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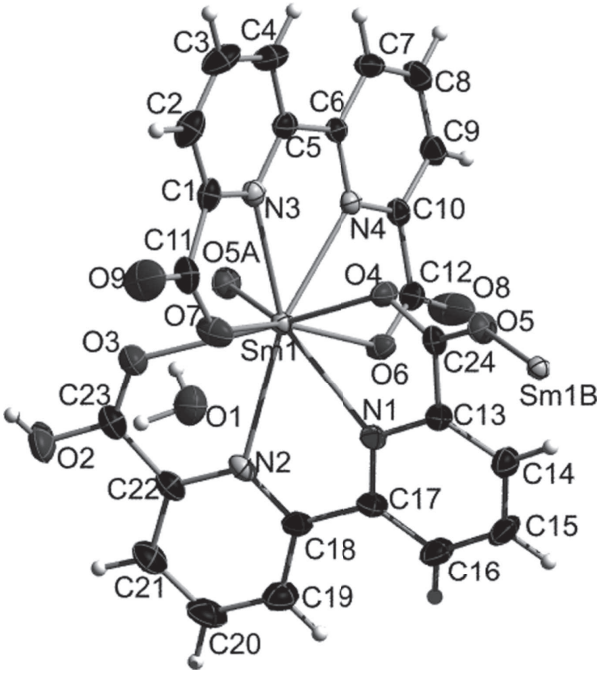
Crystal structure of catena-poly[2,2′-bipyridinyl-6,6′-dicarboxylato-κ^4N,N',O,O')-(μ_2-2,2′-bipyridinyl-6′-carboxyl-6-carboxylato-κ^5N,N',O,O':O″)samarium(III)] monohydrate, $C_{24}H_{13}N_4O_8Sm \cdot H_2O$



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Abstract

$C_{24}H_{15}N_4O_9Sm$, monoclinic, $P2_1/n$, $a = 6.780(2)$ Å, $b = 27.939(8)$ Å, $c = 11.546(4)$ Å, $\beta = 101.630(4)°$, $V = 2142.1(12)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0221$, $wR_{ref}(F^2) = 0.0587$, $T = 296(2)$ K.

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Table 1: Data collection and handling.

Crystal:	Colourless, block, size 0.25×0.38×0.47 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	28.11 cm^{-1}
Diffractometer, scan mode:	CCD area detector, φ and ω scans
$2\theta_{max}$:	50°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	10789, 3758
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3532
$N(param)_{refined}$:	344
Programs:	SHELX [9]

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

Atom	Site	x	y	z	U_{iso}
H(1W)	4e	0.6101	0.1147	0.7417	0.061
H(2W)	4e	0.6228	0.1407	0.6425	0.061
H(2)	4e	1.4042	0.0829	0.5677	0.064
H(2A)	4e	0.7787	0.2796	0.5612	0.040
H(3)	4e	0.7556	0.3433	0.4311	0.044
H(4)	4e	0.7488	0.3290	0.2334	0.038
H(7)	4e	0.7842	0.3102	0.0519	0.033
H(8)	4e	0.7847	0.2837	−0.1368	0.036
H(9)	4e	0.7748	0.2019	−0.1756	0.031
H(14)	4e	0.0816	0.0614	0.0857	0.035
H(15)	4e	0.1757	−0.0163	0.0492	0.044
H(16)	4e	0.4976	−0.0419	0.1300	0.039
H(19)	4e	0.7886	−0.0642	0.2362	0.043
H(20)	4e	1.1026	−0.0819	0.3459	0.049
H(21)	4e	1.2991	−0.0206	0.4448	0.043

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.

