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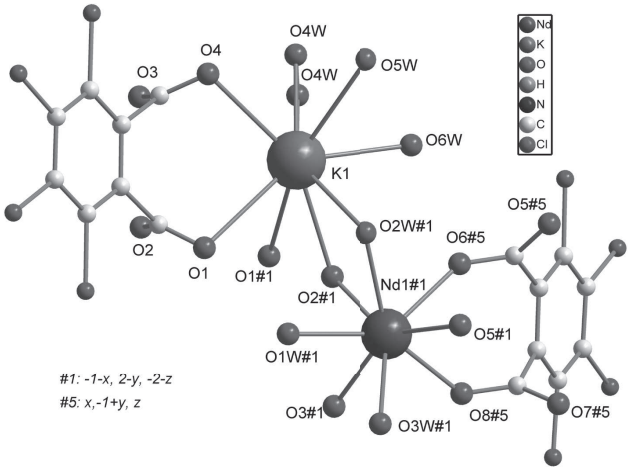
Fan Zhang, Ya-Jie Qu, Wen-Hua Wu and Yu-Heng Deng*

Crystal structure of a poly[bis(3,4,5,6-tetrachlorophthalato)neodym(III)potassium(I)] — 4,4′-bipyridine — water (1/1/5.5)



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Abstract

$C_{26}H_{19}Cl_8KN_2NdO_{13.5}$, triclinic, $P\bar{1}$ (no. 2), $a = 8.6114(17)$ Å, $b = 12.665(3)$ Å, $c = 16.997(3)$ Å, $\alpha = 96.53(3)°$, $\beta = 103.28(3)°$, $\gamma = 97.89(3)°$, $V = 1766.6(6)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0254$, $wR_{ref}(F^2) = 0.0838$, $T = 293$ K.

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The crystal structure is shown in the figure, Tables 1–3 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

All chemicals and solvents purchased were of reagent grade and used without further purification. Neodymium(III) nitrate hexahydrate (0.438 g, 1 mmol), 3,4,5,6-tetrachlorophthalic acid (0.608 g, 2 mmol) and 4,4′-bipyridine (0.312 g, 2 mmol) were mixed in ethanol (80 ml). The pH value of the mixture was adjusted to about 6.5 by the potassium hydroxide solution, and then stirred at 80°C for 8 hours. After filtration, the resulting solution was stood at room temperature for several days. Crystals suitable for X-ray analysis were collected by filtration.

Table 1: Data collection and handling.

Crystal:	Colorless, block, size 0.28×0.42×0.68 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	22.60 cm^{-1}
Diffractometer, scan mode:	CCD area detector, φ and ω scans
$2\theta_{max}$:	50.1°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	6180, 6180
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 5990
$N(param)_{refined}$:	481
Programs:	SHELX [12], Diamond [13]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	Site	x	y	z	U_{iso}
H(1WA)	2*i*	−0.2183	1.1661	−1.1141	0.068
H(1WB)	2*i*	−0.3381	1.1082	−1.0840	0.068
H(2WA)	2*i*	−0.5541	1.2237	−1.1414	0.056
H(2WB)	2*i*	−0.6430	1.2908	−1.0997	0.056
H(3WA)	2*i*	−0.047(5)	1.424(3)	−1.053(2)	0.061
H(3WB)	2*i*	0.023(3)	1.341(3)	−1.010(3)	0.061
H(5WA)	2*i*	0.082(6)	0.861(3)	−0.791(1)	0.080
H(5WB)	2*i*	−0.019(6)	0.769(2)	−0.848(3)	0.080
H(6WA)	2*i*	−0.2423	0.7084	−1.0603	0.075
H(6WB)	2*i*	−0.1040	0.7791	−1.0611	0.075
H(17)	2*i*	−0.2288	1.2098	−1.3682	0.058
H(18)	2*i*	−0.3086	1.1417	−1.5050	0.051
H(21)	2*i*	−0.4833	1.0262	−1.6167	0.052
H(22)	2*i*	−0.5548	0.9499	−1.7508	0.059
H(23)	2*i*	−0.2018	0.7866	−1.7178	0.053
H(24)	2*i*	−0.1210	0.8541	−1.5810	0.048
H(25)	2*i*	−0.1605	0.8675	−1.4492	0.050
H(26)	2*i*	−0.0839	0.9443	−1.3144	0.054

