



Structures of Ca and Sr salts with $[W(CN)_6(bpy)]^-$ ion. Comparative studies to alkali metal salts analogues



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ABSTRACT

Five complexes with the alkaline earth metals salts (Be^{2+} , Mg^{2+} , Ca^{2+} , Sr^{2+} and Ba^{2+}) and $[W(CN)_6(bpy)]^-$ ion have been synthesized. Two of them, $Ca[W(CN)_6(bpy)]ClO_4 \cdot 3H_2O$ and $Sr[W(CN)_6(bpy)]NO_3 \cdot 2H_2O$, were structurally characterized based on the X-ray analysis of single crystals and compared with series of $Me_2[W^{IV}(CN)_6(bpy)]$ and $Me[W^{V}(CN)_6(bpy)]$ complexes (where Me = alkali metal) previously studied. The structure of salt with Ca^{2+} shows a layered system of cations and anions, with a clearly defined inorganic and organic (bpy) layer, which are connected by $\pi \cdots \pi$ interactions. For structure of Sr^{2+} , the 2,2'-bipyridine ligands present in the structure do not form $\pi \cdots \pi$ interactions as is the case with Ca^{2+} or the other structures previously studied.

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1. Introduction

Cyanido ligands, because of their interesting properties are widely used in synthesis of new coordination compounds, this includes charge-transfer interaction through CN bond, possibility of bridges formation due to electron free pair on the nitrogen end (in synthesis of polymeric materials), stabilization of low oxidation stated (due to π -back bonding), linear chain formation (due to sp hybridization in cyanides) etc. They can stabilize metal atoms on different oxidation states, both low and high, what is observed for example in Cu(I) and Mo(V) complexes [1–4]. Due to their small size, CN^- ligands can make strong interaction with the metal ions, which have high, rare coordination numbers 7, 8 or 9, for example in cyanometallate anions $[Mo(CN)_7]^{4-}$, $[Re(CN)_8]^{3-}$, $[M(CN)_8]^{3-/4-}$ and $[M(CN)_9]^{4-}$ (where M = Mo, W) [5–8]. Additionally, due to the presence of two coordinating atoms, cyanido ligands easily make bridging structures between different or the same metal centers [9–11]. Polymeric structures with cyanido-bridges can extend in one, two or three dimensions [12,13].

For several decades, hexacyanidometallate and octacyanidometallate anions – respectively $[M(CN)_6]^{n-}$ and $[M(CN)_8]^{n-}$ (M = Mo, W, Nb, Fe, Co etc.) have been widely used in structural and

physicochemical studies [14–19]. Metal–cyanido frameworks are of central interest due to their wide range of applications, for example, as molecular magnets, spin-crossover or charge transfer systems, porous materials and multifunctional systems [20–23]. Nowadays, the only known group of heteroleptic, octacoordinated complexes of W(IV/V), having similar properties is type $[W^{IV/V}(CN)_6(LL)]^{-/2-}$, where LL means bidentate ligand 2,2'-bipyridine (bpy) or 1,10-phenanthroline (phen). Comparing $[W^{IV/V}(CN)_6(bpy)]^{-/2-}$ with $[W^{IV/V}(CN)_8]^{3-/4-}$ anion, it can be noticed that replacing two CN^- with 2,2'-bipyridine cause reduction of negative charge and removing two potentially bridging ligands. Presence of organic ligand (bpy) results in occurring of intense MLCT (*metal-to-ligand charge-transfer*) bands. For this reason, in comparison light-yellow octacyanotungstate(IV), $[W^{IV}(CN)_6(bpy)]^{2-}$ has intense color, which depends on the type of solvent due to very strong solvatochromic effect. Its acetonitrile solution is green, methanol is navy blue and water solution is violet. Additionally, two aromatic rings in 2,2'-bipyridine ligand can make $\pi \cdots \pi$ interactions, which helps to stabilize the crystal structure.

In our previous publications we described compounds with $[W^{IV/V}(CN)_6(bpy)]^{-/2-}$ anion and simple, mono-positive alkali metal cations [24–28]. In case of the W(IV) anion we obtained and characterized structures with Li^+ (2 structures) [24], Na^+ (2 structures) [25], K^+ , Rb^+ [26], and Cs^+ [27] cations, but also we isolated three complexes with alkali heterocation systems: Na^+/K^+ ; Na^+/Rb^+ ; Na^+/Cs^+ [29]. Salts with $[W^{IV}(CN)_6(bpy)]^-$ anion are

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known with sodium, potassium and rubidium cations [28]. In structures of W(IV), the anionic to cationic charge ratio is 2:1 and layered arrangement with inorganic and organic layers, interconnected by $\pi \cdots \pi$ interactions is observed [24–27]. Compounds containing W(V) has one-negative anion and one-positive cation; salts form much more complex structural systems, the arrangement of which is based on an extensive network of bridging cyanido ligands. This network is additionally stabilized by $\pi \cdots \pi$ type interactions [28].

