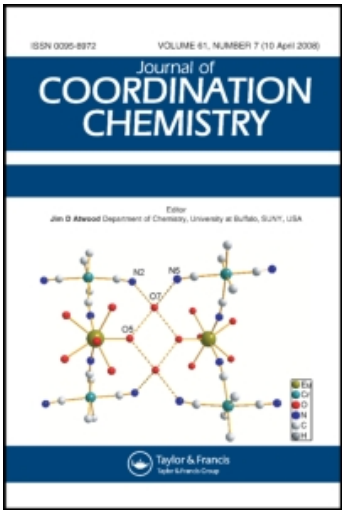

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Tris(Trifluoroacetylacetonato)(4,4'-bipyridyl-N,N'-dioxido)Lanthanum(III): A One-dimensional Polynuclear Complex

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TRIS(TRIFLUOROACETYLACETONATO) (4,4′-BIPYRIDYL-N,N′-DIOXIDO) LANTHANUM(III): A ONE-DIMENSIONAL POLYNUCLEAR COMPLEX

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A novel one-dimensional polynuclear complex, tris(trifluoroacetylacetonato)(4,4′-bipyridyl-*N*,*N*′-dioxido)lathanum(III), was synthesized and characterized by elemental analysis and IR spectroscopy. X-ray structure analysis revealed that the complex has an infinite one-dimensional polynuclear 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 and two from two 4,4′-bipyridyl-*N*,*N*′-dioxide molecules to form a slightly distorted square antiprismatic coordination polyhedron. The coordination moiety was linked through 4,4′-bipyridyl-*N*,*N*′-dioxide forming a one-dimensional chain.

Keywords: Lanthanum; Complex; Trifluoroacetylacetone; 4,4′-bipyridyl-*N*,*N*′-dioxide; Polynuclear

INTRODUCTION

Some binary rare earth-2,2′-bipyridyl-*N*,*N*′-dioxide complexes and ternary rare earth-β-diketone-2,2′-bipyridine-*N*,*N*′-dioxide complexes have been studied [1, 2]. These have good thermodynamic stability and the Eu^{3+}, Tb^{3+} complexes possess unique luminescence properties. They find potential applications in technical fields. Very little work dealing with 4,4′-bipyridyl-*N*,*N*′-dioxide complex has appeared [3]. In previous work, some ternary complexes of europium with the β-diketones dibenzoylmethane

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(DBM), thenoyl trifluoroacetone (TTA) and 4,4′-bipyridyl-*N*,*N*′-dioxide have been isolated and characterized [4]. They have formula $Ln(\beta\text{-dik})_3 \cdot 0.5(bipyN_2O_2)$ which may imply a dimeric structure with the 4,4′-bipyridyl-*N*,*N*′-dioxide molecule as a bridging ligand. We failed to prepare the complexes $Ln(\beta\text{-dik})_3 \cdot (bipyN_2O_2)$ for β-diketones DBM and TTA. This is presumably because of the hindrance of benzene and thenyl rings. It is reasonable to predict the exist of the complexes $Ln(\beta\text{-dik})_3 \cdot (bipyN_2O_2)$ when the β-diketones are less bulky. Here we report a new ternary complex $[La(bipyN_2O_2)(TFA)_3]_n$. Crystal structure analysis shows it has an infinite one-dimensional polynuclear structure.

EXPERIMENTAL

Instrumentation

Elemental analysis (C, H, N) was carried out on a Perkin-Elmer 240C instrument. IR spectra of the solid complex and ligands were recorded on a Nicolet 170SX FT-IR spectrometer, using KBr pellets.