***Corresponding author: Yu-Heng Deng,** Department of Chemistry, Capital Normal University, Beijing 100048, P. R. China, e-mail: dyh@mail.cnu.edu.cn
Fan Zhang, Ya-Jie Qu and Wen-Hua Wu: Department of Chemistry, Capital Normal University, Beijing 100048, P. R. China

Table 3: Atomic displacement parameters (Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Nd(1)	2*i*	−0.31203(2)	1.31807(1)	−0.982877(8)	0.0259(1)	0.0240(1)	0.0174(1)	0.00682(7)	0.00679(7)	0.00051(7)
K(1)	2*i*	−0.2435(1)	0.92989(8)	−0.94078(7)	0.0705(6)	0.0494(5)	0.0651(6)	−0.0085(4)	0.0308(5)	−0.0195(4)
O(1)	2*i*	−0.5139(4)	1.0253(2)	−0.8879(2)	0.086(2)	0.031(1)	0.037(1)	−0.014(1)	0.010(1)	0.001(1)
O(1W)	2*i*	−0.2738(3)	1.1674(2)	−1.0787(2)	0.054(2)	0.034(1)	0.048(2)	−0.001(1)	0.028(1)	−0.013(1)
O(2)	2*i*	−0.4633(3)	1.1692(2)	−0.9430(1)	0.071(2)	0.043(1)	0.024(1)	−0.019(1)	0.001(1)	0.005(1)
O(2W)	2*i*	−0.5672(3)	1.2537(2)	−1.0965(1)	0.038(1)	0.044(1)	0.025(1)	0.011(1)	0.0032(9)	−0.0033(9)
O(3)	2*i*	−0.1128(3)	1.2364(2)	−0.8940(2)	0.052(1)	0.070(2)	0.037(1)	0.037(1)	0.027(1)	0.027(1)
O(3W)	2*i*	−0.0571(3)	1.3745(2)	−1.0235(2)	0.038(1)	0.044(1)	0.046(1)	0.010(1)	0.020(1)	0.007(1)
O(4)	2*i*	−0.0450(3)	1.1052(2)	−0.8257(2)	0.052(1)	0.039(1)	0.039(1)	0.024(1)	0.019(1)	0.008(1)
O(4W)	2*i*	0.0490(8)	1.0016(6)	−0.9608(5)	0.069(4)	0.063(4)	0.098(5)	−0.005(3)	0.043(4)	0.009(4)
O(5)	2*i*	−0.3416(3)	1.4681(2)	−1.0548(1)	0.040(1)	0.039(1)	0.028(1)	0.005(1)	0.0023(9)	0.0115(9)
O(5W)	2*i*	0.0337(4)	0.8328(2)	−0.8406(2)	0.066(2)	0.053(2)	0.037(1)	−0.006(1)	0.020(1)	−0.010(1)
O(6)	2*i*	−0.4709(2)	1.6077(2)	−1.0634(1)	0.027(1)	0.045(1)	0.031(1)	0.0082(9)	0.0067(9)	−0.013(1)
O(6W)	2*i*	−0.1611(3)	0.7568(2)	−1.0298(2)	0.037(1)	0.059(2)	0.052(2)	0.005(1)	0.014(1)	−0.008(1)
O(7)	2*i*	−0.8208(3)	1.3689(2)	−1.1405(2)	0.039(1)	0.048(1)	0.043(1)	0.004(1)	0.021(1)	0.013(1)
O(8)	2*i*	−0.8165(2)	1.5462(2)	−1.1311(1)	0.023(1)	0.047(1)	0.030(1)	0.0099(9)	0.0054(9)	−0.012(1)
N(1)	2*i*	−0.1482(4)	1.0843(3)	−1.3278(2)	0.051(2)	0.055(2)	0.030(2)	0.000(1)	0.013(1)	−0.004(1)
N(2)	2*i*	−0.3851(4)	0.8600(3)	−1.7474(2)	0.053(2)	0.050(2)	0.030(2)	0.007(1)	0.008(1)	−0.000(1)
C(1)	2*i*	−0.4615(3)	1.1207(2)	−0.8835(2)	0.020(1)	0.026(1)	0.023(1)	0.002(1)	0.007(1)	−0.001(1)
C(2)	2*i*	−0.3794(3)	1.1853(2)	−0.7995(2)	0.022(1)	0.026(1)	0.021(1)	0.003(1)	0.006(1)	0.003(1)
C(3)	2*i*	−0.4704(3)	1.2125(2)	−0.7445(2)	0.020(1)	0.035(2)	0.026(2)	0.006(1)	0.009(1)	0.003(1)
C(4)	2*i*	−0.3956(4)	1.2668(2)	−0.6669(2)	0.028(1)	0.034(2)	0.026(2)	0.008(1)	0.015(1)	0.001(1)
C(5)	2*i*	−0.2274(4)	1.2942(2)	−0.6428(2)	0.030(1)	0.030(2)	0.020(1)	0.004(1)	0.005(1)	−0.001(1)
C(6)	2*i*	−0.1372(3)	1.2679(2)	−0.6983(2)	0.020(1)	0.030(1)	0.025(1)	0.004(1)	0.006(1)	0.002(1)
