

Synthesis and crystal structure of heteronuclear La(III)-Cu(II) complex $\{[\text{LaCu}_2(\text{NTA})_2(4,4'\text{-bpy})(\text{H}_2\text{O})_3]\text{NO}_3 \cdot 5\text{H}_2\text{O}\}_n$

LIANG, Fu-Pei(梁福沛) CHEN, Zi-Lu(陈自卢) HU, Rui-Xiang(胡瑞祥)

LIANG, Hong*(梁宏) ZHANG, Man-Bo(张曼波)

Department of Chemistry, Guangxi Normal University, Guilin, Guangxi 541004, China

YU, Kai-Bei(郁开北)

Analysis Center, Chengdu Branch of Chinese Academy of Science, Chengdu, Sichuan 610041, China

A novel La(III)-Cu(II) heterometallic coordination polymer $\{[\text{LaCu}_2(\text{NTA})_2(4,4'\text{-bpy})(\text{H}_2\text{O})_3]\text{NO}_3 \cdot 5\text{H}_2\text{O}\}_n$, where H_3NTA denotes nitrilotriacetic acid and 4,4'-bpy denotes 4,4'-bipyridine, was synthesized and characterized by IR spectrum, elemental analysis and X-ray diffraction. The complex crystallizes in the triclinic space group $P\bar{1}$ with cell parameters $a = 1.33710(10)$ nm, $b = 1.44530(10)$ nm, $c = 1.0949(2)$ nm, $\alpha = 71.905(7)^\circ$, $\beta = 74.327(7)^\circ$, $\gamma = 64.427(9)^\circ$, $V = 1.7912(4)$ nm³ and $Z = 2$. It consists of heterometallic units, in which each La(III) ion is coordinated in a distorted mono-capped square antiprism by three oxygen atoms from water molecules and six carboxyl oxygen atoms from five NTA^{3-} ions, and each Cu(II) ion is coordinated by one nitrogen atom from 4,4'-bpy and one nitrogen atom, three oxygen atoms from NTA^{3-} . In the title complex, La(III) ions and Cu(II) ions are connected by the heterometallic bridging of NTA^{3-} , constructing a two-dimensional network structure along the [110]. And it is extended into an infinite three-dimensional network structure by the formation of homometallic bridging of Cu-4,4'-bpy-Cu, exhibiting a certain inclusion ability.

Keywords Nitrilotriacetic acid, 4,4'-bipyridine, La(III)-Cu(II) heterometallic complex, three-dimensional network structure, inclusion, bridging

Heteronuclear and/or polynuclear complexes have attracted considerable interests in the last two decades. Especially great attention has been paid to the heteronuclear complexes containing both lanthanide(III) and 3dⁿ transition metal ions¹⁻¹¹ due to their interesting structures

and various properties. To look for novel molecular functional materials, all sorts of complexes owning one-, two-, or three-dimensional structures have been flourishing out, such as linear,¹² ladders,^{13,14} layered network,³ clusters^{4,15-17} or helical¹⁸⁻²¹ and other complicated 3D network structures.²² These kinds of complexes provide models for investigations of magnetic exchange interactions between transition metal and rare-earth metal ions in bridging systems;^{23,24} they are also possible precursors for the production of high temperature superconductors.^{25,26} Besides these, there can still be used to develop luminescent structural probes in biological materials.²⁷

In the rare earth and transition metal heterometal complex systems, the finite and/or simple structures have been sufficiently studied, however, the infinite and/or poly-dimensional complicated structures are less reported. The bridging ligand is designed from simple heteronuclear ligand to segmental ligand or 'complex ligand'. But still less investigated was the amino polycarboxylic acid^{6,28} or amino acid^{5,17} as the heterometallic bridging of rare earth and transition metals. Furthermore, the application of this type of complex is still not enough developed, especially in biological and medical fields. In this paper, nitrilotriacetic acid was chosen as heterometallic bridging. And another ligand of 4,4'-bipyridine was added as homometallic bridging. Therefore, we obtained a novel complex containing two differ-

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ent kinds of ligands acting as heterometallic and homometallic bridges respectively in the same complex simultaneously.

Experimental

Lanthanum oxide and absolute ethanol were of analytical grade, other reagents used in the synthesis were of reagent grade. Among them, nitrilotriacetic acid was purified by recrystallizing before using. Elemental analysis (C, H, N) was performed by a German EL-CHNS-O elemental analyser. Infrared spectrum was measured with an American Nicolet 5DXB FT-IR spectrophotometer on KBr disk.

