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MOF Formation vs. Reversible High Ligand Uptake in Anhydrous Halides: Two Opposing Aspects of ${}^{3}_{\infty}[La_2Cl_6(4,4'\text{-bipy})_5]\cdot 4(4,4'\text{-bipy})$

Christoph J. Höller,[a] Philipp Matthes,[a] Jens Beckmann,[b] and Klaus Müller-Buschbaum*[a]

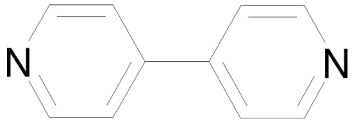
Dedicated to Professor Hans-Jörg Deiseroth on the Occasion of His 65th Birthday

Keywords: Lanthanum; Metal-organic frameworks; Ln–N-MOFs; Reversibility; 4,4'-Bipyridine

Abstract. Construction of the framework structure ${}^{3}_{\infty}[La_2Cl_6(\text{bipy})_5]\cdot$4bipy (**1**), bipy = 4,4'-bipyridine, $C_{10}H_8N_2$, is achieved by reaction of the anhydrous halide $LaCl_3$ with molten 4,4'-bipyridine. Five equivalents of bipyridine are used for the framework construction linking $LaCl_3$ units to give an extended, three-dimensional MOF. Furthermore, four additional equivalents of bipyridine per $LaCl_3$ unit are incorporated within the crystalline MOF, which is thereby completely filled with bipy molecules. This compound formation results in the extraordinary high uptake of nine equivalents of bipyridine per equivalent of the formula and a volume increase of eight times the volume of $LaCl_3$. Further heating of the MOFs results in a stepwise release of all nine equivalents of bipyridine and reformation of the anhydrous chloride at 425 °C. Formation and disassembly can be run in cycles and are reversible. Thus two interesting yet opposing aspects are the reversible construction and disassembly of the MOF framework.

Introduction

Usually, the construction of MOFs is described as an intended one way reaction of metal salts and complexes with a suitable linker to give a multi-dimensional framework structure [1–6]. The way back and thereby decomposition of the MOF structures is fairly unwanted. This includes the N ligand containing *Ln*–N-MOFs we have elaborated from ligand melts [7]. Nonetheless decomposition is a prominent feature of all solvent containing MOFs that enforce a thermal activation in order to gain porous materials by evaporation of incorporated solvate ligands [8–10]. As collapse of the referring frameworks is likely for highly solvent containing MOFs it is also limiting the interest in such materials. We discovered for the series of two-dimensional 4,4'-bipyridine containing *Ln*–N-MOFs of the formula ${}^{2}_{\infty}[Ln_2Cl_6(\text{bipy})_3]\cdot$2bipy, with *Ln* = Ce, Pr, Nd, Sm, Eu, Tb, bipy = 4,4'-bipyridine ($C_{10}H_8N_2$, see Scheme 1) [11] that their formation is thermally reversible. Construction of the MOFs and disassembly into the reagents can be directed depending on the temperature. We now found that the number of equivalents that are reversibly incorporated in LnX_3 can be further increased for lanthanum up to nine equivalents per formula unit including the reversible character of the reactions. Accordingly, formation and disassembly reactions of MOFs can be equally interesting for such a high and reversible ligand uptake in anhydrous halides of the rare earth elements.



Scheme 1. The amine ligand 4,4'-bipyridine.

Experimental Section

All manipulations were carried out under inert atmospheric conditions using glove box, ampoule as well as vacuum line techniques. Heating furnaces were equipped with Al_2O_3 tubes and EUROTHERM 2416 control elements. For ${}^{3}_{\infty}[La_2Cl_6(\text{bipy})_5]\cdot$4bipy (**1**), the trichloride $LaCl_3$, was prepared according to the known ammonium halide route [12] using the oxide La_2O_3 (ChemPur, 99.9 %), HCl solution (10 $mol\cdot l^{-1}$, reagent grade) and ammonium chloride (Fluka, 99.5 %), and purified by decomposition of the trivalent ammonium chlorides under vacuum and subsequent sublimation of the products. 4,4'-bipyridine (ACROS, 98 %) was used as purchased. All products are air and moisture sensitive. The IR spectra were recorded using a BRUKER FTIR-IS66V-S spectrometer. KBr pellets for Mid IR investigation and PE pellets for Far IR were used under vacuum. Only the crystalline product was

