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Crystal structure of bis(2,2'-bipyridine- κ^2N,N')-tetrakis(μ_2 -3-(phenylsulfonamido)propanoato- $\kappa^2O:O'$)-bis(3-(phenylsulfonamido)propanoato- κ^2O,O')digadolinium(III) – 2,2'-bipyridine (1/1), $C_{84}H_{84}Gd_2N_{12}O_{24}S_6$

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.32 × 0.28 × 0.25 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	1.71 mm ⁻¹
Diffractometer, scan mode:	CCD, φ and ω
$\theta_{\max}$, completeness:	25.0°, 99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	15497, 7752, 0.051
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 6039
$N(\text{param})_{\text{refined}}$:	577
Programs:	Bruker [1], SHELX [2, 3], Olex2 [4]

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Abstract

$C_{84}H_{84}Gd_2N_{12}O_{24}S_6$, triclinic, $P\bar{1}$, $a = 9.733(2)$ Å, $b = 11.3610(8)$ Å, $c = 21.4970(3)$ Å, $\alpha = 89.635(3)^\circ$, $\beta = 82.334(3)^\circ$, $\gamma = 69.794(3)^\circ$, $V = 2208.8(5)$ Å³, $Z = 1$, $R_{\text{gt}}(F) = 0.0467$, $wR_{\text{ref}}(F^2) = 0.0925$, $T = 293(2)$ K.

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The molecular structure is shown in the figure (The uncoordinated 2,2'-bipyridine molecule is omitted for clarity). Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

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Source of material

A mixture of $Gd(NO_3)_3$ (137.3 mg, 0.4 mmol), 3-(phenylsulfonamido)propanoic acid (*Hnbsa*) (231.2 mg, 1.2 mmol) and 2,2'-bipyridine (2,2'-bipy) (124.9 mg, 0.8 mmol) was dissolved in 8 mL mixed solution of methanol and water (methanol: water = 1:1). Then the pH of the mixture was adjusted to 6 with 1 mol/L NaOH aqueous solution, stirred and refluxed for 1 h at 80 °C. After filtration, the filtrate was naturally evaporated for 3 days to give a colorless rod crystal.

Experimental details

The structure was solved with the ShelXT [2] structure solution program using Intrinsic Phasing and refined with the ShelXL [3] refinement package using Least Squares minimisation.

Comment

In the recent years, rare earth metal coordination polymers have attracted increasing attention because of their particular properties in photoluminescence and photovoltaic conversion [5–9]. It is well known that rare earth metals have an abundant electronic structure with their 4f electronic number, so that they have relatively high coordination number which provides a way to design new structures, and they are suitable for luminescent centers owing to their high luminescent quantum yield, long lifetime and large Stokes shifts