NTA (0.1915 g, 1.0 mmol) was dissolved in water (10 mL) at 80°C and the pH value of the solution was adjusted to 6.0 with 0.2 mol/L NaOH solution, then aqueous solution (5 mL) of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.2418 g, 1.0 mmol) was added stepwise with stirring. The resulting blue solution was adjusted to pH = 5 and then stirred at 80°C for 5 h. After that, the mixture was cooled to room temperature and 5 mL of aqueous solution containing 1 mmol of $\text{La}(\text{NO}_3)_3$ (pH = 5) was added with stirring. 1 h later, 0.5 mmol of 4,4'-bpy in absolute ethanolic solution (5 mL) was added rapidly. The resulting solution was kept on stirring for 12 h, then left to evaporate for one day, giving blue needle crystals of the complex. A single crystal suitable for X-ray analysis

was obtained from the mother solution of the filtration by evaporating the solvent at room temperature for one month. Anal. $\text{C}_{22}\text{H}_{36}\text{Cu}_2\text{LaN}_5\text{O}_{23}$. Calcd.: C, 26.30; H, 3.62; N, 6.97. Found: C, 26.63; H, 3.45; N, 6.99. Infrared data: 3375 (s, br.), 2976.6 (w), 2936.7 (w), 1608.6 (vs), 1575.4 (s), 1489 (w), 1455 (m), 1402.7 (s), 1323 (m), 1250 (w), 1223.4 (w), 1110.5 (w), 1070.7 (w), 1017.6 (w), 918 (w), 818.4 (w), 732 (w), 652 (w), 532.8 (w).

Results and discussion

A summary of selected crystallographic data for the complex is given in Table 1. The diffraction data of the single crystal was collected on a Siemens P4 diffractometer using graphite-monochromated $\text{Mo K}\alpha$ ($\lambda = 0.071073$ nm) radiation in the ω -scan mode at 296(2) K. Cell parameters of the complex were determined from 29 reflections in the θ range of $3.67 < \theta < 16.54^\circ$. An empirical absorption correction was applied to the original data set. The structure was solved using direct methods and refined by a full-matrix least-squares on F_2 technique using the SHLXL-97 program package. Hydrogen atoms of the ligands were generated geometrically. The weighting schemes are $w = 1/[\sigma^2 F_o^2 + (0.0508 P)_2 + 3.7820 P]$, where $P = (F_o^2 + 2F_c^2)/3$. Selected bond lengths and bond angles are listed in Table 2. The positional parameters are given in Table 3.

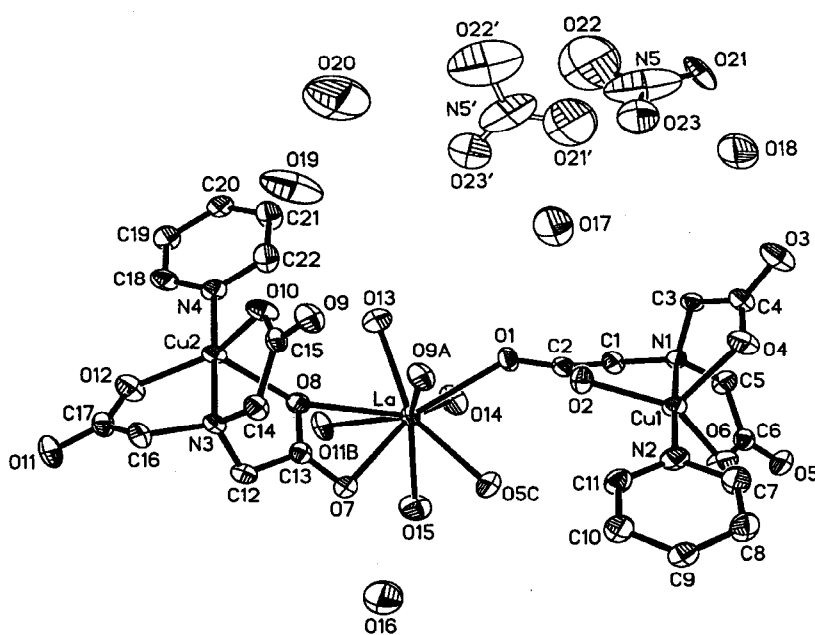


Fig. 1 Asymmetric unit content along with the atom labelling.

