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SYNTHESIS AND CRYSTAL STRUCTURE OF THE DINUCLEAR COMPLEX OF 6-METHYLPICOLINIC ACID *N*-OXIDE WITH LANTHANUM(III)

LAN YAN, JIANMIN LIU, XIN WANG, RUDONG YANG* and FANGLIANG SONG

Department of Chemistry, Lanzhou University, Lanzhou 730000, P. R. China

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Abstract—A new dinuclear complex of 6-methylpicolinic acid *N*-oxide (6-mepicno) with lanthanum(III) ion, La_2(6-mepicno)$_6 \cdot 6H_2O$, was synthesized and characterized by elemental analysis, molar conductance, thermogravimetric analysis and IR spectra. The structure of the complex was determined by single-crystal X-ray diffraction. In the complex, the two lanthanum(III) ions were coordinated by six 6-mepicno and two water molecules, and the coordination number of the lanthanum(III) ion is nine. However, the 6-mepicno adopted different coordination modes, acting as both chelating bidentate and bridging bidentate ligands. The coordination polyhedron is a distorted tricapped trigonal prism. The La—O bond lengths are in the range of 0.2441(2)–0.2760(2) nm.

Picolinic acid *N*-oxide and its substituted derivatives as mono- and bidentate ligands were able to form complexes with various metals, such as transition metals, alkaline earths etc.[1,2] A number of the complexes of picolinic acid *N*-oxide with lanthanide(III) ions have been inverstigated.[3–6] However, little has been published about the structure of the complexes. In order to study the coordination modes of picolinic acid *N*-oxide with lanthanide(III) ions, we herein first report the synthesis and X-ray crystal structure of the 6-methylpicolinic acid *N*-oxide (6-mepicno)–lanthanum(III) complex. The structure analysis show that the 6-mepicno acts as chelating bidentate and bridging bidentate ligands.

EXPERIMENTAL

Synthesis of La_2(6-mepicno)$_6 \cdot H_2O$

La_2O_3 (2 mmol) and 6-mepicno (6 mmol) were added to 30–40 cm^3 of distilled water and the reaction mixture was stirred at reflux temperature for 12 h. After cooling to room temperature, the surplus reactants were removed by filtration and the filtrate was concentrated by evaporation. To the concentrated solution, 20 cm^3 ethanol was added, then suitable ether was added dropwise. A precipitate gradually appeared and was filtered, washed three times with ether and dried to constant weight at room temperature in a vacuum drier. Found: C, 38.1: H, 3.3; N, 6.3. Calc. for La_2(6-mepicno)$_6 \cdot H_2O$: C, 38.8; H, 3.7; N, 6.5%.

The product was dissolved in ethanol–water. Slow evaporation of the resulting solution gave, after several months, crystals suitable for X-ray diffraction studies.

Chemical and physical measurements

The lanthanum ion content was determined by EDTA titration using Xylenol Orange as an indicator. The carbon, nitrogen and hydrogen contents were determined on a Carlo-Erba 1106 elemental analyser. The IR spectra was recorded over the range 4000–200 cm^{-1} on a 170 SX FTR spec-

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*Author to whom correspondence should be addressed.

trometer using KBr discs. The conductance measurements were carried out with a DDS-11A type conductometer. The thermogravimetric measurement was performed on a PCT-2 differential thermal analyser in air at a heating rate of 10°C min^{-1}.

Crystal structure determination

Crystal data: $C_{42}H_{48}La_2N_6O_{24}$, $M_r = 1298.7$, monoclinic, space group $P2_1/c$, $a = 1.6208$ (2), $b = 1.0570$ (2), $c = 2.9678$ (3) nm, $\beta = 99.86$ (2)°, $Z = 4$, $V = 5.0092$ nm^3, $D_c = 1.722$ g cm^{-3}, $\mu = 139.451$ cm^{-1}, $F(000) = 2592$.

