

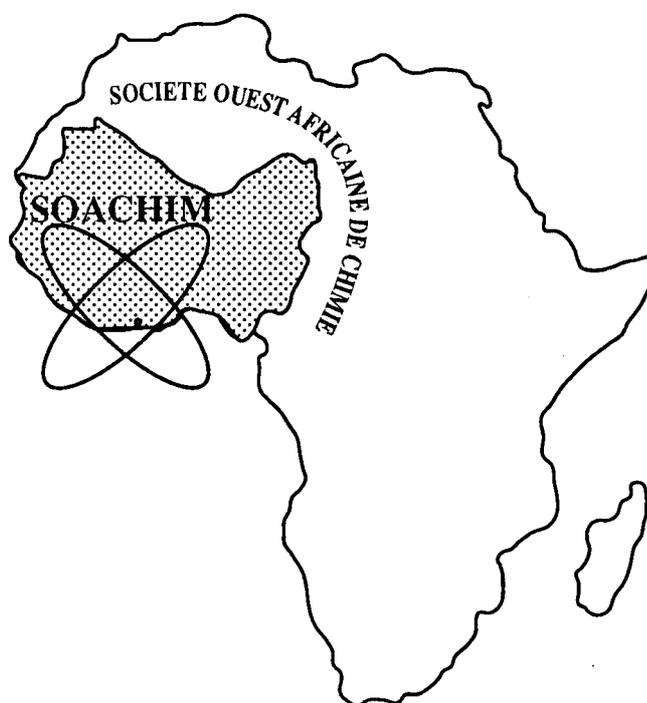
Synthesis, crystal structure and magnetic properties of a novel Nd(III)-Cu(II) heterometallic coordination polymer based on pyridine-3,5-dicarboxylate and oxalate ligands

**Mamoudou Diallo, Magatte Camara, Nicolas Claiser,
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D. Luneau,**

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Synthesis, crystal structure and magnetic properties of a novel Nd(III)-Cu(II) heterometallic coordination polymer based on pyridine-3,5-dicarboxylate and oxalate ligands

Mamoudou Diallo^{a,b}, Magatte Camara^{a*}, Nicolas Claiser^b, Insa Badiane^a, Claude Lecomte^b, Mohamed Souhassou^b, D. Luneau^c,

^[a] *LCPM—Groupe ‘‘Matériaux Inorganiques: Chimie Douce et Cristallographie’’, Université Assane SECK de Ziguinchor, BP 523 Ziguinchor, Sénégal*

^[b] *Laboratoire Cristallographie, Résonance Magnétique et Modélisations, CRM2, UMR 7036, Institut Jean Barriol, Université de Lorraine et CNRS, BP70239, F54506 Vandœuvre-lès-Nancy, France*

^[c] *Laboratoire des Multimatériaux et Interfaces, Groupe de Cristallographie et Ingénierie Moléculaire (UMR 5615), Université Claude Bernard Lyon 1.69622 Villeurbanne cedex*

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Abstract: A novel 3d–4f heterometallic coordination polymer, $\{[\text{NdCu}(3,5\text{-pdc})_2(\text{Oxa})_{0.5}(\text{H}_2\text{O})_8]2\text{H}_2\text{O}\}_n$ (3,5-pdc=pyridine-3,5 dicarboxylate, Oxa=oxalate), has been successfully synthesized through slow diffusion in agar-agar gel medium and characterized by X-ray single-crystal diffraction at 100K. The structure is composed of infinite dinuclear chains sandwiching oxalate ligands. The three-dimensional network is ensured by hydrogen bonds involving water molecules and stabilized by $\pi\text{-}\pi^*$ stacking interactions. Magnetic properties of the complex were investigated by variable temperature magnetic susceptibility and reveal the occurrence of overall antiferromagnetic interactions within $\text{Nd}^{3+}\text{-Nd}^{3+}$ dinuclear units through the exchange pathway provided by the oxalate bridges.

Keywords: Slow diffusion, Agar-agar gel medium, Neodymium – Copper mixed compound, molecular materials.

