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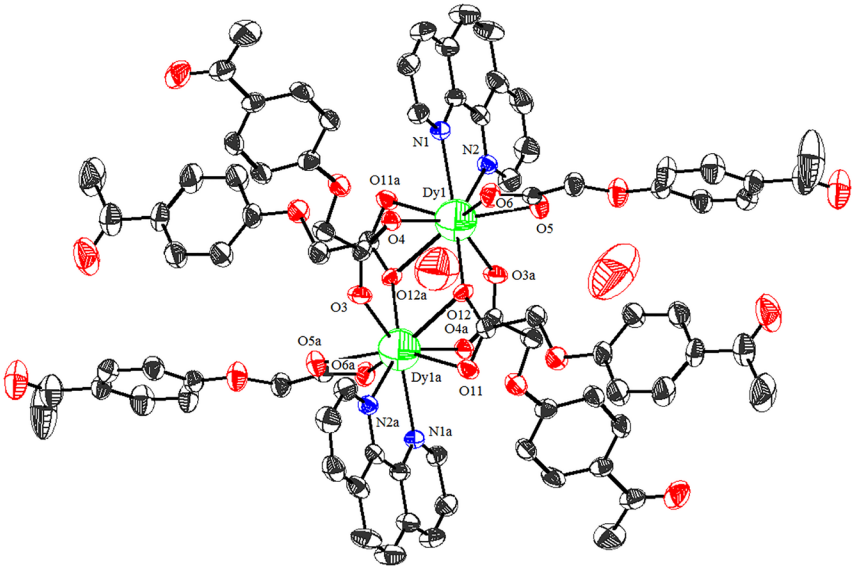
Crystal structure of bis{μ_2-(4-acetyl-phenoxy) acetato-$\kappa^2O:O'$}-bis{μ_2-(4-acetyl-phenoxy)acetato-$\kappa^3O,O':O$)- bis{(4-acetyl-phenoxy)acetato-κ^2O,O'}-bis(phenanthrolin-κ^2N,N')didysprosium(III) tetrahydrate, $C_{84}H_{78}N_4O_{28}Dy_2$



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Abstract

$C_{84}H_{78}N_4O_{28}Dy_2$, triclinic, $P\bar{1}$ (no. 2), a = 12.3134(5) Å, b = 12.7705(5) Å, c = 14.5150(6) Å, α = 70.852(1)°, β = 80.298(1)°, γ = 65.726(1)°, V = 1964.05(14) Å^3, Z = 1, $R_{gt}(F)$ = 0.0381, w$R_{ref}(F^2)$ = 0.0682, T = 296.15 K.

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Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.15 × 0.12 × 0.11 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	1.98 mm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD 6000, ω
θ_{max}, completeness:	25.1°, 99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	54,137, 6967, 0.076
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 5875
$N(param)_{refined}$:	541
Programs:	Bruker [1], Olex2 [2], SHELX [3], Diamond [4]