The main goal of this work is to find the correlation between the synthesis and the structure of compounds containing the 6-cyanide complex anion $[W^V(CN)_6(bpy)]^-$. Although the method of synthesizing this type of systems has been known since the 1980s, unfortunately, due to the difficult and chimeric synthesis, very few research groups around the world have focused on the study of this type of compounds. The issues discussed in the work lie in the field of crystal engineering, coordination chemistry and inorganic synthesis. In this context, in this work, we decided to investigate complexes with a system based on a mono-negative anion $[W^V(CN)_6(bpy)]^-$ and alkaline earth metals bi-positive cations as Be^{2+} , Mg^{2+} , Ca^{2+} , Sr^{2+} and Ba^{2+} . Such a combination should result in the formation of separate monomeric or one-dimensional polymer structures. We determined the crystal structure for calcium and strontium salts, while for the remaining metal salts we proved their formation based on the results of IR spectra. It should be emphasized that the tested systems are part of the series of systematic studies of the salt $[W^{V/IV}(CN)_6(bpy)]^{-/2-}$ with all known s-block elements, which allows to summarize the entire group and show structural changes from the smallest and most covalent cations to the largest, with the largest ionic radius, and therefore with the greatest polarizability and the most ionic character.

2. Experimental section

2.1. General methods and materials

$(PPh_4)_2[W(CN)_6(bpy)] \cdot 4H_2O$ and $(PPh_4)[W(CN)_6(bpy)]$ were synthesized as we described earlier [30,31]. All other chemicals were of analytical grade (Aldrich) and were used as supplied. IR spectra were recorded on a Nicolet iS5 FT-IR spectrophotometer.

2.2. Preparation of $Ca[W(CN)_6(bpy)]ClO_4 \cdot 3H_2O$ (1)

The $(PPh_4)[W(CN)_6(bpy)]$ salt was dissolved in water and to the resulting solution a drop of 5 M $HClO_4$ was added. The obtained solid PPh_4ClO_4 was filtered and to the filtrate solid CaO was then added in quantitative amount. The mixture was left for crystallization in the dark to avoid photolysis. After four days, the formed red crystals were washed with small amount of MeCN. IR-ATR [cm^{-1}]: ν_{CN} 2161, 2144, 2134, 2127.

2.3. Preparation of $Sr[W(CN)_6(bpy)]NO_3 \cdot 2H_2O$ (2)

The $(PPh_4)_2[W(CN)_6(bpy)] \cdot 4H_2O$ complex (0.5074 g; 0.407 mmol) was dissolved in 15 ml MeCN and passed through Amberlite IR 120 ion exchange in the H^+ form. To the obtained solution of $H_2[W(CN)_6(bpy)]$ a few drops of concentrated H_2O_2 and HNO_3 was added, and mixture was heated until solution color changed to very light pink. To the resulted $H[W(CN)_6(bpy)]$, a water solution of strontium nitrate was then added in a quantitative amount, and the mixture was left for crystallization in the dark to avoid photolysis. The formed crystals were filtered off and washed with very small amount of ethanol, acetone and mixture

of ethanol and acetone. Yield 23.66% (0.0663 g). IR-ATR [cm^{-1}]: ν_{CN} 2161, 2155, 2137, 2121.

2.4. Preparation of $[W(CN)_6(bpy)]^-$ salts with Be^{2+} (3), Mg^{2+} (4) and Ba^{2+} (5)

The syntheses were performed as for **2**, but as alkaline earth metals salts we used $BeSO_4 \cdot 4H_2O$, $MgSO_4 \cdot 7H_2O$ and $BaCl_2$ (for **3–5**, respectively). IR-ATR [cm^{-1}]: ν_{CN} 2190, 2179, 2156, 2131 (for **3**), ν_{CN} 2185, 2155 (for **4**) and ν_{CN} 2173, 2163, 2152 (for **5**).

2.5. Single-crystal X-ray diffraction

Diffraction intensity data for the single crystal of two new compounds were collected: for **1** at 293 K and for **2** at 100 K on a Rigaku XtaLAB Synergy-S diffractometer with mirror-monochromated $Mo K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Cell refinement and data reduction were performed using firmware [32]. The positions of all non-hydrogen atoms were determined using SHELXT software [33,34]. All non-hydrogen atoms were refined anisotropically using weighted full-matrix least-squares on F^2 . Refinement and further calculations were carried out using SHELXL software (ver. 2019/2 for **1** and ver. 2017/1 for **2**) [33,34]. All hydrogen atoms joined to carbon atoms were positioned with idealized geometries and refined using a riding model with $U_{iso}(H)$ fixed at 1.2 $U_{eq}(C_{arom})$. The hydrogen atoms of all water molecules for both structures are indeterminate. The figures were made using Diamond ver. 4.6.1 software [35]. CCDC 2161967 and 2084090 contain the supplementary crystallographic data for **1** and **2**.