Synthèse, caractérisation structurale et étude des propriétés magnétiques d’un nouveau polymère de coordination hétérométallique Nd(III)-Cu(II) à base du ligand 3,5-pyridinedicarboxylate et du ligand oxalate

Résumé: Un nouveau polymère de coordination hétérométallique Nd(III)-Cu(II) $\{[\text{NdCu}(3,5\text{-pdc})_2(\text{Oxa})_{0.5}(\text{H}_2\text{O})_8]2\text{H}_2\text{O}\}_n$ (3,5-pdc=pyridine-3,5 dicarboxylate, Oxa=oxalate) a été obtenu par diffusion lente en milieu gel agar-agar et structuralement caractérisé par la diffraction des rayons-X sur monocristal à une température de 100K. La structure du composé est constituée de chaînes binucléaires reliées entre elles par des ligands oxalates et la cohésion de la structure est assurée par les liaisons hydrogène impliquant des molécules d’eaux associée à des interactions $\pi\text{-}\pi^*$. L’étude des propriétés magnétiques du composé réalisée, en mesurant la variation de la susceptibilité magnétique χT en fonction de la température, montre qu’il présente un comportement antiferromagnétique entre les centres dinucléaires $\text{Nd}^{3+}\text{-Nd}^{3+}$ pontés par les ligands oxalates.

Mots-clés : Diffusion lente, Milieu gel agar-agar, Composés mixtes néodyme-cuivre, matériaux moléculaires.

* Corresponding author : mcamara@univ-zig.sn; Tel. (+221) 77 608 03 01. Fax: (+221) 33 991 68 09 To whom correspondence should be addressed

1. Introduction

The field of coordination polymers has experienced impressive growth in the past decade. The process of mixing readily available metal ions with organic linkers has captured the imagination of chemists and materials scientists worldwide due to their application for catalysis, separation, magnetism and sensor technologies^[1,2]. Within this context, lanthanide-transition metals (3d–4f) heterometallic coordination polymers, featuring the characteristics of both 3d- and 4f -block elements, are particularly notable because they not only inherit the intrinsic properties of 3d- and 4f-block coordination polymers but also extract some unique cooperative properties^[3]. Currently, such compounds have attracted enormous interest in magnetism due to the development of new functional molecule-based materials^[4]. However, they remain largely unexplored owing to their synthetic challenges^[5,6]. Various multifunctional nitrogen-containing organic ligands such as imidazolecarbonates, pyridinedicarboxylates, pyridinephosphonates and triazolcarbonates are employed to help overcome these difficulties. Dinicotinate or pyridine-3,5-dicarboxylate(3,5-pcd²⁻) is one of these ligands largely employed to construct 3d–4f heterometallic coordination polymers because it can coordinate both transition metal ions through its pyridine nitrogen and trivalent lanthanides ions with its opposite side carboxylate groups in a bridging and/or chelating mode, acting as a rigid V-shaped organic linker^[6,7]. Other types of ligands frequently utilized in the construction of 3d–4f heterometallic complexes are auxiliary ligands. The most popular ones documented in the literature are oxalate, 1,2-benzenedicarboxylate and 1,3-benzenedicarboxylate^[8–10]. The introduction of oxalate as a co-ligand, for instance, helps not only to control the structural stability of complexes but also to exclude water molecules from the first coordination sphere of the lanthanide ions. Hence it serves as an excellent spacer within 3D structures. Herein, we report the synthesis, crystal structure and magnetic properties of a new Nd(III)-Cu(II) heterometallic coordination polymer of formula [NdCu(3,5-pdc)₂(Oxa)_{0.5}(H₂O)₈].2H₂O.

2. Experimental

2.1. Materials

Dinicotinic acid, oxalic acid, copper(II) nitrate, neodymium(III) nitrate, and potassium hydroxide were obtained from Aldrich Chemical Co. Agar-agar powder was purchased from Acros Organics

and all products were used without further purification. All other chemicals and solvents were reagent grade.

