

Article

Coordination Chemistry of Polynitriles, Part XI. Influence of 4,4'-Bipyridine and Solvent on the Crystal and Molecular Structures of Alkaline Earth Pentacyanocyclopentadienides

Patrick R. Nimax and Karlheinz Sünkel * 

Department of Chemistry, Ludwig Maximilians University Munich, Butenandtstr. 5-13, 81377 Munich, Germany

* Correspondence: suenk@cup.uni-muenchen.de

Abstract: The reaction of alkaline earth pentacyanocyclopentadienides with 4,4'-bipyridine in MeOH yielded undefined products of composition $[M(\text{PCC})_2(\text{Bipy})_x(\text{MeOH})_y(\text{H}_2\text{O})_z]$ ($\text{PCC} = [\text{C}_5(\text{CN})_5]^-$). Recrystallization from MeOH, EtOH, or n-BuOH gave crystals of $[\text{Mg}(\text{H}_2\text{O})_4(4,4'\text{-bipy})_2](\text{PCC})_2 \cdot 2\text{BuOH}$ (1), $[\text{Ca}(\text{H}_2\text{O})_4(4,4'\text{-bipy})_2](\text{PCC})_2 \cdot (4,4'\text{-bipy})$ (2), $[\text{Sr}(\text{MeOH})_8](\text{PCC})_2 \cdot 3(4,4'\text{-bipy})$ (3), $[\text{Sr}_2(\text{H}_2\text{O})_4(\text{BuOH})_4(\text{PCC})_2(\mu\text{-PCC})_2(\mu\text{-}4,4'\text{-bipy})] \cdot 4(4,4'\text{-bipy}) \cdot 0.29(\text{BuOH})$ (4), $[\text{Ba}_3(\text{H}_2\text{O})_4(\text{EtOH})_{10}(\text{PCC})_2(\mu\text{-PCC})_2(\mu\text{-}4,4'\text{-bipy})_2(4,4'\text{-bipy})](\text{PCC})_2 \cdot 3(4,4'\text{-bipy}) \cdot 2\text{EtOH} \cdot \text{H}_2\text{O}$ (5) and $[\text{Ba}_4(\text{H}_2\text{O})_8(\text{BuOH})_6(\text{PCC})_2(\mu\text{-PCC})_6(4,4'\text{-bipy})_6] \cdot 3(4,4'\text{-bipy})$ (6). 4,4'-Bipyridine functions either as monodentate or bidentate ligand and is present in all cases except for 2 as lattice guest. While in compounds 1 and 2 only water is present as O-donor, the alcohol coordinates in the other compounds either exclusively (3) or together with water (4–6). The pentacyanocyclopentadienide does not coordinate in 1–3, but is present as mono-, bi-, or tridentate ligand in 4–6. In all compounds, a more or less complicated interplay of hydrogen bridges and π – π stacking is observed.

Keywords: polynitrile anions; 4,4'-bipyridine; pentacyanocyclopentadienide; alkaline-earth metal; coordination polymer; hydrogen bonding; π – π interactions



Citation: Nimax, P.R.; Sünkel, K. Coordination Chemistry of Polynitriles, Part XI. Influence of 4,4'-Bipyridine and Solvent on the Crystal and Molecular Structures of Alkaline Earth

Pentacyanocyclopentadienides.

Chemistry **2022**, *4*, 1524–1545.

<https://doi.org/10.3390/chemistry4040101>

chemistry4040101

Academic Editor: Katharina Fromm

Received: 16 October 2022

Accepted: 7 November 2022

Published: 10 November 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Crystal engineering, since its beginnings around 30 years ago [1], is still an exponentially growing field of solid-state research. While originally developed for organic chemistry, it has nowadays become an invaluable tool in inorganic chemistry [2]. There were two apparently contradictory synthetic goals: the creation of “porous” structures, mainly porous coordination networks, often called “metal-organic frameworks” (MOFs) on the one hand [3], and the intentional directed synthesis of cocrystals [4]. One of the major approaches used for the preparation of MOFs was the “node and linker (spacer)” design developed originally by Wells in 1954 and systematically used by the Robson group starting from 1989 [5,6]. One of the most promising linkers besides the dicarboxylic acids was for transition metals 4,4'-bipyridine (also often called 4,4'-bipyridyl) [7,8]. While indeed this molecule formed numerous linear bridges between pairs of metals, it was soon found out, that also monodentate coordination was possible, quite often combined with additional involvement of hydrogen bonding and π – π interactions [9,10]. A higher level of designing MOFs was reached by the introduction of “the concept of mixed organic ligands” [11]. As mentioned before, most of the metals used as “nodes” in the networks were transition metals. However, there are also examples of “coordination polymer networks with s-block metal ions”, quite often with mixed-ligand systems, also including 4,4'-bipyridine [12]. While most of the anionic bridging ligands used in these networks are of the di- or polycarboxylate type, there is also a small sub-group that uses polynitrile anions as ligands [13], however, so far only with transition metals. Our group is investigating the coordination chemistry of polycyanocyclopentadienides for quite a while [14]. Since we found quite interesting coordination polymers with the alkaline earth metal ions and

the $[C_5(CN)_5]^-$ ("PCC") anion [15], we regarded it worthwhile to look at the influence of adding 4,4'-bipyridine to these systems.

2. Materials and Methods

All solvents were obtained commercially (analytical grade) and were used as such. The chlorides $MgCl_2 \cdot 6H_2O$, $CaCl_2$, $SrCl_2 \cdot 6H_2O$, and $BaCl_2 \cdot 2H_2O$ were also obtained commercially and were stored in a desiccator prior use. The starting complexes $[Mg(PCC)_2(MeOH)(H_2O)_6]$, $[Ca(PCC)_2(H_2O)_6]$, $[Sr(PCC)_2(MeOH)_{0.5}(H_2O)_2]$, and $[Ba(PCC)_2(H_2O)_3]$ were obtained as described by us previously [15].

Synthesis of $[Ag(PCC)(4,4'-bipy)(H_2O)_{1.25}]$

A solution of $AgPCC$ (149 mg, 0.50 mmol) in MeOH (50 mL) was treated with a solution of 4,4'-bipyridine (77 mg, 0.5 mmol) in MeOH (5 mL) and heated to 60 °C for five hours. After filtration the solution was evaporated nearly to dryness, and the title compound was precipitated as a yellow powder by addition of CH_2Cl_2 , which was dried in vacuo. Yield: 200 mg (0.42 mmol, 84%).

MS: (FAB+): $m/z = 157.0$ $[C_{10}H_8N_2]$; (FAB-): $m/z = 191.3$ $[C_{10}N_5^-]$

EA: $AgC_{20}H_{10.5}N_7O_{1.25}$ $[M = 476.65]$: calc/ found: C: 50.39/ 51.10; H: 2.20/ 2.31; N: 20.56/ 20.94%.

General procedures for the syntheses of $[M(PCC)_2(4,4'-bipy)_x(MeOH)_y(H_2O)_z]$

Procedure A:

A suspension of $[Ag(PCC)(4,4'-bipy)(H_2O)_{1.25}]$ in MeOH (20 mL) was treated with a solution of the alkaline earth dichloride in MeOH (20 mL) with exclusion of light. Stirring was continued for three days at room temperature. The obtained suspension was filtered and the filtrate concentrated in vacuo until a further precipitate formed. After renewed filtration, the solution was evaporated in vacuo to give a white powder. The residue was taken up in an alcohol and allowed to stand in a small Erlenmeyer flask either in a refrigerator (MeOH, EtOH) or at room temperature (n-BuOH) until crystals formed.

Details:

- $MgCl_2 \cdot 6H_2O$ (51 mg, 250 μ mol) and $[Ag(PCC)(4,4'-bipy)(H_2O)_{1.25}]$ (235 mg, 556 μ mol)
Product data: 1H -NMR (270 MHz, CD_3OD): $\delta = 8.69$ (m, 4H), 7.83 (m, 4H); $^{13}C\{^1H\}$ (69 MHz, CD_3OD): $\delta = 151.2$, 147.4, 123.2 (4,4'-bipy), 114.0, 103.4 (PCC).
- $CaCl_2$ (28 mg, 250 μ mol) and $[Ag(PCC)(4,4'-bipy)(H_2O)_{1.25}]$ (235 mg, 556 μ mol)
Product data: 1H -NMR (270 MHz, CD_3OD): $\delta = 8.69$ (m, 4H), 7.83 (m, 4H); $^{13}C\{^1H\}$ (69 MHz, CD_3OD): $\delta = 151.2$, 147.4, 123.2 (4,4'-bipy), 114.0, 103.4 (PCC).
- $SrCl_2 \cdot 6H_2O$ (49 mg, 185 μ mol) and $[Ag(PCC)(4,4'-bipy)(H_2O)_{1.25}]$ (177 mg, 371 μ mol)
- $BaCl_2 \cdot 2H_2O$ (61 mg, 250 μ mol) and $[Ag(PCC)(4,4'-bipy)(H_2O)_{1.25}]$ (235 mg, 556 μ mol)
Product data: 1H -NMR (270 MHz, CD_3OD): $\delta = 8.69$ (m, 4H), 7.83 (m, 4H); $^{13}C\{^1H\}$ (69 MHz, CD_3OD): $\delta = 151.2$, 147.4, 123.2 (4,4'-bipy), 113.9, 103.4 (PCC).

Procedure B:

A solution of the pentacyanocyclopentadienide complex $[M(PCC)_2(MeOH)_x(H_2O)_y]$ in MeOH was treated with an excess of 4,4'-bipyridine with stirring for 2 h. The obtained solution was concentrated to a volume of ca. 1 mL. Addition of CH_2Cl_2 produced a white precipitate, which was isolated by filtration and dried in vacuo. The residue was taken up in an alcohol and allowed to stand in a small Erlenmeyer flask either in a refrigerator (MeOH, EtOH) or at room temperature (n-BuOH) until crystals formed.

Details

- $[Mg(PCC)_2(MeOH)(H_2O)_6]$: (37 mg, 67 μ mol) and 4,4'-bipy (14 mg, 90 μ mol)
Product Data: MS (FAB+): $m/z = 157.0$ ($C_{10}H_8N_2$); (FAB-): $m/z = 190.3$ ($C_{10}N_5$)
- $[Ca(PCC)_2(H_2O)_6]$: (16 mg, 30 μ mol) and 4,4'-bipy (12 mg, 77 μ mol)
Product Data: MS (FAB+): $m/z = 157.0$ ($C_{10}H_8N_2$); (FAB-): $m/z = 190.3$ ($C_{10}N_5$)

- $[\text{Sr}(\text{PCC})_2(\text{MeOH})_{0.5}(\text{H}_2\text{O})_2]$: [35 mg, 67 μmol] and 4,4'-bipy (29 mg, 186 μmol)
Product Data: MS (FAB+): $m/z = 157.0$ ($\text{C}_{10}\text{H}_8\text{N}_2$); (FAB-): $m/z = 190.3$ (C_{10}N_5)
- $[\text{Ba}(\text{PCC})_2(\text{H}_2\text{O})_3]$: (15 mg, 27 μmol) and 4,4'-bipy (15 mg, 96 μmol).
Product Data: MS (FAB+): $m/z = 157.0$ ($\text{C}_{10}\text{H}_8\text{N}_2$); (FAB-): $m/z = 190.3$ (C_{10}N_5)

Elemental analyses were obtained for all the crude reaction products, but their results turned out to be useless. Although it was possible to calculate “fitting” formulae of the type $\text{M}(\text{PCC})_2 \cdot x [4,4'\text{-bipy}] \cdot y \text{MeOH} \cdot z \text{H}_2\text{O}$, their results did not allow to say anything, if the products were pure or just mixtures. In particular, these algebraic results usually did not show any correlations with the stoichiometries of the obtained crystal structures: For example, the crude product obtained from the strontium reaction according to procedure A was analyzed as $[\text{Sr}(\text{H}_2\text{O})_5(\text{MeOH})(\text{PCC})_2(4,4'\text{-bipy})_2]$, while the product obtained according to procedure B was analyzed as $[\text{Sr}(\text{MeOH})_8(\text{PCC})_2(4,4'\text{-bipy})_3]$, which is the composition of the crystals **3** described here later (as can be derived from the reaction stoichiometries, the Sr–(4,4'-bipy) ratio of the elemental analysis corresponds to the reaction stoichiometry). The crystals used for the structure determination, however, came from procedure A!

Most of the crystals described here came from reactions according to procedure A (**2**, **3**, **4**, **6**). Unfortunately, the amount of obtained single-crystalline material was not sufficient to obtain any further characterization.