3. Results and discussion

3.1. General remarks to the isolated compounds

The various methods of synthesis of Be-Ba salts of $[W(CN)_6(bpy)]^-$ anion were used. The simplest one was a reaction of $H[W(CN)_6(bpy)]$ with 2nd group of elements in form of NO_3^- , SO_4^{2-} or Cl^- salts but only the crystals with Sr^{2+} cation were of quality suitable for X-Ray single crystal measurements, for other salts (Be^{2+} , Mg^{2+} , Ba^{2+}), very fine crystals or oils were formed. The second method was to use acidic $H[W(CN)_6(bpy)]$ and alkaline MeO, $MeCO_3$ or $Me(OH)_2$ as cation source to avoid co-crystallization of metal nitrates, sulfates or chlorides. With the use of this method, single crystals of Ca^{2+} salt were isolated using CaO as a substrate. The other cation salts formed glasses and no crystals could be isolated. This was probably caused by too high solubility of salts in water and no seeds of crystallization. We could not use other solvents, as MeOH is oxidized with W(V) anion, and water-solvents mixtures (H_2O -MeCN or H_2O -acetone) gave too fine crystals in solvent diffusion method.

All salts are very light brown and are very soluble in polar solvents (H_2O) and insoluble in non-polar solvents. The crystals, due to high solubility, could not be separated from respective nitrates or sulfates by other methods as manual separation. Thus, we did not have suitable amounts of samples for elemental analysis, but the single crystals separated manually were also used for IR measurements, which are included in the Supplementary Materials. The ν_{CN} bands in the IR spectra of all the salts studied are much different from those of the substrates used in synthesis and indicate on cation exchange. The number of bands, their position, and intensities are much more different than those of M^+ cations [28] and are rather similar to the salts described earlier with Zn^{2+} and Cd^{2+} [36]. Described methods can be used to synthesize compounds **3–5**, based in the resulted IR pattern, but without any further evidence we are unable to further clearly prove the presence of **3–5** in the given formula.

Table 1
Crystal data and structure refinement for **1** and **2**.

	1	2	
Empirical formula	C ₃₂ H ₁₆ Ca ₂ Cl ₂ N ₁₆ O ₁₄ W ₂	C ₃₂ H ₁₆ N ₁₈ O ₁₀ Sr ₂ W ₂	
Formula weight	1367.37	1355.57	
Temperature [K]	293(2)	100(2)	
Wavelength [Å]	0.71073	0.71073	
Crystal system	Monoclinic	Monoclinic	
Space group	P 2 ₁ /c	P 2 ₁ /n	
Unit cell dimensions	a [Å]	13.8368(5)	8.0297(2)
	b [Å]	12.3020(5)	30.2195(8)
	c [Å]	13.4804(5)	8.8565(3)
	α [°]	90	90
	β [°]	100.112(4)	106.888(3)
	γ [°]	90	90
Volume [Å ³]	2258.99(15)	2056.38(11)	
Z	2	2	
Density (calculated) [g/cm ³]	2.010	2.189	
Absorption coefficient [mm ⁻¹]	5.514	8.233	
F(000)	1308	1276	
Crystal size [mm ³]	0.200 × 0.100 × 0.020	0.200 × 0.150 × 0.100	
Theta range for data collection [°]	2.231 to 30.758	2.496 to 33.659	
Index ranges	-17 ≤ h ≤ 19 -15 ≤ k ≤ 16 -15 ≤ l ≤ 16	-11 ≤ h ≤ 12 -46 ≤ k ≤ 46 -13 ≤ l ≤ 13	
Reflections collected	17,877	71,769	
Independent reflections	5630 [R(int) = 0.0379]	7491 [R(int) = 0.1317]	
Completeness to theta	99.9%	99.9%	
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²	
Data / restraints / parameters	5630 / 0 / 307	7491 / 0 / 289	
Goodness-of-fit on F ²	1.032	1.054	
Final R indices [I > 2σ(I)]	R1 = 0.0356, wR2 = 0.0810	R1 = 0.0408, wR2 = 0.0808	
R indices (all data)	R1 = 0.0537, wR2 = 0.0899	R1 = 0.0601, wR2 = 0.0863	
Largest diff. peak and hole [e/Å ³]	1.708 and -1.827	1.973 and -1.602	

3.2. Crystallographic studies

The crystal data and structure refinement parameters for complexes **1** and **2** are collected in Table 1, while selected bond lengths and angles are listed in the Table S1 in the Supplementary Materials.