Table 1 Crystallographic data

Empirical formula	C ₂₂ H ₃₆ Cu ₂ LaN ₅ O ₂₃	Crystal size, mm	0.50 × 0.32 × 0.18
Crystal system	Triclinic	<i>T</i> , K	296(2)
Space group	<i>P</i> $\bar{1}$	θ	1.70 to 25.00°
<i>a</i> , nm	1.33710(10)	Index range	0 ≤ <i>h</i> ≤ 15, -15 ≤ <i>k</i> ≤ 16, -12 ≤ <i>l</i> ≤ 13
<i>b</i> , nm	1.44530(10)	μ , mm ⁻¹	2.44
<i>c</i> , nm	1.0949(2)	Refl. collected/unique	13557/6260 [<i>R</i> (int) = 0.0129]
α , deg	71.905(7)	Max. and min. transm.	0.6675 and 0.3747
β , deg	74.327(7)	Refinement method	Full-matrix least-squares on <i>F</i> ²
γ , deg	64.427(9)	Parameters	505
<i>V</i> , nm ³	1.7912(4)	Goodness-of-fit on <i>F</i> ²	1.046
Formula weight	1004.5	Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.032, ωR ₂ = 0.0861
λ , nm	0.071073	<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0353, ωR ₂ = 0.0885
<i>Z</i>	2	Extinction coefficient	0.0032(4)
<i>D</i> _x , g/cm ³	1.863	Largest diff. peak and hole	1303 and -601 e/nm ³
<i>F</i> (000)	1004.0		

Table 2 Selected bond lengths (nm) and bond angles (deg)

La—O1	0.2511(3)	Cu1—N1	0.1996(3)
La—O5C	0.2534(3)	Cu1—N2	0.1958(4)
La—O7	0.2579(3)	Cu1—O2	0.1997(3)
La—O8	0.2674(3)	Cu1—O4	0.2133(3)
La—O9A	0.2506(3)	Cu1—O6	0.2004(3)
La—O11B	0.2533(3)	Cu2—N3	0.2010(3)
La—O13	0.2539(3)	Cu2—N4	0.1976(3)
La—O14	0.2523(3)	Cu2—O8	0.2214(3)
La—O15	0.2665(3)	Cu2—O10	0.1964(3)
		Cu2—O12	0.1963(3)
O9A—La—O1	72.44(10)	O9A—La—O14	139.04(11)
O1—La—O14	67.95(11)	O9A—La—O11B	133.76(10)
O1—La—O11B	136.40(10)	O14—La—O11B	74.80(11)
O9A—La—O5C	77.955(10)	O1—La—O5C	78.12(10)
O14—La—O5C	103.22(11)	O11B—La—O5C	133.48(11)
O9A—La—O13	85.81(12)	O1—La—O13	75.20(11)
O14—La—O13	74.59(13)	O11B—La—O13	73.74(12)
O5C—La—O13	151.94(11)	O9A—La—O7	75.82(10)
O1—La—O7	139.91(10)	O14—La—O7	144.25(11)
O11B—La—O7	83.60(10)	O5C—La—O7	71.77(10)
O13—La—O7	126.24(11)	O9A—La—O15	140.67(11)
O1—La—O15	117.31(11)	O14—La—O15	70.51(12)
O11B—La—O15	67.59(11)	O5C—La—O15	68.19(11)
O13—La—O15	133.07(12)	O7—La—O15	75.05(11)
O9A—La—O8	65.47(10)	O1—La—O8	130.40(10)
O14—La—O8	139.13(11)	O11B—La—O8	69.60(10)
O5C—La—O8	115.64(9)	O13—La—O8	76.72(10)
O7—La—O8	49.61(9)	O15—La—O8	111.81(10)
O9A—La—C13	67.61(10)	O1—La—C13	140.05(11)
O14—La—C13	150.86(11)	O11B—La—C13	76.45(10)
O5C—La—C13	93.12(11)	O13—La—C13	101.72(12)
O7—La—C13	24.66(10)	O15—La—C13	94.20(11)
O8—La—C13	25.00(10)	N2—Cu1—N1	177.54(15)
N2—Cu1—O2	98.52(14)	N1—Cu1—O2	83.27(13)
N2—Cu1—O6	93.41(14)	N1—Cu1—O6	84.13(13)
O2—Cu1—O6	134.21(14)	N2—Cu1—O4	98.21(14)
N1—Cu1—O4	82.58(13)	O2—Cu1—O4	113.05(13)
O6—Cu1—O4	108.65(14)	O12—Cu2—O10	145.68(14)
O12—Cu2—N4	96.55(14)	O10—Cu2—N4	94.00(14)
O12—Cu2—N3	83.67(13)	O10—Cu2—N3	85.41(13)
N4—Cu2—N3	179.22(15)	O12—Cu2—O8	111.37(13)
O10—Cu2—O8	98.66(12)	N4—Cu2—O8	100.19(13)
N3—Cu2—O8	80.41(12)	C1—N1—C3	111.8(3)