Ligand Synthesis

4,4′-Bipyridyl-*N*,*N*′-dioxide was synthesized by an adaptation of the method described for preparing 2,2′-bipyridyl-*N*,*N*′-dioxide [5], by heating 4,4′-bipyridine (2.0 g), glacial acid (75 cm^3) and 30% hydrogen peroxide (30 cm^3) together at $70 \sim 80°C$ for 3 hr. An additional 3 cm^3 of 30% hydrogen peroxide was added and the temperature maintained at $70 \sim 80°C$ for a further 20 hr. On addition of acetone (300 cm^3), 4,4′-bipyridyl-*N*,*N*′-dioxide precipitated. The material was recrystallized from hot water by the addition of a large excess of acetone, washed with acetone, and dried at 70°C to yield a pale yellow powder. The product was characterized by elemental analysis and IR absorption spectroscopy. *Anal.* Calcd. for $C_{10}H_8N_2O_2$ (%): C, 63.82; H, 4.30; N, 14.89. Found: C, 63.30; H, 4.27; N, 14.50. IR: 1241 cm^{-1}(vs), for ν (N–O); 1186 cm^{-1}(s), for δ (C–H, in plane); 1474 cm^{-1}(s), for ν (ring); 842 cm^{-1}(m), for δ (N–O).

Complex Synthesis

A solution of HTFA (0.231 g, 1.5 mmol) in 3 cm^3 of MeOH was added to a stirred solution of $LaCl_3 \cdot 6H_2O$ (0.177 g, 0.5 mmol) in MeOH (5 cm^3). The

reaction solution was adjusted to pH 6.2 with dilute NaOH. A solution of 4,4′-bipyridyl-*N*,*N*′-dioxide (0.0941 g, 0.5 mmol) in 6 cm^3 of MeOH was added to the reaction solution. After 2 hr reflux, some white powder precipitated from solution with a yield of 60%. The product was characterized as having a formula of $La(TFA)_3(bipyN_2O_2)$. *Anal.* Calcd. for $C_{25}H_{20}O_8N_2F_9La$ (%): C, 38.18; H, 2.56; N, 3.56; La, 17.66. Found: C, 37.85; H, 2.40; N, 3.23; La, 18.11. The mother liquor was stored at room temperature for two weeks when some colourless rectangle crystals were obtained which were suitable for X-ray analysis.

X-ray Crystallography

A crystal with dimensions $0.40 \times 0.25 \times 0.15$ mm was selected for the X-ray diffraction experiment. $La(TFA)_3(bipyN_2O_2)$, $Mr = 786.34$, is monoclinic, space group $C2/c$, with $Z = 8$, $a = 25.336(5)$, $b = 14.954(3)$, $c = 19.452(4)$ Å, $\beta = 126.50(3)^\circ$, $V = 5924(2)$ $Å^3$, $Dc = 1.763$ Mg/m^3. The cell parameters were obtained from 24 reflections with $13.3 < \theta < 16.0^\circ$. Some 5357 reflections were collected on a Rigaku AFC6S four-circle diffractometer at 293 K with graphite-monochromated Mo-*Ka* radiation ($\lambda = 0.71073$ Å) using the $\omega - 2\theta$ scan mode in the range $2.14^\circ < \theta < 25.00^\circ$. The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2 using the SHELXS-97 program. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located at calculated positions and assigned isotropic displacement parameters. The final R factor was 0.077, $Rw = 0.147$ for 5232 independent reflections with $I > 2\sigma(I)$.

RESULTS AND DISCUSSION

Table I shows some relevant IR absorption frequencies related to ligands and complex. It can be observed that for the free ligand, 4,4′-$bipyN_2O_2$,

TABLE I Relevant infrared absorption frequencies for the complex and ligands (cm^{-1})

	Assignments				
	v (*N*–*O*)	*δ* (*C*–*H*, *in plane*)	*v* (*C*=*O*)	*v* (*ring*)	*v* (*M*–*O*)
$La(bipyN_2O_2)(tfa)_3$	1224(s)	1183(s)	1632(sh)	1466(vs)	457(w)
			1628(vs)		410(w)
tfa			1665(sh)		
			1604(vs)		
$bipyN_2O_2$	1241(vs)	1186(s)		1474(vs)	

