# Crystal structure of diaquabis(1,10-phenanthroline)dilanthanum(III) tris($\mu$-1,4-benzenedicarboxylate), $La_2(H_2O)_2(C_{12}H_8N_2)_2(C_8H_4O_4)_3$

X. Li*[I], D.-Y. Wang[II] and H.-M. Hu[II]

[I] Capital Normal University, Department of Chemistry, Beijing, 100037 P. R. China
[II] Northwest University, Department of Chemistry, Xian, 710069 P. R. China

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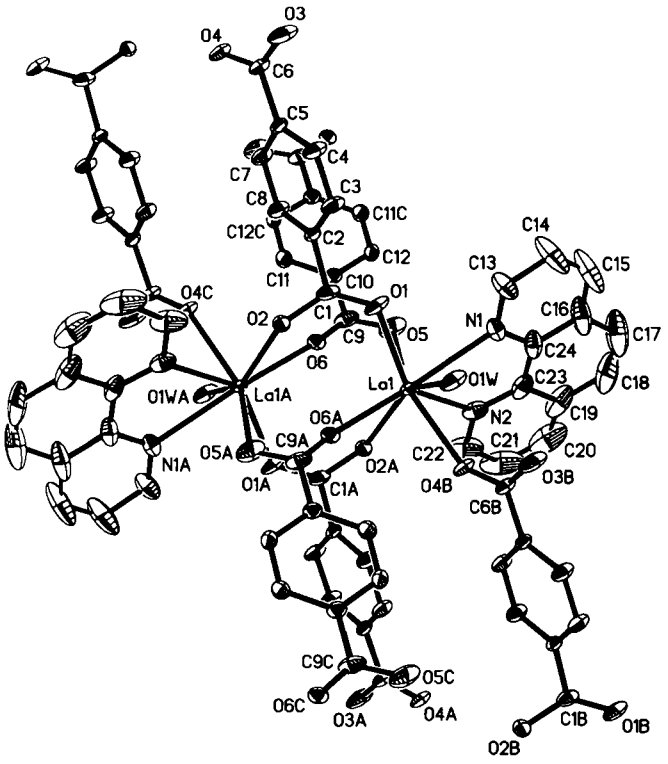


**Abstract**

$C_{24}H_{16}LaN_2O_7$, triclinic, $P\bar{1}$ (no. 2), $a$ = 10.424(1) Å, $b$ = 10.8499(9) Å, $c$ = 11.448(2) Å, $\alpha$ = 109.435(6)°, $\beta$ = 92.016(4)°, $\gamma$ = 112.162(3)°, $V$ = 1111.5 Å$^3$, $Z$ = 2, $R_{gt}(F)$ = 0.029, $wR_{ref}(F^2)$ = 0.071, $T$ = 293 K.

**Source of material**

Sodium 1,4-benzenedicarboxylate (164 mg, 1.0 mmol) and 1,10-phenanthroline (90 mg, 0.5 mmol) were dissolved in aqueous solution of agar. The mixture was heated and placed to gel. Aqueous solution of $La(NO_3)_3 \cdot 6H_2O$ (217 mg, 0.5 mmol) was added to the top of it. Single crystals were obtained after one month.

**Experimental details**

While hydrogen atoms attached to carbon atoms were calculated using common restraints, the positions of the aqua H atoms were located from Fourier difference maps and refined.

* Correspondence author (e-mail: zouyq@263.net)

**Discussion**

Recently, lanthanide coordination polymers using phthalic acid by hydrothermal method have been reported, such as complexes $[Ln_2(bdc)_3(H_2O)]_n$ ($Ln$ = La, Eu, Tb; $H_2bdc$ = 1,2-benzenedicarboxylic acid) [1], $[Ln_4(mbdc)_6(phen)]_n$ ($Ln$ = Tb, Er; $H_2bdc$ = 1,3-benzenedicarboxylic acid; phen = 1,10-phenanthroline) [2], and $Tb_2(bdc)_3(H_2O)_4$ ($H_2bdc$ = 1,4-benzenedicarboxylic acid) [3].