Crystal Structure Determinations:

All the crude products obtained from the before-mentioned reactions were recrystallized from MeOH, EtOH, and n-BuOH. The crystals obtained from the Mg compound in MeOH had the approximate composition $[\text{Mg}(\text{PCC})_2(\text{MeOH})_6(4,4'\text{-bipy})]$, as could be shown by the obtained structure solution. The 4,4'-bipyridine apparently was disordered over three positions, which could not be resolved. Only the crystals **1** obtained from BuOH were of sufficient quality to allow for full refinement. With the Ca compound only the crystals **2** obtained from MeOH were of X-ray quality. The Sr compound yielded from MeOH and BuOH were X-ray quality crystals **3** and **4** that also allowed full refinement. Recrystallization of the Ba product gave X-ray quality crystals **5** and **6** from EtOH and BuOH, respectively. Recrystallization of the Sr compound from EtOH and of the Ba compound from MeOH did not give single-crystalline material. All crystals were measured on a BRUKER D8VENTURE system. The experimental details of the structure determinations are collected in Table S3 of the Supporting Information. The software package WINGX [16] was used for structure solution (SHELXT, [17], refinement (SHELXL 2018/3, [18]), evaluation (PLATON, [19]), and graphical representation (ORTEP3 and MERCURY [16]). Carbon-bound hydrogen atoms were treated with a riding model, using the AFIX command of SHELXL. The positions of alcohol and water hydrogen atoms were determined using the program subroutine CALC-OH. The found positions were either refined using SHELX restraints, or were fixed, when refinement was not possible. In the following, some remarks are given on the individual crystal structure determinations:

- Compound **1**: Structure solution with SHELXS. Refinement with omission of two low-angle reflections.
- Compound **2**: Structure solution with SHELXS. The crystal turned out to be a racemic twin. Refinement was performed with omission of six low-angle reflections and using the TWIN card with a final BASF value of 0.45459. It was also necessary to restrain the water molecules (O–H and H–H distances). When applying the program subroutine ADDSYM of PLATON, a non-crystallographic inversion center was detected. Refinement in a higher symmetric spacegroup was, however, not possible.
- Compound **3**: Structure solution with SIR97. Although there was some indication of twinning, the results of the twin-search routine of PLATON were not conclusive. Instead, a rather large number (16) of low-angle reflections was omitted from the refinement.
- Compound **4**: Structure solution with DIRDIF. PLATON analysis showed the presence of 4.7% solvent accessible voids, and actually it was possible to locate a disordered

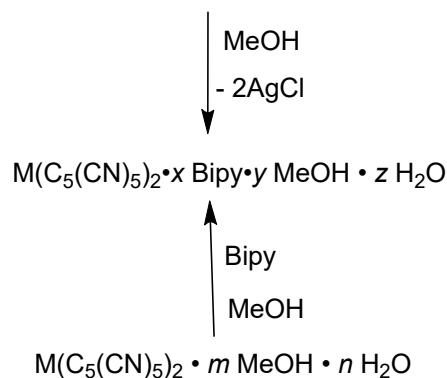
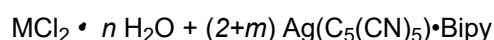
butanol molecule with low occupancy. Refinement with omission of six low-angle reflections. It was also necessary to restrain the water molecules (O–H and H–H distances) and the disordered solvent molecule.

- **Compound 5:** Structure solution with SHELXT. The crystal turned out to be a racemic twin. Refinement was performed with SHELXL 2018/3 with omission of 22 low-angle reflections and using the TWIN card with a final BASF value of 0.34643. Since there was severe disorder within the ethanol molecules, a large number of restraints had to be applied on them.
- **Compound 6:** Structure solution with SIR97. Refinement with omission of ten low-angle reflections. Since there was severe disorder within two butanol molecules, a large number of restraints had to be applied on them.

3. Results

3.1. Synthesis

We applied two different synthetic approaches (Scheme 1). Either a metal dichloride (hydrated or anhydrous) was treated with an excess of the preformed silver bipyridine pentacyanocyclopentadienide (2.22 equivalents for Mg, Ca, Ba, or 2.00 equivalents for Sr) or the preformed alkaline earth bis-pentacyanocyclopentadienide solvate was treated in methanol solution with an excess of 4,4'-bipyridine (1.34 equiv. for Mg, 2.57 equiv. for Ca, 2.78 equiv. for Sr and 3.56 equiv. for Ba). The crude products obtained after filtration and evaporation always contained water, MeOH, and “free” 4,4'-bipyridine and were therefore taken up in the minimum amount of MeOH, EtOH, and *n*-BuOH for recrystallization. When the first crystals appeared, they were placed on an X-ray diffractometer and a data collection was started.



Scheme 1. Synthetic approaches for the alkaline earth—4,4'-bipyridine-pentacyanocyclopentadienides. “Bipy” stands for 4,4'-bipyridine.

3.2. Crystal and Molecular Structures

It should be noted here that reactions of MI_2 ($\text{M} = \text{Mg}, \text{Sr}, \text{Ba}$) with 4,4'-bipy in either MeOH ($\text{M} = \text{Mg}$) or *n*-PrOH were reported to yield crystals of *cis*- $[\text{Mg}(\text{H}_2\text{O})_4(4,4'\text{-bipy})_2]\text{I}_2 \cdot (4,4'\text{-bipy})$, and $[\text{MI}_2(\text{n-PrOH})_2(4,4'\text{-bipy})_{3/2}] \cdot (4,4'\text{-bipy})$ ($\text{M} = \text{Sr}, \text{Ba}$) [20,21].

3.2.1. Magnesium Pentacyanocyclopentadienides

The crystals obtained from *n*-BuOH turned out to be $[\text{Mg}(\text{H}_2\text{O})_4(4,4'\text{-bipy})_2](\text{PCC})_2 \cdot 2\text{BuOH}$ (**1**) and were of sufficient quality for full refinement and are therefore discussed in the following.

Compound **1** crystallizes in the monoclinic space group $\text{C2}/c$ with half a formula unit in the asymmetric unit. Figure 1 shows an ORTEP3 representation of the asymmetric unit, Figure 2 the full coordination sphere of the metal ion together with all hydrogen bonds involving the coordinated water molecules. The Mg^{2+} ion resides on an inversion center

and is coordinated to four water molecules and two terminal 4,4'-bipyridine ligands. Due to this inversion center the 4,4'-bipy ligands are in mutual *trans* orientation, in contrast to the *cis*-orientation in the above-mentioned MgI_2 complex. Important bond parameters are collected in Table 1.

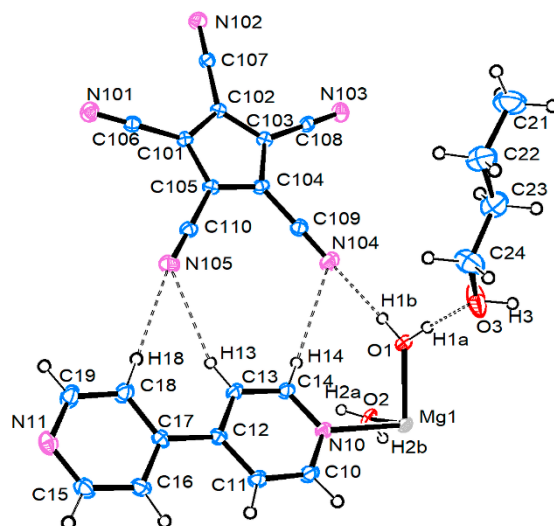


Figure 1. ORTEP3 representation of the asymmetric unit of compound 1. Thermal ellipsoids are drawn at the 30% probability level.

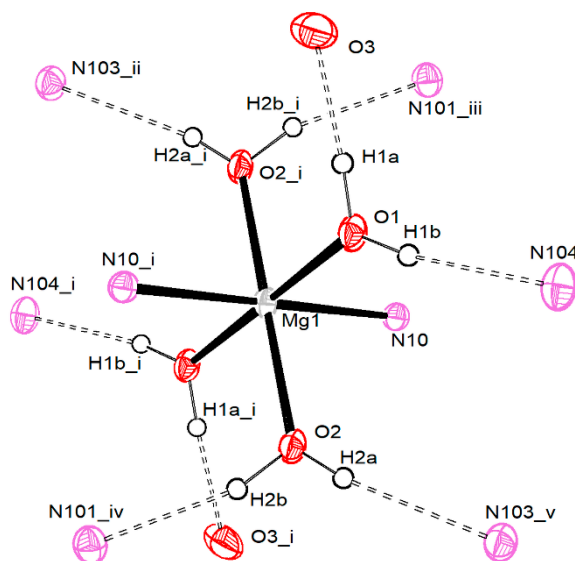


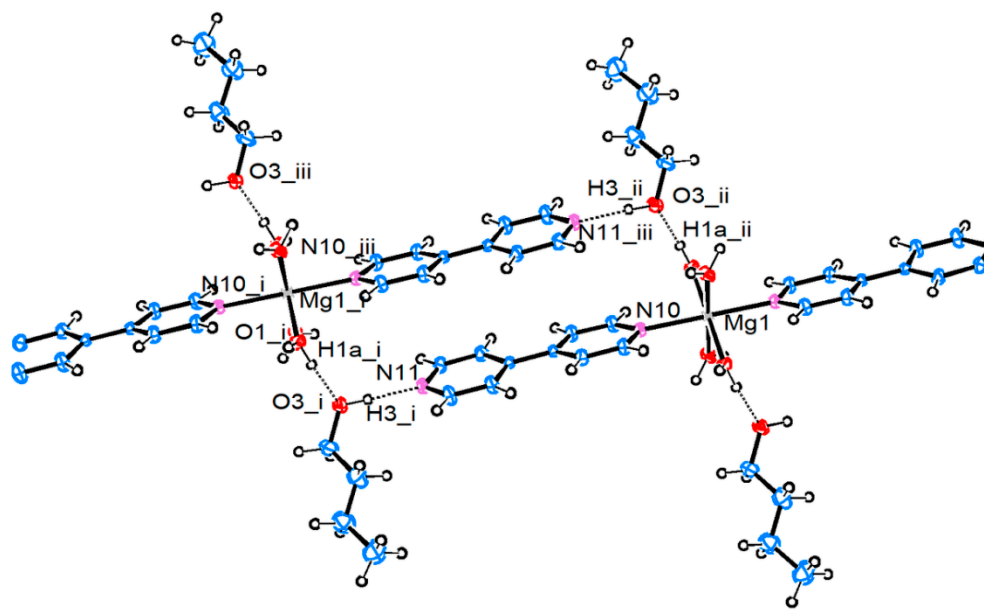
Figure 2. The coordination sphere of Mg^{2+} together with the hydrogen bonds involving water molecules.

The two halves of the 4,4'-bipy ligand are nearly coplanar (interplanar angle 6°). Water oxygen O1 (and its inversion related counterpart as well) donates hydrogen bonds to the oxygen atom O3 of a lattice butanol molecule and cyano nitrogen N104 of the PCC anion, while water oxygen O2 donates two hydrogen bonds to cyano nitrogens N101 and N103 from two different PCC anions. The cyano nitrogens N105 and N102 accept three C-H hydrogen bonds from the bipyridine ligand (H13, H18, and H16, respectively). Thus, all the cyano groups are involved in hydrogen bonds. When this structure is compared to the one of $[\text{Mg}(\text{H}_2\text{O})_6](\text{PCC})_2$, it becomes clear that 4,4' bipyridine is a better ligand for Mg^{2+} than PCC and has comparable ligand strength with water.

Table 1. Important bond lengths [Å] and angles [°] of compounds **1** and **2**.

Compound 1			
Mg1–O1	2.030 (2)	N10–Mg1–N10'	180
Mg1–O2	2.060 (2)	C11–C12–C17–C16	5.9 (4)
Mg1–N10	2.224 (2)	Mg1–N10 ... C12	178
C12–C17	1.490 (4)		
Compound 2			
Ca1–O1	2.322 (3)	C13–C18	1.484 (6)
Ca1–O2	2.318 (3)	C23–C28	1.485 (6)
Ca1–O3	2.329 (3)	N1–Ca1–N3	177.70 (12)
Ca1–O4	2.325 (3)	Ca1–N1 ... C3	176
Ca1–N1	2.516 (4)	Ca1–N3 ... C13	176
Ca1–N3	2.490 (4)	C2–C3–C8–C9	17.2 (6)
C3–C8	1.499 (6)	C12–C13–C18–C19	−15.0 (6)
		C22–C23–C28–C29	−27.8 (7)

While one of the bipyridine nitrogen atoms coordinates to the Mg ion, the other accepts a hydrogen bond from a butanol proton of a neighboring molecule, thus forming a dimeric substructure (Figure 3).

**Figure 3.** The dimeric substructure in the crystal of compound **1**.

The centroids of the symmetry-related 4,4'-bipy ligands are 3.980(2) Å apart, with a perpendicular distance of 3.521(1) Å, and one can therefore postulate a very weak π – π interaction. With all the mentioned weak intermolecular interactions in mind, a short look at the packing diagram seems appropriate (Figure 4). As can be seen, compound **1** forms a layer structure consisting of the MgO4N2 and [PCC] units, that are connected via hydrogen bonds within and between the layers and butanol molecules in-between. Tables S1 and S2 of the Supporting Information collect all the hydrogen bond parameters.