2.2. Preparation of Ligands

The ligands used in this study are shown in Figure 1. Sodium pyridine-3,5-dicarboxylate and sodium oxalate were prepared according to the procedure described in reference^[11]. An aqueous solution of 1.48 M NaOH was added dropwise to an aqueous solution (75 cm³) of oxalic acid (5 g, 0.055 mol) until a pH value between 6 and 7 is attained, the solution is then evaporated to dryness at 90°C using a rotary evaporator. The obtained salt is dissolved in ether and absolute ethanol for crystallization. The powder is finally washed with diethyl ether then dried under vacuum over silica gel. Similarly was prepared the sodium pyridine-3,5 dicarboxylate.

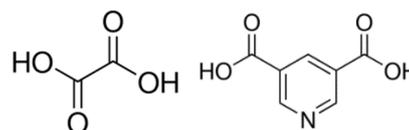


Figure 1: Chemical formulas of oxalic acid (left) and pyridine-3,5 dicarboxylic acid (right)

2.3. Preparation of the complex

Gelation of agar-agar was made according to established procedure^[12,13] and complexation according to the literature^[14,15]. To prepare a gel of 0.5% density, 50mg of agar-agar powder was dissolved in 10mL of demineralized water. While the mixture was boiled under stirring, sodium pyridine-3,5 dicarboxylate (0.0211g, 0.10 mmol) and sodium oxalate (0.0134g, 0.10 mmol) are added and the warm solution is poured in a test tube for gelation about 24 hours at room temperature. After gelation, a solution of NdCl₂.6H₂O (0.0359g, 0.10 mmol) and Cu(NO₃)₂.x H₂O (0.0187g, 0.10 mmol) in 10 mL H₂O was slowly layered on top of the gel in a test tube. After a few weeks of diffusion at room temperature, blue single crystals were obtained in the gel/solution interface.

2.4. Crystal Structure Determination and Refinement

The single crystal X-ray diffraction data were collected with Mo K α radiation ($\lambda = 0.71073$ Å) using a Rigaku SuperNova diffractometer. The sample was cooled down to 100 K using an N2 Oxford cryostream cooling device. The SuperNova control software, CrysAlisPro^[16], was used for data

collection and also for indexing the diffraction peaks. The same software was used for data reduction (Intensity integrating, scaling and averaging). The structure was solved by direct methods and refined by full-matrix least-squares method using SHELXT and SHELXL programs respectively^[17] with Olex2 interface^[18]. Atomic displacement parameters of all the non-H atoms were refined in the anisotropic approximation. The refinement was conducted against F^2 of all reflections with 2 sigma cutoff ($I > 2 \cdot \sigma(I)$). We have used constraints for accurate description of O-H bond length treatments. One coordination water molecule (O7W) on the Nd^{3+} ion shows has been disordered that has been refined over two positions. The final geometrical calculations and graphical illustrations were carried out with *Mercury*^[19] and *DIAMOND* program^[20]. A summary of the crystal data and refinement conditions are reported in Table I, whereas selected bond lengths and angles are given in Table II.

2.5 Magnetic measurements

Magnetic susceptibility measurement was carried out on a polycrystalline sample with a Quantum Design MPMS-XL5 superconducting quantum interference device (SQUID) magnetometer equipped with a magnet-reset at a temperature range of 1.8-400 K in the field of 0-5 T. The values of the experimental magnetic susceptibility data were corrected for the

diamagnetic contribution of the constituent atoms, as well as for the magnetization sample holder.

3. Results and discussion:

Single crystal X-ray diffraction studies revealed that this compound is a three-dimensional heterometallic coordination framework constructed from dinuclear chains interconnected by oxalate ligands and water molecules. It crystallizes in the triclinic P-1 space group, its asymmetric unit consists of one unique Nd^{3+} cation, one Cu^{2+} cation, two independent 3,5-pdc²⁻ ligands, half an oxalate ligand, eight coordination water molecules and two lattice water molecules (Figure 2).