Dimeric units $La_2(bdc)_3(phen)_2(H_2O)_2$ may be viewed as building blocks of the title crystal structure ($H_2bdc$ = 1,4-benzenedicarboxylic acid, phen = 1,10-phenanthroline). Each La(III) ion is coordinated by five oxygen atoms of $bdc^{2-}$ dianions, two nitrogen atoms of phen and one oxygen atom of water molecule. The coordination polyhedron of the La ion is a square antiprism with atoms O1W, O4B, N1, N2 and O1, O5, O2A, O6A, respectively, as the two square planes. The dihedral angle between the planes is 4.8°.

The La—O (carboxylate groups) distances vary from 2.416(4) Å to 2.510(4) Å with an average distance of 2.468 Å. The bond length La1—O6A is the smallest of them, and O6···La1 is also the shortest distance of second coordination sphere (3.212(6) Å). The O–La–O angles are in the range of 67.8(1)° – 141.3(1)°. The distance between coordinated water and La ion is 2.586(3) Å. Phen ligand coordinates to the La ion in a bidentate-chelating coordination mode with the La—N lengths of 2.691(3) Å and 2.723(3) Å, and an N–La–N bond angle being 60.2(1)°. $bdc^{2-}$ dianions adopt two coordination modes: tridentate coordination mode (one carboxylate group of $bdc^{2-}$ dianion is in monodentate, another is in bridging bidentate) and tetradentate coordination mode (both carboxylate groups of $bdc^{2-}$ dianion are in bridging). In a $La_2(bdc)_3(phen)_2(H_2O)_2$ building block, the two La ions are then linked to each other by four $COO^-$ groups (O1–C1–O2, O1A–C1A–O2A, O5–C9–O6 and O5A–C9A–O6A) being bidentate-bridging. The dimer has a centre of symmetry and the distance between La1 and La1A is 4.2249(5) Å.

The neighboring building blocks are connected to a 1D chain through one $^-OOCC_6H_4COO^-$ unit in tetradentate coordination mode and to another 1D chain through two $^-OOCC_6H_4COO^-$ units in tridentate mode. Two types of 1D chains are connected to a 2D open channel structure containing a regular rhombus being parallel to the $a,b$ plane. If viewed along the $c$ axis, the $\pi$-$\pi$ stacking interactions of benzene rings exist in the crystal. Hydrogen bonds occur in the crystal. The coordinated aqua ligand forms two hydrogen bonds with the uncoordinated carboxylate oxygen of the monodentate $bdc^{2-}$ anion [O1W–H1WB···O3($x$+1,$y$+1,$z$), 2.766(5) Å, 167(6)°, O1W–H1WA···O3(–$x$,–$y$,–$z$), 2.823(5) Å, 167(7)°]. Adjacent 2D layers parallel to $a,b$ plane are interlinked by these hydrogen bonds along $c$ axis to form a 3D supermolecular structure.

**Table 1.** Data collection and handling.

| | |
|---|---|
| Crystal: | colorless block, size 0.14 × 0.18 × 0.28 mm |
| Wavelength: | Mo $K_\alpha$ radiation (0.71073 Å) |
| $\mu$: | 19.71 $cm^{-1}$ |
| Diffractometer, scan mode: | Rigaku R-AXIS RAPID IP, $\varphi/\omega$ |
| $2\theta_{max}$: | 50° |
| $N(hkl)_{measured}$, $N(hkl)_{unique}$: | 3824, 3824 |
| Criterion for $I_{obs}$, $N(hkl)_{gt}$: | $I_{obs} > 2\,\sigma(I_{obs})$, 3677 |
| $N(param)_{refined}$: | 314 |
| Programs: | SHELXS-97 [4], SHELXL-97 [5] |