Table 3 Atomic coordinates and equivalent isotropic displacement parameters [$\times 10^4 \text{ nm}^2$] for the complex. $U(\text{eq})$ is defined as one third of the trace of orthogonalized U_{ij} tensor

	<i>x</i>	<i>y</i>	<i>z</i>	$U(\text{eq})$
La	0.1798(1)	0.2316(1)	0.7764(1)	2.0(1)
Cu1	0.3975(1)	0.0627(1)	0.3187(1)	2.3(1)
Cu2	-0.1233(1)	0.5614(1)	0.8096(1)	2.1(1)
N1	0.3455(3)	-0.0535(3)	0.4221(3)	2.1(1)
N2	0.4551(3)	0.1724(3)	0.2180(4)	2.9(1)
N3	-0.0194(3)	0.6380(3)	0.7185(3)	1.9(1)
N4	-0.2268(3)	0.4876(3)	0.8976(3)	2.6(1)
O1	0.1814(3)	0.1209(2)	0.6383(3)	3.1(1)
O2	0.2690(3)	0.1468(2)	0.4336(3)	2.8(1)
O3	0.2474(3)	-0.0417(3)	0.1427(3)	4.5(1)
O4	0.3465(3)	0.0413(3)	0.1643(3)	3.5(1)
O5	0.6414(3)	-0.2200(2)	0.3850(3)	3.2(1)
O6	0.5507(3)	-0.0467(2)	0.3441(3)	3.6(1)
O7	0.2199(2)	0.3962(2)	0.7525(3)	2.8(1)
O8	0.0392(2)	0.4255(2)	0.8040(3)	2.4(1)
O9	-0.1052(3)	0.6466(2)	0.4264(3)	3.2(1)
O10	-0.1525(3)	0.5817(2)	0.6349(3)	3.0(1)
O11	-0.1238(3)	0.7623(2)	0.9850(3)	3.7(1)
O12	-0.1473(3)	0.6297(3)	0.9504(3)	3.5(1)
O13	-0.0105(3)	0.2162(3)	0.8482(4)	4.6(1)
O14	0.2190(3)	0.0431(3)	0.8982(3)	4.2(1)
O15	0.3569(3)	0.1613(3)	0.8954(3)	4.4(1)
C1	0.2977(4)	-0.0296(3)	0.5519(4)	2.5(1)
C2	0.2441(4)	0.0884(3)	0.5418(4)	2.5(1)
C3	0.2592(4)	-0.0469(3)	0.3561(4)	2.4(1)
C4	0.2875(4)	-0.0144(3)	0.2093(4)	2.8(1)
C5	0.4437(4)	-0.1545(3)	0.4220(5)	2.9(1)
C6	0.5532(4)	-0.1392(3)	0.3818(4)	2.5(1)
C7	0.5339(4)	0.1510(4)	0.1136(5)	3.8(1)
C8	0.5903(4)	0.2166(4)	0.0445(5)	3.9(1)
C9	0.5687(4)	0.3064(3)	0.0857(4)	2.7(1)
C10	0.4859(4)	0.3280(4)	0.1924(5)	3.5(1)
C11	0.4314(4)	0.2599(4)	0.2560(5)	3.1(1)
C12	0.0913(4)	0.5722(3)	0.7602(4)	2.5(1)
C13	0.1193(3)	0.4564(3)	0.7724(4)	2.2(1)
C14	-0.0137(4)	0.6563(3)	0.5762(4)	2.5(1)
C15	-0.0971(4)	0.6275(3)	0.5427(4)	2.3(1)
C16	-0.0716(4)	0.7354(3)	0.7696(4)	2.5(1)
C17	-0.1174(4)	0.7073(3)	0.9137(4)	2.6(1)
C18	-0.2926(4)	0.5017(4)	1.0114(4)	3.2(1)
C19	-0.3624(4)	0.5017(4)	1.0733(5)	3.3(1)
C20	-0.3637(4)	0.3731(3)	1.0176(4)	2.9(1)
C21	-0.2986(4)	0.3628(4)	0.8969(5)	3.9(1)
C22	-0.2307(4)	0.4194(4)	0.8408(5)	3.7(1)
O16	0.4443(4)	0.3316(4)	0.7867(5)	7.1(1)
O17	-0.0063(5)	0.0961(4)	0.5074(5)	8.2(2)
O18	0.0466(5)	-0.0712(5)	0.2264(6)	8.5(2)
O19	-0.3174(5)	0.5586(5)	0.5482(5)	8.8(2)
O20	-0.4183(7)	0.4239(7)	0.5874(8)	14.0(3)
N5	-0.1535(8)	0.1814(6)	0.1520(9)	11.6(7)
O21	-0.1217(7)	0.1027(5)	0.1051(7)	4.5(2)
O22	-0.2386(11)	0.2010(11)	0.2409(14)	15.6(7)
O23	-0.1115(8)	0.2506(6)	0.0989(10)	7.6(3)
N5'	-0.2352(7)	0.2611(7)	0.3787(9)	8.5(5)
O21'	-0.1625(10)	0.2000(10)	0.3078(9)	12.1(5)
O22'	-0.3340(8)	0.3129(10)	0.3524(12)	13.7(6)
O23'	-0.2108(7)	0.2695(6)	0.4757(8)	5.8(2)

