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Synthesis and Characterization of Lanthanoid(III) Complexes with a Pentadentate Ligand Derived from 2,6-Diacetylpyridine and Benzoylhydrazide

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Abstract

The pentadentate ligand 2,6-diacetylpyridine-bis(benzoylhydrazone) (abbreviated as dapph) was shown to form lanthanoid(III) complexes with the general formula Ln(dapph)$(NO_3)_3(H_2O)_n$ ($n = 0$–2); the La to Eu complexes were obtained as monohydrates, the Tb to Lu complexes as dihydrates, and the Gd complex as an anhydrate. The complexes are classified into two groups based on IR spectral patterns of the nitrate ions: the La to Gd complexes and the Tb to Lu complexes. In the former complexes all three nitrate ions function as bidentate ligands, whereas the latter complexes contain both bidentate and unidentate nitrate ions. Based on ^{13}C NMR spectra, it was suggested that the ligand dapph forms more stable complexes with the heavier metal ions (Tb–Lu) compared to the lighter metal ions (La–Gd).

Introduction

It is known that lanthanoid(III) ions function as effective templating agents in the syntheses of macrocyclic Schiff bases containing 2,6-diacetylpyridine, 2,6-diformylpyridine or 2,6-diformyl-4-methylphenol and primary diamines [1–7]. During the course of the systematic investigation on template syntheses of macrocyclic lanthanoid(III) complexes, the present author was successful in the isolation of binuclear lanthanoid(III) complexes of the 2:2 condensation product of 2,6-diacetylpyridine and 1,3-diamino-2-propanol, abbreviated as H_2apdapy (see Fig. 1) [8]. This has stimulated interest in examining the complexation behavior of 2,6-diacetylpyridine-bis(benzoylhydrazone) (abbreviated as dapph), which can be presumed to be half of H_2apdapy and thence is expected to form 1:1 complexes with lanthanoid(III) ions (Fig. 2).

In this paper complexing behavior of dapph toward the lanthanoid(III) ions was examined, and some properties of the dapph complexes are discussed in comparison with those of the apdapy complexes.

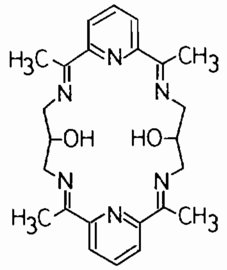

Fig. 1. Structure of H_2apdapy.

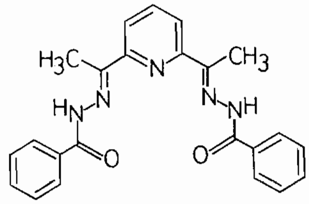

Fig. 2. Structure of dapph.

Experimental

Commercial reagent grade of 2,6-diacetylpyridine and benzoylhydrazide were purchased from Wako Chemical Co. and used for the preparation of the ligand dapph without further purification. The synthesis of dapph was carried out according to the method reported by Nishida *et al.* [9]. Hydrated lanthanoid(III) nitrates were prepared in the usual way, by evaporating the solution of Ln_2O_3, Pr_6O_{11} or Tb_4O_7 in HNO_3 to dryness.

Preparation of Complexes

The dapph (1 mmol) was added to 40 cm^3 of methanol and the temperature was raised to 50–60 °C. To the resulting transparent solution, 10 cm^3 of methanolic solution of $Ln(NO_3)_3 \cdot nH_2O$ (1 mmol) was added. After the mixture was refluxed under stirring for 2–3 h, a microcrystalline precipitate was filtered, washed with methanol and then diethyl ether, and dried in open air.

Analytical results are summarized in Table I.

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TABLE I. Elemental Analyses and Magnetic Moments of Complexes

Complex	*Anal.* found (calc.)[a] (%)					μ_{eff} (BM)
	Ln	C	H	N	H_2O [b]	
La	18.76	37.68	2.98	15.23	~2.2	dia.
	(18.71)	(37.21)	(3.12)	(15.09)	(2.43)	
Pr	18.56	36.98	3.09	14.96	~2.5	3.32
	(18.93)	(37.11)	(3.11)	(15.05)	(2.42)	
Nd	19.03	36.78	3.00	14.92	~2.5	3.30
	(19.29)	(36.95)	(3.10)	(14.99)	(2.41)	
Sm	19.58	36.58	3.07	14.80	~2.5	1.62
	(19.95)	(36.65)	(3.08)	(14.86)	(2.39)	
Eu	19.88	36.42	3.07	14.74	~2.5	3.31
	(20.12)	(36.57)	(3.07)	(14.83)	(2.30)	
Gd	20.94	37.04	2.86	15.01		7.91
	(21.17)	(37.19)	(2.85)	(15.09)	(0.00)	
Tb	20.34	35.84	3.20	14.37	~4.6	9.49
	(20.36)	(35.40)	(3.23)	(14.36)	(4.62)	
Dy	20.66	35.51	3.21	14.24	~4.6	10.28
	(20.73)	(35.24)	(3.21)	(14.29)	(4.60)	
Ho	20.91	35.48	3.21	14.23	~4.6	10.37
	(20.97)	(35.13)	(3.20)	(14.25)	(4.58)	
Er	21.13	35.12	3.20	14.18	~4.6	9.25
	(21.21)	(35.02)	(3.19)	(14.21)	(4.57)	
Lu	21.81	34.92	3.12	14.09	~4.5	dia.
	(21.97)	(34.68)	(3.16)	(14.07)	(4.52)	