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	U_{iso}^*/U_{eq}
Gd1	0.83560(3)	0.11496(2)	−0.04110(2)	0.02220(9)
S1	0.7796(3)	0.53217(17)	0.24398(11)	0.0752(7)
S2	0.7572(2)	−0.18006(16)	−0.34248(8)	0.0504(5)
S3	0.78975(18)	0.05922(15)	0.27480(8)	0.0432(4)
O1	0.9924(4)	0.0922(3)	0.04991(16)	0.0280(9)
O2	0.8095(4)	0.2679(3)	0.04533(17)	0.0394(10)
O3	0.7952(7)	0.6017(5)	0.1890(3)	0.102(2)
O4	0.8303(7)	0.5570(5)	0.2994(3)	0.113(2)
O5	0.8496(4)	0.0917(3)	−0.15444(17)	0.0333(9)
O6	0.7081(4)	0.0017(3)	−0.10152(18)	0.0354(9)
O7	0.6853(6)	−0.2330(4)	−0.3822(2)	0.0721(15)
O8	0.9085(5)	−0.2441(4)	−0.3354(2)	0.0709(15)
O9	0.7498(4)	0.0134(3)	0.04240(17)	0.0323(9)
O10	0.9336(4)	−0.1322(3)	0.08139(16)	0.0305(9)
O11	0.6431(5)	0.1368(4)	0.2668(2)	0.0608(13)
O12	0.8956(5)	0.1203(4)	0.2774(2)	0.0567(12)
C1	0.4638(6)	0.1849(5)	0.0030(3)	0.0376(15)
H1	0.504160	0.106530	0.019614	0.045*
C2	0.3114(6)	0.2382(5)	0.0089(3)	0.0409(15)
H2	0.250827	0.196273	0.027648	0.049*
C3	0.2532(7)	0.3548(6)	−0.0141(3)	0.0541(19)
H3	0.151271	0.394496	−0.010641	0.065*
C4	0.3459(7)	0.4127(6)	−0.0422(3)	0.0479(18)
H4	0.306726	0.492622	−0.057301	0.057*
C5	0.4978(6)	0.3530(5)	−0.0482(3)	0.0312(14)
C6	0.6023(7)	0.4099(5)	−0.0792(3)	0.0328(14)
C7	0.5551(8)	0.5293(5)	−0.1029(3)	0.0479(17)
H7	0.455193	0.578094	−0.097225	0.057*
C8	0.6572(8)	0.5748(6)	−0.1346(3)	0.0545(19)
H8	0.626903	0.653624	−0.151683	0.065*
C9	0.8042(8)	0.5026(5)	−0.1409(3)	0.0504(18)
H9	0.875465	0.531167	−0.162194	0.061*
C10	0.8440(7)	0.3860(5)	−0.1146(3)	0.0452(16)
H10	0.943996	0.337847	−0.118231	0.054*
C11	0.9143(6)	0.2017(5)	0.0721(3)	0.0342(14)
C12	0.9497(7)	0.2473(6)	0.1312(3)	0.0527(19)
H12A	0.994712	0.175258	0.155419	0.063*
H12B	1.022451	0.287266	0.119825	0.063*
C13	0.8243(8)	0.3353(6)	0.1710(3)	0.0572(19)
H13A	0.773639	0.404005	0.146051	0.069*
H13B	0.755582	0.293085	0.185939	0.069*
C14	0.5936(9)	0.5504(6)	0.2600(3)	0.060(2)
C15	0.5446(12)	0.4707(8)	0.2985(4)	0.080(3)
H15	0.613069	0.405596	0.316433	0.095*
C16	0.3955(14)	0.4855(9)	0.3109(4)	0.095(3)
H16	0.364743	0.429733	0.335964	0.114*
C17	0.2963(11)	0.5818(9)	0.2860(4)	0.095(3)
H17	0.196093	0.593695	0.294830	0.114*
C18	0.3417(12)	0.6631(8)	0.2476(4)	0.083(3)
H18	0.272247	0.729180	0.230585	0.099*
C19	0.4883(12)	0.6467(7)	0.2344(4)	0.078(3)
H19	0.518070	0.700995	0.207918	0.094*

Table 2 (continued)