The crystal structure of the complex consists of $[\text{LaCu}_2(4,4'\text{-bpy})(\text{NTA})_2(\text{H}_2\text{O})_3]^+$ cation, NO_3^- anion, and lattice water molecules in an asymmetric unit, as shown in Fig. 1, in which the NO_3^- anion is disordered in the two positions with equal occupancies. Each La^{3+} ion is coordinated by six carboxylate oxygen atoms from five NTA^{3-} ions and three oxygen atoms from coordinated water molecules, forming a distorted monocapped square antiprismatic coordination polyhedron (Fig. 2 (a)) with the bond lengths of $\text{La}-\text{O}$ in the range of 0.2506(3)–0.2674(3) nm. The symmetry transformations used to generate equivalent atoms:

$$\begin{aligned} A &-x, -y+1, -z+1; B -x, -y+1, -z+1; \\ C &-x+1, -y, -z+1. \end{aligned}$$

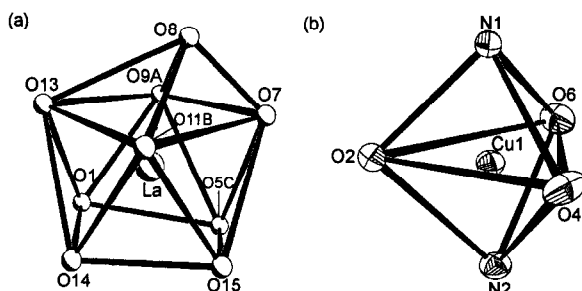


Fig. 2 (a) Lanthanum coordination polyhedron; (b) Cupric coordination polyhedron.

The distance from $\text{La}(\text{III})$ ion to the bridged oxygen atom O8 is a bit longer than those of $\text{La}(\text{III})$ ion to the other eight non-bridged oxygen atoms. Every $\text{Cu}(\text{II})$ ion is coordinated by one nitrogen atom from 4,4'-bipyridine molecule and one nitrogen atom, three oxygen atoms from NTA^{3-} anion. In the distorted trigonal bipyramid environments (Fig. 2(b)) of both Cu1 and Cu2, the distance from $\text{Cu}(\text{II})$ ion to the nitrogen atom of NTA (Cu1–N1: 0.1996(3) nm, Cu2–N3: 0.2010(3) nm) is longer than that of $\text{Cu}(\text{II})$ ion to the nitrogen atom from 4,4'-bipyridine molecule (Cu1–N2: 0.1958(4) nm, Cu2–N4: 0.1976(3) nm). And it is noteworthy that the bond lengths of $\text{Cu}(\text{II})$ ions to the nitrogen atoms from 4,4'-bpy molecules are a little shorter than those reported (Cu–N: 0.1983(9)–0.2049(6) nm),^{29–33} resulting the rather short separations of two $\text{Cu}(\text{II})$ ions in the Cu-4,4'-bpy-Cu (Cu··Cu: 1.0941 nm).