3.2.1. The anion structure in **1** and **2**

In the structures of both compounds, **1** and **2**, the anionic complex molecule [W(CN)₆(bpy)]⁻ exhibits a square antiprism geometry as shown in Fig. 1. The mean W-C distances for all six ligands

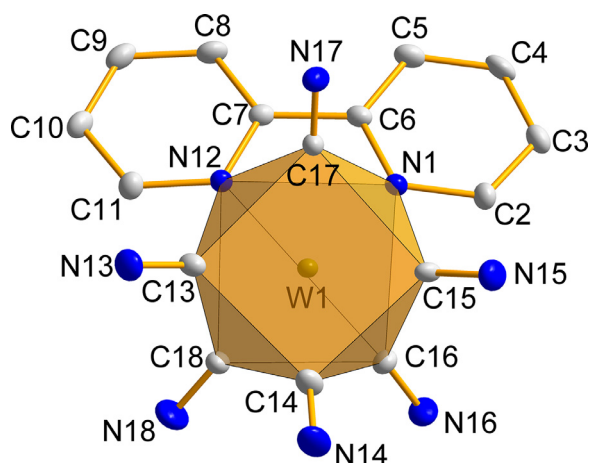


Fig. 1. Structure of an anionic complex molecule [W(CN)₆(bpy)]⁻ on the example of structure **1** with the adopted numbering scheme. The coordination environment around the tungsten atom is in the shape of a slightly distorted square antiprism. The nitrogen atoms are marked in blue and the carbon atoms in gray. All H atoms are omitted for clarity. All non-hydrogen atoms are represented at 30% probability thermal ellipsoids.

are 2.153(3) and 2.156(2) Å, for structures **1** and **2**, respectively. Based on previously published data [28], it can be concluded that there is no influence of the cation type or spatial arrangement of the structure over the W-C_{cyanido} distance. The same is true for the W-N_{cyanido} distance where the average length is 3.297(1) Å, regardless of the cation type. Also, the lengths of W-N_{bpy} interactions do not differ significantly between systems with different types of cations (compounds **1**, **2** and alkali metals) as well as between the salts of the W^{IV} and W^V analogues [24–28]. In the case of both structures of compounds **1** and **2**, three cyanido ligands (C13N13, C14N14 and C16N16 in **1** and C12N5, C11N3 C13N6 in **2**) are involved in the anionic-cationic interaction, while the other three cyanido ligands are “free”. Occurring in the structures and constituting the immediate coordination environment of the tungsten atom in [W(CN)₆(bpy)]⁻, the bidentate bipyridyl ligand (bpy) has an almost completely flat molecular geometry.

3.2.2. The cations structures

The structure of the asymmetric part of unit cell of the compound **1** is shown in Fig. 2. It consists of two anion molecules, one [W(CN)₆(bpy)]⁻ and one perchlorate ClO₄⁻, one cation Ca²⁺ and three water molecules. There are seven atoms in the immediate vicinity of the calcium cation (heptacoordinated), therefore the coordination environment around the cation adopts the geometry of a slightly distorted capped trigonal prism (Fig. 3) in which the three cyanido nitrogen atoms N13, N14, N16 and the oxygen atom O2 of the water molecule occupy four vertices (equatorial positions) of the base of the complex. The remaining three vertices are occupied by three oxygen atoms, including two from water molecules (O1 and O3) and one from the perchlorate anion. In other words, three nitrogen atoms and three oxygen atoms, O2, O3, O5, form the prism, while O1 covers the rectangular base of the prism. It should be emphasized that mentioned geometry of coordination of the calcium atom in systems containing cyanide

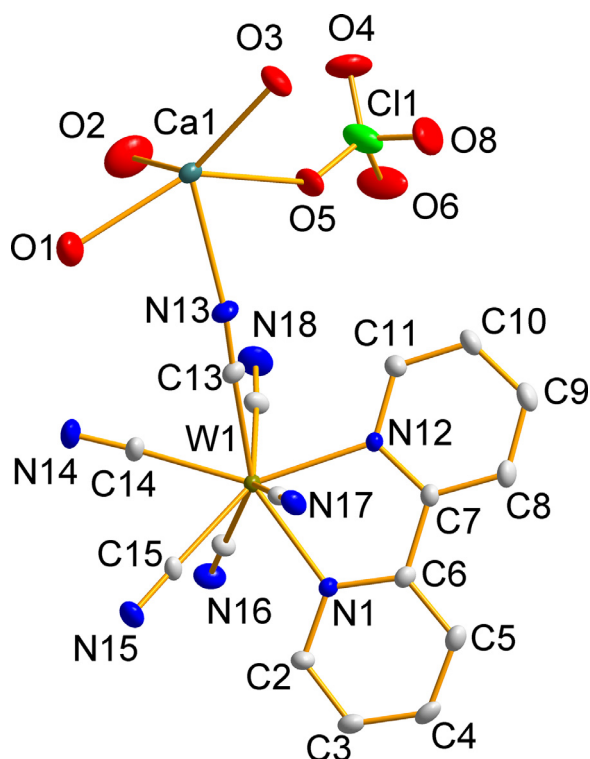


Fig. 2. The asymmetric part of the cell unit of the compound **1** with the adopted numbering scheme. All hydrogen atoms of the bipyridyl ligand are omitted for clarity. All non-hydrogen atoms are represented at 30% probability thermal ellipsoids.