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* PD Dr. K. Müller-Buschbaum
Fax: +49-89-2180-77851
E-Mail: kmbch@cup.uni-muenchen.de
[a] Department für Chemie und Biochemie
Ludwig-Maximilians-Universität München
Butenandtstr. 5–13 (D)
81377 München, Germany
[b] Institut für Chemie und Biochemie
Anorganische Chemie
Freie Universität Berlin
Fabeckstraße 34–36
14195 Berlin, Germany

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used for micro analyses on a Vario Microcube (Elementar) elemental analyzer. The yield of the reaction was calculated according to the amount of ligand used for the synthesis. For thermal analysis the bulk product of ${}^{3}_{\infty}[La_2Cl_6(4,4'\text{-bipy})_5]\cdot 4(4,4'\text{-bipy})$ was studied using simultaneous DTA/TG (TG-DTA92 Setaram). 17,5 mg of ${}^{3}_{\infty}[La_2Cl_6(4,4'\text{-bipy})_5]\cdot 4(4,4'\text{-bipy})$ were heated from 25 °C to 700 °C in a constant helium flow of 50ml·min^{-1} with a heating rate of 10 °C·min^{-1}.

Synthesis of ${}^{3}_{\infty}[La_2Cl_6(bipy)_5]\cdot 4bipy$

$LaCl_3$ (0.25 mmol, 62 mg) and 4,4'-bipyridine (bipy, 1.25 mmol, 195 mg) were sealed in an evacuated DURAN^{TM} glass ampoule and heated to 90 °C in 7 h and then to 120 °C within 30 h. The temperature was held for 48 h and afterwards cooled to 95 °C in 250 h and finally to room temperature in further 14 h. The reaction resulted in high reflecting colorless crystals of the product and an amount of unreacted $LaCl_3$ in the bulk. Yield: 199 mg = 84 %. Anal. calcd. $La_2Cl_6C_{90}H_{72}N_{18}$; M = 1896.22 g·mol^{-1}: C, 57.01; N, 13.30; H, 3.83. Found: C, 56.74; N, 12.98; H, 3,95 %. **MIR** (KBr): (3129 s, 1591 m, 1532 w, 1489 w, 1403 s, 1231 w, 1066 w, 1011 w, 868 w, 822 msh, 801 s, 733 w, 614 m, 571 w, 474 w) cm^{-1}. **FIR** (PE): (570 m, 474 m, 236 w, 214 m, 179 m, 160 w, 143 w) cm^{-1}.

Studies concerning the reversibility of formation and disassembly of the framework compound were performed with the same amounts of the reagents but shortened in annealing and reaction times for each step. Only one tenth annealing (24 h) and the half reaction time (24 h) were applied. Therefore, no complete reaction occurred and the crystallinity degrades. These conditions were chosen in order to keep a reasonable timeframe for multiple repetitions. Therefore an amount of 25 % of unreacted halide $LaCl_3$ remains.

Table 1. Crystallographic data for ${}^{3}_{\infty}[La_2Cl_6(bipy)_5]\cdot 4bipy$. Deviations are given in brackets.

formula	$C_{90}H_{72}N_{18}La_2Cl_6$
formula weight	1896.18
crystal system	triclinic
space group	$P\bar{1}$
a /pm	1344.7(3)
b /pm	1371.5(3)
c /pm	1430.1(3)
α /°	79.48(3)
β /°	63.90(3)
γ /°	65.68(3)
V /10^6 pm^3	2158.3(11)
Z	1
$d_{calcd.}$ /g· cm^{-3}	1.459
μ/cm^{-1}	12.2
T /K	173(2)
data range	$3.18 \leq 2\theta \leq 54.66$
X-ray radiation /pm	Mo-K_α, λ = 71.073
diffractometer	STOE **I**mage **P**late **D**iffraction **S**ystem II
no. of unique reflections	9557
no. of refined parameters / refl./ parameter ratio	567 / 17
R_1 $^{a)}$ for n reflections with $F_o > 4\sigma(F_o)$; n	0.0447; 5743
R_1 (all)	0.0965
wR_2 $^{b)}$ (all)	0.0951
remaining electron density /e· pm·10^{-6}	+0.85/–2.13

a) $R_1 = \Sigma[|F_o|-|F_c|]/\Sigma\,[|F_o|$. b) $wR_2 = (\Sigma w(F_o^2-F_c^2)^2/(\Sigma w\,(F_o^4))^{1/2}$ [14].