In one unit, $\text{La}(\text{III})$ and $\text{Cu}(\text{II})$ 1 ions are

bridged by one carboxylate group of NTA in a coordination mode of $\text{La}-\text{O}-\text{C}-\text{O}-\text{Cu}$, that is, one of the carboxylate oxygen atoms coordinates to $\text{La}(\text{III})$ ion and the other coordinates to $\text{Cu}(\text{II})$ ion. In contrast to this coordination mode, one oxygen atom of the carboxylate group connecting $\text{La}(\text{III})$ and $\text{Cu}(\text{II})$ 2 ions, acting as a μ -coordination atom, coordinates both to $\text{La}(\text{III})$ and to $\text{Cu}(\text{II})$ ion while the other oxygen atom coordinated only to $\text{La}(\text{III})$ ion. This bridge mode between $\text{La}(\text{III})$ and $\text{Cu}(\text{II})$ 2 results in a shorter distance of $\text{La}\cdots\text{Cu}2$ (0.4784 nm) than that of $\text{La}\cdots\text{Cu}1$ (0.5472 nm). We can also consider that two $\text{Cu}(\text{II})$ ions and one $\text{La}(\text{III})$ are bridged by the ligand of NTA in the form of $\text{Cu}1(\text{carboxylate})\text{La}(\text{carboxylate})\text{Cu}2$ in the unit. As a result, the sequence of atoms $\text{Cu}1\cdots\text{La}\cdots\text{Cu}2$ makes a broken line with an angle of 127.9°.

Actually, in the title complex, $\text{La}(\text{III})$ ions and $\text{Cu}(\text{II})$ ions are connected by the heterometallic bridgings of $\text{La}-\text{NTA}-\text{Cu}$, constructing an infinite two-dimensional network structure along the $[110]$ (Fig. 3). Then the two-dimensional networks are extended into an infinite three-dimensional network structure by the formation of homometallic bridging of $\text{Cu}-4,4'\text{-bpy}-\text{Cu}$, as depicted in Fig. 3. This kind of transition metal and lanthanide heteronuclear complex, in which two different kinds of ligands exist as homometal and heterometal bridgings simultaneously, is not ever reported. In the network, the nearest $\text{Cu}1\cdots\text{Cu}1$, $\text{Cu}1\cdots\text{Cu}2$, $\text{Cu}2\cdots\text{Cu}2$, $\text{La}\cdots\text{Cu}1$, $\text{La}\cdots\text{Cu}2$ and $\text{La}\cdots\text{La}$ distances are larger than 0.4867 nm, 0.576 nm, 0.5401 nm, 0.5472 nm, 0.4784 nm and 0.8620 nm respectively.

The NO_3^- anion and uncoordinated water molecules are trapped in the lattice of the three dimensional network (Fig. 3) as guests. The separations of $\text{O}13\cdots\text{O}23$ (0.2805 nm) and $\text{O}14\cdots\text{O}21$ (0.2927 nm) demonstrate the presence of hydrogen bonds between NO_3^- and coordinated water molecules. Some uncoordinated water molecules and coordinated water molecules also form hydrogen bond with $\text{O}13\cdots\text{O}18$ and $\text{O}15\cdots\text{O}16$ contacts of 0.2728 nm and 0.2958 nm, respectively. It is very interesting that the complicated network is served as hosts for guest molecules or ions. This kind of inclusion phenomenon has ever been reported in the network formed by transition metal and 4,4'-bipyridine molecule.^{29,30} However, it is rarely found in the rare earth and transition metal heterometal system.

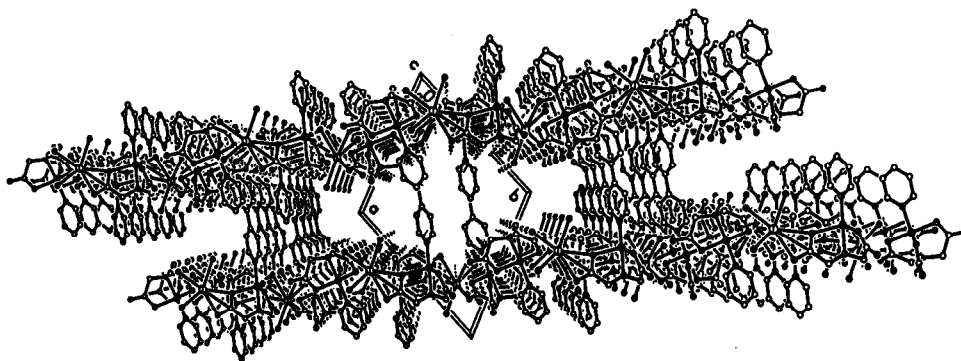


Fig. 3 Three dimensional crystal packing not including NO_3^- and uncoordinated water molecules.

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