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Synthesis and Molecular Structure of Europium(III) Complex with 2,6-Diacetylpyridine Bis(2-pyridylhydrazone)

Masatomi Sakamoto,* Naohide Matsumoto,*,† and Hisashi Ōkawa†
Department of Industrial Chemistry, Faculty of Engineering, Ehime University, Matsuyama 790
†Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812

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Synopsis. The title complex, $[Eu(NO_3)_2(L)(CH_3OH)]NO_3$, has been synthesized and its molecular structure has been determined by a single crystal X-ray analysis, where L denotes 2,6-diacetylpyridine bis(2-pyridylhydrazone). The complex has a ten-coordinate structure with quinquedentate L, two bidentate NO_3^- ions, and monodentate CH_3OH.

Lanthanoid ions are classified into "hard acids" in the HSAB sence and generally have a low affinity toward nitrogen donor atom. Therefore, lanthanoid complexes derived from nitrogenous ligands (with only nitrogen donor atoms) are still limited to those of phthalocyanine, porphyrines, *o*-phenanthroline, 2,2′-bipyridyl, and aliphatic polyamines.

In 1979, Backer-Dirks et al.[1a)] reported the synthesis of lanthanum(III) complex of a Schiff base derived from 2,6-diacetylpyridine and ethylenediamine. Thereafter some synthetic investigations of lanthanoid complexes have been undertaken using related nitrogenous ligands.[1—4)] Those previous studies suggest that despite low affinity to nitrogen donor atom lanthanoid ions form significantly stable complexes when a multidentate nitrogenous ligand is appropriately chosen. In this study a quinquedentate nitrogenous ligand, 2,6-diacetylpyridine bis(2-pyridylhydrazone) (abbreviated as L), obtained by the condensation of 2,6-diacetylpyridine and 2-pyridylhydrazine in the 1 : 2 ratio, has been utilized for the synthesis of europium(III) complex. This paper describes the synthesis and single crystal X-ray analysis of $[Eu(NO_3)_2(L)(CH_3OH)]NO_3$.

Experimental

Synthesis of Ligand (L). To a solution of 2,6-diacetylpyridine (10 mmol) and 2-pyridylhydrazine (20 mmol) in ethanol (25 cm^3) was added one drop of concentrated hydrochloric acid, and the mixture was heated at about 60 °C with stirring to give a pale yellow precipitate. After further heating with stirring at this temperature for 1 h, the mixture was allowed to stand overnight at room temperature. The precipitate was collected by filtration, washed with ethanol, and dried in the open air. The yield was 2.3 g (60%).

Found: C, 60.08; H, 5.89; N, 25.72%. Calcd for $C_{19}H_{19}N_7\cdot 2H_2O$: C, 59.83; H, 6.08; N, 25.70%.

$[Eu(NO_3)_2(L)(CH_3OH)]NO_3$. To a solution of the ligand (L, 1 mmol) in hot methanol (90 cm^3) was added europium(III) nitrate hexahydrate (1 mmol) in methanol (10 cm^3). The solution was refluxed with stirring for 2 h and set aside at room temperature overnight to give orange crystals, which were collected on a glass filter, washed with methanol, and dried in the open air. The yield was 0.54 g (77%).

Found: C, 32.58; H, 3.09; N, 19.72; Eu, 21.49%. Calcd for $C_{19}H_{21}EuN_{10}O_{10}$: C, 32.54; H, 3.02; N, 19.97; Eu, 21.67%.

Recrystallization of the above complex from hot methanol formed single crystals suitable for X-ray analysis.

Measurements. Elemental analyses were carried out at Advanced Instrumentation Center for Chemical Analysis, Ehime University. Molar conductances were measured in methanol (concn 1×10^{-3} mol dm^{-3}) at 25 °C with a Toa CM-S Conductivity Meter. Infrared spectra were recorded on KBr disks with a JASCO IR-G Spectrometer.