**Table 2.** Atomic coordinates and displacement parameters (in $Å^2$).

| Atom | Site | $x$ | $y$ | $z$ | $U_{iso}$ |
|---|---|---|---|---|---|
| H(3A) | 2*i* | 0.0525 | 0.1447 | 0.1373 | 0.053 |
| H(4A) | 2*i* | –0.1513 | –0.0610 | 0.0869 | 0.051 |
| H(7A) | 2*i* | –0.0246 | –0.1218 | 0.3885 | 0.049 |
| H(8A) | 2*i* | 0.1730 | 0.0901 | 0.4444 | 0.049 |
| H(11A) | 2*i* | 0.4073 | 0.1516 | 0.6207 | 0.050 |
| H(12A) | 2*i* | 0.6389 | 0.0650 | 0.3594 | 0.046 |
| H(13A) | 2*i* | 0.4182 | 0.2004 | 0.0553 | 0.088 |
| H(14A) | 2*i* | 0.4339 | 0.0510 | –0.1347 | 0.155 |
| H(15A) | 2*i* | 0.6463 | 0.0753 | –0.1828 | 0.161 |
| H(17A) | 2*i* | 0.9082 | 0.1990 | –0.1207 | 0.160 |
| H(18A) | 2*i* | 1.1006 | 0.3615 | 0.0228 | 0.141 |
| H(20A) | 2*i* | 1.2041 | 0.5402 | 0.2462 | 0.156 |
| H(21A) | 2*i* | 1.1750 | 0.6723 | 0.4407 | 0.150 |
| H(22A) | 2*i* | 0.9439 | 0.6417 | 0.4733 | 0.102 |
| H(1WA) | 2*i* | 0.513(5) | 0.562(6) | 0.122(6) | 0.080 |
| H(1WB) | 2*i* | 0.403(6) | 0.446(5) | 0.084(4) | 0.080 |