Crystal Structure Determination

The best suitable single crystal of the compound ${}^{3}_{\infty}[La_2Cl_6(4,4'\text{-bipy})_5]\cdot 4(4,4'\text{-bipy})$ (**1**) was selected for single-crystal X-ray investigation under glovebox conditions and sealed in a glass capillary. Data collection was carried out on a STOE IPDS-II diffractometer (Mo-K_α radiation λ = 0.7107 Å) at 170 K. The structure was determined using direct methods [13]. All non hydrogen atoms were refined anisotropically by least-squares techniques [14]. All hydrogen positions were calculated into pre-set positions adjusting their thermal parameters to 1.2 of the referring carbon atoms. The compound crystallizes in the triclinic space group $P\bar{1}$. Because of the free rotation of the pyridine rings in 4,4'-bipyridine one incorporated bipy molecule is disordered (see Supporting Information). Integrity of symmetry and extinction were checked and no higher symmetry could be found [15]. A numerical absorption correction was applied [16]. For crystallographic data see Table 1. Further information was deposited at the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223336033 or E-Mail: deposit@ccdc.cam.ac.uk) and may be requested by citing the deposition number CCDC-740032, the names of the authors and the literature citation.

Results and Discussion

Reversible Formation and High Ligand Uptake

We elaborated that the use of melts of organic ligands like N-heterocyclic amines is a suitable alternative to solvent treatments if co-coordination of the solvent is to be avoided [17]. Depending on the ligands used and the reaction conditions a large structural variety ranging from small molecular complexes [17a, 18] to coordination polymers and MOFs [19] can be obtained. The ligand melt can be directly used for oxidizing reactive metals like the lanthanides acting as weak N–H acids using various activation methods for the metals [17a, 20]. The method can also be used for other ligands like phenols [21] or thioles [22] to yield amides, phenolates and thiolates of the rare earth elements together with hydrogen gas. It can be further expanded to ligands that cannot be utilized in a redox reaction. Instead of metals, we successfully used anhydrous halides of the rare earth elements to yield nitriles [23] of the lanthanides including the first dinitrile *Ln*–N-MOFs of the referring elements [24, 25]. Accordingly, the 4,4'-bipyridine ligand that has been used for MOF constructions of transition metals already [26–28] was most promising for our synthesis strategy together with lanthanide halides. 4,4'-bipyridine acts as chemical scissors and cuts down the halide structure. It also controls the formation of coordination polymers by interlinking $LnCl_3$ units. For numerous lanthanides this can lead to 2D-nets of the formula ${}^{2}_{\infty}[Ln_2Cl_6(bipy)_3]\cdot 2bipy$, with *Ln* = Ce, Pr, Nd, Sm, Eu, Tb, [11]. In addition to three interlinking ligands per two $LnCl_3$ units, two equivalents of bipy are incorporated in cavities within and in between the sheets. For the larger trivalent ion La^{3+} we now found that an extraordinary increase in the 4,4'-bipyridine uptake is observed according to the reaction [Equation (1)]:

$$2\ LaCl_3 + 9\ C_{10}H_8N_2 \xrightarrow[120\ °C]{C_{10}H_8N_2\ melt} {}^{3}_{\infty}[La_2Cl_6(C_{10}H_8N_2)_5]\cdot 4(C_{10}H_8N_2) \quad (1)$$

At temperatures starting from 155 °C the MOF begins to release the incorporated bipyridine equivalents in three steps.

Removal of the template bipyridine is in principle possible by evaporation, as thermal investigations reveal. But as this does not lead to suitable crystals, it has yet not been possible to refine the structure of this new template free high temperature compound. At temperatures between 330–425 °C also the linking bipyridine equivalents are released in two steps under re-formation of $LaCl_3$ [Equation (2)], as observed by simultaneous DTA/TG (see Figure 1):