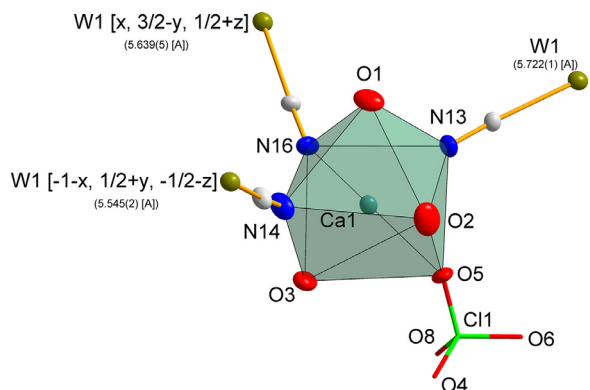


Fig. 3. The geometry of the coordination environment of the calcium cation in compound **1**, along with the metallic environment. W-Ca distances in angstroms are given in parentheses.

bridges is extremely rare, and so far, to the best of our knowledge, has been observed only once by Perruchas et al. [37].

The mean Ca-N and Ca-O distances are 2.482(6) and 2.432(5) Å, respectively. The length of the Ca-N bonds is similar to the values reported in the literature for similar systems [37] or, for example, for calcium carbazole derivatives [38]. Note that the oxygen atom O2 is clearly closer to the Ca(II) ion (2.379(6) Å) than the two oxygen atoms, O3 and O5, forming one edge of the trigonal prism (2.418(5) and 2.454(7) Å) (Table S1), which is probably due to steric factors. Each molecule of the anion $[W(CN)_6(bpy)]^-$ is connected to three calcium cations through three cyanido ligands forming typical “end-on” type bridges. In the intermediate vicinity of the calcium atom there are three symmetrically dependent tungsten atoms, with an average distance of 5.635(3) Å (Fig. 3). The perchlorate anion only performs the functions of coordinating the calcium cation and does not participate in other interactions.

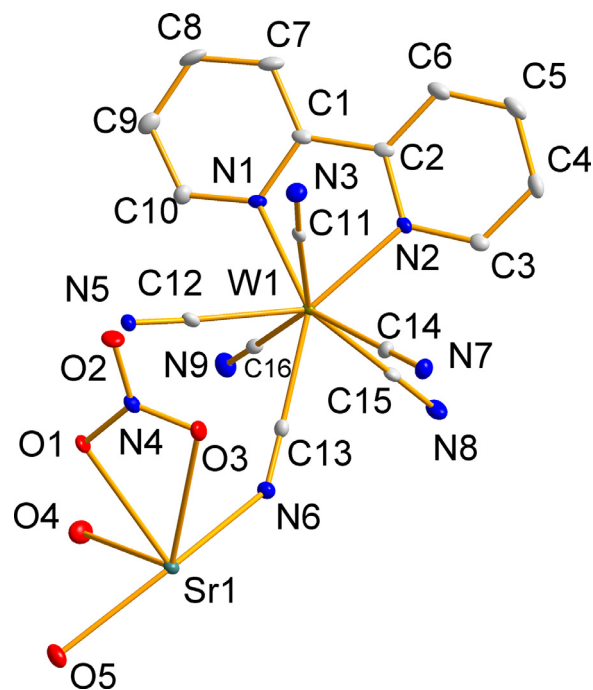


Fig. 4. The asymmetric part of the cell unit of the compound **2** with the adopted numbering scheme. For clarity, all hydrogen atoms were omitted. Tungsten atoms and their immediate coordination environment, as well as water molecules represented with a 30% probability of a thermal ellipsoid.

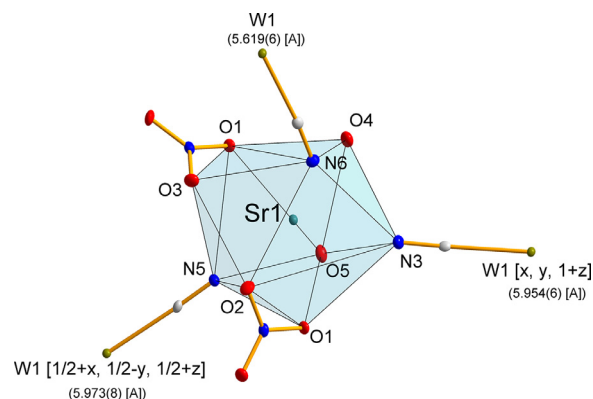


Fig. 5. The geometry of the coordination environment of the strontium cation in compound **2**, along with the metallic environment. W-Sr distances in angstroms are given in parentheses.