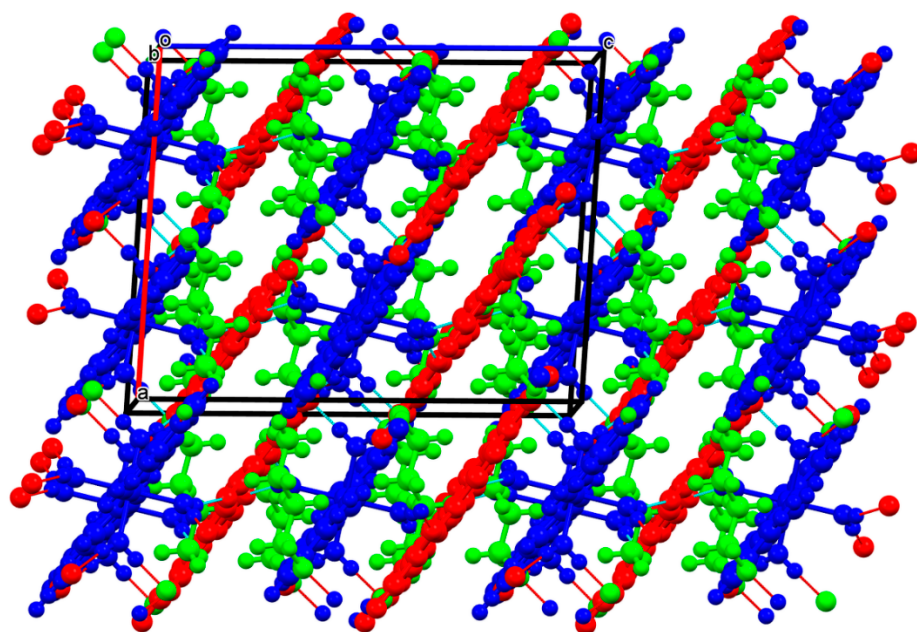


Figure 4. Packing diagram of compound 1, watched along *b*. Color code: dark blue: the $[\text{Mg}(\text{H}_2\text{O})_4(4,4'\text{-bipy})_2]$ unit; red: the cyclopentadienide anions; green: the butanol molecules.

3.2.2. Calcium Pentacyanocyclopentadienides

Only the recrystallization from methanol yielded crystalline material. Compound 2, $[\text{Ca}(\text{H}_2\text{O})_4(4,4'\text{-bipy})_2](\text{PCC})_2 \cdot (4,4'\text{-bipy})$, crystallized in the monoclinic space group $P2_1$ with one molecule in the asymmetric unit (Figure 5). Two bipyridine molecules are coordinated in relative trans position via only one N atom each; however, donating a total of 4 C–H hydrogen bonds to two coordinated water molecules. A third 4,4'-bipy molecule functions as lattice guest, acting as hydrogen bond acceptor toward one coordinated water molecule. Both anions are not coordinated. The coordinated bipyridines are less twisted (interplanar angles $17.6(2)$ and $14.8(2)^\circ$) than the lattice 4,4'-bipy (interplanar angle $27.0(3)^\circ$). Presumably it is this latter torsion that prevents the local centrosymmetry at Ca to propagate through the whole crystal: O2 hydrogen-bonds to a translation-generated 4,4'-bipy nitrogen N5, which is approximately inversion-related to the N6 atom shown in Figure 5, however, the carbon atoms C21'–C25' are not inversion related to C26–C30.

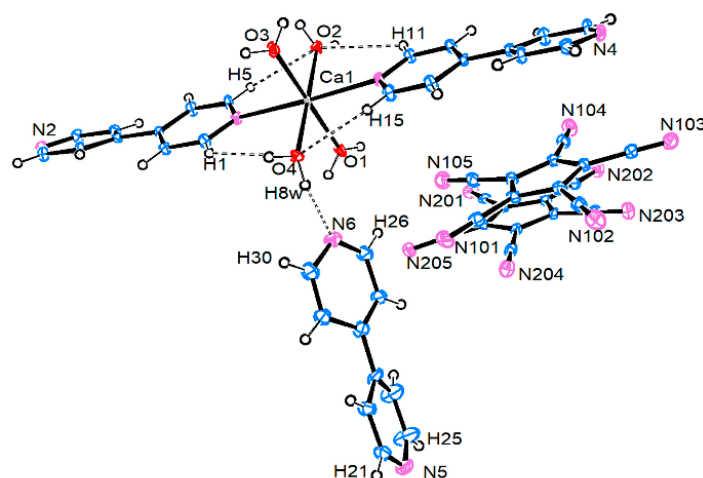


Figure 5. The asymmetric unit of compound 2. Thermal ellipsoids at the 30% probability level.

The coordination sphere around the Ca^{2+} ion resembles fully the situation in compound 1 (Figure 6). All water molecules donate both hydrogen atoms for hydrogen bonds to

nitrogen atoms. One H atom each is used for interaction with an uncoordinated bipyridine nitrogen (N2, N4, N5, N6), and the other one interacts with a nitrile nitrogen (N101, N103, N203, N205). Important bond parameters are collected in Table 1.

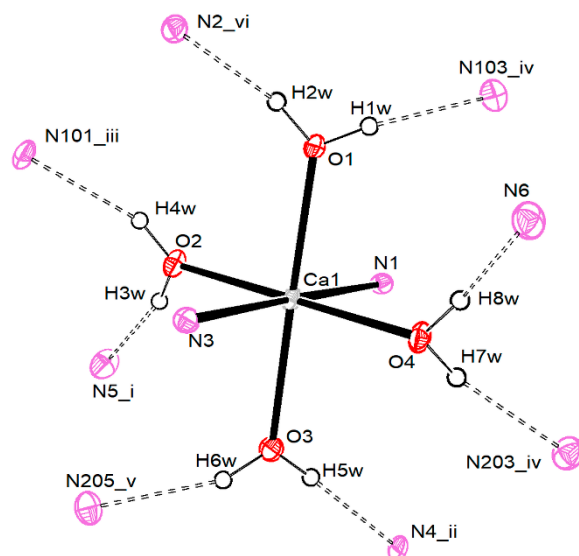


Figure 6. The coordination sphere around Ca^{2+} in compound **2**, with all the donated hydrogen bonds.

Thus, in contrast to compound **1**, each PCC anion uses only two of its nitrile groups as hydrogen bond acceptors (Figure S1). For understanding the packing pattern, it is better to look first at the situation without the anions. The left side of Figure 7 shows the (modified) packing watched along the crystallographic *a* axis, while the right side displays the view along the crystallographic *b* axis.

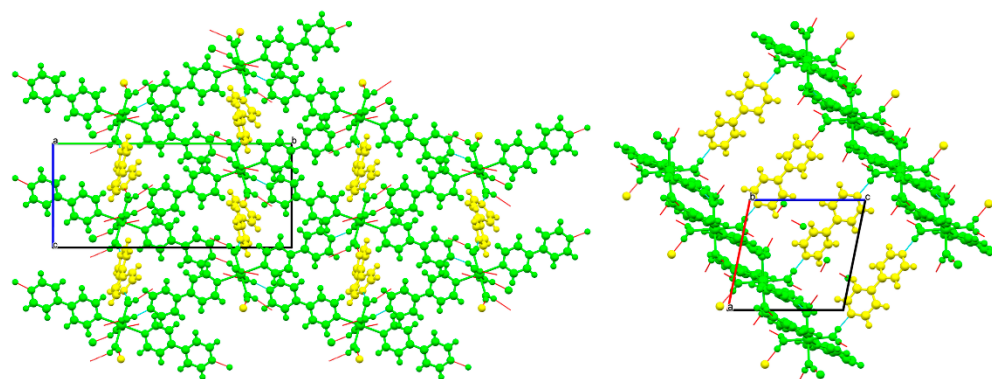


Figure 7. Packing diagrams of compound **2** (anions omitted) watched along *a* (left) and *b* (right). Color coding: green: the $[\text{Ca}(\text{H}_2\text{O})_4(4,4'\text{-bipy})_2]$ cations; yellow: the lattice bipyridines.

The cations form polymeric chains along both *bc* diagonals as well as one *ac* diagonal and are connected along the other *ac* diagonal with the lattice bipyridines. When the PCC anions are also considered, an even more complicated picture arises (Figure 8). The anions π -stack on top of the coordinated 4,4'-bipy ligands in the way that orthogonal C–N ... centroid interactions arise (C107–N101 ... CT2, C111–N105 ... CT3, C207–N202 ... CT1 and C208–N203 ... CT4, where CT*n* is the centroid of the pyridine ring containing nitrogen atom *Nn*, have distances of 3.44–3.54 Å and angles of 83–91°).

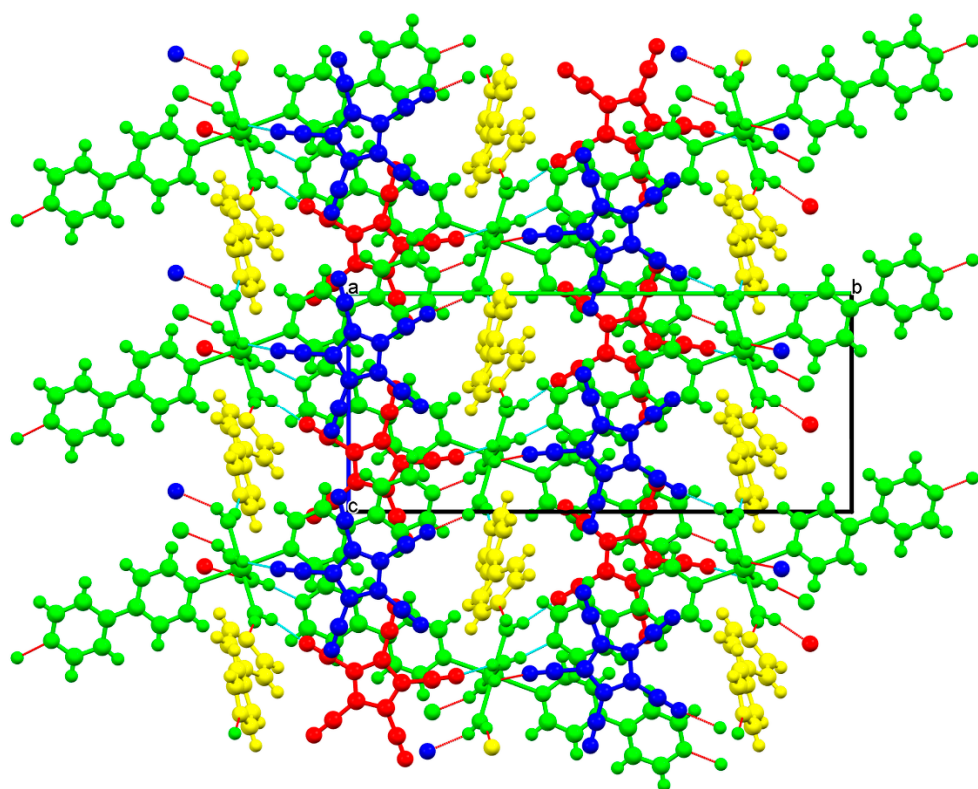


Figure 8. Complete packing diagram of compound 2, watched along *a*. Color coding: green and yellow: see Figure 7; red and blue: the two independent anions.

The parameters of the hydrogen bonds are collected in Tables S1 and S2.

3.2.3. Strontium Pentacyanocyclopentadienides

Crystals could be obtained from MeOH and from *n*-BuOH. The former yielded compound 3, $[\text{Sr}(\text{MeOH})_8](\text{PCC})_2 \cdot 3(4,4'\text{-bipy})$, while the latter produced compound 4, $[\text{Sr}_2(\text{H}_2\text{O})_4(\text{BuOH})_4(\text{PCC})_2(\mu\text{-PCC})_2(\mu\text{-}4,4'\text{-bipy})] \cdot 4(4,4'\text{-bipy}) \cdot 0.29(\text{BuOH})$.

Compound 3 crystallizes in the monoclinic space group $P2_1/c$ with two formula units in the asymmetric unit (Figure 9). The Sr^{2+} ions are eight-fold coordinated exclusively by MeOH ligands. Both anions and all 4,4'-bipy molecules are uncoordinated, but take part in hydrogen bonding. The first and second coordination spheres of both Sr^{2+} ions are very similar. In both cations, six methanol molecules donate hydrogen bonds to six 4,4'-bipy nitrogen atoms each, and two donate hydrogen bonds to two cyano nitrogens of four different anions (Figure 10).

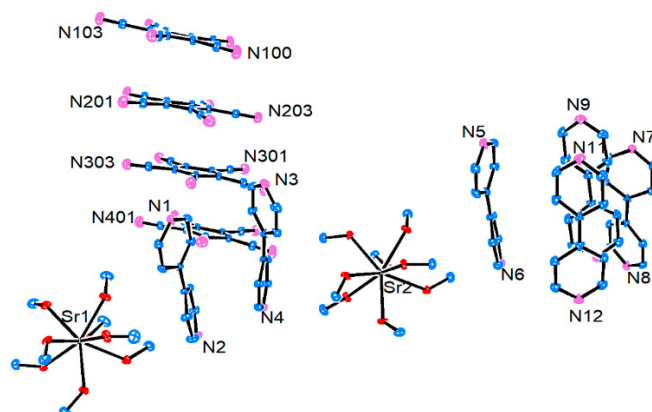


Figure 9. The asymmetric unit of compound 3. Thermal ellipsoids are drawn at the 30% probability level.