The Nd^{3+} ion is nine-coordinated by 9 oxygen atoms: (O3, O9, and O10) of 3,5-pdc²⁻ ligands, (O1 and O2) of oxalate ligand and four (O5W, O6W, O7W and O8W) from coordination water molecules (Figure 3 left). All these donor atoms construct a distorted monocapped square antiprism around the trivalent Nd^{3+} cation. The Nd–O bond distances are in the range of 2.3825(5) – 2.5941(6) Å, all these values are comparable to those observed in similar lanthanides-pyridinecarboxylates complexes^[21–24]. The bond angles O–Nd1–O are in the range of 65.838 (17) – 139.94 (2)°. The square-planar base of Nd(1) polyhedron is defined by [O8W, O9, O10 and O1 oxygen atoms while the upper square-planar is built by O2, O3, O5W and O7W oxygen atoms (Figure 3, left). The dihedral angle between the two square bases is 8.249 ° and the antiprism is capped by the O6W water molecule.

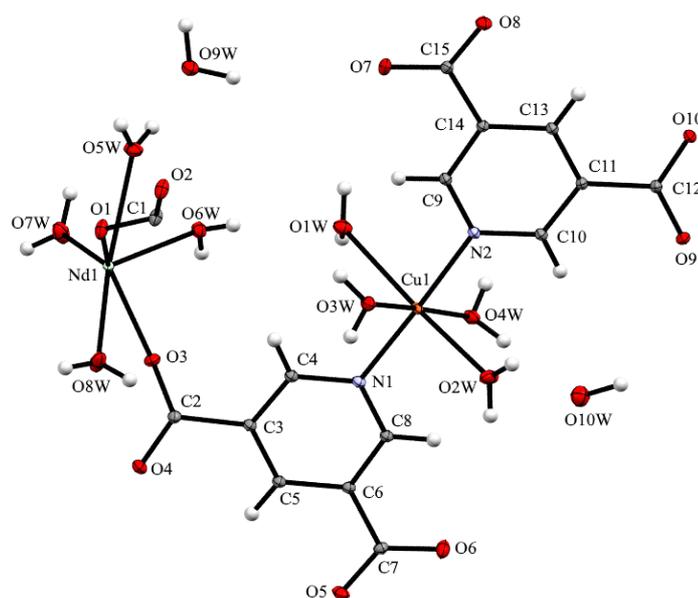


Figure2: Mercury representation of the asymmetric unit at 100K (50% probability ellipsoids)

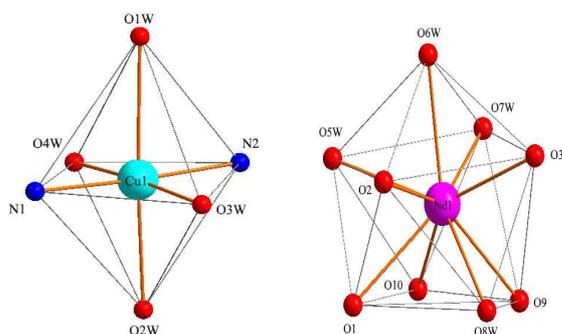


Figure 3: Coordination polyhedron of Nd³⁺ (left) and Cu²⁺ ions (right)

The geometry of copper Cu²⁺ ion is a six-coordinate elongated octahedron (Figure 3, right). It is surrounded by four oxygen atoms from coordination water molecules O1W, O2W, O3W and O4W and two nitrogen atoms N1 and N2 from two different 3,5-pdc²⁻ ligands. N1, O3W, N2 and O4W atoms are in the equatorial plane and O1W

and O2W in the axial position. The Cu–O bonds length is ranging from 1.9796(5) to 2.4918(6) Å (table II) and the Cu–N bond length are 2.0244 (5) and 2.0261 (5) Å for Cu–N1 and Cu–N2, respectively. The mean value of the axial Cu–O water bonded length 2.3818(6) Å is larger than the equatorial bond length 1.9871(6) Å due to the Jahn-Teller effect (Table II). All these structural features are comparable with those previously reported in related Cu²⁺ complexes containing 3,5-pdc²⁻ ligand^[25,26]. The 3,5-pdc²⁻ ligand exhibits two kinds of different coordination modes A and B as depicted in the Figure 4. In coordination mode A, the nitrogen atom coordinates the copper center and one of the carboxylate groups chelate the neodymium center in the $\mu_2\text{-}\eta^1\text{:}\eta^1\text{:}\eta^0\text{:}\eta^0$ bridging mode. In coordination mode B, the ring nitrogen coordinates the copper center whereas one of the carboxylate groups coordinates the neodymium center with the $\mu_2\text{-}\eta^1\text{:}\eta^1\text{:}\eta^0\text{:}\eta^0$ bridging mode.