The asymmetric part of the unit cell of compound **2** is shown in Fig. 4 and contains anion molecules $[W(CN)_6(bpy)]^-$ and NO_3^- , a strontium cation Sr^{2+} and two water molecules represented by oxygen atoms O4 and O5. Each anion $[W(CN)_6(bpy)]^-$ is linked to three strontium cations by “end-on” type bridges formed by cyanido ligands (Fig. 5). The Sr-N bond lengths assume similar values and are 2.658(4) Å, 2.694(3) Å and 2.708(4) Å for Sr1-N3 [x,y,z + 1], Sr1-N5 [x + 1/2, -y + 1/2, z + 1/2] and Sr1-N6 bonds, respectively. Two of the three angles between the Sr-N≡C bonds are close to 170°. These values are equal to 172.6° for the C11-N3-Sr1 [x,y,z-1] angle and 170.6° for the C12-N5-Sr1 [x-1/2, -y + 1/2, z-1/2] angle, while the third C13-N6-Sr1 angle has a much lower value of 140.8°. The strongest bond between the cyanido bridge and the strontium cation occurs for Sr1-N3, for which the Sr-N≡C angle is closest to the linear one. Apart from the previously mentioned three CN⁻ ligands, the strontium cation is bound to two water molecules, O4, O5 and two NO₃⁻ ions (Fig. 5) which coordinate

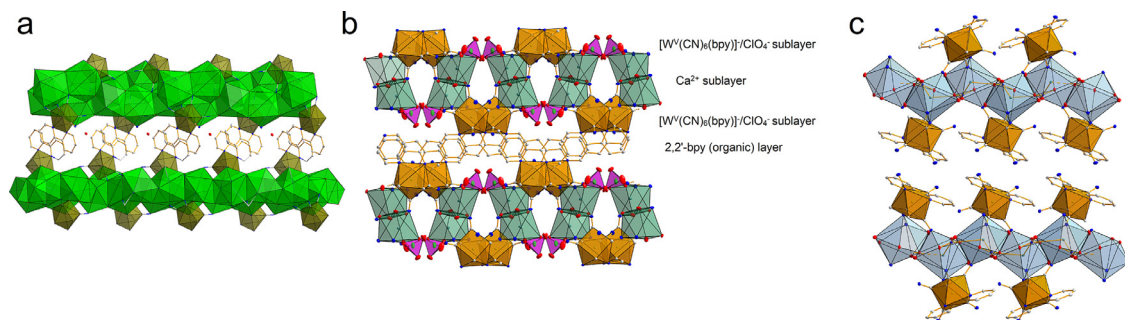


Fig. 6. (a) A typical packing pattern for structures for W^{IV} with alkali metals (Rb^+) view toward [001] direction [26]. (b) The packing observed in the structure of compound **1** visible in the [001] direction, a clear analogy to the systems based on $W(IV)$ and alkali metals is visible. (c) The packing observed in the structure of compound **2** seen towards [001]. All non-hydrogen atoms are represented at 30% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. The following colors of coordination polyhedra were used: bright green - Rb^+ , orange - W^V (Fig. 6b and c) or W^{IV} (Fig. 6a), pink - ClO_4^- , light green - Ca^{2+} , light blue - Sr^{2+} .

through two O atoms. The coordination number Sr^{2+} is 9 and it adopts the geometry of a capped square antiprism. Each NO_3^- ion is involved in the formation of bridges between the two Sr^{2+} cations, so it simultaneously binds with all three oxygen atoms, one of them being bonded to both cations. The bond lengths of $Sr-O_{NO_3}$ are similar and are 2.676(3) Å, 2.729(3) Å, 2.758(3) Å and 2.761(3) Å for $Sr1-O1$, $Sr1-O1 [x + 1/2, -y + 1/2, z + 1/2]$, $Sr1-O2$ and $Sr1-O3$, respectively. The average bond length is 2.731 Å. The valence angles between the O-Sr-O bonds where both oxygen atoms belong to one nitrate ion (V) are nearly identical, approximately equal to 46°. In the case of coordinated water molecules, the $Sr-O_{H_2O}$ bond lengths are similar and their mean value is 2.548 Å.

3.2.3. Packing of the structures of compounds 1 and 2

Based on the analysis of the spatial structure of both tested compounds (Fig. 6), two similar ways of spatial arrangement of molecules and ions can be concluded. The structure of compound **1** is characterized by packing analogous to the previously described salts of the anion $[W^{IV}(CN)_6(bpy)]^{2-}$ with alkali metal cations (Li^+ , Na^+ , K^+ , Rb^+ , Cs^+) and thallium cation (Fig. 6a), which means that the structure **1** shows a layered system of cations and anions, with a clearly defined inorganic and organic (bpy) layer, and most importantly, which are connected by $\pi \cdots \pi$ interactions [24–27,39].