ν(N–O) is 1241 cm^{-1}; when coordinated to the La(III), it is shifted to 1224 cm^{-1}; $\Delta\nu$ is −17, whereas δ(C–H, in plane), 1186 cm^{-1}, decreases by 3 cm^{-1}. The ring absorption of 4,4′-bipyN_2O_2, (1474 cm^{-1}) in the free ligand shifts to 1466 cm^{-1} in the complex; $\Delta\nu$ is −8 cm^{-1}. These results suggest that the oxygen atoms of 4,4′-bipyN_2O_2 are coordinated to the metal ion. For tfa two bands (ν(C═O)) were observed. They are related to the two different carbonyl groups, one linked to methyl and the other linked to trifluoromethyl groups. In the complex frequency changes follow different trends; $\Delta\nu$ is +24 cm^{-1} and −33 cm^{-1}. The negative shift of ν(C═O) indicates bonding between >C═O (which linked to $-CH_3$) and La(III). Taking into account the structure of trifluoroacetylacetone, the existence of an appreciable amount of enol form in this β-diketone molecule should lead to an unusually low frequency of >C═O (1604 cm^{-1}) because the enol forms of most β-diketone molecules form intramolecular hydrogen bonds, and weaken the carbonyl bond significantly. On coordination of lathanum(III) to the β-diketone molecule, the intramolecular hydrogen bonds have been disrupted, and therefore the frequency of the >C═O group increases, $\Delta\nu = +24\,cm^{-1}$, in comparison with the free ligand. Two weak bands 457 and 410 cm^{-1} in the spectra of the complex can be assigned to metal-oxygen coordination bond stretches; 457 cm^{-1} from La-O(diketone) and 410 cm^{-1} from La-O(bipyN_2O_2) (see structure analysis below).

Table II presents crystallographic parameters, Table III final non-hydrogen positions and Table IV selected bond distances and angles. From

TABLE II Summary of data collection and crystal parameters

Empirical formula	$C_{25}H_{20}F_9LaN_2O_8$
Formula weight	786.34
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, $C2/c$
Unit cell dimensions	$a = 25.336(5)$ Å,
	$b = 14.954(3)$ Å, $\beta = 126.50(3)°$
	$c = 19.452(4)$ Å
Volume	5924(2) $Å^3$
Z, Calculated density	8, 1.763 g/cm^3
Absorption coefficient	1.548 mm^{-1}
$F(000)$	3088
Crystal size	0.40 × 0.25 × 0.15 mm
θ range for data collection	2.14–25.00°
Index ranges	$0 \leqslant h \leqslant 30$, $0 \leqslant k \leqslant 17$, $-23 \leqslant l \leqslant 18$
Reflections collected/unique	5357/5232 [R(int) = 0.0353]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5232/0/409
Googness-of-fit on F^2	1.044
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.077$, $wR2 = 0.147$

TABLE III Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for the complex U(eq) is defined as one third of the trace of the orthogonalized *Uij* tensor