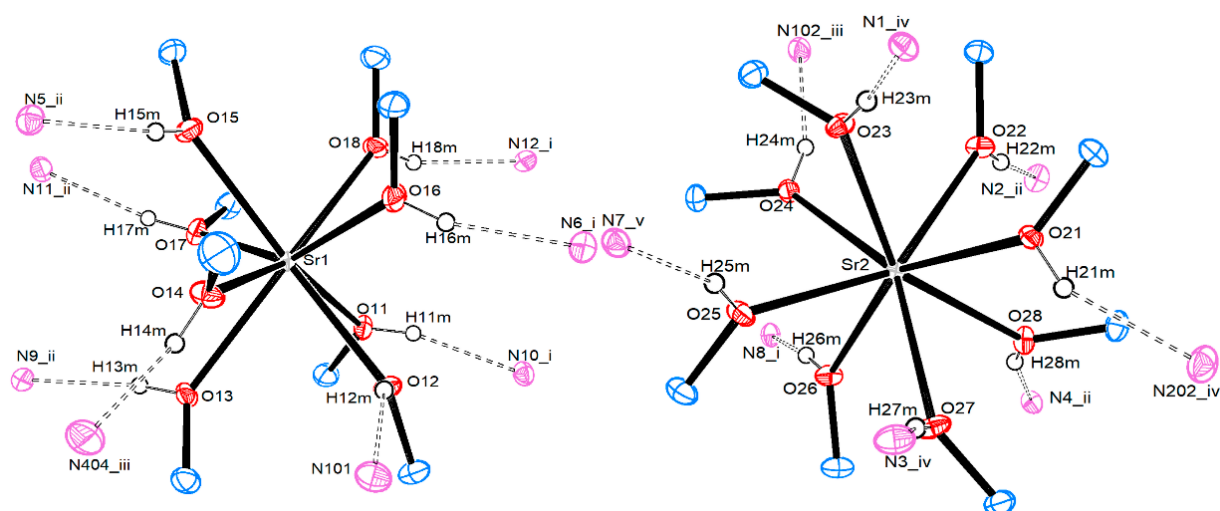


Figure 10. The first and second coordination spheres of the Sr^{2+} ions in compound 3.

Closer inspection of these coordination spheres shows that each metal ion hydrogen bonds exclusively to both ends of a set of three bipyridines: Sr1 to N5/N6, N9/N10 and N11/N12, while Sr2 employs hydrogen bonds to N1/N2, N3/N4, and N7/N8. Because of this, two independent cylindrical columns form and extend along the a axis (Figure 11). All bipyridines are significantly twisted, with interplanar angles ranging from 23 to 40°. Parallel to this, the PCC anions form π -stacks also along the a axis. The distances between the cyclopentadienyl centroids vary between 3.65 and 3.89 Å, while the perpendicular distances are in the range 3.36 to 3.54 Å, which means there is a significant “slippage” (Figure 12). Combination of both stacks leads to the final packing diagram (Figure 13). The individual stacks are partially connected by hydrogen bonds (shown as light blue lines). Again, Tables S1 and S2 collect all the relevant hydrogen bond parameters. Table 2 collects important bond parameters

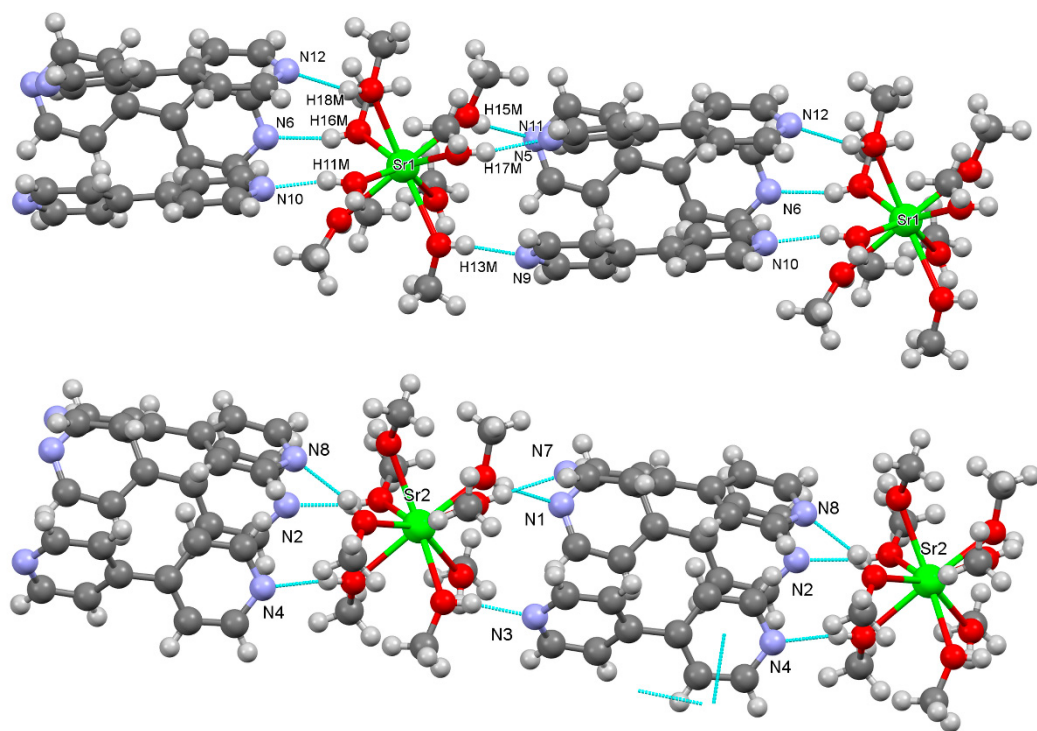


Figure 11. The two independent $[\text{Sr}(\text{MeOH})_8(4,4'\text{-bipy})_3]_x$ columns.

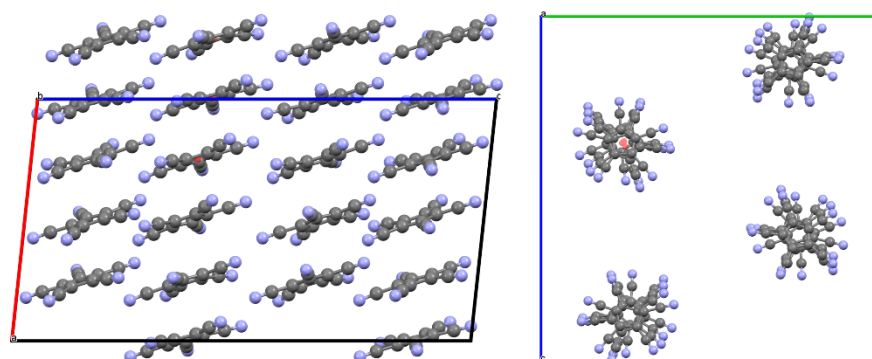


Figure 12. The π stacking of the anions, watched along b (left) and along a (right).

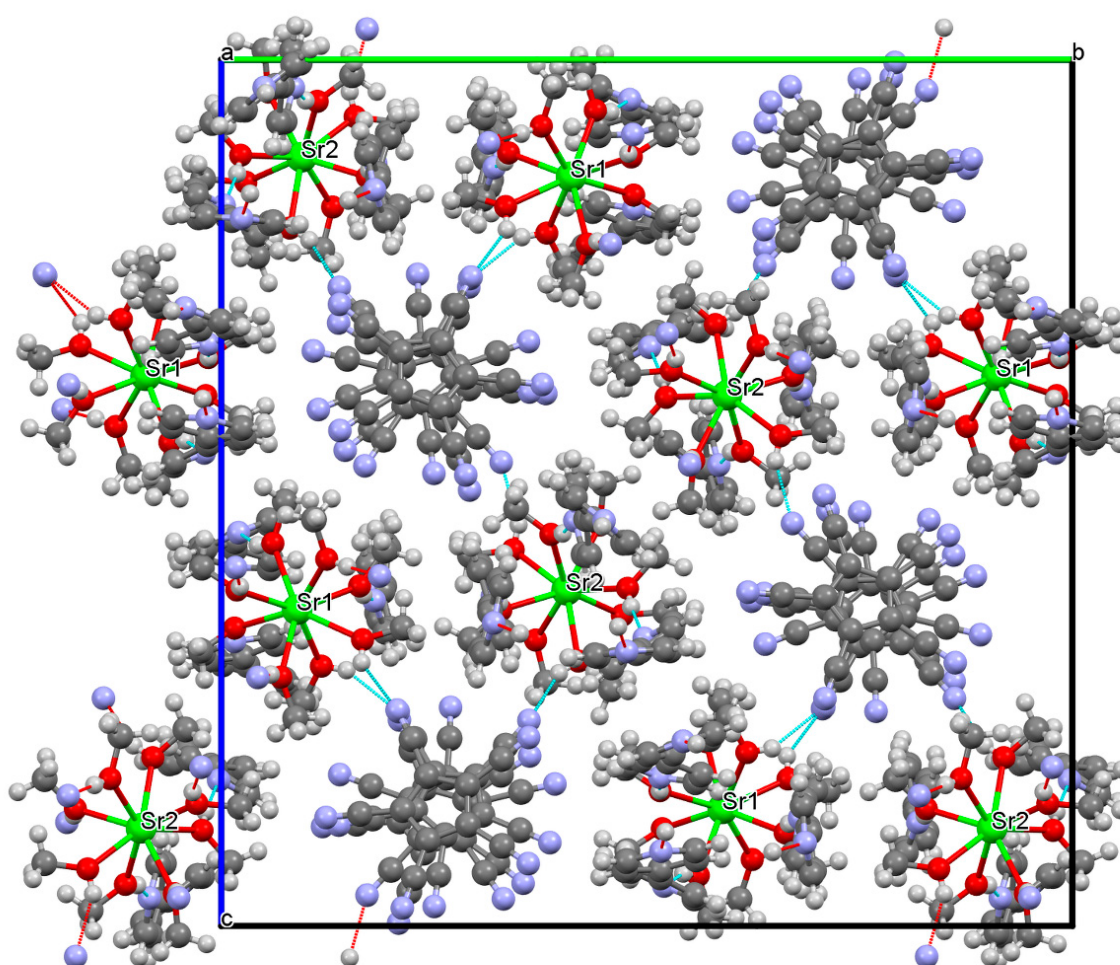
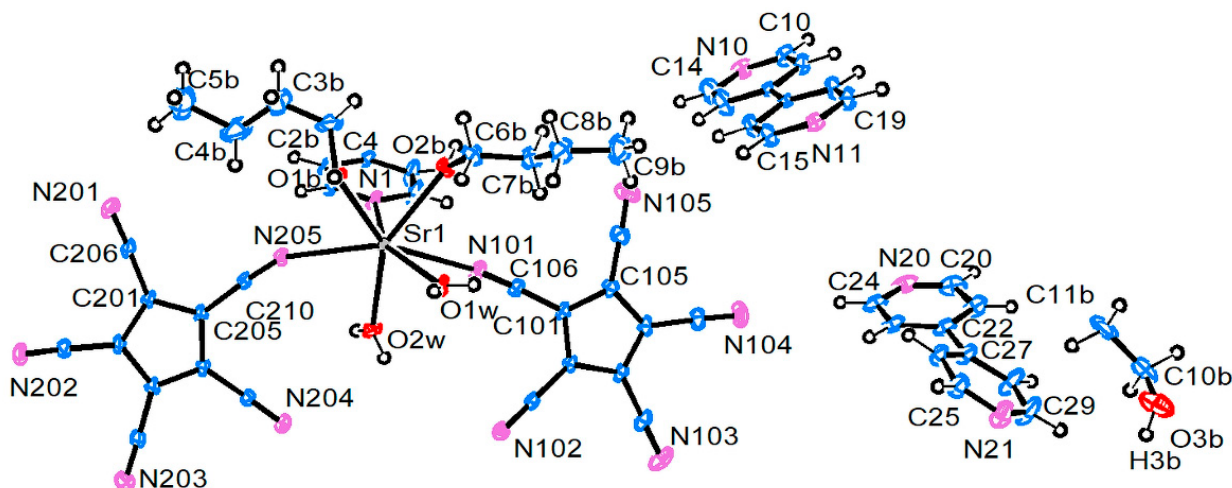


Figure 13. Complete packing diagram of compound 3.

Compound 4 crystallizes in the triclinic space group $P-1$ with one molecule in the asymmetric unit (Figure 14). The molecular unit consists of a complex fragment $[\text{Sr}(\text{H}_2\text{O})_2(\text{BuOH})_2(\text{PCC})_2(4,4'\text{-bipy})_{0.5}]$ and two lattice 4,4'-bipy molecules and a disordered half butanol (with partial occupancy). The disordered butanol is generated by an inversion center close to carbon atom C11b. The end atoms of the generated six atom chain are either a OH or a methyl hydrogen group.