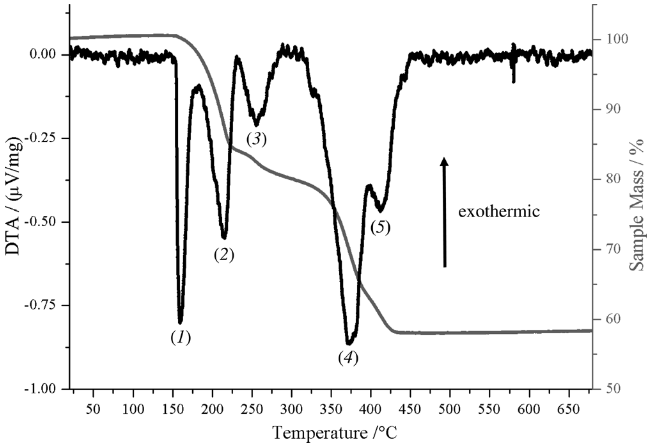

Figure 1. Simultaneous DTA/TG of $^{3}_{\infty}[La_2Cl_6(bipy)_5]\cdot 4bipy$ (**1**) reveals a five step release of 4,4'-bipyridine from the framework. The first three signals correspond to intercalated bipy equivalents; the forth and fifth signal above 350 °C indicate the framework disassembly and reformation of the reagents.

$$^{3}_{\infty}[La_2Cl_6(C_{10}H_8N_2)_5]\cdot 4(C_{10}H_8N_2) \xrightarrow{155\text{–}425\ °C} 2\ LaCl_3 + 9\ C_{10}H_8N_2 \uparrow \quad (2)$$

If the bipy equivalents released from the MOF are recovered, the formation reaction can be started over. Thus formation and disassembly of the framework are reversible. Formation and disassembly can be run in cycles as powder diffraction indicates, (see Figure 2) [29]. Some unreacted $LaCl_3$ in the product pattern originates from incomplete reaction because of shorter reaction and annealing times, which had to be chosen in order to allow multiple reversible processes in a reasonable timeframe. Reversibility is further supported by IR spectroscopy. Mid IR spectra of the product contain bands that can be identified with the ν(C–N) stretching modes. They are shifted to smaller wave numbers compared to the free ligand because of binding to the metal ions and thus weakening of the C–N bonds at 1011 cm^{-1}. The ν(C=N) ring vibrations of the uncoordinated 4,4'-bipyridine are observed at 1591 cm^{-1}. Furthermore, the Far IR spectra of framework **1** contain bands that indicate ν(*Ln*–N) stretching modes between 236–214 cm^{-1} [30]. Only the *Ln*–Cl stretching and deformation bands at 571 and 474 cm^{-1} [31] are found after disassembly.

That leads us to describing the compound presented here with two equally interesting features: As the first feature a MOF structure is formed that is able to incorporate a large number of additional bipy equivalents as well as these incorporated molecules can all be thermally released. Moreover, as the linking bipyridine equivalents can also be released reversibly, another interesting point can be raised as the second feature: Anhydrous halides LnX_3 can show an extraordinary high uptake of the organic ligand 4,4'-bipyridine with formation of N-donor complexes as thermal intermediates and re-formation of the halides at suitable temperatures.

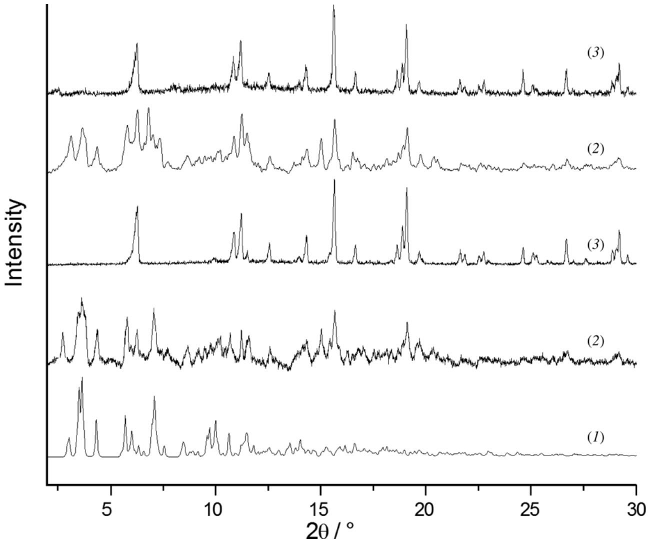

Figure 2. Simulated powder pattern (*1*) of $^{3}_{\infty}[La_2Cl_6(bipy)_5]\cdot 4bipy$ (**1**) (from bottom to top) as well as powder diffractogram of the bulk product of the MOF formation (*2*) in comparison to diffractograms after disassembly of the MOF to $LaCl_3$ (*3*). Both reactions can be run in cycles as the repetitions of patterns indicate (Mo-$K_{\alpha 1}$ radiation, λ = 0.7107 Å).