	x/*a*	*y*/*b*	*z*/*c*	*U*(*eq*)
La(1)	626 (1)	2242 (1)	1095 (1)	37 (1)
F(1)	915 (4)	3497 (6)	−1041 (5)	146 (3)
F(2)	1966 (4)	3406 (8)	−317 (5)	196 (5)
F(3)	1386 (6)	2313 (7)	−842 (6)	179 (4)
F(4)	641 (5)	5760 (5)	2370 (5)	205 (5)
F(5)	967 (7)	4666 (6)	3168 (6)	205 (6)
F(6)	1466 (6)	5102 (9)	2732 (9)	244 (7)
F(7)	1410 (4)	297 (6)	3627 (5)	141 (3)
F(8)	2348 (4)	472 (9)	4011 (5)	196 (5)
F(9)	1839 (8)	−667 (6)	3410 (8)	261 (8)
O(1)	−212 (2)	1869 (4)	1333 (3)	52 (1)
O(2)	−241 (2)	1348 (3)	−218 (3)	45 (1)
O(3)	1837 (2)	2577 (4)	2049 (3)	54 (1)
O(4)	946 (2)	2887 (3)	229 (3)	56 (1)
O(5)	−273 (2)	3365 (3)	164 (3)	57 (1)
O(6)	766 (3)	3569 (4)	1931 (3)	62 (1)
O(7)	1156 (3)	1016 (4)	851 (4)	69 (2)
O(8)	1112 (2)	1148 (4)	2272 (3)	60 (1)
N(1)	−836 (2)	2095 (4)	956 (3)	40 (1)
N(2)	−197 (2)	1294 (4)	−870 (3)	37 (1)
C(1)	−1016 (4)	2400 (6)	1425 (5)	62 (2)
C(2)	−1668 (4)	2567 (6)	1063 (5)	64 (2)
C(3)	−2145 (3)	2432 (4)	204 (4)	38 (1)
C(4)	−1927 (4)	2179 (6)	−274 (5)	58 (2)
C(5)	−1280 (3)	2005 (6)	110 (5)	59 (2)
C(6)	−319 (3)	2024 (4)	−1344 (4)	42 (2)
C(7)	−254 (3)	1986 (4)	−1990 (4)	42 (2)
C(8)	−53 (3)	1213 (4)	−2161 (4)	34 (1)
C(9)	44 (3)	471 (4)	−1675 (4)	39 (1)
C(10)	−27 (3)	513 (4)	−1039 (4)	40 (1)
C(11)	2966 (4)	2482 (9)	2660 (7)	104 (4)
C(12)	2249 (4)	2611 (6)	1888 (6)	61 (2)
C(13)	2105 (4)	2756 (6)	1077 (6)	68 (2)
C(14)	1484 (4)	2887 (5)	322 (6)	64 (2)
C(15)	1436 (5)	3090 (8)	−453 (6)	75 (3)
C(16)	−1058 (4)	4518 (7)	−484 (6)	98 (4)
C(17)	−421 (4)	4130 (5)	255 (5)	58 (2)
C(18)	−38 (4)	4631 (6)	999 (6)	77 (3)
C(19)	509 (4)	4330 (6)	1754 (5)	65 (2)
C(20)	866 (7)	4980 (8)	2493 (8)	107 (4)
C(21)	1956 (6)	110 (8)	938 (9)	131 (5)
C(22)	1618 (5)	475 (7)	1327 (9)	95 (4)
C(23)	1821 (5)	214 (7)	2174 (8)	105 (4)
C(24)	1546 (4)	556 (6)	2549 (6)	75 (3)
C(25)	1785 (5)	160 (8)	3386 (8)	97 (4)

these data, it is apparent that 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 opposite sides.

TABLE IV Selected bond lengths (Å) and angles (°) for $La(bipyN_2O_2)(tfa)_3$

Bond lengths			
La(1)–O(6)	2.454 (5)	La(1)–O(4)	2.459 (5)
La(1)–O(8)	2.465 (5)	La(1)–O(7)	2.478 (5)
La(1)–O(1)	2.490 (4)	La(1)–O(3)	2.516 (5)
La(1)–O(5)	2.527 (5)	La(1)–O(2)	2.541 (4)
O(1)–N(1)	1.331 (6)	O(2)–N(2)	1.341 (6)
O(3)–C(12)	1.257 (9)	O(4)–C(14)	1.264 (9)
O(5)–C(17)	1.248 (9)	O(6)–C(19)	1.254 (9)
O(7)–C(22)	1.262 (12)	O(8)–C(24)	1.255 (10)
Bond angles			
O(6)–La(1)–O(4)	99.22 (18)	O(6)–La(1)–O(8)	97.20 (18)
O(4)–La(1)–O(8)	135.24 (16)	O(6)–La(1)–O(7)	147.50 (18)
O(4)–La(1)–O(7)	73.87(19)	O(8)–La(1)–O(7)	70.06 (19)
O(6)–La(1)–O(1)	82.00 (19)	O(4)–La(1)–O(1)	151.62 (16)
O(8)–La(1)–O(1)	71.89 (16)	O(7)–La(1)–O(1)	119.26 (19)
O(6)–La(1)–O(3)	73.60 (17)	O(4)–La(1)–O(3)	70.94 (17)
O(8)–La(1)–O(3)	74.38 (17)	O(7)–La(1)–O(3)	74.17 (18)
O(1)–La(1)–O(3)	135.01 (16)	O(6)–La(1)–O(5)	69.55 (17)
O(4)–La(1)–O(5)	76.83 (17)	O(8)–La(1)–O(5)	147.79 (17)
O(7)–La(1)–O(5)	135.61 (18)	O(1)–La(1)–O(5)	77.13 (17)
O(3)–La(1)–O(5)	125.44 (17)	O(6)–La(1)–O(2)	142.09 (16)
O(4)–La(1)–O(2)	87.62 (15)	O(8)–La(1)–O(2)	103.87 (17)
O(7)–La(1)–O(2)	70.23 (16)	O(1)–La(1)–O(2)	75.28 (15)
O(3)–La(1)–O(2)	142.36 (15)	O(5)–La(1)–O(2)	75.99 (16)
N(1)–O(1)–La(1)	134.8 (4)	N(2)–O(2)–La(1)	118.2 (3)
C(12)–O(3)–La(1)	130.8 (5)	C(14)–O(4)–La(1)	131.9 (5)
C(17)–O(5)–La(1)	136.6 (5)	C(19)–O(6)–La(1)	134.8 (5)
C(22)–O(7)–La(1)	134.8 (7)	C(24)–O(8)–La(1)	133.9 (6)