Table 1. Positional Parameters

Atom	x	y	z	B_{eqv}/Å^2
Eu	0.15267(5)	0.28634(4)	0.54933(5)	2.0
N1	−0.0208(9)	0.2661(6)	0.6007(10)	2.9
N2	0.0140(9)	0.1288(7)	0.6406(10)	3.0
N3	0.1008(8)	0.1403(6)	0.5994(9)	2.4
N4	0.2732(8)	0.1707(6)	0.5196(8)	2.2
N5	0.3288(8)	0.3223(6)	0.5216(9)	2.6
N6	0.3559(8)	0.4026(6)	0.5311(10)	2.8
N7	0.2099(8)	0.4307(6)	0.6097(9)	2.5
C1	−0.0848(12)	0.3277(10)	0.6055(13)	3.7
C2	−0.1742(11)	0.3210(10)	0.6461(13)	3.8
C3	−0.2030(11)	0.2454(11)	0.6846(13)	4.2
C4	−0.1408(11)	0.1803(10)	0.6806(13)	3.7
C5	−0.0520(10)	0.1934(8)	0.6385(11)	2.8
C6	0.1520(10)	0.0779(8)	0.5817(11)	2.6
C7	0.1225(13)	−0.0076(8)	0.6087(14)	3.7
C8	0.2458(10)	0.0923(7)	0.5319(10)	2.4
C9	0.3012(12)	0.0287(8)	0.4951(13)	3.5
C10	0.3856(12)	0.0446(9)	0.4487(14)	3.7
C11	0.4169(12)	0.1264(9)	0.4416(13)	3.6
C12	0.3587(10)	0.1862(8)	0.4817(10)	2.4
C13	0.3896(10)	0.2732(8)	0.4830(11)	2.5
C14	0.4887(11)	0.2946(9)	0.4548(15)	5.3
C15	0.2936(9)	0.4565(7)	0.5739(10)	2.2
C16	0.3207(12)	0.5392(8)	0.5799(13)	3.4
C17	0.2599(13)	0.5912(8)	0.6281(13)	3.8
C18	0.1720(12)	0.5652(8)	0.6685(12)	3.5
C19	0.1511(11)	0.4834(8)	0.6567(12)	3.0
OM	0.0804(7)	0.2152(6)	0.3680(8)	3.3
CM	−0.0164(13)	0.2220(11)	0.3156(16)	5.2
N8	0.1031(10)	0.4028(8)	0.3591(11)	4.0
O1	0.1836(7)	0.3697(6)	0.3636(8)	3.4
O2	0.0777(13)	0.4523(11)	0.2824(14)	9.5
O3	0.0460(7)	0.3853(6)	0.4346(8)	3.1
N9	0.2019(9)	0.3017(6)	0.8053(9)	3.1
O4	0.2592(8)	0.2709(6)	0.7380(8)	3.5
O5	0.1170(7)	0.3137(6)	0.7596(8)	3.5
O6	0.2246(11)	0.3181(8)	0.9077(9)	5.5
N10	0.0861(9)	0.0421(7)	1.2183(10)	3.2
O7	0.0464(10)	−0.0075(8)	1.1521(12)	6.1
O8	0.1178(11)	0.1061(8)	1.1821(14)	7.0
O9	0.0929(11)	0.0286(9)	1.3244(10)	6.2

X-Ray Crystallography. Reflection data were measured on a Rigaku Denki AFC-5 automated four-circle diffractometer with graphite-monochromatized Mo *Kα* radiation at room temperature. The details of data collection and crystallographic data are as follows:

$[Eu(NO_3)_2(L)(CH_3OH)]NO_3$, formula=$C_{20}H_{23}EuN_{10}O_{10}$, F.W.=715.4, monoclinic, space group $P2_1/n$, a=13.978(4), b=16.487(4), c=11.443(2) Å, β=95.02(2)°, V=2626.9(11) Å^3, D_x =1.808 g cm^{-3}(Z=4), crystal size 0.3×0.3×0.4 mm, μ(Mo $K\alpha$) =18.16 cm^{-1}, scan mode θ-2θ, scan range 2.5—52°, scan width (1.2+0.35 tan θ)°, octant measured $+h$, $+k$, $\pm l$, number of observed reflections with $|F_o|>3\sigma$ ($|F_o|$) 4284, R=7.22%, R_w=8.81%, highest peak on the final D-Fourier 4.3 e Å^{-3} around Eu atom.