The three sublayers form an inorganic layer, the inner part of which is made of calcium cations linked by cyano bridges and water molecules. On both sides of this calcium sublayer there are sublayers made of the ClO_4^- and $[W^V(CN)_6(bpy)]^-$ anions, which hold the sublayers together via cyanido “end-on” bridging interactions. The very usual is the position of ClO_4^- anions. Typically, in other previously described systems, if additional anions (apart from $[W(CN)_6(bpy)]^{n-}$) are present, they are positioned inside the cation layer. Here, they are positioned just between tungsten anions, thus inorganic layer is composed by exclusively anions, cations (two layers) and anion sub-layers. It would be rather expected that small ClO_4^- anion will be placed between calcium cations. Anion ClO_4^- in addition to its essential coordination role, also participates in the non-classical hydrogen interaction of the C–H...O type (C3–H3...O8 $[x, -1 + y, z]$, distance $D \cdots A = 3.200(15)$ Å, angle $D-H \cdots A = 123.29(5)^\circ$, dist $H \cdots A = 2.594(15)$ Å).

The organic layer is built on the basis of 2,2'-bpy ligands, which are connected to $W(V)$ tungsten atoms in two different inorganic layers. Bpy ligands play a key role in creating interactions that stabilize the structure of the compound. The occurrence of hydrogen bonds and interactions between the delocalized electrons of the π orbitals and nitrogen atoms can be observed (Tables S2–S4). Therefore, it can be concluded that, similarly to the $W(IV)$ systems, the $\pi \cdots \pi$ interactions play a dominant role in the stabilization of the structure. An interesting fact is that in the previ-

ously published $W(V)$ systems with alkali metals, no layered packing of the structure was observed, but only a 3D layout. In the structures analogous to **1** in terms of packing [24–27], is based on the $[W^{IV}(CN)_6(bpy)]^{2-}$ anion, the structure is mainly determined by the $\pi \cdots \pi$ interactions of bpy ligands, which results in a layered packing similar to a capacitor system. Each layer has a neutral charge, so the packing of the layers is forced, not by electrostatic interactions, which are rather repulsive, as the anions occupy the surface of the layer, but by very weak intermolecular interactions, and since bpy ligands are directed to the interlayer space, the weak interactions are solely responsible for resisting and compensating for the repulsive forces between the layers, and therefore for the stability of the crystal.

The spatial structure of compound **2** is apparently similar to that in **1**, and in the previously described salts of the anion $[W^{IV}(CN)_6(bpy)]^{2-}$ with alkali cations (Li^+ , Na^+ , K^+ , Rb^+ and Cs^+) [24–27].

Fact, analyzing Fig. 6c, one can see the alternation of the characteristic inorganic and organic layers, and the inorganic layer, as in **1**, consists of three parts arranged sequentially “side by side”, of which the inner part is composed of strontium cations connected by the nitrate(V) bridges discussed earlier, and water molecules. On both outer sides of this part are tungsten atoms and cyanido ligands. However, the main structural difference between the structures of compounds **1** and **2** is due to the fact that there are no $\pi \cdots \pi$ interactions in **2** (Fig. 7). The 2,2'-bpy ligands present in the structure do not form $\pi \cdots \pi$ interactions, as is the case with **1** or the other structures already mentioned. Only the presence of hydrogen bonds and interactions between delocalized electrons of π orbitals and nitrogen atoms can be observed (Tables S2–S4). Both types of interactions are formed by N8 and N9 atoms, belonging to cyanido ligands unbound to the strontium cation.

The striking difference between packing observed in **1** and **2** is that the NO_3^- anions are now in the cation layer and the cation layer is single. Comparing packing in **1** and **2** the inorganic layer has 7.247 Å and 8.722 Å thickness, while the distance to next inorganic layer (thus organic layer thickness) is of 6.375 Å and 6.388 Å, respectively. Thus the overall thickness of both layers is 13.622 Å in **1** and 15.110 Å in **2**. This is in contrary to density of the crystals, which is higher for **2** than that of **1**. This is caused by the much denser packing in one of other direction, as shown in Fig. 6b, where two tungsten anions are very close to each other.