Table 2. Important bond lengths [Å] and angles [°] of compounds **3** and **4**.

Compound 3			
Sr1–O11	2.555 (2)	Sr2–O21	2.595 (2)
Sr1–O12	2.641 (2)	Sr2–O22	2.558 (2)
Sr1–O13	2.620 (2)	Sr2–O23	2.579 (2)
Sr1–O14	2.602 (2)	Sr2–O24	2.616 (2)
Sr1–O15	2.589 (2)	Sr2–O25	2.562 (2)
Sr1–O16	2.608 (2)	Sr2–O26	2.569 (2)
Sr1–O17	2.591 (2)	Sr2–O27	2.581 (2)
Sr1–O18	2.611 (2)	Sr2–O28	2.587 (2)
C3–C8	1.477 (4)	C33–C38	1.480 (4)
C13–C18	1.477 (4)	C43–C48	1.479 (4)
C23–C28	1.481 (4)	C53–C58	1.473 (4)
C2–C3–C8–C7	−32.4 (4)	C32–C33–C38–C37	28.5 (4)
C12–C13–C18–C17	39.5 (4)	C42–C43–C48–C47	−31.1 (4)
C22–C23–C28–C27	−22.4 (4)	C52–C53–C58–C57	−32.6 (4)
Compound 4			
Sr1–O1W	2.505 (2)	Sr1–N1	2.704 (2)
Sr1–O2W	2.518 (2)	Sr1–N101	2.817 (3)
Sr1–O1B	2.526 (2)	Sr1–N205	2.782 (2)
Sr1–O2B	2.567 (2)	Sr1–N102′	2.815 (3)
C4–C4′	1.486 (5)	C3–C4–C4′–C5′	0.1 (4)
C12–C17	1.488 (3)	C11–C12–C17–C18	−1.5 (4)
C22–C27	1.482 (4)	C21–C22–C27–C28	−32.1 (4)
Sr1–N1 ... C4	179		
Sr1–N101–C106	164.8 (2)	Sr1–N205–C210	152.8 (2)
N101–Sr1–N205	135.72 (7)	N101–Sr1–N102′	129.10 (6)

**Figure 14.** The asymmetric unit of compound **4**. Thermal ellipsoids at the 30% probability level.

The Sr^{2+} ion is eight-coordinated, by two water and butanol oxygens each, by three nitrile nitrogens and one Bipy nitrogen (Figure 15). Important bond parameters are collected in Table 2.

Water molecule O1w donates hydrogen bridges to one nitrile and one lattice 4,4′-bipy nitrogen and accepts one hydrogen bridge from water molecule O2w of another molecular entity. O2w also donates a hydrogen bridge to another lattice 4,4′-bipy nitrogen. The two butanol molecules donate one hydrogen bridge each to two different lattice bipyridines. One of the anions uses two nitrile functions in relative 1,2-position to bridge two metal anions coordinatively, while the other supports this bridge via combination of nitrile coordination and H-bond acceptor. Thus a “dimeric subunit” is formed (Figure 16). The bridging is also supported by weak π -stacking of two pairs of anions. The interplanar angle

is ca. 4° , the distance of the two ring centroids is ca. 3.81 Å with a perpendicular distance of ca. 3.36 Å.

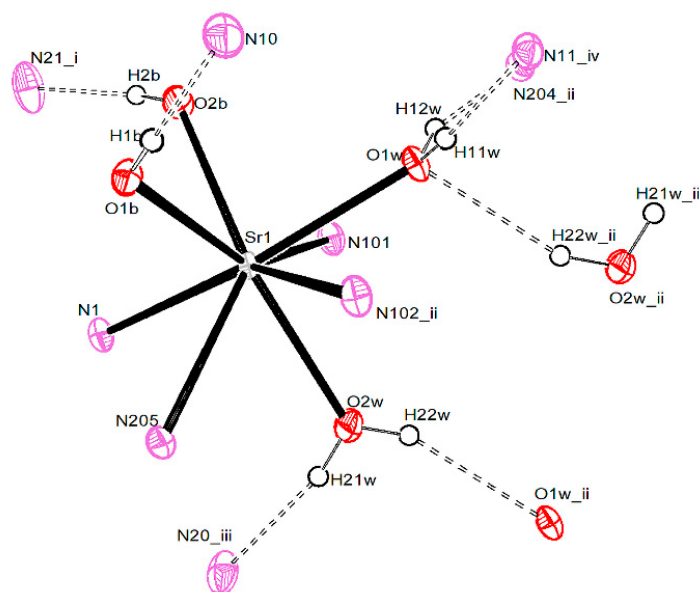


Figure 15. The first and second coordination spheres of Sr^{2+} in compound **4**. Symmetry operators: i: x, y, z ; ii: $-x, -y, 1 - z$; iii: $1 - x, -y, 1 - z$; iv: $-x, 1 - y, 1 - z$.

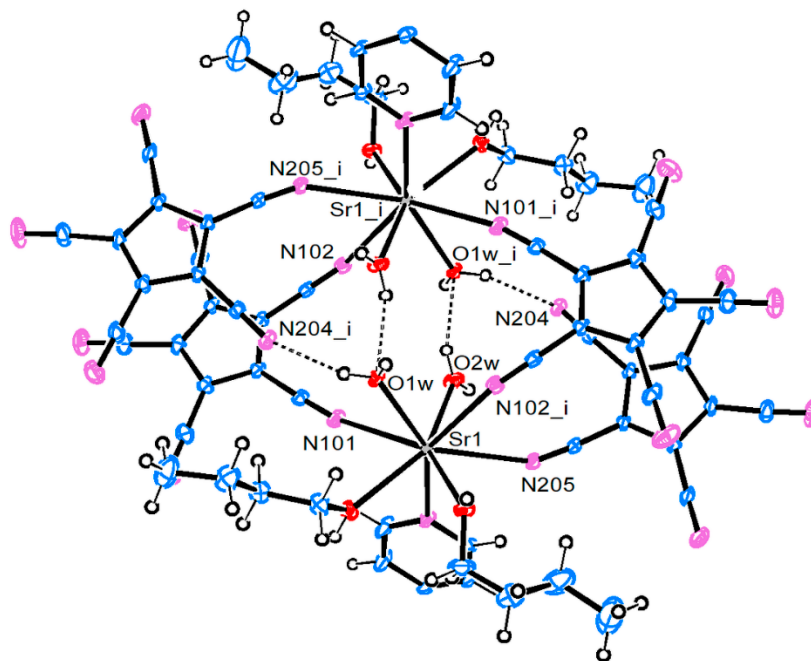


Figure 16. The dimeric quadruply anion-bridged subunit of compound **4**. Symmetry operator: i: $-x, -y, 1 - z$.

The figure also shows that both Sr^{2+} ions coordinate to half a 4,4'-bipy molecule each, and thus it is clear that the real description of the structure is linear polymeric (Figure 17). Because of symmetry both halves of this 4,4'-bipy molecule are coplanar.

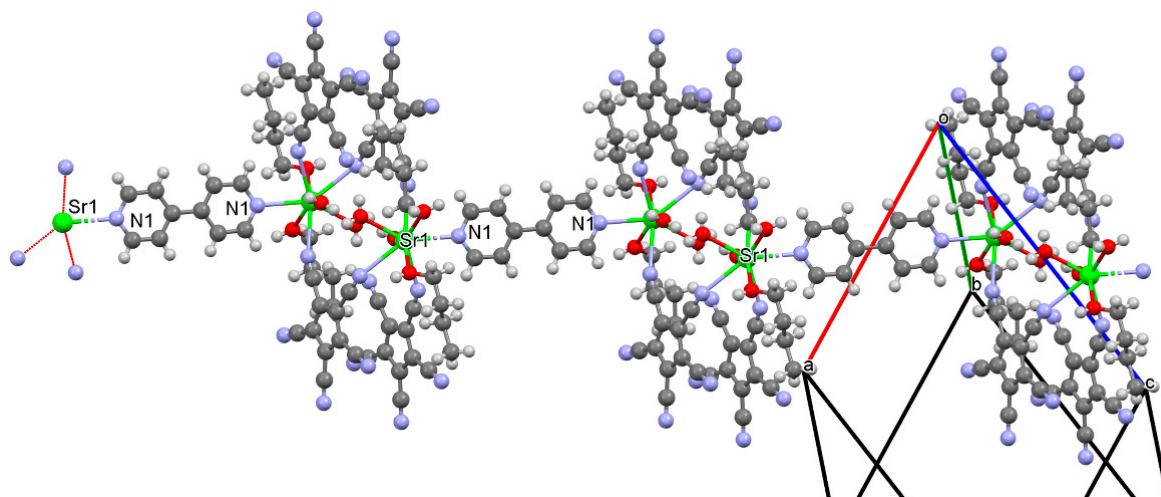


Figure 17. The linear 4,4'-bipy-bridged arrangement of the dimeric subunits of Figure 16.

The two remaining 4,4'-bipy molecules fill the voids between the polymeric chains (Figure 18). One of them (containing N11/ N12, blue-colored in Figure 18)) is nearly planar (angle between the two molecule halves $1.3 (1)^\circ$, while the other (containing N21/ N22, red-colored in Figure 18)) is severely twisted (interplanar angle $33.6 (2)^\circ$). Two symmetry related “blue” bipyridines show weak π -stacking (distance between centroids ca. $3.83 \text{ \AA}$ with a perpendicular distance of ca. $3.45 \text{ \AA}$). There is also weak π -stacking between a “red” and a “blue” bipyridine (centroid distance ca. $3.77 \text{ \AA}$, perpendicular distance $3.62 \text{ \AA}$) and between a “red” and a “green” bipyridine (centroid distance ca. $3.70 \text{ \AA}$, perpendicular distance ca. $3.17 \text{ \AA}$).

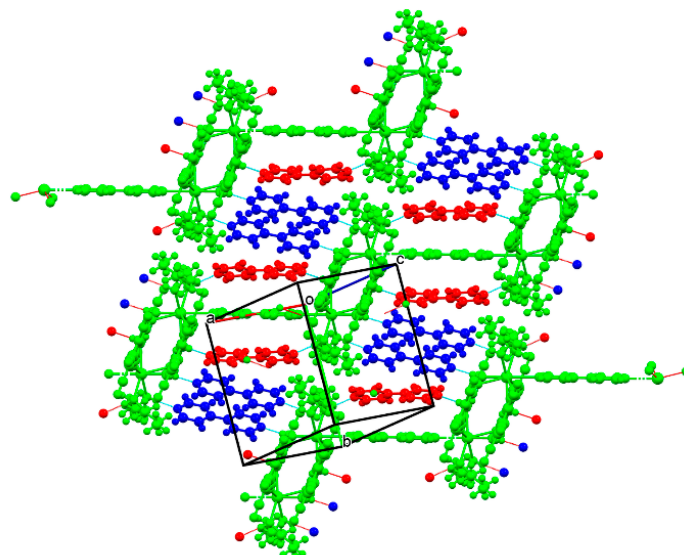


Figure 18. The complete packing arrangement in compound 4.

3.2.4. Barium Pentacyanocyclopentadienides

Both recrystallizations from EtOH and *n*-BuOH yielded X-ray quality crystals, while from MeOH only a microcrystalline substance could be obtained.

Compound 5, $[\text{Ba}_3(\text{H}_2\text{O})_4(\text{EtOH})_{10}(\text{PCC})_2(\mu\text{-PCC})_2(4,4'\text{-bipy})] (\text{PCC})_2 \cdot 3 (4,4'\text{-bipy}) 2\text{EtOH} \cdot \text{H}_2\text{O}$, crystallizes as a racemic twin in the monoclinic space group *Pc* with one “molecule” in the asymmetric unit. It contains a complicated trinuclear dication with coordinated water, ethanol, 4,4'-bipy molecules. Four PCC anions are coordinated and two are “free”. In addition, there are three uncoordinated bipyridines as well as lattice solvents EtOH and water (Figure 19).