A transparent colourless crystal of approximate dimensions $0.2 \times 0.2 \times 0.3$ mm was used for data collection on an Enraf–Nonius CAP-4 diffractometer with graphite monochromatized Cu-K_α radiation ($\lambda = 1.5418$ Å). The ω–2θ scan technique was used. The cell parameters were refined by a least-squares method on the basis of 25 reflections with $10 < \theta < 18°$. Three standard reflections were monitored every 90 min and showed no significant change (<2.5%). A total of 6598 independent reflections were collected in the range $2 < 2\theta < 108°$ ($h = -17$ to 17; $k = 0$–11; $l = 0$–31) in which 4582 strong reflections with $I > 3\sigma(I)$ were used in the calculations. Lorentz, polarization and absorption corrections were made. The structure was solved by direct methods. The atomic coordinates of the two lanthanum(III) ions were first obtained by analysing the Patterson function. The other non-hydrogen atom coordinates were gradually obtained using a subsequent difference-Fourer technique. Finally, the coordinates and the anisotropic thermal parameters of non-hydrogen atoms were refined by full-matrix least-squares. The final values $R = 0.032$ and $R_w = 0.036$ were obtained for all observed reflections.

RESULTS AND DISCUSSION

Characterization of the complex

The elemental analysis result was in agreement with the proposed formula, $La_2(6\text{-mepicno})_6 \cdot 6H_2O$. The molar conductance of the complex was 1.58 S cm^2 mol^{-1} in absolute ethanol and so it is a non-electrolyte. The TG curve indicated that the complex begins losing four water molecules at 80°C, and then loses two coordinated water molecules at 185°C. The anhydrous complex decomposes through three processes to La_2O_3 at 800°C.

IR spectra of the complex

A comparison of the IR spectral data of the ligand with that of complex indicates that the carboxyl and N—O groups of the ligand were coordinated to lanthanum(III). The ν(COO) and ν(N—O) of the ligand observed at 1680 and 1223 cm^{-1} shift to 1624 and 1209 cm^{-1} in the complex, respectively, while the δ(N—O) appearing at 829 cm^{-1} in the ligand shifts to 850 cm^{-1}. The ν(COO) mode at 1391 cm^{-1} in the ligand splits into 1397 and 1370 cm^{-1} in the complex, which demonstrates that the carboxylates have different coordination behaviours. A broad band in the complex observed at 3309 cm^{-1} indicates the existence of water molecules.

Crystal structure

Selected bond lengths and angles are listed in Tables 1 and 2, respectively. Figure 1 shows the structure of the complex $La_2(6\text{-mepicno})_6 \cdot 6H_2O$. In the complex, 6-mepicno acts as both chelating bidentate and bridging ligands. The two nine-coordinated lanthanum(III) ions were bridged through two 6-mepicno groups in which μ_3-O [O(12), O(22)] of the carboxylate, with N—O [O(11), O(21)] and with another oxygen of the carboxylate chelated, respectively, to two lanthanum(III) ions. The remaining four 6-mepicno moieties chelated through N—O and one of the carboxylate oxygens chelated symmetrically to two lanthanum(III) ions; the nine-coordination about each lanthanum(III) ion is completed by one water molecule. The coordination geometry is a distorted tricapped trigonal prism, which is shown in Fig. 2. O(1), O(11) and O(42) form the top plane of the trigonal prism and the bottom plane is formed by O(22), O(31) and O(32); O(12), O(23) and O(41) cap each quadrilateral face of the trigonal prism. The La—$O_{(H_2O)}$ bonds range from 0.2546 to 0.2596 nm, average 0.2571 nm; the La—$O_{(N—O)}$ bonds range from 0.2441 to 0.2492 nm, average 0.2484 nm, and the La—$O_{(\mathrm{carboxylate})}$ bonds vary from 0.2490 to 0.2760 nm, average 0.2575 nm. The distance from lanthanum(III) to oxygen of the carboxylate of the bridging ligands is the longest.