Crystal Structure

The crystal structure of $^{3}_{\infty}[La_2Cl_6(bipy)_5]\cdot 4bipy$ (**1**), bipy = 4,4'-bipyridine, $C_{10}H_8N_2$, constitutes to a three-dimensional framework. It is built up by trivalent lanthanum ions linked by 4,4'-bipyridine ligands and chloride ions. $^{3}_{\infty}[La_2Cl_6(bipy)_5]\cdot 4bipy$ exhibit a CN of eight consisting of three halide atoms each as well as two additional nitrogen atoms, resulting in a

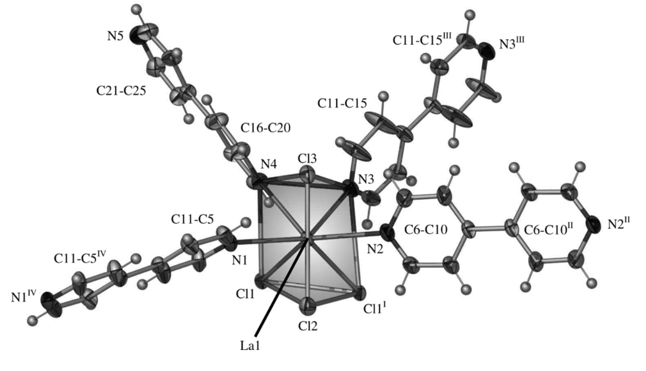

Figure 3. The double capped trigonal prismatic coordination sphere of nitrogen and chlorine atoms around La^{III} in $^{3}_{\infty}[La_2Cl_6(bipy)_5]\cdot 4bipy$ as well as the thermal ellipsoids of the atoms reflecting 50 % probability. Symmetry operations: I: 1 –*x*, 2 –*y*, 1 –*z*, II: 2 –*x*, 1 –*y*, 1 –*z*, III: 2 –*x*, 2 –*y*, 1 –*z*, IV: –*x*, 2 –*y*, 2 –*z*.

double nitrogen capped trigonal prism around lanthanum. Three bipyridine ligands coordinate rather symmetrically μ-η^1:η^1 to two different lanthanide cations with each nitrogen atom of the pyridine rings. The double capping nitrogen atoms exhibit an N–La–N angle of 135.7(2)° (ideal 120°). A fourth bipyridine molecule coordinates end-on η^1 to only one lanthanide ion. Four chloride ions complete the coordination sphere of every lanthanide atom (see Figure 3, for selected interatomic distances and angles see Table 2). Edge sharing of the double capped trigonal prisms leads to the formation of a three-dimensional framework. The CN of lanthanum in **1** is higher than for the series of lanthanides of the formula $^{2}_{\infty}[Ln_2Cl_6(\mathrm{bipy})_3]\cdot$2bipy, with *Ln* = Ce, Pr, Nd, Sm, Eu, Tb [11], which exhibit pentagonal-bipyramidal coordination. This corroborates the fact that La^{3+} is the largest of the Ln^{3+} ions [32]. Double capped trigonal prisms around lanthanum atoms can also be found in $La_3OCl[AsO_3]_2$ as well as in $[La_2(aib)_4(H_2O)_8](ClO_4)_6$ (aib = α-aminoisobutyric acid) [33, 34], although the most numerous coordination polyhedron for La^{3+} with CN eight is the square antiprism, especially regarding nitrogen coordination [35]. The La–N distances in **1** range from 274.9(4) to 281.8(4) pm. Because of the large La^{3+}-ion and the high coordination number of eight, the La–N distances are about 20 pm larger than the ones e.g. found for $^{2}_{\infty}[Sm_2Cl_6(\mathrm{bipy})_3]\cdot$2bipy of 258–263 pm [11]. In $^{3}_{\infty}[La_2Cl_6(\mathrm{bipy})_5]\cdot$4bipy two of the chloride ions also link between different lanthanide ions forming a “double bridge” [36]. The La–Cl distances range from 276.0(2) to 296.4(2) pm and match with the trichloride [37]. Figure 4 depicts the crystal structure of **1**.