The intensity data were corrected for Lorentz and polarization effects but not for absorption and extinction effects. The structure was solved by the standard heavy-atom method and refined by the block-diagonal least-squares method, in which the function minimized was $\sum w(|F_o|-|F_c|)^2$ and the equal weight w=1 was adopted for all the reflections. The atomic scattering factors were taken from Ref. 5. All computations were performed on a FACOM M 780 computer at the Computer Center of Kyushu University using UNICS III program system.[6] The final atomic coordinates are given in Table 1. Tables of observed and calculated structure factors, listing of atomic positional and anisotropic thermal parameters, and complete lists of bond distances and angles with their estimated standard deviations have been deposited as Document No. 9101 at the office of the Editor of Bull. Chem. Soc. Jpn.

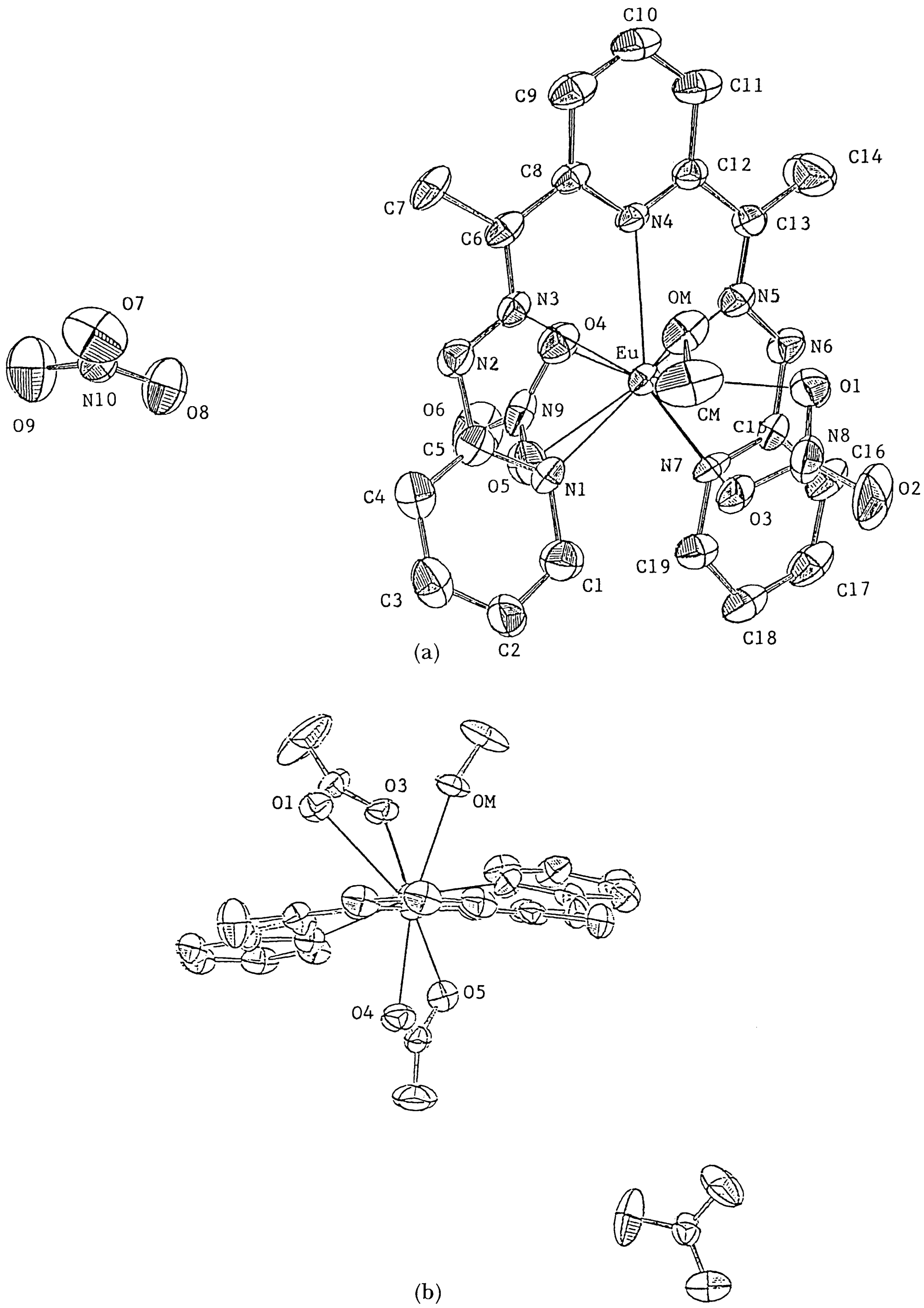

Fig. 1. Molecular structure of $[Eu(NO_3)_2(L)(CH_3OH)]$ NO_3 (a) and the side view (b) drawn by ORTEP.

Table 2. Selected Bond Distances(Å) and Angles(deg)

(a) Bond distance/Å

Eu-N1	2.566(12)	Eu-N3	2.594(10)	Eu-N4	2.587(10)
Eu-N5	2.579(11)	Eu-N7	2.585(9)	Eu-O1	2.599(9)
Eu-O3	2.503(9)	Eu-O4	2.526(9)	Eu-O5	2.540(9)
Eu-OM	2.516(9)				

(b) Bond angle/deg

N1-Eu-N3	62.6(3)	N3-Eu-N4	62.7(3)
N4-Eu-N5	60.9(3)	N5-Eu-N7	62.9(3)
N1-Eu-N7	109.6(3)	O1-Eu-O3	50.2(3)
O4-Eu-O5	50.1(3)	Eu-OM-CM	127(1)

Results and Discussion

Some typical IR bands of the free ligand shifted significantly on complexation: ν(C=N), from 1600 cm^{-1} to 1575 cm^{-1}; skeletal bands of pyridine, from 1565 and 1575 cm^{-1} to 1595 and 1612 cm^{-1}, respectively. The shifts of the skeletal bands toward higher frequencies suggest the coordinations of pyridine rings.[2b,d,e] Two nitrate vibrations were observed around 1450 and 1380 cm^{-1}, suggesting the presence of bidentate and non-coordinating groups within a molecule.[1b,2c–e,3b,7] Electrical conductivity in methanol was 101 S cm^2 mol^{-1}, indicating that the complex functions as a 1 : 1 electrolyte in this solvent.[8]