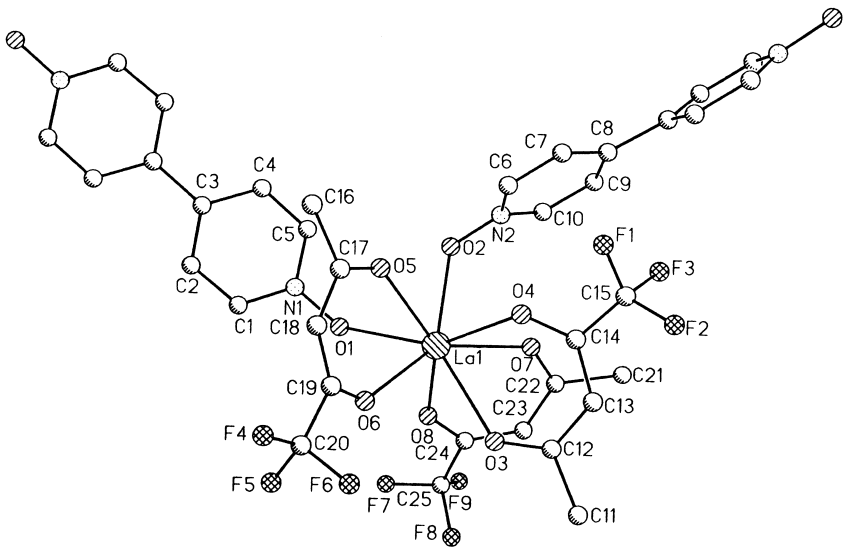

FIGURE 1 ORTEP representation of the complex showing the atom labelling scheme.

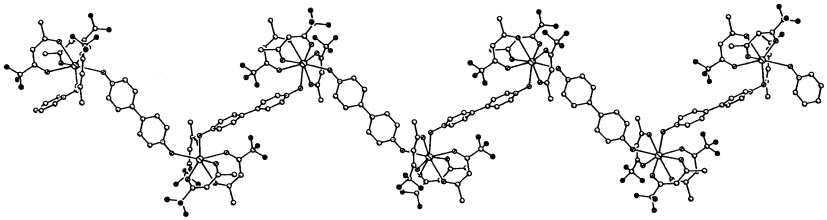

FIGURE 2 The one-dimensional polynuclear structure of the complex.

Figure 1 shows an ORTEP representation of complex moiety $La(TFA)_3$ ($bipyN_2O_2$). The coordination polyhedron is a distorted square antiprism.

It is apparent from Figure 1 that the three β-diketonato groups are located to one side of the metal ion and two bridging bipyridyl-dioxide molecules on the other. In one bipyridyl-dioxide, the two pyridine rings are nearly coplanar, but the two bipyridyl-dioxide molecular planes intersect at an angle of 91.88°. La–O distances for dipyridyl-dioxide are 2.490(4) Å and 2.541(4) Å, for β-diketonate ions; however, the average La–O distance, 2.483 Å, is shorter than those for bipyridyl-dioxide. This may be attributed to the extensive conjugation in the β-diketonate ions 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 is arranged along the *c* axis, as shown in Figure 2.

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