Table I. Crystal data and Details of Structure Determination	
Chemical formula	C ₁₅ H ₁₈ CuN ₂ NdO ₁₇ ·3(H ₂ O)
<i>M_r</i> (g.mol ⁻¹)	760.14
Crystal system, space group	Triclinic, <i>P</i> -1
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	8.5606(1), 11.8223(1), 13.0552(1)
α , β , γ (°)	104.217(1), 104.530(1), 95.2788(9)
<i>V</i> (Å ³)	1223.11(2)
<i>Z</i>	2
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	3.07
Crystal size (mm)	0.33 × 0.18 × 0.08
Diffractometer	SuperNova, Dual, Cu at zero, Atlas
<i>T</i> _{min} , <i>T</i> _{max}	0.294, 1.000
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	134213, 20585, 19427
<i>R</i> _{int}	0.043
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	1.003
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.018, 0.045, 1.08
No. of reflections	19427
No. of parameters	452
No. of restraints	18
H-atom treatment	All H-atom parameters refined
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.98, -1.40

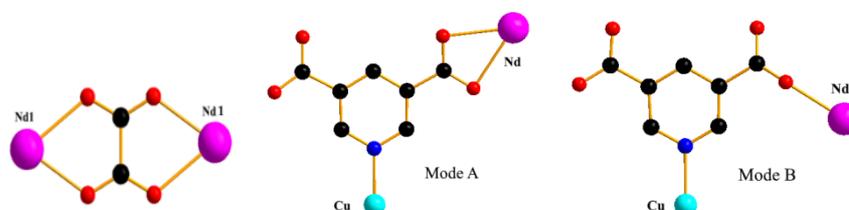


Figure 4: The two coordination modes of dinicotinate and oxalate ligands

With these two coordination modes along with coordination water molecules, the metal centers are bridged to form a one-dimensional zigzag dinuclear $[\text{NdCu}(3,5\text{-pdc})_2(\text{H}_2\text{O})_8]$ heterometallic organic chains (Figure 5). These one-dimensional chains are further interlinked by oxalate ligands through bis-chelating coordination mode to form a two-dimensional ladder-like framework (Figure 6).

The values of the intrachain distances $\text{Nd}^{3+}\text{-Nd}^{3+}$ [13.9438(1) Å] and $\text{Cu}^{2+}\text{-Cu}^{2+}$ [13.9438(1) Å] are greater than those of the interchain $\text{Nd}^{3+}\text{-Nd}^{3+}$ and $\text{Cu}^{2+}\text{-Cu}^{2+}$ distances [6.3446(1) Å and 8.8121(1) Å, respectively] the shortest intrachain $\text{Nd}^{3+}\text{-Cu}^{2+}$ separation is 6.2273(1) Å. Due to the presence of uncoordinated water molecules acting as space-filling particles between the chains, are involved in the three-dimension network formed through hydrogen bonding interactions (see Table VI). Another interesting feature of the

structure of this compound is the presence of $\pi\text{-}\pi^*$ stacking interactions between the aromatic rings of 3,5-pdc²⁻ ligands. The centroid-centroid distances within the chains are 3.693 Å and those between two adjacent chains are 3.639 Å (Figure 7). These distances are a slightly larger than the standard face-to-face $\pi\text{-}\pi^*$ interactions between the pyridine rings (3.45 Å), but they are similar to values reported in the literature for structures involving the same organic ligand^[25,27]. The hydrogen bonds of water molecules assisted by these $\pi\text{-}\pi^*$ stacking interactions ensure the overall cohesion and the stability of the tridimensional network of the polymeric structure.