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

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sm(1)	4*e*	0.81656(2)	0.133295(6)	0.26401(1)	0.0153(1)	0.0154(1)	0.0186(1)	0.00105(6)	0.00314(7)	0.00051(6)
N(1)	4*e*	0.5436(4)	0.0659(1)	0.2258(2)	0.018(1)	0.019(2)	0.022(2)	0.002(1)	0.006(1)	0.000(1)
N(2)	4*e*	0.9194(4)	0.0429(1)	0.3166(3)	0.021(2)	0.023(2)	0.024(2)	0.007(1)	0.006(1)	0.004(1)
N(3)	4*e*	0.7985(4)	0.2204(1)	0.3252(2)	0.016(1)	0.021(2)	0.023(2)	−0.000(1)	0.002(1)	−0.001(1)
N(4)	4*e*	0.7802(4)	0.1969(1)	0.1030(2)	0.014(1)	0.017(2)	0.021(2)	0.001(1)	0.002(1)	0.000(1)
O(1)	4*e*	0.5348(4)	0.1218(1)	0.6666(3)	0.038(2)	0.047(2)	0.035(2)	−0.001(1)	0.005(1)	−0.002(1)
O(2)	4*e*	1.3768(4)	0.0624(1)	0.5160(3)	0.030(2)	0.046(2)	0.043(2)	0.013(1)	−0.011(1)	−0.005(1)
O(3)	4*e*	1.1437(4)	0.11408(9)	0.4272(2)	0.031(2)	0.029(2)	0.034(2)	0.003(1)	−0.003(1)	0.001(1)
O(4)	4*e*	0.4632(3)	0.15854(8)	0.2283(2)	0.016(1)	0.018(1)	0.037(1)	−0.000(1)	0.004(1)	−0.000(1)
O(5)	4*e*	0.1340(4)	0.14418(9)	0.1990(2)	0.017(1)	0.029(1)	0.038(2)	0.005(1)	0.006(1)	−0.001(1)
O(6)	4*e*	0.7548(4)	0.10380(9)	0.0665(2)	0.030(1)	0.021(1)	0.022(1)	−0.003(1)	0.007(1)	−0.002(1)
O(7)	4*e*	0.7649(5)	0.1452(1)	0.4577(2)	0.050(2)	0.028(1)	0.024(1)	0.007(1)	0.013(1)	0.002(1)
O(8)	4*e*	0.7763(6)	0.1117(1)	−0.1207(3)	0.110(3)	0.031(2)	0.024(2)	−0.001(2)	0.015(2)	−0.005(1)
O(9)	4*e*	0.7688(6)	0.1902(1)	0.6154(2)	0.081(2)	0.052(2)	0.022(2)	−0.009(2)	0.016(2)	−0.006(1)
C(1)	4*e*	0.7884(5)	0.2288(1)	0.4377(3)	0.017(2)	0.033(2)	0.023(2)	−0.001(2)	0.003(1)	−0.005(2)
C(2)	4*e*	0.7773(6)	0.2745(2)	0.4815(4)	0.029(2)	0.040(2)	0.032(2)	−0.006(2)	0.009(2)	−0.015(2)
C(3)	4*e*	0.7640(6)	0.3121(2)	0.4042(4)	0.039(2)	0.025(2)	0.049(3)	−0.006(2)	0.015(2)	−0.014(2)
C(4)	4*e*	0.7630(6)	0.3038(1)	0.2869(4)	0.033(2)	0.019(2)	0.044(2)	−0.003(2)	0.012(2)	−0.003(2)
C(5)	4*e*	0.7834(5)	0.2573(1)	0.2491(3)	0.015(2)	0.022(2)	0.030(2)	−0.001(1)	0.003(1)	0.001(1)
C(6)	4*e*	0.7838(5)	0.2442(1)	0.1256(3)	0.016(2)	0.019(2)	0.026(2)	0.001(1)	0.001(1)	0.001(1)
C(7)	4*e*	0.7835(5)	0.2776(1)	0.0357(3)	0.025(2)	0.019(2)	0.037(2)	−0.001(1)	0.005(2)	0.005(2)
C(8)	4*e*	0.7822(6)	0.2618(1)	−0.0764(3)	0.027(2)	0.034(2)	0.028(2)	−0.001(2)	0.004(2)	0.012(2)
C(9)	4*e*	0.7771(5)	0.2132(1)	−0.0996(3)	0.025(2)	0.032(2)	0.021(2)	−0.002(2)	0.002(2)	0.006(2)
C(10)	4*e*	0.7754(5)	0.1820(1)	−0.0071(3)	0.016(2)	0.025(2)	0.021(2)	0.000(1)	0.002(1)	0.002(1)
C(11)	4*e*	0.7757(6)	0.1847(2)	0.5109(3)	0.025(2)	0.040(2)	0.021(2)	0.004(2)	0.002(2)	−0.003(2)
C(12)	4*e*	0.7677(6)	0.1282(1)	−0.0231(3)	0.028(2)	0.024(2)	0.020(2)	−0.001(1)	0.002(2)	−0.002(2)
C(13)	4*e*	0.3553(5)	0.0803(1)	0.1806(3)	0.018(2)	0.022(2)	0.021(2)	0.000(1)	0.007(1)	0.000(1)
C(14)	4*e*	0.2117(6)	0.0506(1)	0.1151(3)	0.021(2)	0.027(2)	0.037(2)	0.000(2)	0.002(2)	−0.004(2)
C(15)	4*e*	0.2673(6)	0.0045(1)	0.0946(4)	0.030(2)	0.025(2)	0.051(3)	−0.008(2)	0.000(2)	−0.012(2)
C(16)	4*e*	0.4591(6)	−0.0106(1)	0.1420(4)	0.031(2)	0.021(2)	0.045(2)	−0.002(2)	0.007(2)	−0.007(2)
C(17)	4*e*	0.5943(5)	0.0207(1)	0.2073(3)	0.022(2)	0.021(2)	0.026(2)	0.001(1)	0.010(2)	0.003(1)
C(18)	4*e*	0.8023(5)	0.0069(1)	0.2658(3)	0.025(2)	0.018(2)	0.030(2)	0.003(1)	0.007(2)	0.001(1)
C(19)	4*e*	0.8699(6)	−0.0399(1)	0.2748(4)	0.031(2)	0.024(2)	0.052(3)	0.003(2)	0.007(2)	−0.003(2)
C(20)	4*e*	1.0560(7)	−0.0505(2)	0.3402(4)	0.040(2)	0.025(2)	0.058(3)	0.016(2)	0.011(2)	0.007(2)
C(21)	4*e*	1.1738(6)	−0.0143(2)	0.3974(4)	0.029(2)	0.034(2)	0.044(2)	0.015(2)	0.007(2)	0.006(2)
C(22)	4*e*	1.1003(5)	0.0320(1)	0.3826(3)	0.025(2)	0.028(2)	0.024(2)	0.008(2)	0.007(2)	0.005(2)
C(23)	4*e*	1.2113(6)	0.0738(1)	0.4444(3)	0.025(2)	0.034(2)	0.025(2)	0.007(2)	0.004(2)	0.004(2)
C(24)	4*e*	0.3136(5)	0.1317(1)	0.2054(3)	0.017(2)	0.027(2)	0.015(2)	0.001(1)	0.005(1)	0.002(1)