C(7)	2*i*	−0.2124(3)	1.2144(2)	−0.7768(2)	0.024(1)	0.024(1)	0.022(1)	0.004(1)	0.008(1)	0.004(1)
C(8)	2*i*	−0.1141(3)	1.1825(2)	−0.8367(2)	0.017(1)	0.029(1)	0.022(1)	0.002(1)	0.005(1)	−0.002(1)
C(9)	2*i*	−0.4316(3)	1.5236(2)	−1.0930(2)	0.018(1)	0.031(1)	0.017(1)	−0.003(1)	0.006(1)	0.002(1)
C(10)	2*i*	−0.4996(3)	1.4886(2)	−1.1850(2)	0.024(1)	0.024(1)	0.018(1)	0.006(1)	0.006(1)	0.002(1)
C(11)	2*i*	−0.3982(3)	1.4800(2)	−1.2373(2)	0.023(1)	0.035(2)	0.024(1)	0.004(1)	0.007(1)	0.004(1)
C(12)	2*i*	−0.4640(4)	1.4473(2)	−1.3213(2)	0.028(1)	0.035(2)	0.022(1)	0.008(1)	0.013(1)	0.003(1)
C(13)	2*i*	−0.6300(4)	1.4255(2)	−1.3521(2)	0.029(1)	0.035(2)	0.016(1)	0.006(1)	0.005(1)	−0.001(1)
C(14)	2*i*	−0.7308(3)	1.4344(2)	−1.2992(2)	0.020(1)	0.036(2)	0.023(1)	0.006(1)	0.006(1)	0.000(1)
C(15)	2*i*	−0.6666(3)	1.4639(2)	−1.2155(2)	0.023(1)	0.026(1)	0.019(1)	0.007(1)	0.006(1)	0.001(1)
C(16)	2*i*	−0.7780(3)	1.4595(2)	−1.1575(2)	0.018(1)	0.040(2)	0.019(1)	0.005(1)	0.003(1)	−0.003(1)
C(17)	2*i*	−0.2144(5)	1.1400(3)	−1.3848(2)	0.058(2)	0.041(2)	0.044(2)	0.005(2)	0.015(2)	−0.005(2)
C(18)	2*i*	−0.2631(5)	1.0996(3)	−1.4675(2)	0.053(2)	0.040(2)	0.035(2)	0.009(2)	0.011(2)	0.005(1)
C(19)	2*i*	−0.2433(4)	0.9961(3)	−1.4936(2)	0.041(2)	0.035(2)	0.029(2)	0.001(1)	0.010(1)	0.004(1)
C(20)	2*i*	−0.2922(4)	0.9492(3)	−1.5815(2)	0.038(2)	0.034(2)	0.029(2)	0.001(1)	0.009(1)	0.004(1)
C(21)	2*i*	−0.4243(5)	0.9769(3)	−1.6354(2)	0.050(2)	0.051(2)	0.034(2)	0.018(2)	0.012(2)	0.008(2)
C(22)	2*i*	−0.4660(5)	0.9310(3)	−1.7160(2)	0.052(2)	0.065(2)	0.030(2)	0.021(2)	0.004(2)	0.006(2)
C(23)	2*i*	−0.2598(5)	0.8347(3)	−1.6968(2)	0.051(2)	0.044(2)	0.038(2)	0.010(2)	0.014(2)	−0.003(2)
C(24)	2*i*	−0.2093(4)	0.8756(3)	−1.6142(2)	0.042(2)	0.043(2)	0.033(2)	0.010(2)	0.007(1)	0.002(1)
C(25)	2*i*	−0.1754(4)	0.9377(3)	−1.4344(2)	0.050(2)	0.039(2)	0.034(2)	0.006(2)	0.007(2)	0.004(1)
C(26)	2*i*	−0.1298(5)	0.9846(3)	−1.3533(2)	0.051(2)	0.051(2)	0.030(2)	0.002(2)	0.007(2)	0.009(2)
Cl(1)	2*i*	−0.67828(9)	1.17683(8)	−0.77380(5)	0.0199(3)	0.0679(6)	0.0359(4)	0.0041(3)	0.0098(3)	−0.0020(4)
Cl(2)	2*i*	−0.5075(1)	1.29910(8)	−0.59812(5)	0.0368(4)	0.0651(6)	0.0313(4)	0.0116(4)	0.0194(3)	−0.0054(4)
Cl(3)	2*i*	−0.1323(1)	1.35821(8)	−0.54555(5)	0.0391(4)	0.0597(5)	0.0231(4)	0.0000(4)	0.0060(3)	−0.0120(3)
Cl(4)	2*i*	0.07051(8)	1.30210(7)	−0.66937(5)	0.0213(3)	0.0503(5)	0.0327(4)	−0.0007(3)	0.0051(3)	−0.0041(3)
Cl(5)	2*i*	−0.19164(9)	1.51251(8)	−1.19966(5)	0.0211(3)	0.0755(6)	0.0287(4)	0.0013(3)	0.0086(3)	0.0072(4)
Cl(6)	2*i*	−0.33980(9)	1.43516(8)	−1.38663(5)	0.0329(4)	0.0674(5)	0.0264(4)	0.0106(4)	0.0170(3)	0.0011(3)
Cl(7)	2*i*	−0.7124(1)	1.38548(8)	−1.45538(4)	0.0365(4)	0.0684(6)	0.0172(4)	0.0084(4)	0.0047(3)	−0.0042(3)
Cl(8)	2*i*	−0.93828(9)	1.40752(8)	−1.33611(5)	0.0206(3)	0.0772(6)	0.0266(4)	0.0061(3)	0.0018(3)	−0.0001(4)