To the best of our knowledge, this compound is the first 3d-4f heterometallic coordination framework based on Neodymium–3,5-pdc–Copper chains and oxalate ligands.

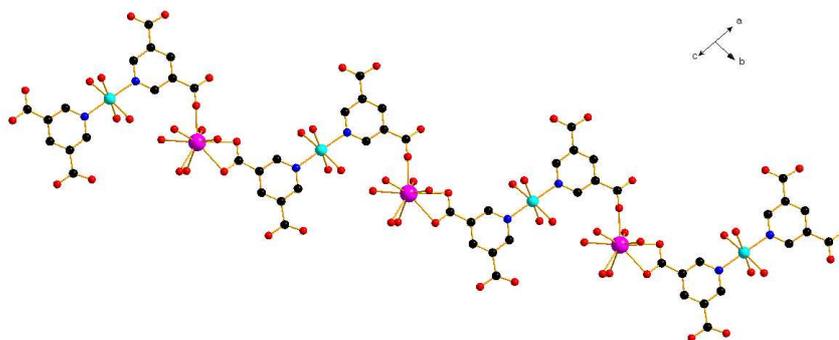


Figure 5: Representation of the zigzag dinuclear $[\text{NdCu}(3,5\text{-pdc})_2(\text{H}_2\text{O})_8]_\infty$ chain

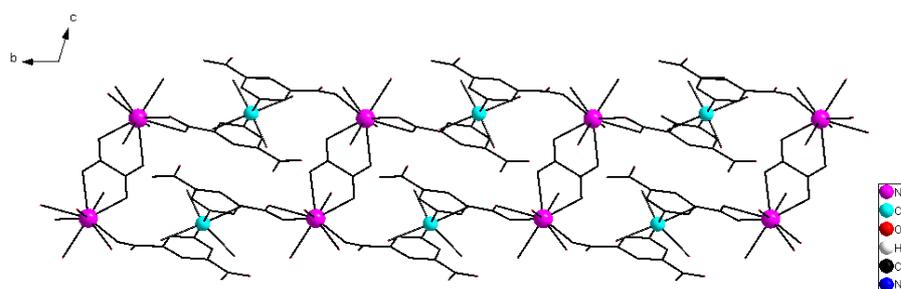


Figure 6: Ladder-like chain $[\text{Nd}_2\text{Cu}_2(3,5\text{-pdc})_4(\text{H}_2\text{O})_{16}]_\infty$ in the (\vec{b}, \vec{c}) plane

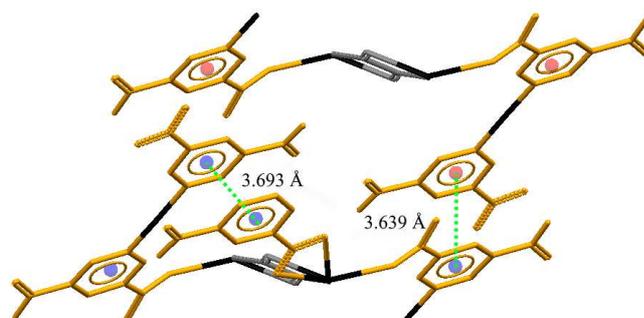


Figure 7: $\pi\text{-}\pi^*$ stacking interactions of dinicotinate aromatic rings (all water molecules were hidden for clarity)

The temperature dependence of the magnetic susceptibility for the compound was measured in the temperature range of 1.8-400 K with an applied field of 0-5 T. The plot of χT versus T for the compound is shown in Figure 8. At room temperature, the product χT is 1.67 emu K mol⁻¹. This is smaller than the expected value (2.02 emu K mol⁻¹) for one Cu²⁺ (0.375 emu K mol⁻¹) and one Nd³⁺ (~1.64 emu K mol⁻¹; S = 3/2, L = 6, 4I9/2, J = 9/2, g = 8/11) without any interaction. Then χT

decrease almost linearly down to 2K where it is 0.8 emu K mol⁻¹. This behavior indicates the existence of antiferromagnetic interaction that may be between the Nd³⁺ ions bridged by the oxalate anions. If the Nd³⁺ ions are antiferromagnetically coupled we can expect to have at low temperature the value for only one Cu²⁺ (0.375 emu K mol⁻¹) but the value at 2K is larger. The field dependence of the magnetization is very small.