Another noticeable structural difference between both compounds studied and all other systems so far described and published containing both $[W^{IV}(CN)_6(bpy)]^{2-}$ and $[W^V(CN)_6(bpy)]^-$ is the fact that there are no “side-on” cyanide intermetallic bridges. This is an astonishing fact, since, based on our existing experience in this area, the presence of such interactions would be expected. Comparing the effective ionic radii by Shannon [40] of,

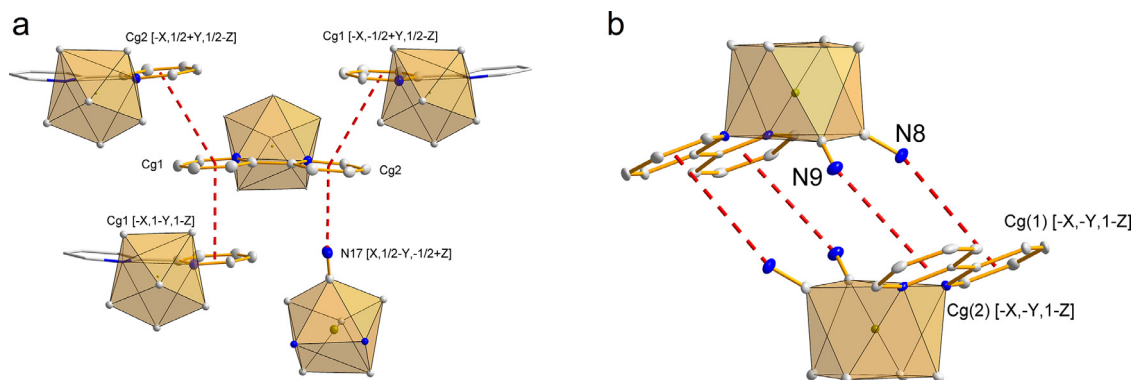


Fig. 7. (a) $\pi \cdots \pi$ and C-N $\cdots\pi$ type interactions observed in bpy layer of the structure **1**; (b) C-N $\cdots\pi$ type interactions observed in bpy layer of the structure **2**.

for example, Ca^{2+} for CN=7 1.06 Å to Na^+ with CN=5 1.14 Å (a sodium cation with a coordination of 5 is described in [28]) or Sr^{2+} (CN=9 1.31 Å) to K^+ (CN=6 1.38 Å [28]), one can see clear analogies in their lengths, and despite this fact, in compounds **1** (Ca) and **2** (Sr), the aforementioned interactions do not occur, in contrast to systems with Na and K and both $[\text{W}^{\text{IV}}(\text{CN})_6(\text{bpy})]^{2-}$ and $[\text{W}^{\text{V}}(\text{CN})_6(\text{bpy})]^-$, in which they play a fundamental structural function [24–28]. The only logical explanation for the absence of cyanide “side-on” bridges in **1** and **2**, is the fact that the Ca^{2+} and Sr^{2+} cations have a much higher charge, which also makes the charge-to-ionic radius ratio compare more favorably for Ca and Sr. In other words, the low charge of the ion, combined with a large ionic radius of cations (easy electron cloud polarizability), favors, or perhaps even forces, the occurrence of intermetallic cyanide “side-on” bridging interactions.

4. Conclusions

The very rare structures of W(V) complexes of anion formula $[\text{W}(\text{CN})_6(\text{bpy})]^-$, described here for two cations, Ca^{2+} and Sr^{2+} show that the structural packing is very sensitive on cation used, contrary to all previously described structures of W(IV) analogues with alkali metal cations. In case of both cations studied, additional anion (ClO_4^- or NO_3^-) is coordinated thus, formally cation is only 1+ charged. For calcium salt, structure resemble those of alkali metals with $\pi-\pi$ interactions within bpy molecules, located roughly perpendicular to inorganic layers, however this interaction is remarkably different from those found earlier. Moreover, anions are arranged in pairs. Even if, at first look, the strontium salt structure resembles those described earlier with layered anion-cation planes, there are no $\pi-\pi$ interaction within bpy molecules, they are arranged almost parallel to inorganic layers and the nitrogen of the cyanido ligands of anions is directed to the center of bpy plane, from adjacent inorganic layer, with very short 3.055 Å distance.

It is very unusual that the very rigid anions studied here, gave so very different structures even for very similar cations as Ca^{2+} and Sr^{2+} . Almost similar structure changes were observed previously for other two very similar cations, Zn^{2+} and Cd^{2+} , with the same W(V) anion. Studies of this intriguing system to understand the intermolecular interactions dependence on cation are in progress as $[\text{W}(\text{CN})_6(\text{bpy})]^{2-/}$ anions were found to be a very promising material for synthesis of modern molecular materials of wide applications.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Maciej Hodorowicz: Methodology, Writing – original draft, Visualization. **Monika Sternal:** Investigation, Writing – original draft. **Anna Jurowska:** Writing – original draft, Visualization. **Janusz Szklarzewicz:** Conceptualization, Methodology, Supervision, Writing – original draft.

Data availability

No data was used for the research described in the article.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.molstruc.2023.135374](https://doi.org/10.1016/j.molstruc.2023.135374).

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