Experimental details

All the H atoms of carbon were treated as riding-model, with C—H = 0.93–0.98 Å, and their $U_{iso} = 1.2U_{eq}$(carrier atom). Water H atoms except O4W were located in a difference Fourier map and refined with O—H = 0.85(1) Å and $U_{iso}(H) = 1.5U_{eq}(O)$. H atoms were not added to water O4W due to its disorder (occupancy factor: 0.5).

Discussion

As a versatile benzendicarboxylate ligand, the tetrachlorophthalate ligand was rarely used to construct complex. By now, there are few of published reports concerning metal complexes with 3,4,5,6-tetrachlorophthalate (tcph), which may play the role of bridging ligand in transition metal complexes [1–6] and terminal ligand in rare earth metal complexes [7–11]. All the reported rare earth metal complexes have a mononuclear structure and contain the $Htcph^-$ or $tcph^{2-}$ ligand in terminal coordinate style. Whereas, this article presents a novel mixed neodymium and potassium complex with a two-dimentional network structure, showing the $tcph^{2-}$ ligand in the polydentate bridging mode.

The title compound contains two kinds of metal ion, Nd^{3+} and K^+ ions. The asymmetric unit contains a $NdK(tcph)_2$ moiety and 5.5 water ligands. Nd(III) ion is eight-coordinated with five oxygen atoms from three $tcph^{2-}$ ligands and three oxygen atoms from three coordination waters. K(I) is also eight-coordinated with four oxygen atoms from two $tcph^{2-}$ ligands and four oxygen atoms from four coordination waters. Ligand $tcph^{2-}$ has two kinds of coordination style in the title complex. Two $tcph^{2-}$ ligands construct two K(I) and two Nd(III) ions into a $[Nd_2K_2(tcph)_2]^{4-}$ tetranuclear unit in a hexadentate chelating-bridging mode, and the other two $tcph^{2-}$ ligands both bridge the two neighboring Nd(III) ions of the tetranuclear unit in tridentate bridging style into an infinite chain along the *b* axis. The adjacent infinite chains are further connected into a 2D network in the *ab* plane by the bridging water O4W between the K(I) ions. The 4,4′-bipyridine molecule connects the 2D networks into a three-dimentional supramolecule *via* N–H···O hydrogen bonds between the coordination waters O2W, O5W and N2, N1 of 4,4′-bipyridine, respectively. Moreover, there are a lot of hydrogen bonds between the coordination waters, carboxylate O atoms and coordination waters in the structure.

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