Table 2. Selected distances /pm and angles /deg between atoms of $^{3}_{\infty}[La_2Cl_6(\mathrm{bipy})_5]\cdot$4bipy. Deviations are given in brackets.

atoms	distances	atoms	angles
La1–N1	279.4(4)	N1–La1–N2	135.70(13)
La1–N2	281.8(4)	N3–La1–N4	66.63(13)
La1–N3	274.9(4)	Cl1–La1–Cl1$^{\#1}$	68.05(5)
La1–N4	276.4(4)	Cl2–La1–Cl3	102.49(5)
La1–Cl1	288.7(2)	Cl1–La1–N3	98.00(10)
La1–Cl1$^{\#1}$	296.4(2)		
La1–Cl2	276.0(2)		
La1–Cl3	280.6(2)		

Symmetry operation: #1 1 –*x*, 2 –*y*, 1 –*z*.

As the linkage leads to a complicated crystal structure, it is reasonable to reduce it to a topological description. $^{3}_{\infty}[La_2Cl_6(\mathrm{bipy})_5]\cdot$4bipy can be identified with two perpendicular 2D-nets that each have a 6,3 topology. Viz., three sixfold bridged rings form a 2D-layer. This gives an overall 3D (6,4) topology (see Figure 5). This topology is e.g. also found for MOFs like $Co(Im)_2$ (Im^- = $N_2C_3H_3$, imidazolate) or $[Eu(pdc)_{1.5}(dmf)]\cdot dmf\cdot(H_2O)_{0.5}$ (pdc^{2-} = pyridine-3,5-dicarboxylate, dmf = dimethylformamid) [38, 39]. The topology description however is based on counting the chloride “double-bridges” as one bridge only. Otherwise the connectivity would be five.

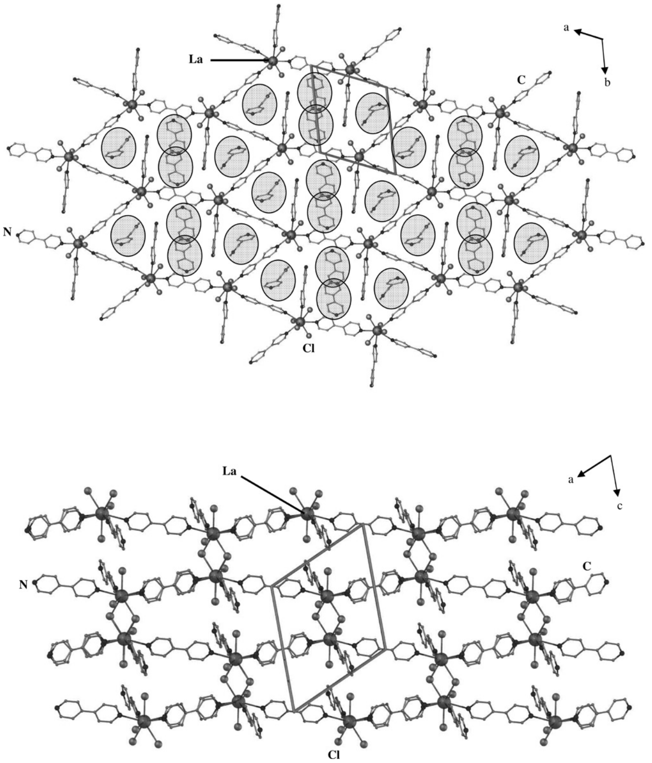

Figure 4. The crystal structure of $^{3}_{\infty}[La_2Cl_6(\mathrm{bipy})_5]\cdot$4bipy with a view along [001] (top) and [010] (bottom). Incorporated bipyridine molecules are either emphasized by ellipsoids (top) or omitted for clarity (bottom). Lanthanum atoms are depicted as large grey balls, nitrogen atoms as dark, carbon atoms as well as chlorine atoms as light grey balls. Hydrogen atoms are omitted for clarity as well.

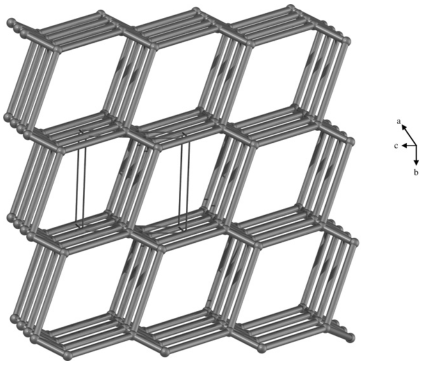

Figure 5. Topological drawing of $^{3}_{\infty}[La_2Cl_6(\mathrm{bipy})_5]\cdot$4bipy with a view along [100]. The framework can be identified with a three-dimensional (6,4) net that consists of two two-dimensional 6,3 nets.

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