Atom	x	y	z	U_{iso}^*/U_{eq}
C20	0.7618(6)	0.0310(5)	−0.1526(3)	0.0287(13)
C21	0.7219(7)	−0.0031(5)	−0.2132(3)	0.0385(15)
H21A	0.625519	0.056096	−0.218824	0.046*
H21B	0.792789	0.006146	−0.247350	0.046*
C22	0.7178(7)	−0.1332(5)	−0.2178(3)	0.0453(17)
H22A	0.816929	−0.192717	−0.217088	0.054*
H22B	0.655631	−0.145784	−0.181102	0.054*
C23	0.7414(8)	−0.0301(6)	−0.3696(3)	0.0443(16)
C24	0.6045(8)	0.0621(7)	−0.3673(3)	0.059(2)
H24	0.519862	0.045437	−0.351270	0.071*
C25	0.5930(11)	0.1794(8)	−0.3890(4)	0.078(3)
H25	0.500330	0.241650	−0.386982	0.094*
C26	0.7162(14)	0.2049(9)	−0.4132(4)	0.094(3)
H26	0.707708	0.283812	−0.428069	0.113*
C27	0.8548(13)	0.1112(10)	−0.4156(4)	0.099(3)
H27	0.939904	0.127210	−0.431669	0.119*
C28	0.8642(9)	−0.0037(8)	−0.3940(4)	0.071(2)
H28	0.956675	−0.066217	−0.395931	0.086*
C29	0.8010(6)	−0.0598(5)	0.0838(3)	0.0283(13)
C30	0.6931(6)	−0.0609(6)	0.1407(3)	0.0450(16)
H30A	0.634606	−0.110011	0.130260	0.054*
H30B	0.626169	0.024380	0.151173	0.054*
C31	0.7650(7)	−0.1139(6)	0.1978(3)	0.0415(15)
H31A	0.688741	−0.114312	0.231745	0.050*
H31B	0.829166	−0.200231	0.187936	0.050*
C32	0.7743(7)	−0.0186(6)	0.3449(3)	0.0460(17)
C33	0.7020(8)	0.0533(7)	0.3991(3)	0.062(2)
H33	0.664154	0.140450	0.398549	0.075*
C34	0.6874(10)	−0.0083(11)	0.4544(4)	0.088(3)
H34	0.639668	0.038365	0.491385	0.106*
C35	0.7422(11)	−0.1368(10)	0.4553(4)	0.088(3)
H35	0.730516	−0.176148	0.492679	0.105*
C36	0.8131(10)	−0.2070(9)	0.4022(4)	0.083(3)
H36	0.849940	−0.294167	0.403083	0.100*
C37	0.4202(7)	0.5153(6)	0.5097(3)	0.0476(17)
C38	0.3410(8)	0.4542(7)	0.4842(4)	0.070(2)
H38	0.388350	0.388931	0.454340	0.084*
C39	0.1932(10)	0.4889(9)	0.5024(5)	0.106(4)
H39	0.138058	0.447190	0.486025	0.128*
C40	0.1275(9)	0.5869(9)	0.5456(4)	0.099(3)
H40	0.025915	0.613821	0.558192	0.119*
C41	0.2094(9)	0.6441(8)	0.5697(4)	0.077(3)
H41	0.162978	0.708345	0.600197	0.092*
C85	0.8301(8)	−0.1480(7)	0.3469(3)	0.0565(19)
H85	0.879736	−0.195878	0.310518	0.068*
N1	0.5561(5)	0.2384(4)	−0.0247(2)	0.0322(11)
N2	0.7473(5)	0.3390(4)	−0.0843(2)	0.0320(11)
N3	0.8642(6)	0.3863(4)	0.2249(2)	0.0548(16)
H3A	0.930932	0.339856	0.245748	0.066*
N4	0.6628(6)	−0.1609(4)	−0.2742(2)	0.0468(14)
H4A	0.576445	−0.166950	−0.270432	0.056*
N5	0.8517(5)	−0.0436(5)	0.2194(2)	0.0440(13)
H5	0.940469	−0.058936	0.200947	0.053*
N6	0.3551(6)	0.6125(5)	0.5519(3)	0.0578(16)

[10–12]. The Gd^{3+} with a large spin ground state S and low-lying excited spin states was preferentially selected to construct molecular units [13, 14]. In this work, we report the synthesis and crystal structure.

Single crystal X-ray structure analysis reveals that the title complex crystallizes in the triclinic system with space group $P\bar{1}$. The structure of this complex unit is centrosymmetric and contains two $Gd(III)$ ions, six *nbsa* ligands, two 2, 2'-bipy ligand and one guest 2,2'-bipy molecule. The $Gd(III)$ atom exhibits a slightly distorted nine-coordination sphere, which is defined by six oxygen atoms from three independent *nbsa* ligands, one carboxyl oxygen atom from a symmetric *nbsa* ligand and two nitrogen atoms from the 2,2'-bipy ligand. $Gd-O$ bond lengths fall in the narrow range 2.343(4) to 2.596(3) Å, and $Gd-N$ bond lengths are 2.570(4) and 2.599(4) Å. These values are within the normal experimental limitation. The extended three-dimensional network was formed by weak $\pi-\pi$ stacking interactions between two pyridine ring of two 2,2'-bipy ligands with centroid-centroid distance 3.729 Å, shift distance 1.372 Å and $N-H\cdots O$ hydrogen bonds ($N4\cdots O11^{#1}$: 2.877(7) Å, $N4-H4A\cdots O11^{#1}$ angle 166.1°; symmetry code: #1 = 1 - X , - Y , - Z).

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