**Table 3.** Atomic coordinates and displacement parameters (in $Å^2$).

| Atom | Site | $x$ | $y$ | $z$ | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| La(1) | 2*i* | 0.58492(2) | 0.49161(2) | 0.33412(2) | 0.0252(1) | 0.0199(1) | 0.0269(1) | 0.00365(9) | 0.00715(8) | 0.01135(9) |
| N(1) | 2*i* | 0.6190(4) | 0.3106(4) | 0.1232(3) | 0.058(2) | 0.052(2) | 0.032(2) | 0.032(2) | 0.011(2) | 0.013(2) |
| N(2) | 2*i* | 0.8464(4) | 0.5004(4) | 0.3068(4) | 0.029(2) | 0.044(2) | 0.082(3) | 0.013(2) | 0.001(2) | 0.030(2) |
| O(1) | 2*i* | 0.3358(3) | 0.3047(3) | 0.2626(3) | 0.030(2) | 0.045(2) | 0.072(2) | –0.005(1) | 0.011(2) | 0.034(2) |
| O(2) | 2*i* | 0.2809(6) | 0.3628(4) | 0.4512(3) | 0.164(5) | 0.035(2) | 0.035(2) | –0.024(2) | –0.024(2) | 0.009(2) |
| O(3) | 2*i* | –0.3150(4) | –0.3022(4) | 0.0945(3) | 0.052(2) | 0.060(2) | 0.055(2) | –0.027(2) | –0.021(2) | 0.035(2) |
| O(4) | 2*i* | –0.2672(3) | –0.3016(3) | 0.2843(3) | 0.032(1) | 0.036(2) | 0.050(2) | 0.001(1) | 0.007(1) | 0.029(1) |
| O(5) | 2*i* | 0.6058(4) | 0.2884(4) | 0.3794(4) | 0.075(2) | 0.051(2) | 0.075(2) | 0.016(2) | 0.007(2) | 0.048(2) |
| O(6) | 2*i* | 0.5245(5) | 0.3576(4) | 0.5484(6) | 0.106(4) | 0.032(2) | 0.228(6) | 0.038(2) | 0.115(4) | 0.049(3) |
| O(1W) | 2*i* | 0.4529(3) | 0.5087(4) | 0.1486(3) | 0.034(2) | 0.052(2) | 0.062(2) | –0.002(1) | –0.004(1) | 0.037(2) |
| C(1) | 2*i* | 0.2591(4) | 0.2792(4) | 0.3392(4) | 0.037(2) | 0.035(2) | 0.038(2) | –0.004(2) | –0.013(2) | 0.018(2) |
| C(2) | 2*i* | 0.1311(4) | 0.1411(4) | 0.2986(3) | 0.027(2) | 0.026(2) | 0.027(2) | 0.002(2) | 0.007(1) | 0.011(2) |
| C(3) | 2*i* | 0.0354(5) | 0.0930(5) | 0.1899(4) | 0.041(2) | 0.041(2) | 0.039(2) | –0.006(2) | –0.004(2) | 0.026(2) |
| C(4) | 2*i* | –0.0857(4) | –0.0316(5) | 0.1585(4) | 0.035(2) | 0.040(2) | 0.039(2) | –0.006(2) | –0.008(2) | 0.024(2) |
| C(5) | 2*i* | –0.1103(4) | –0.1131(4) | 0.2328(3) | 0.023(2) | 0.030(2) | 0.032(2) | 0.004(2) | 0.007(1) | 0.015(2) |
| C(6) | 2*i* | –0.2399(4) | –0.2493(4) | 0.2002(4) | 0.026(2) | 0.032(2) | 0.045(2) | 0.003(2) | 0.006(2) | 0.023(2) |
| C(7) | 2*i* | –0.0110(4) | –0.0669(5) | 0.3389(4) | 0.040(2) | 0.039(2) | 0.040(2) | 0.003(2) | 0.003(2) | 0.026(2) |
| C(8) | 2*i* | 0.1080(4) | 0.0596(5) | 0.3720(4) | 0.034(2) | 0.039(2) | 0.035(2) | –0.002(2) | –0.004(2) | 0.020(2) |
| C(9) | 2*i* | 0.5549(4) | 0.2685(5) | 0.4709(5) | 0.027(2) | 0.033(2) | 0.082(3) | 0.013(2) | 0.007(2) | 0.027(2) |
| C(10) | 2*i* | 0.5278(4) | 0.1304(4) | 0.4880(4) | 0.030(2) | 0.026(2) | 0.037(2) | 0.012(2) | 0.006(2) | 0.015(2) |
| C(11) | 2*i* | 0.4447(5) | 0.0907(4) | 0.5720(4) | 0.051(3) | 0.029(2) | 0.051(2) | 0.023(2) | 0.026(2) | 0.014(2) |
| C(12) | 2*i* | 0.5829(5) | 0.0390(4) | 0.4161(4) | 0.050(2) | 0.034(2) | 0.036(2) | 0.018(2) | 0.021(2) | 0.017(2) |
| C(13) | 2*i* | 0.5071(7) | 0.2105(7) | 0.0372(5) | 0.092(4) | 0.078(4) | 0.038(3) | 0.043(4) | –0.007(3) | –0.002(3) |
| C(14) | 2*i* | 0.515(1) | 0.120(1) | –0.0777(7) | 0.153(9) | 0.154(9) | 0.055(4) | 0.099(8) | –0.012(5) | –0.028(5) |
| C(15) | 2*i* | 0.640(1) | 0.135(1) | –0.1050(7) | 0.18(1) | 0.19(1) | 0.042(4) | 0.131(9) | 0.003(5) | –0.011(5) |
| C(16) | 2*i* | 0.765(1) | 0.237(1) | –0.0195(7) | 0.135(7) | 0.154(7) | 0.076(4) | 0.120(7) | 0.062(5) | 0.055(5) |
| C(17) | 2*i* | 0.898(1) | 0.255(2) | –0.0431(9) | 0.157(9) | 0.24(1) | 0.101(6) | 0.16(1) | 0.075(7) | 0.084(8) |
| C(18) | 2*i* | 1.012(1) | 0.350(1) | 0.043(1) | 0.122(7) | 0.20(1) | 0.149(8) | 0.137(8) | 0.114(7) | 0.122(8) |
| C(19) | 2*i* | 1.0039(7) | 0.4378(9) | 0.1685(9) | 0.050(4) | 0.119(6) | 0.157(7) | 0.053(4) | 0.048(4) | 0.098(6) |
| C(20) | 2*i* | 1.1139(9) | 0.529(1) | 0.261(1) | 0.061(5) | 0.127(8) | 0.26(1) | 0.057(6) | 0.063(7) | 0.122(9) |
| C(21) | 2*i* | 1.0976(7) | 0.6086(9) | 0.377(1) | 0.038(4) | 0.081(5) | 0.22(1) | 0.007(4) | –0.034(5) | 0.044(6) |
| C(22) | 2*i* | 0.9570(6) | 0.5893(7) | 0.3956(8) | 0.040(3) | 0.058(3) | 0.134(6) | 0.013(3) | –0.021(3) | 0.021(4) |
| C(23) | 2*i* | 0.8679(6) | 0.4235(6) | 0.1934(6) | 0.057(3) | 0.070(3) | 0.087(4) | 0.046(3) | 0.043(3) | 0.055(3) |
| C(24) | 2*i* | 0.7481(6) | 0.3231(6) | 0.0980(5) | 0.075(4) | 0.079(4) | 0.049(3) | 0.056(3) | 0.031(3) | 0.036(3) |

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