Table 1. Selected bond lengths (nm) for $[La_2L_6(H_2O)_2]\cdot 4H_2O$

La(1)—O(1)	0.2596(3)	O(11)—N(1)	0.1327(7)
La(1)—O(11)	0.2492(5)	O(12)—C(16)	0.1259(6)
La(1)—O(12)	0.2490(4)	O(13)—C(16)	0.1228(6)
La(1)—O(22)	0.2642(3)	O(21)—N(2)	0.1318(5)
La(1)—O(23)	0.2760(2)	O(22)—C(26)	0.1276(2)
La(1)—O(31)	0.2491(4)	O(23)—C(26)	0.1227(4)
La(1)—O(32)	0.2511(2)	O(31)—N(3)	0.1324(5)
La(1)—O(41)	0.2462(5)	O(32)—C(36)	0.1267(6)
La(1)—O(42)	0.2457(2)	O(33)—C(36)	0.1226(4)
La(2)—O(2)	0.2546(3)	O(41)—N(4)	0.1322(7)
La(2)—O(12)	0.2644(4)	O(42)—C(46)	0.1255(6)
La(2)—O(13)	0.2668(4)	O(43)—C(46)	0.1238(4)
La(2)—O(21)	0.2489(2)	O(51)—N(5)	0.1326(5)
La(2)—O(22)	0.2518(3)	O(52)—C(56)	0.1244(3)
La(2)—O(51)	0.2441(2)	O(53)—C(56)	0.1245(6)
La(2)—O(52)	0.2483(4)	O(61)—N(6)	0.1330(4)
La(2)—O(61)	0.2468(4)	O(62)—C(66)	0.1257(5)
La(2)—O(62)	0.2575(2)	O(63)—C(66)	0.1233(5)

Table 2. Selected bond angles (°) for $[La_2L_6(H_2O)_2]\cdot 4H_2O$

O(1)—La(1)—O(11)	75.5(1)	O(2)—La(2)—O(12)	72.1(9)
O(1)—La(1)—O(12)	72.2(9)	O(2)—La(2)—O(13)	100.8(9)
O(1)—La(1)—O(22)	82.7(1)	O(2)—La(2)—O(21)	115.3(2)
O(1)—La(1)—O(23)	70.1(9)	O(2)—La(2)—O(22)	72.5(8)
O(1)—La(1)—O(31)	132.5(7)	O(2)—La(2)—O(51)	74.7(2)
O(1)—La(1)—O(32)	147.1(9)	O(2)—La(2)—O(52)	76.0(9)
O(1)—La(1)—O(41)	133.1(1)	O(2)—La(2)—O(61)	151.5(7)
O(1)—La(1)—O(42)	74.8(1)	O(2)—La(2)—O(62)	141.0(9)
O(11)—La(1)—O(12)	65.1(1)	O(12)—La(2)—O(13)	48.6(2)
O(11)—La(1)—O(22)	128.8(1)	O(12)—La(2)—O(21)	123.4(9)
O(11)—La(1)—O(23)	145.6(1)	O(12)—La(2)—O(22)	63.8(2)
O(11)—La(1)—O(31)	148.3(1)	O(12)—La(2)—O(51)	100.1(1)
O(11)—La(1)—O(32)	97.6(1)	O(12)—La(2)—O(52)	147.9(9)
O(11)—La(1)—O(41)	73.6(2)	O(12)—La(2)—O(61)	124.7(1)
O(11)—La(1)—O(42)	84.5(1)	O(12)—La(2)—O(62)	73.2(8)
O(12)—La(1)—O(22)	64.2(2)	O(13)—La(2)—O(21)	138.5(7)
O(12)—La(1)—O(23)	104.4(9)	O(13)—La(2)—O(22)	109.5(2)
O(12)—La(1)—O(31)	130.5(2)	O(13)—La(2)—O(51)	70.8(2)
O(12)—La(1)—O(32)	75.8(9)	O(13)—La(2)—O(52)	137.1(8)
O(12)—La(1)—O(41)	122.5(9)	O(13)—La(2)—O(61)	81.2(1)
O(12)—La(1)—O(42)	139.5(1)	O(13)—La(2)—O(62)	68.0(7)
O(22)—La(1)—O(23)	48.2(5)	O(21)—La(2)—O(22)	66.1(2)
O(22)—La(1)—O(31)	76.3(1)	O(21)—La(2)—O(51)	136.4(1)
O(22)—La(1)—O(32)	76.9(9)	O(21)—La(2)—O(52)	74.4(8)
O(22)—La(1)—O(41)	144.1(1)	O(21)—La(2)—O(61)	76.7(1)
O(22)—La(1)—O(42)	133.3(6)	O(21)—La(2)—O(62)	71.1(9)
O(23)—La(1)—O(31)	64.1(9)	O(22)—La(2)—O(51)	146.6(1)
O(23)—La(1)—O(32)	111.8(9)	O(22)—La(2)—O(52)	110.1(2)
O(23)—La(1)—O(41)	131.4(2)	O(22)—La(2)—O(61)	134.1(6)
O(23)—La(1)—O(42)	85.5(7)	O(22)—La(2)—O(62)	76.5(9)
O(31)—La(1)—O(32)	66.8(7)	O(51)—La(2)—O(52)	67.1(2)
O(31)—La(1)—O(41)	75.3(1)	O(51)—La(2)—O(61)	79.3(9)
O(31)—La(1)—O(42)	89.5(1)	O(51)—La(2)—O(62)	129.3(1)
O(32)—La(1)—O(41)	71.9(2)	O(52)—La(2)—O(61)	83.3(1)
O(32)—La(1)—O(42)	137.4(2)	O(52)—La(2)—O(62)	138.1(8)
O(41)—La(1)—O(42)	67.9(9)	O(61)—La(2)—O(62)	66.4(9)