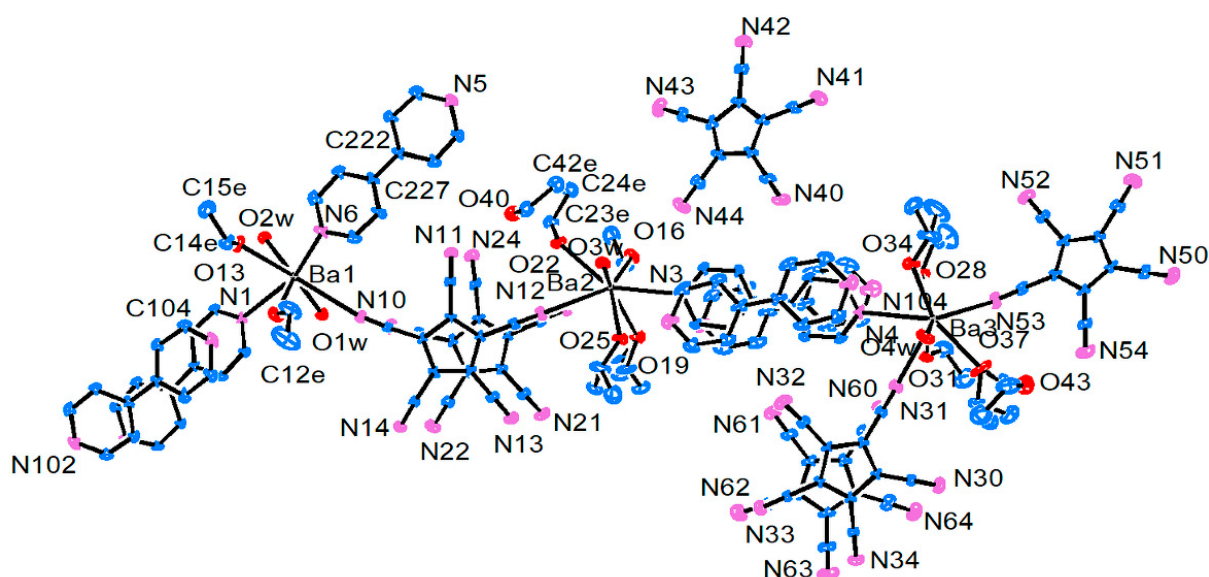


Figure 19. The asymmetric unit in the crystal of compound 5.

To understand the complicated trinuclear cation, it is best to look first at the coordination spheres of the three independent Ba^{2+} ions. Ba1 is coordinated by two water and two ethanol oxygens as well as by three bipyridine nitrogens and one nitrile nitrogen. Both water molecules and one ethanol molecule donate one hydrogen bond each to nitrile nitrogens as well (Figure 20). Important bond parameters are collected in Table 3.

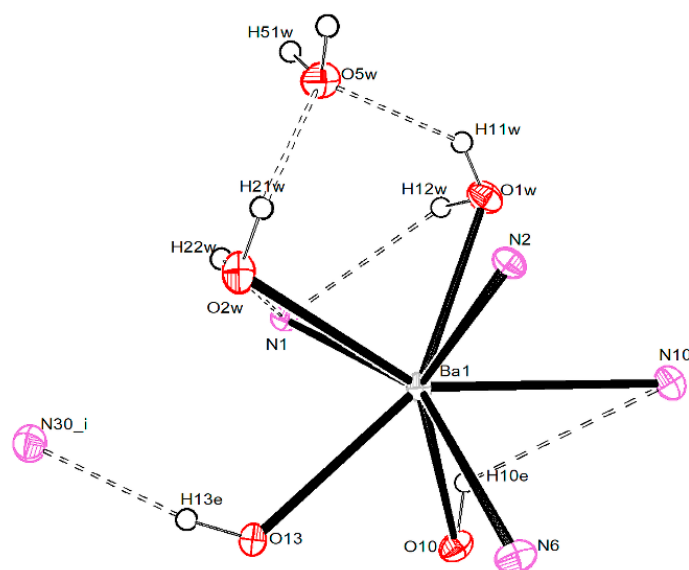
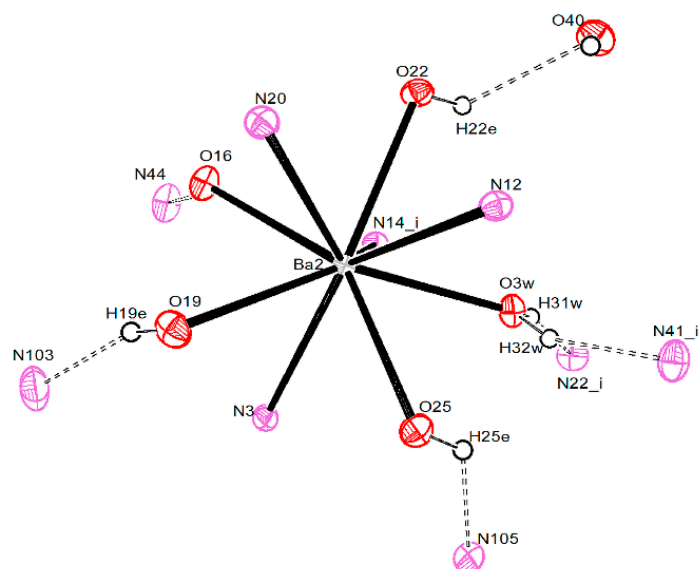


Figure 20. The first and second coordination spheres of Ba1.

The “central” Ba2 is eight-coordinated by one water and three ethanol oxygens, one 4,4'-bipy and three nitrile nitrogens. The coordinated EtOH molecules act as hydrogen bond donors to two bipyridine and one nitrile nitrogen as well as to a lattice ethanol oxygen, while the water molecule donates two H bonds to one coordinated and one uncoordinated anion (Figure 21). Ba3 is nine-coordinated by four EtOH and one water oxygen as well as three nitrile and one bipyridine nitrogen (Figure 22). The coordinated EtOH molecules donate one H bond to a nitrile and two H bonds to bipyridines as well as to a lattice EtOH, while the coordinated water donates two H-bonds to two different anions.

Table 3. Important bond parameters [$\text{\AA}$, $^\circ$] of compound 5.

Ba1–O1W	2.694 (3)	Ba2–O3W	2.733 (4)	Ba3–O4W	2.741 (4)
Ba1–O2W	2.759 (3)	Ba2–O16	2.754 (4)	Ba3–O28	2.777 (4)
Ba1–O10	2.710 (4)	Ba2–O19	2.826 (4)	Ba3–O31	2.744 (4)
Ba1–O13	2.741 (3)	Ba2–O22	2.751 (4)	Ba3–O34	2.804 (4)
Ba1–N1	2.960 (4)	Ba2–O25	2.818 (4)	Ba3–O37	2.712 (4)
Ba1–N2'	3.017 (4)	Ba2–N3	2.920 (4)	Ba3–N4	2.961 (4)
Ba1–N6	2.929 (4)	Ba2–N12	3.120 (5)	Ba3–N31	3.035 (5)
Ba1–N10	3.189 (4)	Ba2–N14'	3.061 (4)	Ba3–N33	3.085 (5)
		Ba2–N20	2.935 (5)	Ba3–N53	2.998 (5)
C102–C107	1.483 (7)	C112–C117	1.472 (9)	C122–C127	1.489 (7)
C202–C207	1.480 (6)	C212–C217	1.476 (6)	C222–C227	1.477 (6)
Ba1–N10–C15	160.9 (4)	Ba2–N12–C17	166.2 (4)	Ba2'–N14–C19	169.1 (4)
Ba2–N20–C25	135.8 (4)	Ba3–N33–C38	162.0 (4)	Ba3–N53–C58	143.9 (4)
C101–C102–C107–C108	−29.5 (5)	C111–C112–C117–C116	30.8 (8)	C121–C122–C127–C126	28.7 (7)
C201–C202–C207–C206	−28.7 (6)	C211–C212–C217–C218	31.2 (7)	C221–C222–C227–C228	30.2 (7)
Ba1–N1 ... C202	170	Ba1–N6 ... C227	138	Ba2–N3 ... C212	177
Ba3–N4 ... C217	174				

**Figure 21.** The first and second coordination spheres of Ba2. Symm. Operators: i: $x, 1 - y, z - \frac{1}{2}$; ii: $x, -y, z + \frac{1}{2}$.

Ba1 and Ba2 are coordinatively bridged by anion I, using the nitrile nitrogens N10 and N12, and additionally by anion II, using the coordinated nitrile N20 and the hydrogen bridge N23/H11W–O1W. At the same time, two symmetry related Ba2 ions are coordinatively bridged by anion I using N12 and N14 and by anions II using N20 and the hydrogen bridge N22/H31W–O3W and anion IV using only the hydrogen bridges O3W–H32W/ N41 and N44/H16E/O16 (Figure 23). As a consequence, Ba1 is also bridged by anion I to the second Ba2 ion via nitriles N10 and N14. Two symmetry related Ba3 ions are similarly triply bridged: coordinatively by anion III using N31 and N33, by anion V using a mix of coordinative and hydrogen bond supported bridge using N53 and N51/H42W–O4W and the doubly hydrogen-bonded anion VI (Figure 23). In all cases, the bridging pentacyanocyclopentadienides show also very weak π – π stacking interactions, with centroid-centroid distances ranging from 3.62 to 3.72 $\text{\AA}$.

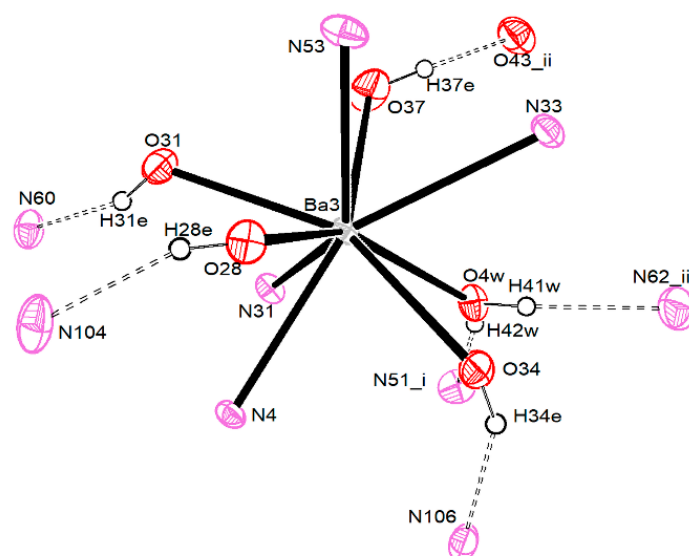


Figure 22. The first and second coordination spheres of Ba3.

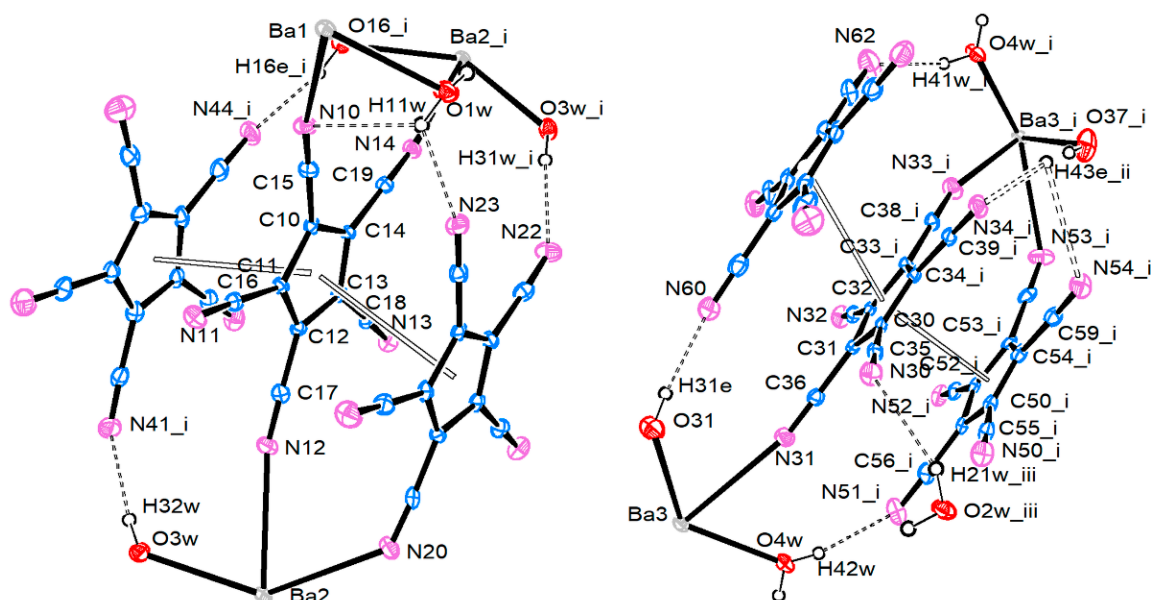


Figure 23. (left) The three anions bridging Ba1, Ba2, and Ba2_i (symm. Code i: $-x, 1 - y, z - \frac{1}{2}$). (right) The three anions bridging Ba3 and Ba3_i (symm. Code i: $-x, 1 - y, z - \frac{1}{2}$).

A related triply bridging occurs between Ba2 and Ba3, however using one coordinated and two hydrogen-bonded bipyridines. The H-bond bridging is supported by four π - π interactions (Figure 24). All three bipyridine are significantly twisted, with interplanar angles ranging from 29 to 33°. The 4,4'-bipy containing nitrogen atoms N1/ N2 bridge two symmetry-related Ba1 ions and also shows weak π - π interactions with a mono-coordinated and an uncoordinated bipyridine (Figure 24). Again, all three involved bipyridines show significant twisting (interplanar angles 29–30°).

The complete packing diagram is shown in Figure 25. It can easily be seen that three parallel strands are formed exclusively by only one type of Ba²⁺ ion each in *c* direction. The Ba3 ions are connected by PCC anions, as are the Ba2 ions, while the Ba1 ions use the 4,4'-bipy ligands for bridging. The different strands are bridged either by 4,4'-bipy (Ba3 and Ba2) or by use of a third nitrile function of an anion (Ba1 and Ba2). As discussed before, additional strengthening of this framework comes by hydrogen bonds and π - π stacking interactions.