[a] $Ln(dapph)(NO_3)_3(H_2O)$, $Ln(dapph)(NO_3)_3$, and $Ln(dapph)(NO_3)_3(H_2O)_2$ for the La–Eu, the Gd and the Tb–Lu complexes, respectively. [b] Determined by TG analyses.

Measurements

Elemental analyses of carbon, hydrogen and nitrogen were carried out at the Service Center of Elemental Analysis, Kyushu University, Japan. Metal contents were determined by EDTA titration. Infrared spectra were measured with a JASCO Model IR-G spectrometer on KBr disks or nujol mulls. Magnetic susceptibilities were measured by the Faraday method at room temperature. Diamagnetic corrections were made using Pascal's constants. The ^{13}C NMR spectra were recorded with a JEOL FX-100 spectrometer in dimethylsulfoxide-d_6 (DMSO-d_6) or dimethylformamide-d_7 (DMF-d_7) at 30 °C. A Cahn 2000 Recording Electrobalance was used for the thermogravimetric (TG) analyses in a helium stream (80 cm^3 min^{-1}). The temperature was raised at the rate of *ca.* 5.6 °C min^{-1}.

Results and Discussion

The TG curves of the complexes except for the Gd complex show a weight loss at ~80 °C, whereas the TG analysis for the Gd complex shows no weight loss below ~160 °C. The weight loss corresponds to one water molecule for the La to Eu complexes, but two water molecules for the Tb to Lu complexes. Therefore, the TG analytical results suggest that the La to Eu, the Gd, and the Tb to Lu complexes are obtained as monohydrate, anhydrate, and dihydrate, respectively, in accordance with the compositions of the complexes determined by elemental analyses. Further heating of these complexes resulted in explosive decomposition at ~250 °C.

Room temperature magnetic moments for the complexes, given in Table I, are quite common for tervalent lanthanoid ions.

The complexes except for the Gd complex show an IR band at 3400–3500 cm^{-1} when measured on nujol mulls. This band is reasonably attributable to the water molecule. On the other hand, such a band was not seen for the Gd complex, consistent with its anhydrous composition predicted from elemental and thermogravimetric analyses. The vibration attributable to the ν(N–H) mode is observed at ~3200 cm^{-1} for all the complexes. This fact suggests that dapph functions as a neutral ligand to lanthanoid(III) ions.

For the La to Gd complexes, the bands assignable to the ν(C=O) and ν(C=N) vibrations are observed at ~1640 and ~1620 cm^{-1}, respectively, whereas the corresponding bands for the free ligand are observed at ~1660 and ~1650 cm^{-1}, respectively. The shifts of the ν(C=O) and ν(C=N) bands toward lower wave number on complexation indicate that all the carbonyl oxygens and the azomethine nitrogens coordinate to the metal. For the Tb to Lu complexes,

TABLE II. Infrared Spectral Data of the Nitrate Groups

Complex	Wavenumber (cm^{-1})				
	Nitrate bands				Δ^a
La	1450	1300, 1285	1025	814	30
Pr	1450	1300, 1285	1025	810	33
Nd	1450	1300, 1285	1025	811	34
Sm	1450	1300, 1285	1025	812	34
Eu	1450	1305, 1290	1029	815	34
Gd	1450	1305, 1290	1029	811	39
Tb	1420–1400	1315, 1290	1035, 1025	820, 812	10, 34
Dy	1420–1400	1315, 1290	1035, 1025	820, 812	10, 35
Ho	1420–1400	1315, 1290	1040, 1028	820, 812	10, 40
Er	1420–1400	1315, 1290	1040, 1028	820, 812	10, 41
Lu	1420–1400	1315, 1290	1035, 1029	820, 812	10, 43

[a] Separation (cm^{-1}) of combination bands.

the $\nu(C{=}O)$ and $\nu(C{=}N)$ vibrations appear at ~1625 and ~1610 cm^{-1}, respectively, both of which are much lower in frequency than the corresponding vibrations of the La to Gd complexes. The in-plane deformation mode of the pyridine ring appears at ~640 cm^{-1}, suggesting that the pyridine nitrogen also coordinates to the metal ion [2, 10]. Based on these facts, dapph presumably acts as a pentadentate ligand to lanthanoid ions. Some transition metal complexes have been obtained with 2,6-diacetylpyridine-bis(semicarbazone) [11, 12] or 2,6-diacetylpyridine-bis(acetohydrazone) [9], which bear a structural similarity to dapph. It has been proved for some of these complexes that the ligands function as planar pentadentate chelates to form pentagonal–bipyramidal complexes with chloro or aqua molecules at the axial sites.