The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
C1	0.6603 (4)	0.3831 (4)	0.5431 (3)	0.0356 (11)
H1	0.646478	0.452580	0.558980	0.043*
C2	0.5732 (4)	0.3351 (5)	0.5699 (3)	0.0452 (13)
H2	0.503101	0.371547	0.602651	0.054*
C3	0.5923 (4)	0.2335 (5)	0.5471 (4)	0.0525 (14)
H3	0.535186	0.199613	0.565080	0.063*
C4	0.6971 (4)	0.1798 (4)	0.4970 (3)	0.0424 (12)
C5	0.7213 (5)	0.0761 (5)	0.4677 (4)	0.0597 (15)
H5	0.665692	0.040419	0.483118	0.072*
C6	0.8217 (5)	0.0294 (5)	0.4188 (4)	0.0555 (15)
H6	0.834164	−0.037648	0.399741	0.067*
C7	0.9114 (4)	0.0798 (4)	0.3946 (3)	0.0400 (12)
C8	1.0193 (5)	0.0316 (4)	0.3452 (3)	0.0473 (13)
H8	1.035537	−0.035667	0.325214	0.057*
C9	1.1002 (5)	0.0832 (4)	0.3267 (4)	0.0483 (13)
H9	1.173247	0.050772	0.295563	0.058*
C10	1.0719 (4)	0.1866 (4)	0.3553 (3)	0.0419 (12)
H10	1.127697	0.221975	0.341283	0.050*
C11	0.8907 (4)	0.1823 (4)	0.4221 (3)	0.0309 (10)
C12	0.7810 (4)	0.2346 (4)	0.4731 (3)	0.0317 (10)
C13	0.7568 (4)	0.5763 (4)	0.3020 (3)	0.0332 (11)
C14	0.6760 (4)	0.6560 (4)	0.2181 (3)	0.0401 (12)
H14A	0.606211	0.636201	0.226051	0.048*
H14B	0.649651	0.739247	0.216655	0.048*
C15	0.5282 (5)	0.8537 (5)	−0.0586 (4)	0.0560 (15)
H15	0.449390	0.907662	−0.065348	0.067*
C16	0.5710 (4)	0.7898 (5)	0.0341 (3)	0.0520 (14)
H16	0.522229	0.802457	0.089043	0.062*
C17	0.6860 (4)	0.7079 (4)	0.0437 (3)	0.0374 (11)
C18	0.7595 (4)	0.6905 (4)	−0.0379 (3)	0.0419 (12)
H18	0.837444	0.634312	−0.030965	0.050*
C19	0.7166 (4)	0.7565 (4)	−0.1289 (3)	0.0429 (12)
H19	0.766744	0.745733	−0.183471	0.052*
C20	0.6001 (5)	0.8392 (4)	−0.1415 (3)	0.0440 (12)
C21	0.5577 (5)	0.9034 (5)	−0.2418 (4)	0.0632 (16)
C22	0.4305 (6)	0.9892 (8)	−0.2555 (5)	0.136 (4)
H22A	0.419158	1.033005	−0.323321	0.204*
H22B	0.411790	1.044232	−0.217880	0.204*
H22C	0.379115	0.945381	−0.234205	0.204*
C23	0.9529 (4)	0.7053 (4)	0.3739 (3)	0.0291 (10)
C24	0.9006 (5)	0.7599 (4)	0.2745 (3)	0.0458 (13)
H24A	0.939029	0.704250	0.235728	0.055*
H24B	0.816199	0.774796	0.281126	0.055*
C25	0.8752 (4)	0.9283 (4)	0.1344 (3)	0.0431 (12)
C26	0.8373 (5)	0.8817 (4)	0.0787 (4)	0.0516 (14)
H26	0.839417	0.803878	0.102679	0.062*
C27	0.7964 (5)	0.9515 (5)	−0.0129 (4)	0.0521 (14)
H27	0.769738	0.920217	−0.049941	0.063*
C28	0.7938 (5)	1.0675 (4)	−0.0514 (3)	0.0459 (13)
C29	0.8360 (6)	1.1093 (5)	0.0052 (4)	0.0637 (17)
H29	0.838102	1.185442	−0.019794	0.076*
C30	0.8748 (6)	1.0426 (5)	0.0970 (4)	0.0641 (17)
H30	0.900878	1.074166	0.134180	0.077*
C31	0.7459 (5)	1.1399 (5)	−0.1497 (4)	0.0589 (15)
C32	0.7537 (7)	1.2603 (6)	−0.1946 (4)	0.094 (2)
H32A	0.729193	1.291207	−0.260827	0.140*
H32B	0.834476	1.252560	−0.193707	0.140*
H32C	0.702539	1.314187	−0.158156	0.140*
C33	0.8186 (4)	0.5575 (4)	0.6346 (3)	0.0299 (10)
C34	0.7216 (4)	0.5837 (4)	0.7129 (3)	0.0382 (12)
H34A	0.748832	0.526195	0.775531	0.046*
H34B	0.702353	0.663387	0.717844	0.046*
C35	0.5214 (4)	0.5934 (4)	0.7511 (3)	0.0351 (11)
C36	0.5209 (4)	0.5993 (4)	0.8447 (3)	0.0414 (12)
H36	0.588654	0.595004	0.868517	0.050*
C37	0.4167 (4)	0.6119 (4)	0.9020 (3)	0.0428 (12)
H37	0.415356	0.615844	0.965064	0.051*
C38	0.3150 (4)	0.6187 (4)	0.8685 (3)	0.0359 (11)
C39	0.3177 (4)	0.6161 (4)	0.7740 (3)	0.0410 (12)
H39	0.248897	0.624390	0.749017	0.049*
C40	0.4197 (4)	0.6015 (4)	0.7163 (3)	0.0405 (12)
H40	0.420589	0.597038	0.653534	0.049*
C41	0.2082 (4)	0.6254 (4)	0.9346 (4)	0.0439 (13)
C42	0.0903 (4)	0.6617 (6)	0.8931 (4)	0.0671 (17)
H42A	0.090499	0.597734	0.872042	0.101*
H42B	0.076873	0.732242	0.838399	0.101*
H42C	0.028030	0.678322	0.942118	0.101*
Dy1	0.91646 (2)	0.42733 (2)	0.45293 (2)	0.02417 (7)
N1	0.7619 (3)	0.3360 (3)	0.4965 (2)	0.0295 (8)
N2	0.9705 (3)	0.2368 (3)	0.4010 (2)	0.0303 (8)
O1	0.2159 (3)	0.6017 (3)	1.0224 (3)	0.0620 (10)
O2	0.6189 (3)	0.5761 (3)	0.6881 (2)	0.0441 (8)
O3	0.9002 (3)	0.5934 (3)	0.6327 (2)	0.0397 (8)
O4	0.8115 (2)	0.5006 (3)	0.5817 (2)	0.0312 (7)
O5	0.8578 (3)	0.5008 (3)	0.2878 (2)	0.0395 (8)
O6	0.7198 (3)	0.5887 (3)	0.3847 (2)	0.0408 (8)
O7	0.7389 (3)	0.6389 (3)	0.1303 (2)	0.0494 (9)
O8	0.6229 (4)	0.8857 (4)	−0.3125 (3)	0.0825 (13)
O9	0.7004 (5)	1.1023 (4)	−0.1929 (3)	0.0906 (15)
O10	0.9166 (3)	0.8691 (3)	0.2265 (2)	0.0552 (10)
O11	1.0091 (3)	0.7479 (3)	0.4032 (2)	0.0363 (7)
O12	0.9374 (2)	0.6100 (2)	0.42534 (19)	0.0295 (7)
O13	1.0167 (8)	0.5591 (9)	0.1299 (8)	0.234 (4)
H13A	1.083383	0.541126	0.098421	0.351*
H13B	1.020099	0.493486	0.172229	0.351*
O14	0.6706 (7)	0.8105 (7)	0.4782 (6)	0.158 (2)
H14C	0.609870	0.846849	0.514905	0.237*
H14D	0.670901	0.742923	0.477089	0.237*