Table II. Selected interatomic distances (Å) and angles in degree(°)

Nd1—O3	2.3825 (5)	Nd1—O8W	2.4865 (6)
Nd1—O5W	2.4757 (6)	Cu1—O1W	2.4918 (6)
Nd1—O1	2.5233 (5)	Cu1—O2W	2.2719 (6)
Nd1—O6W	2.5324 (6)	Cu1—O3W	1.9796 (5)
Nd1—O2	2.4231 (5)	Cu1—O4W	1.9946 (6)
Nd1—O9 ⁱ	2.5941 (6)	Cu1—N1	2.0244 (5)
Nd1—O10	2.5392 (5)	Cu1—N2	2.0261 (5)
Nd1—O7W	2.4621 (6)		
O3—Nd1—O5W	139.94 (2)	O2—Nd1—O7W	139.93 (2)
O3—Nd1—O1	133.911 (2)	O2—Nd1—O8W	77.09 (2)
O3—Nd1—O6W	72.065 (2)	O10—Nd1—O9 ⁱ	50.745 (1)
O3—Nd1—O2	83.644 (2)	O7W—Nd1—O5W	83.81 (2)
O3—Nd1—O9 ⁱ	89.698 (2)	O7W—Nd1—O1	137.05 (2)
O3—Nd1—O10	139.413 (2)	O7W—Nd1—O6W	68.40 (2)
O3—Nd1—O7W	88.46 (2)	O7W—Nd1—O9 ⁱ	74.27 (2)
O3—Nd1—O8W	69.61 (2)	O7W—Nd1—O10	73.71 (2)
O5W—Nd1—O1	67.86 (2)	O7W—Nd1—O8W	135.79 (2)
O5W—Nd1—O6W	68.54 (2)	O8W—Nd1—O1	70.41 (2)
O5W—Nd1—O9 ⁱ	125.190 (2)	O8W—Nd1—O6W	132.53 (2)
O5W—Nd1—O10	75.161 (2)	O8W—Nd1—O9 ⁱ	67.96 (2)
O5W—Nd1—O8W	137.18 (2)	O8W—Nd1—O10	98.13 (2)
O1—Nd1—O6W	123.886 (2)	O4W—Cu1—N1	88.39 (2)
O1—Nd1—O9 ⁱ	95.847 (2)	O4W—Cu1—N2	90.80 (2)
O1—Nd1—O10	68.349 (2)	O4W—Cu1—O2W	89.26 (3)
O6W—Nd1—O9 ⁱ	138.461 (2)	N1—Cu1—N2	177.26 (2)
O6W—Nd1—O10	129.307 (2)	N1—Cu1—O2W	92.74 (2)
O2—Nd1—O5W	77.64 (2)	O3W—Cu1—O4W	176.17 (2)
O2—Nd1—O1	65.838 (1)	O3W—Cu1—N1	91.99 (2)
O2—Nd1—O6W	71.795 (2)	O3W—Cu1—N2	89.00 (2)
O2—Nd1—O9 ⁱ	144.52 (2)	O3W—Cu1—O2W	86.91 (2)
O2—Nd1—O10	132.755 (2)	N2—Cu1—O2W	89.86 (2)

Symmetry code(s): (i) x-1, y-1, z.