Table II summarizes the infrared spectral data of the nitrate groups. The bands at 1450, 1285–1305, ~1025, and ~815 cm^{-1} found for the La to Gd complexes can be assigned to the nitrate ions which coordinate to the metal as bidentate ligands [13, 14]. The spectra for the Tb to Lu complexes differ from those of the La to Gd complexes and show more complicated bands attributable to the nitrate ions (see Table II). The rather low frequency of the ~1410 cm^{-1} band is probably due to a slight distortion from the C_{2v} symmetry of the nitrate ions [15].

It has been pointed out by Lever *et al.* [16] that the splitting of combination bands in the 1700–1800 cm^{-1} region is 5–26 for unidentate nitrate ion, whereas it is 20–66 cm^{-1} for bidentate nitrate ion, and this has often been used as a diagnosis of the bonding mode of nitrate ion [13, 14]. The separation of the combination bands for the present complexes are also included in Table II. The separation for the La to Gd complexes falls in the range 30–39 cm^{-1} and indicates that all of the nitrate ions coordinate as bidentate ligands in these complexes to form an eleven-coordinate geometry around the metal. On the other hand, two types of combination modes for the Tb to Lu complexes (10 cm^{-1} and 34–43 cm^{-1}) suggest that each of these complexes contains two types of nitrate ions, namely bidentate and unidentate ions. It is likely that the Tb to Lu complexes prefer a coordination number smaller than eleven with unidentate nitrate ion(s) because of their relatively small ionic radii.

The ^{13}C NMR spectral data of the La and Lu complexes are given in Table III. The spectrum of the La complex in DMSO-d_6 bears a marked similarity to that of the free ligand, demonstrating that this complex readily undergoes dissociation in this solvent. In DMF-d_7, on the other hand, this complex shows some signals in addition to the signals observed for the free ligand. For instance, a pair of signals are clearly seen for both the methyl and carbonyl carbons. From these observations, it may be concluded that the La complex partially dissociates in DMF. The ^{13}C NMR spectra of the Lu complex in DMSO-d_6 and in DMF-d_7 also demonstrate partial dissociation of the complex in these solvents. That is, the spectra contain both signals due to the coordinated and free ligands. Inspection of the signals of the methyl and carbonyl carbons reveals that in DMSO-d_6 the signal due to the free ligand (12.6 and 165.3 ppm, respectively) dominates, but in DMF-d_7 the signal due to the coordinated ligand (14.6 and 172.9 ppm, respectively) becomes more intense. Hence, it is evident that the Lu complex, as well as the La complex, is more readily dissociated in DMSO than in DMF. From the NMR spectral investigation, it is also shown that the Lu complex is more stable compared to the La complex in solution.

It should be mentioned that in the binuclear lanthanum(III) complexes of apdapy, $La_2(apdapy)(NO_3)_4(H_2O)_5$ and $La_2(apdapy)(NCS)_4(H_2O)_4$, no metal–ligand dissociation occurs even in DMSO [8].

TABLE III. ^{13}C NMR Spectral Data

Solvent	Complex	Chemical shifts (ppm)		
		Methyl	Pyridine, benzene and azomethine	Carbonyl
DMSO-d_6	dapph	12.3	120.3, 128.0, 131.3, 133.9, 136.8, 154.1	164.9
	La complex	12.4	120.4, 128.3, 131.6, 133.9, 137.1, 154.1	165.3
	Lu complex	12.6, 14.4	120.6, 125.6, 128.3, 128.9, 130.6, 131.7, 134.0, 137.2, 138.0, 142.9, 154.3, 156.6	165.3, 171.7
DMF-d_7	dapph	12.3	121.1, 128.9, 132.1, 135.0, 137.5, 153.9, 155.3	165.6
	La complex	12.3, 15.9	121.1, 127.3, 129.2, 129.5, 132.2, 134.3, 137.2, 142.1, 154.1, 158.9	165.6, 170.4
	Lu complex	12.3, 14.6	121.1, 126.6, 128.9, 129.3, 129.9, 130.6, 132.2, 134.4, 137.5, 143.6, 155.1, 157.6	166.6, 172.9

The higher stability of the apdapy complexes relative to the dapph complexes in solution may be attributed to the fact that apdapy acts as a dinegative ligand whereas dapph acts as a neutral ligand. The macrocyclic effect may also contribute to the increased stability of the apdapy complexes.

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