1 Source of materials

The dinuclear Dy(III) complex was synthesized according to the following method: 0.1257 g dysprosium chloride hexahydrate (0.033 mmol), 0.194 g (4-acetyl-phenoxy)acetic acid (1.0 mmol), 0.040 g NaOH (1.0 mmol), and 0.090 g 1,10-phenantroline (0.5 mmol) were dissolved in 20 mL of ethanol-water (1:1, v/v) solution with stirring. Then the mixture was heated at 80 °C for 6 h. After cooling to room

temperature, the solution was filtered to a small beaker, evaporated quietly and slowly. The clear light colourless block crystals of the dinuclear Dy(III) complex were collected after 10 days.

2 Experimental details

The hydrogen atoms were positioned geometrically (C–H = 0.93–0.97 Å, and O–H = 0.85–0.89 Å). Their U_{iso} values were set to 1.2 U_{eq} or 1.5 U_{eq} of the parent atoms.

3 Comment

Due to their unique electronic structure and high coordination numbers, rare earth complexes show for example excellent properties in aspects such as catalyst for isoprene polymerization [5], pharmacological activity [6], copolymerization of cyclohexene oxide with cyclic anhydrides [7], magnetic property [8], selective catalytic reduction of NO with NH_3 [9], and optical, electrochemical property [10]. Our research group has been working on the structure and property of metal complexes [11].

Here we report a new dinuclear Dy(III) complex which was synthesized using a facile one-pot method with dysprosium chloride hexahydrate, (4-acetyl-phenoxy) acetic acid, NaOH, and 1,10-phenantroline as materials. Single crystal X-ray diffraction analysis shows that the dinuclear Dy(III) complex crystallizes in the triclinic space group $P\bar{1}$. The molecular structure of the dinuclear Dy(III) complex is shown in Figure. The asymmetrical unit of dinuclear Dy(III) complex consists of one Dy(III), three (4-acetyl-phenoxy)acetate ligands, one 1,10-phenantroline ligand, and two uncoordinated water molecules. Each Dy(III) atom is nine-coordinated by seven oxygen atoms (O3a, O4, O5, O6, O11a, O12, O12a, or O3, O4a, O5a, O6a, O11, O12, O12a) from five (4-acetyl-phenoxy)acetate ligands and two nitrogen atoms (N1, N2, or N1a, N2a) from one 1,10-phenantroline ligand. The carboxylate groups of (4-acetyl-phenoxy)acetate ligands display three different coordination modes: four adopt two different bridging modes and the other two adopt a simple k2O,O′ chelating mode (see the figure). The Dy–O bond lengths range from 2.319(3) to 2.541(3) Å, and the Dy–N bond lengths range from 2.514(3) to 2.575(3) Å, respectively. Two symmetry-related Dy(III) ions are connected by four carboxylate groups to form a dinuclear $[Dy_2(COO)_4]$ unit with a Dy···Dy distance of 3.911 Å.

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