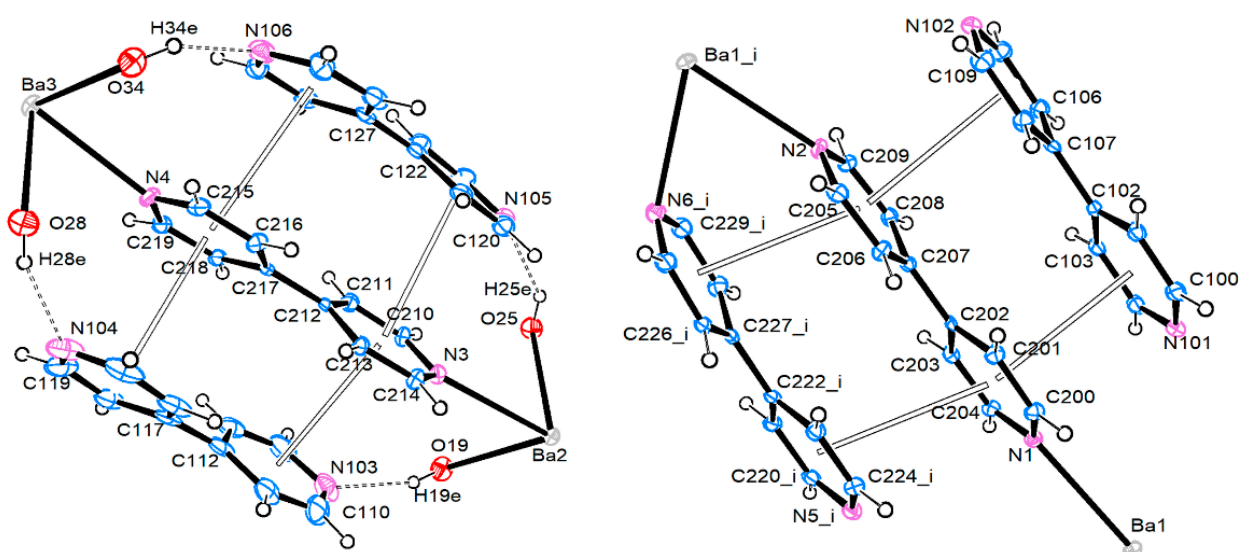


Figure 24. (left) The triple 4,4'-bipy bridging between Ba2 and Ba3. (right) The single 4,4'-bipy bridging between two symmetry-related Ba1 ions, supported by π - π -stacking interactions with two more bipyridines.

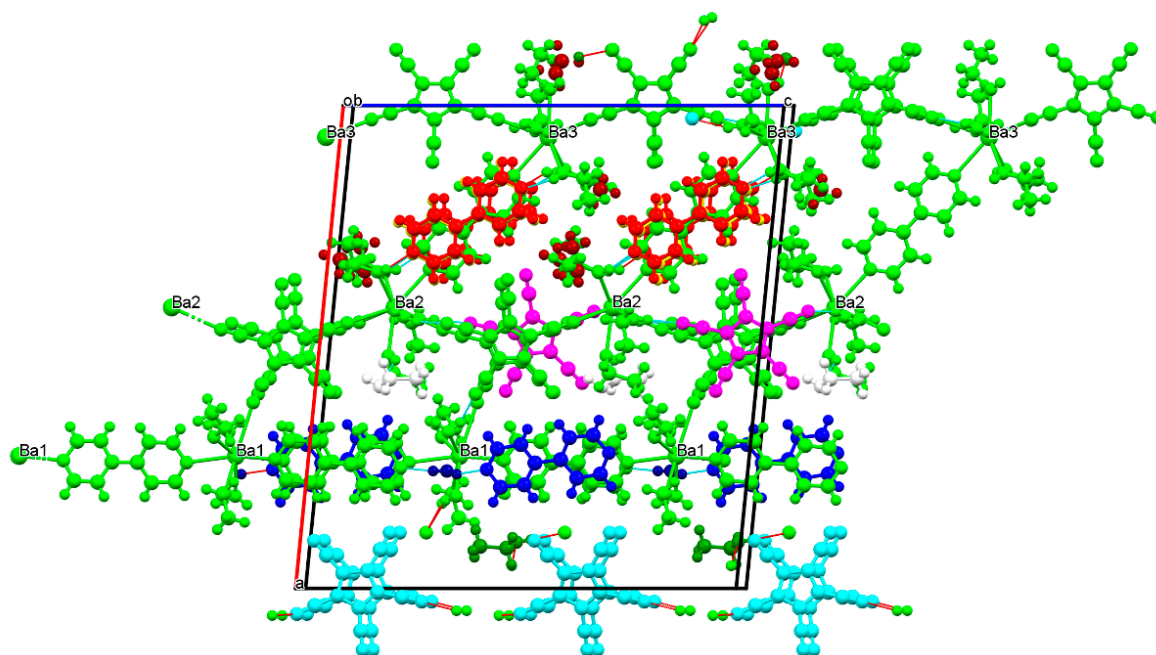


Figure 25. The complete packing diagram of compound 5, watched along *b*. Color coding: Green is the basic trinuclear cation system; dark blue, yellow and red are the lattice bipyridines, light blue and magenta the free anions, and dark red and white the lattice solvent molecules. Thin blue and red lines symbolize the hydrogen bridges.

Compound 6, $[\text{Ba}_4(\text{H}_2\text{O})_8(\text{BuOH})_6(\text{PCC})_2(\mu\text{-PCC})_6(4,4'\text{-bipy})_6]\cdot 3(4,4'\text{-bipy})$, crystallizes in the monoclinic space group $P2_1/n$ with half a molecule in the asymmetric unit (Figure S2). Since the view of the asymmetric unit is very confusing due to severe disorder within the $\text{H}_2\text{O}/\text{BuOH}$ part, it is better to look first at the tetranuclear unit first (H atoms and the alkyl chains of the butanol molecules omitted, Figure 26).

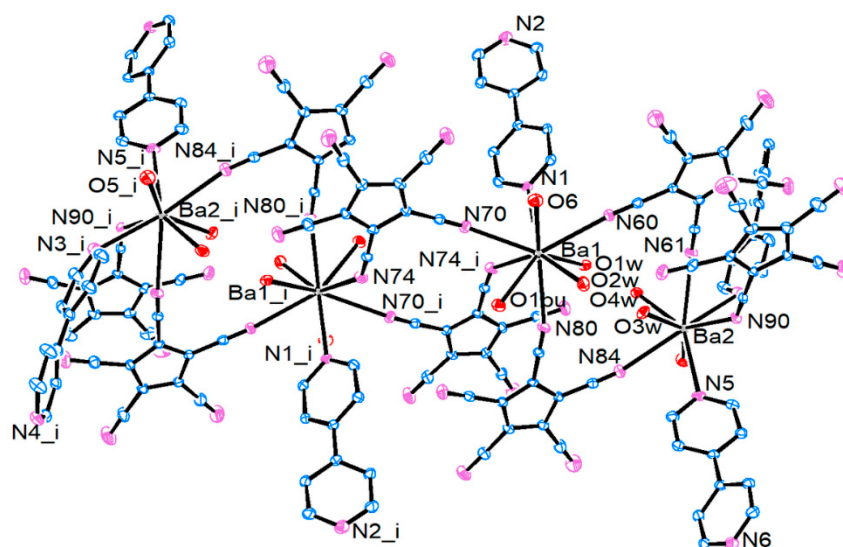


Figure 26. The tetranuclear unit of compound **6** (H atoms and C_4H_9 residues of the butanol molecules omitted). Thermal ellipsoids at the 30% probability level.

As can be seen, two dimeric units $[Ba_2(H_2O)_4(BuOH)_3(\mu-PCC)_2(PCC)(4,4'-bipy)_3]$ are bridged by two bidentate anions to give the tetrameric unit. Thus, Ba1 has a BaN_5O_4 coordination polyhedron (with four nitrile and one 4,4'-bipy nitrogen donors), while Ba2 is eight-coordinated within a BaN_5O_3 polyhedron (with three nitrile and two 4,4'-bipy nitrogen donors, Figure 27). The coordinated water and butanol molecules donate hydrogen bonds to other water molecules (O3W to O1W), nitrile nitrogens (N70, N73, N91, N94), and bipyridine nitrogens (N2, N6, N8, N9). There are also many C–H ... N hydrogen bonds from the 4,4'-bipy units, which are shown in Figures S3–S6 of the Supporting Information. The parameters of these hydrogen bonds are collected in Tables S1 and S2. Important bond parameters are collected in Table 4.

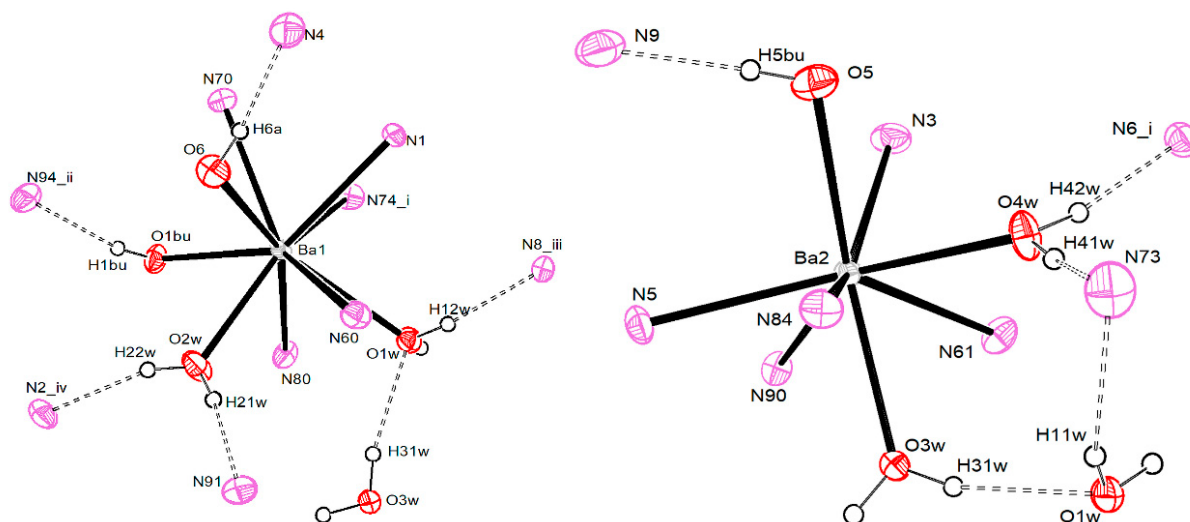
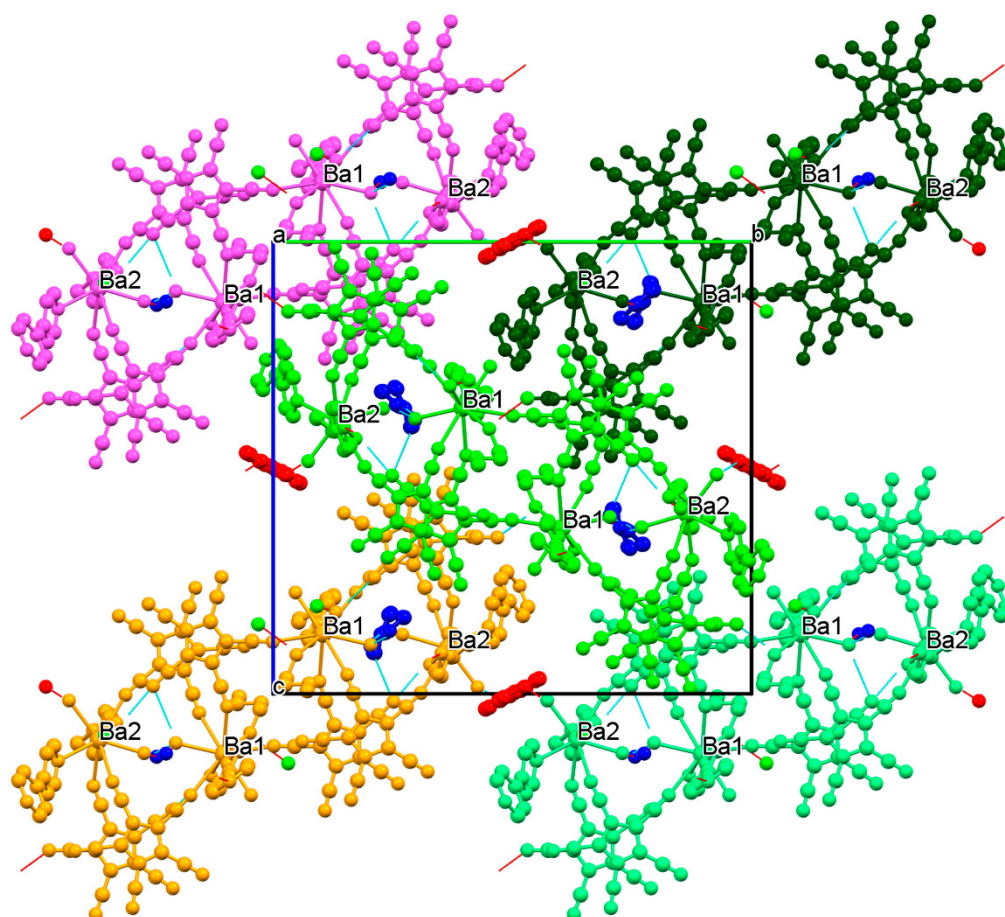


Figure 27. The first and second coordination spheres of Ba1 and Ba2.