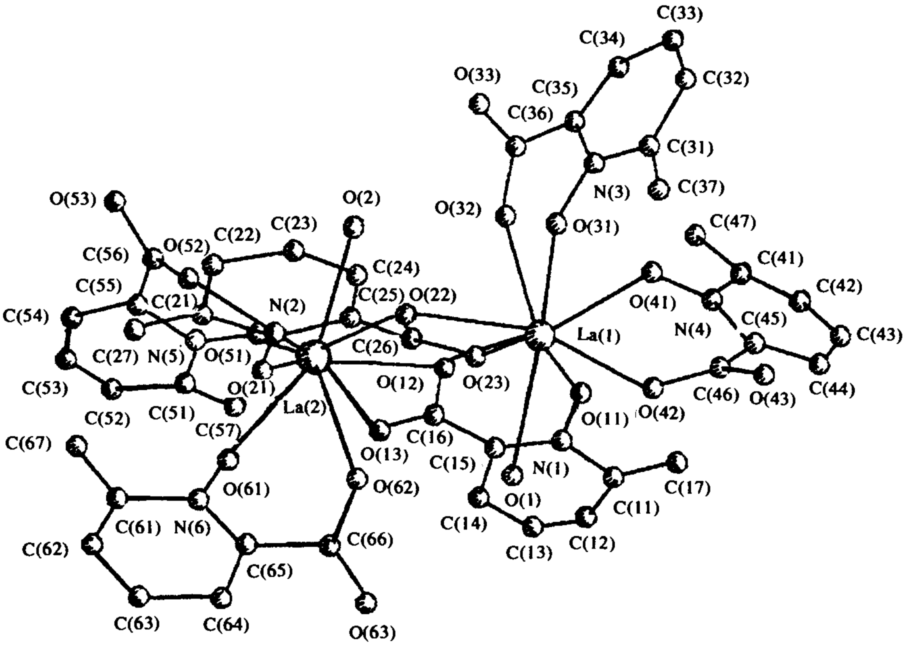

Fig. 1. The molecular structure of $La_2(6\text{-mepicno})_6 \cdot 6H_2O$.

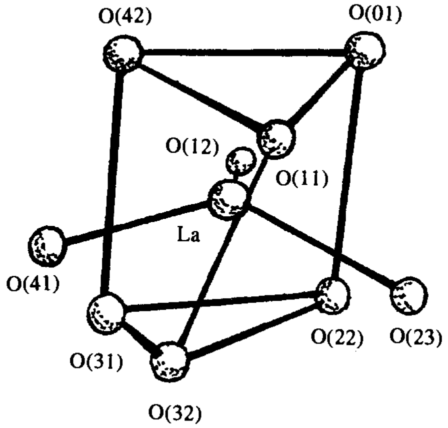

Fig. 2. The coordination polyhedron.

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