Source of material

A mixture of $Sm(NO_3)_3 \cdot 6H_2O$ (0.1 mmol, 44 mg), 2,2′-bipyridinyl-6,6′-dicarboxylic acid, (0.1 mmol, 24 mg) was dissolved in 8 mL H_2O. Then the solution was heated in a 25 mL Teflon-lined autoclave under autogenous pressure at 443 K for four days. After cooling to room temperature colourless block shaped crystals were collected.

Results and discussion

The metal ion is usually achieved by energy transfer from the bonded ligands, a process termed antenna effect [1] in reference to the naturally occurring phenomenon encountered in green plants [2]. The higher molar absorbance of the organic shell allows a better collection of the incident photons when compared to the free metal ions. This is especially true for lanthanide metal ions, for which the various selection rules make their electronic transitions strongly forbidden with molar absorption coefficients rarely higher than a few $M^{-1} \cdot cm^{-1}$ [3]. Present-day technology in supramolecular chemistry allows a precise control of the metal coordination spheres and permits a fine-tuning of the energy-transfer processes either in simple devices used as luminescent stains [4] or in more elaborate molecular wires and sensors [5]. The choice of the ligand remains however a crucial point and molecules containing

aromatic moieties are usually found to be good sensitisers for LnIII ions [6] but more rarely meet all the above-mentioned criteria [7].

In an effort to bring further understanding to the relationship between the ligand structure and the efficiency of the energy transfer process and, also, to unravel suitable synthons for the design of elaborate compartmental ligands, we have turned our attention to 2,2-bipyridine-6,6-dicarboxylic acid, H2L. Thanks to its aromatic core, combined with a four-site pincer-shaped coordinating pattern, H2L appears as an interesting candidate for use as a light-harvesting moiety for lanthanide complexes.

The asymmetric unit of the title structure contains one Sm(III) ion, and one water molecule and two anionic 2,2′-bipyridinyl-6,6′-dicarboxylato ligands (see the figure) to construct a new coordination polymer. The samarium atom is nine-coordinated by five oxygen atoms (O3, O4, O5a, O6 and O7) and four nitrogen atoms (N1, N2, N3 and N4) from three 2,2′-bipyridinyl-6,6′-dicarboxylato ligands. The Sm—O bond lengths are from 2.356(3) to 2.659(3) Å, and the Sm—N bond lengths are from 2.545(3) to 2.659(3) Å, respectively. The bond angles of O—Sm—O are in the range of 65.24(9)° to 157.95(9)°, the N—Sm—N are in the range of 59.91(9)° to 150.56(9)°. Water molecules and oxygen atoms of the carboxylic groups form hydrogen bonds: O(2)—H(2)...O(1)#1 [O...O = 2.485(4) Å, O–H...O = 161.8°]; O(1)—H(2W)...O(9) [O...O = 2.625(5) Å, O–H...O = 164.5°]; O(1)—H(1W)...O(8)#3 [O...O = 2.678(4) Å, O–H...O = 168.9°]. All the oxygen atoms of the carboxylic groups participate in the hydrogen bonding, contributing to packing stability [8]. Thus these interactions result in the infinite threedimensional architecture.

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