There occurs also weak π – π stacking between the cyclopentadienyl rings, with interplanar angles between 3.7 and 5.3° , centroid-centroid distances of 3.80 – 3.86 Å and perpendicular distances between 3.55 and 3.65 Å (Figure S7). All the 4,4'-bipy molecules are severely twisted, with interplanar angles ranging from 26 to 36° . There also occurs some π -stacking between the bipyridines, however, it is more of the C–H ... π type (Figure S8). The interplay of all these interactions leads to a rather dense packing (Figure 28).

Table 4. Important bond parameters [$\text{\AA}$, $^\circ$] of compound **6**.

Ba1–O1W	2.798 (3)	Ba2–O3W	2.663 (3)
Ba1–O2W	2.649 (3)	Ba2–O4W	2.617 (3)
Ba1–O1Bu	2.753 (3)	Ba2–O5	2.777 (3)
Ba1–O6	2.740 (3)	Ba2–N3	2.919 (4)
Ba1–N1	2.895 (3)	Ba2–N5	2.892 (3)
Ba1–N60	2.968 (4)	Ba2–N61	2.986 (4)
Ba1–N70	2.937 (4)	Ba2–N84	2.956 (4)
Ba1–N74'	2.967 (4)	Ba2–N90	2.931 (4)
Ba1–N80	3.006 (4)		
C12–C17	1.481 (5)	C22–C27	1.476 (6)
C32–C37	1.479 (6)	C42–C47	1.479 (6)
C52–C52'	1.488 (11)		
Ba1–N60–C65	173.9 (3)	Ba2–N61–C66	153.5 (4)
Ba1–N70–C75	159.3 (4)	Ba2–N84–C89	164.7 (3)
Ba1'–N74–C79	145.4 (4)	Ba2–N90–C95	140.3 (3)
Ba1–N80–C85	163.1 (4)	Ba2–N3 ... C22	143
Ba1–N1 ... C12	178	Ba2–N5 ... C32	166
C11–C12–C17–C18	28.8 (6)	C21–C22–C27–C26	−31.2 (7)
C31–C32–C37–C38	35.0 (6)	C41–C42–C47–C46	26.0 (4)
C51–C52–C52'–C53'	−0.4 (8)		

**Figure 28.** Complete packing plot (H atoms omitted as well as disordered BuOH molecules) of compound **6**, watched along *a*. Color coding: light-green. Dark green, turquoise, yellow, and magenta are five symmetry-related tetranuclear units, while red and dark blue are the uncoordinated bipyridines. Light-blue lines symbolize hydrogen bonds.

4. Discussion

Polycyanocyclopentadienides $[\text{C}_5(\text{CN})_4\text{X}]^-$ ($\text{X} = \text{H}, \text{CN}$) act usually as triply-bridging ligands toward Ca^{2+} , Sr^{2+} , and Ba^{2+} , together with additional aqua ligands, while only Mg^{2+} prefers exclusive coordination by water ligands [15]. In the presence of 4,4'-bipy, the coordination behavior of the PCC anion depends on both the metal and the solvent. In MeOH, Mg^{2+} , Ca^{2+} , Sr^{2+} (no crystals could be obtained with Ba^{2+} from this solvent) do not coordinate the anion at all. While Mg^{2+} and Sr^{2+} coordinate only MeOH ligands (six with the former and eight with the latter), the Ca^{2+} coordinates besides four water molecules two monodentate bipyridines in mutual trans position. In ethanol, with Ba^{2+} the PCC anion acts either as a monodentate or a (1,3-) bridging bidentate or a (1,2,4-) bridging tridentate ligand (no crystals were obtained from this solvent with the other alkaline earth metal ions). With *n*-butanol as solvent, Mg^{2+} still does not coordinate the anion, but besides four water molecules two 4,4'-bipy ligands in mutual trans position act as monodentate ligands. From this solvent and Sr^{2+} or Ba^{2+} as cation, PCC anion acts both as monodentate and (1,2-) bridging bidentate ligand. In addition, water, butanol and either N, N'-bridging bidentate (Sr^{2+}) or monodentate (Ba^{2+}) 4,4'-bipy complete the coordination sphere. Thus, the presence of 4,4'-bipyridine reduces the denticity of the anion (except for the Ba^{2+} / EtOH system).

While it is clear that the “harder” cations Mg^{2+} and Ca^{2+} prefer the “harder” oxygen donor ligands over the softer bipyridine- and nitrile nitrogen donors, it seems strange, that the relatively soft Sr^{2+} ion prefers an exclusively hard oxygen donor sphere in compound 3 and allows coordination of both nitrile and 4,4'-bipy nitrogens in compound 4.

Except for the Mg compound 1, 4,4' bipy acts in all crystals as lattice guest molecule. In addition, it acts in all crystals (except for the Sr^{2+} compound 3) as terminal monodentate ligand, and only in compounds 4 and 5 as bridging bidentate ligand. Although in all reactions were used similar stoichiometries, the obtained crystals show a very different content of 4,4'-bipy: in compounds 1 and 5 a metal: 4,4'-bipy ratio of 1:2, in compounds 2 and 3 of 1:3, in 4 of 2:5, and in 6 of 4:9 are found. This great variability has certainly to do with the ability of both PCC and 4,4'-bipy to act as hydrogen bond acceptors as well as to undergo π - π interactions. Therefore, it seems very difficult to prepare mixed ligand complexes in these systems with a predictable stoichiometry. There will be a lot of research necessary to actually carry out “crystal engineering” with these systems.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/chemistry4040101/s1>, Table S1: Hydrogen bond parameters of O–H donors; Table S2: Hydrogen bond parameters of the C–H donors; Table S3: Experimental details of the data collections; Figure S1: The pentacyanocyclopentadienides in compound 2 as H-bond acceptors; Figure S2: The asymmetric unit of compound 6; Figure S3: The hydrogen bonds around Bipyridine I; Figure S4: The hydrogen bonds around Bipyridine II; Figure S5: The hydrogen bonds around Bipyridine III; Figure S6: The hydrogen bonds around Bipyridine IV; Figure S7: The π -stacking of pentacyanocyclopentadienides in 6: side view and top view; Figure S8: The π -stacking of Bipyridines in 6: side view and top view.

Author Contributions: Conceptualization, P.R.N. and K.S.; methodology, P.R.N.; validation, P.R.N. and K.S.; formal analysis, P.R.N.; investigation, P.R.N.; resources, K.S.; data curation, K.S.; writing—original draft preparation, K.S.; writing—review and editing, K.S.; visualization, K.S.; supervision, K.S. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: CCDC 2213249–2213254 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223336033.

Acknowledgments: We thank P. Mayer for performing the X-ray data collections.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Desiraju, G.R. *Crystal Engineering: The Design of Organic Solids*; Elsevier: Amsterdam, The Netherlands, 1989.
2. Grepioni, F.; Casali, L.; Fiore, C.; Mazzei, L.; Sun, R.; Shemchuk, O.; Braga, D. Steps towards a nature inspired inorganic crystal engineering. *Dalton Trans.* **2022**, 51, 7390–7400. [[CrossRef](#)] [[PubMed](#)]
3. O'Hearn, D.J.; Bajpai, A.; Zaworotko, M.J. The “Chemistree” of Porous Coordination Networks: Taxonomic Classification of Porous Solids to Guide Crystal Engineering Studies. *Small* **2021**, 17, 2006351. [[CrossRef](#)] [[PubMed](#)]
4. Sun, L.; Zhu, W.; Zhang, X.; Li, L.; Dong, H.; Hu, W. Creating Organic Functional Materials beyond Chemical Bond Synthesis by Organic Cocrystal Engineering. *J. Am. Chem. Soc.* **2021**, 143, 19243–19256. [[CrossRef](#)] [[PubMed](#)]
5. Wells, A.F. The Geometrical Basis of Crystal Chemistry I. *Acta Cryst.* **1954**, 7, 535–544. [[CrossRef](#)]
6. Hoskins, B.F.; Robson, R. Infinite polymeric frameworks consisting of three-dimensionally linked rod-like segments. *J. Am. Chem. Soc.* **1989**, 111, 5962–5964. [[CrossRef](#)]
7. Biradha, K.; Sarkar, M. Rajput Crystal engineering of coordination polymers using 4,4'-bipyridine as a bond between transition metal atoms. *Chem. Commun.* **2006**, 40, 4169–4179. [[CrossRef](#)] [[PubMed](#)]
8. Darwish, S.; Wang, S.-Q.; Croker, D.M.; Walker, G.M.; Zaworotko, M.J. Comparison of Mechanochemistry vs Solution Methods for Synthesis of 4,4'-Bipyridine-Based Coordination Chemistry. *ACS Sustain. Chem. Eng.* **2019**, 7, 19505–19512. [[CrossRef](#)]
9. Carlucci, L.; Ciani, G.; Proserpio, D.M.; Sironi, A. Extended networks via hydrogen bond cross-linkages of [M(bipy)] (M = Zn²⁺ or Fe²⁺; bipy = 4,4'-bipyridyl) linear coordination polymers. *Dalton Trans.* **1997**, 11, 1801–1803. [[CrossRef](#)]
10. Roesky, H.W.; Andruh, M. The interplay of coordinative, hydrogen bonding and π - π stacking interactions in sustaining supramolecular solid-state architectures. A study case of bis(4-pyridyl)- and bis(4-pyridyl-N-oxide) tectons. *Coord. Chem. Rev.* **2003**, 236, 91–119. [[CrossRef](#)]
11. Yin, Z.; Zhou, Y.-L.; Zeng, M.-H.; Kurmoo, M. The concept of mixed organic ligands in metal-organic frameworks: Design, tuning and functions. *Dalton Trans.* **2015**, 44, 5258–5275. [[CrossRef](#)] [[PubMed](#)]
12. Fromm, K.M. Coordination polymer networks with s-block metal ions. *Coord. Chem. Rev.* **2008**, 252, 856–885.
13. Benmansour, S.; Armani, C.; Setifi, F.; Triki, S.; Marchivie, M.; Gomez-Garcia, C.J. Polynitrile anions as ligands: From magnetic polymeric architectures to spin crossover materials. *Coord. Chem. Rev.* **2010**, 254, 1468–1478. [[CrossRef](#)]
14. Sünkel, K.; Reimann, D. Coordination Chemistry of Polynitriles, I. Syntheses and Crystal Structures of [Ag(PCC)(DMF)], [Ni(DMF)₆](PCC)₂ and [Co(DMF)₆](PCC)₂ (PCC = [C₅(CN)₅][−], DMF = N,N-dimethylformamide). *Z. Nat. B* **2013**, 68, 546–550. [[CrossRef](#)]
15. Sünkel, K.; Nimax, P.R. Structural diversity in the alkaline earth metal compounds of tetra- and pentacyanocyclopentadienide. *Dalton Trans.* **2018**, 47, 409–417. [[CrossRef](#)] [[PubMed](#)]
16. Farrugia, L.J. WINGX and ORTEP for Windows: An update. *J. Appl. Crystallogr.* **2012**, 45, 849–854. [[CrossRef](#)]
17. Sheldrick, G.M. Crystal Structure Refinement with SHELXL. *Acta Crystallogr. Sect. C Struct. Chem.* **2015**, C71, 3–8. [[CrossRef](#)] [[PubMed](#)]
18. Sheldrick, G.M. SHELXT- integrated space group and crystal structure determination. *Acta Crystallogr. Sect. A Found. Adv.* **2015**, A71, 3–8. [[CrossRef](#)] [[PubMed](#)]
19. Spek, A.L. PLATON squeeze: A tool for the calculation of the disordered solvent contribution to the calculated structure factors. *Acta Crystallogr. Sect. C: Struct. Chem.* **2015**, C71, 9–18. [[CrossRef](#)] [[PubMed](#)]
20. Skelton, B.W.; Waters, A.F.; Whitaker, C.R.; White, A.H. Magnesium iodide-4,4'-bipyridine-water (1/3/4) and strontium iodide-4,4'-bipyridine-propan-1-ol (1/2.5/2). *Acta Crystallogr. Sect. C.* **2003**, 59, m435–m438. [[CrossRef](#)] [[PubMed](#)]
21. Kepert, D.L.; Waters, A.F.; White, A.H. Synthesis and Structural Systematics of Nitrogen Base Adducts of Group 2 Salts. VIII. Some Mixed-Ligand Complexes of Group 2 Metal Halides with Aromatic N,N'-Bidentate and Oxygen Donors. *Aust. J. Chem.* **1996**, 49, 117–135. [[CrossRef](#)]