The ORTEP drawing of the complex with atom numbering scheme is shown in Fig. 1. The selected bond distances and angles with standard deviations are given in Table 2.

The X-ray structural result demonstrates that the geometry around the europium(III) ion is of ten-coordination with quinquedentate L, two bidentate nitrate ions, and a methanol oxygen. The quinquedentate ligand L forms the basal coordination plane, in which the atoms N_1, N_3, N_4, N_5, and N_7 deviate by −0.27, 0.30, −0.08, −0.16, and 0.23 Å from the best plane of the basal donor atoms, respectively. The third nitrate ion is free from coordination and captured in the crystal lattice. One of the bidentate nitrate ions is situated on one side of the coordination plane formed by the ligand L, with similar Eu-O4 and Eu-O5 bond distances (2.526 and 2.540 Å, respectively). Another bidentate nitrate ion and the methanol molecule are situated on the other side, with the Eu-O1 and Eu-O3 bond distances of 2.599 and 2.503 Å, respectively, and the Eu-OM distance of 2.516 Å. The Eu-O1 bond is significantly elongated probably because of a steric effect from the neighboring methanol molecule. The Eu-N bond distances fall in the range 2.566—2.594 Å, which are short compared with the Sm-N bond distances (2.620—2.655 Å) found for a samarium(III) complex of 3,6,14,17,23,24-hexaazatricyclo[17.3.1.1^{8,12}]tetracosa-1(23),2,6,8,10,12(24),13,17,19,21-decaene[3b] but long on the whole compared with the Gd-N bond distances (2.500—2.606 Å) found for a gadolinium(III) complex of *N,N′*-bis(2-pyridylmethylene)ethylenediamine.[9] This trend is in line with that ionic radii of lanthanoid ions decrease with increasing atomic number (lanthanide contraction), i.e., r(Sm)$>r$(Eu)$>r$(Gd).

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