Tableau III: Hydrogen-bond geometry (Å, °)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O3W—H3WA···O1 ⁱⁱ	0.947	1.741	2.669	165.7 (2)
O2W—H2WA···O8 ⁱⁱ	0.937	1.884	2.790	162.2 (2)
O3W—H3WB···O8 ⁱⁱⁱ	0.862	1.904	2.736	162.1 (2)
O9W—H9WB···O9	0.964	1.801	2.757	170.7 (2)
O2W—H2WB···O10 ⁱⁱⁱ	0.960	1.777	2.733	174.2 (2)
O6W—H6WA···O1W	0.960	1.990	2.928	165.4 (2)
O6W—H6WB···O6 ^{iv}	0.937	1.935	2.858	168.1 (2)
O1W—H1WA···O4 ^v	0.962	1.914	2.847	162.8 (2)
O10W—H10A···O9W	0.958	1.840	2.768	162.4 (2)
O10W—H10B···O4 ^{vii}	0.955	1.948	2.835	153.6 (2)
O5W—H5WA···O9W ^v	0.946	1.782	2.724	174.1 (2)
O5W—H5WB···O8 ^{viii}	0.966	1.852	2.816	176.9 (2)
O4W—H4WA···O10W ⁱ	0.945	1.813	2.742	167.2 (2)
O4W—H4WB···O5 ⁱ	0.944	1.713	2.634	164.0 (2)
O1W—H1WB···O5 ^{iv}	0.959	1.730	2.680	170.3 (2)
O8W—H8WA···O7 ^{ix}	0.937	1.830	2.760	171.4 (2)
O8W—H8WB···O7 ⁱⁱⁱ	0.935	1.829	2.759	173.4 (2)

Symmetrycodes: (i) $x-1, y-1, z$; (ii) $-x, -y+1, -z+1$; (iii) $x, y-1, z$; (iv) $-x, -y, -z$; (v) $x-1, y, z$; (vi) $x, y+1, z$; (vii) $-x+1, -y+1, -z$; (viii) $-x, -y+2, -z+1$; (ix) $-x+1, -y+2, -z+1$.

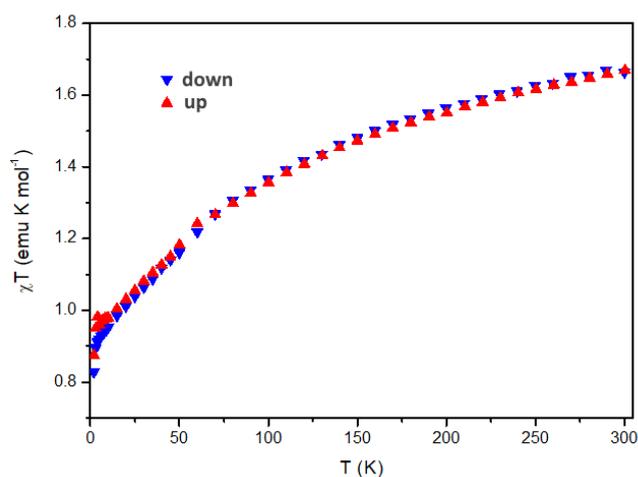


Figure 8: Temperature dependence of the product of the magnetic susceptibility(χT) with temperature.

4. Conclusion

In summary, we have synthesized and characterized a new 3d–4f heterometallic coordination polymer containing mixed 3,5-pdc²⁻ and oxalate ligands from slow diffusion in agar-agar gel media. The compound presents a three-dimensional network in which infinite one-dimensional [NdCu(3,5-pdc)₂(H₂O)₈] chains are interlinked by oxalate ligands to form ladder-like chains compound comprising 3d and 4f metal ions. The π - π^* stacking interactions between the aromatic rings contribute significantly to the stabilization of the three-dimensional structure. The magnetic properties of the compound were investigated by variable temperature magnetic susceptibility and suggest that overall antiferromagnetic interactions are present between the Nd³⁺ ions bridged by oxalate ligands. The systematic investigation of this complex not only provides examples of 3d–4f heterometallic coordination polymers but also opens up alternative approaches for constructing new functional materials.

5. Supporting information

Full details of the X-ray structure determination of [NdCu(3,5-pdc)₂(Oxa)_{0.5}(H₂O)₈].2H₂O have been deposited with the Cambridge Crystallographic Data Center under the depository number CCDC-1871649, and can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internet.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk], on request, from the authors and the reference to this publication.

6. Acknowledgment:

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7. References

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