were added to an aqueous solution (1 mL) containing the $K_6[Mo_4Te_4(CN)_{12}] \cdot 12H_2O$ complex (20 mg). After 3 days, black bulk crystals precipitated from the solution. The crystalline compound was filtered through a paper filter, washed with a 70% aqueous solution of ethanol, and dried in air for 1 h. The results of elemental analysis, yields, and IR spectroscopic data are given in Table 1.

X-ray diffraction analysis. The crystallographic characteristics and details of X-ray diffraction studies are given in Tables 3 and 4. The unit cell parameters of complexes **4** and **8** are given in Table 5. The X-ray diffraction data were collected on an automated four-circle Stoe STADI4 diffractometer (Mo-Kα radiation, graphite monochromator, standard procedure) at −70 °C under a stream of dry nitrogen. The absorption correction was applied using the azimuth scanning curves. The structures were solved by direct methods and refined by the full-matrix least-squares method with anisotropic thermal parameters for non-hydrogen atoms using the SHELX97 program package.[24] The hydrogen atoms of the DMF molecules were refined geometrically. The hydrogen atoms of the water molecules were not located. All crystals are as a whole chiral because their space group does not contain inversion centers and symmetry planes. However, no special experiments were carried out with the aim of determining the absolute configuration. The atomic coordinates and tables of bond lengths and bond angles were deposited with the Cambridge Structural Database and can also be obtained from the authors.

Table 5. Unit cell parameters of complexes **4** and **8**

Parameter	**4**	**8**
a/Å	11.037(4)	11.059(9)
b/Å	16.180(7)	16.197(12)
c/Å	16.306(9)	16.30(4)
β/deg	94.17(7)	94.32(25)
V/Å^3	2904(1)	2911(7)

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