

Synthesis and Structural Characterization of One-dimensional Polynuclear Complex $[\text{La}(\text{bipyN}_2\text{O}_2)(\text{TFA})_3]_n$

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Abstract: A novel polymeric complex $[\text{La}(\text{bipyN}_2\text{O}_2)(\text{TFA})_3]_n$ (TFA= trifluoroacetylacetone) was prepared. The X-ray structure analysis revealed that the complex has an infinite one-dimensional supramolecule structure with the 4,4'-bipyridyl-N,N'-dioxide as a bridge. La(III) is coordinated to eight oxygen atoms, six from three trifluoroacetylacetonate anions, two from two 4,4'-bipyridyl-N,N'-dioxide molecules.

Keywords: Lanthanum polynuclear complex, trifluoroacetylacetone, 4,4'-bipyridyl-N,N'-dioxide.

Some of rare earth- β -diketone-2,2'-bipyridyl-N,N'-dioxide ternary complexes have been studied^{1,2}. Very few work dealing with 4,4'-bipyridyl-N,N'-dioxide complex appeared. In our previous work, some ternary complexes of europium with β -diketones and 4,4'-bipyridyl-N,N'-dioxide with the formula of $\text{Ln}(\beta\text{-dik})_3 \cdot 0.5(\text{bipyN}_2\text{O}_2)$ have been isolated and well characterized.³ Here we report a newly synthesized ternary complex $[\text{La}(\text{bipyN}_2\text{O}_2)(\text{TFA})_3]_n$. Crystal analysis showed it had an infinite one-dimensional polynuclear structure.

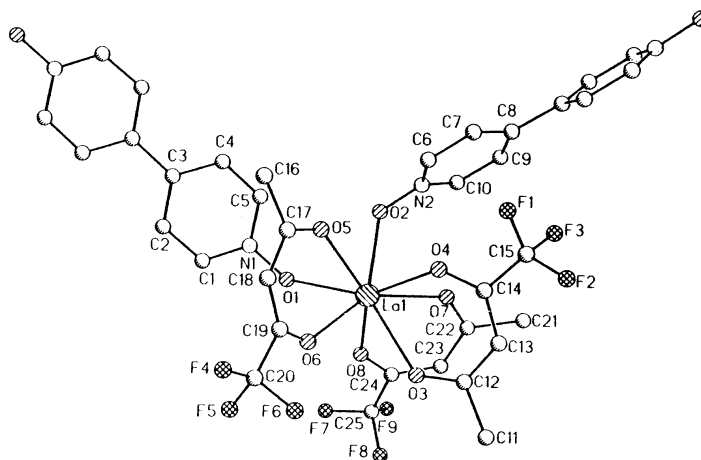
A solution of HTFA (0.231g, 1.5 mmol) in 3 cm³ of MeOH was added to a stirred solution of $\text{LaCl}_3 \cdot 6\text{H}_2\text{O}$ (0.177g, 0.5 mmol) in MeOH (5 cm³). A solution of 4,4'-bipyridyl-N,N'-dioxide (0.0941g, 0.5 mmol) in 6 cm³ of MeOH was added to the reaction solution. After 2 hr of reflux, white powder precipitated from solution with a yield of 60%. The product was characterized having a formula of $\text{La}(\text{TFA})_3(\text{bipyN}_2\text{O}_2)$. Found: C, 37.85; H, 2.40; N, 3.23; La, 18.11%. Calc. for $\text{C}_{25}\text{H}_{20}\text{O}_8\text{N}_2\text{F}_9\text{La}$: C, 38.18; H, 2.56; N, 3.56; La, 17.66%. Some colorless rectangle crystals suitable for X-ray crystal analysis were obtained from the mother liquor.

A crystal with a dimension of 0.40 x 0.25 x 0.15 mm was selected for X-ray diffraction experiment. Crystal $\text{La}(\text{TFA})_3(\text{bipyN}_2\text{O}_2)$, $M_r=786.34$, monoclinic, space group $C2/c$, with $Z=8$, $a=25.336(5)$, $b=14.954(3)$, $c=19.452(4)\text{\AA}$, $\beta=126.50(3)^\circ$, $V=5924(2)\text{\AA}^3$, $D_c=1.763\text{Mg/m}^3$. The structures were solved by direct methods and refined by full-matrix least-squares methods on F^2 using SHELXS-97 program. The final R factor was 0.0483, R_w 0.1311 for 5232 independent reflections of $I>2\sigma(I)$.

The coordination sphere of the lanthanum (III) cation is completed by three bidentate β -diketonato groups in the *syn*-form fashion and two bridging

bipyridyl-dioxide ligands on the opposite side. The coordination polyhedron is a distorted square antiprism. An ORTEP representation of complex moiety La (TFA)₃(bipyN₂O₂) is shown in **Figure 1**.

Figure 1. ORTEP representation of the coordination moiety



It is apparent from **Figure 1** that the three β -diketonato groups located on one side, two bridging bipyridyl-dioxide molecules on the other side. The La-O distances for bipyridyl-dioxide are 2.490(4) Å and 2.541(4) Å, for β -diketone anions, however, the average La-O distance, 2.483 Å is shorter than that for the bipyridyl-dioxide. This may be attributed to the extensive conjugation in β -diketone anions and their chelating effect. The subunit [La(TFA)₃] is linked by the bridging ligand bipyridyl-dioxide leading to an infinite one-dimensional zigzag chain, which then in unit cell is arranged along the c axis in 011 plane.

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