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# Template Synthesis of Binuclear Lanthanoid Complexes with Macrocyclic Schiff Base Constituted of 2,6-Diacetylpyridine and 1,3-Diamino-2-propanol

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**Synopsis.** Reaction of 2,6-diacetylpyridine with 1,3-diamino-2-propanol in the presence of lanthanoid(III) ions gave complexes of (2+2) macrocyclic tetraimine ligand, $H_2$apdapy. Complexes synthesized have the composition of $Ln_2(apdapy)(NO_3)_4(H_2O)_5$ (Ln=La or Pr) or $Ln_2$(apdapy) $(NCS)_4$ $(H_2O)_4$ (Ln=La, Pr, Nd, Sm, or Eu). It is suggested that the complexes are considerably stable and maintain the binuclear structure in dimethylsulfoxide solution.

It is well known that some metal ions function as effective templating agents in the syntheses of macrocyclic Schiff bases constituted of 2,6-diacetylpyridine or 2,6-diformylpyridine and a primary diamine.[1-5] The success in such template syntheses depends upon the conformity in shape and size between the templating ions and the macrocycles thus formed. In this point of view lanthanoid ions have been used for the systematic investigations on template syntheses of macrocyclic complexes.[6-10] The lanthanoid complexes so far characterized, however, are almost limited to those of mononucleating macrocycles, and lanthanoid complexes of binucleating macrocycles have been only reported by Kahwa et al.,[11] in spite of much interest in physicochemical properties[12] and quantum efficiency of luminescence in the condensed systems of f-block elements.[13]

Recently, Bailey et al. have reported that a template reaction of 2,6-diacetylpyridine and 1,3-diamino-2-propanol in the presence of barium perchlorate forms a macrocyclic complex, $Ba(H_2apdapy)(ClO_4)_2 \cdot 2H_2O$ (see Fig. 1).[14,15] This complex was then used for the synthesis of a binuclear copper(II) complex, $Cu_2(Hapdapy)(ClO_4)_3 \cdot 2H_2O$, by the transmetallation.[14,15] X-ray crystal analysis[15] for the dicopper(II) complex demonstrates a relatively large internal cavity size of $H_2$apdapy and significant flexibility of propanol site, suggesting that the macrocycle, $H_2$apdapy, can also function as a binucleating ligand toward lanthanoid(III)ions. Therefore, it was attempted in this study to synthesize binuclear lanthanoid complexes of $H_2$apdapy by template reaction. This paper deals with the synthesis and characterization of $Ln_2(apdapy)(NO_3)_4(H_2O)_5$ and $Ln_2(apdapy)(NCS)_4(H_2O)_4$.

## Experimental

**Preparations of Complexes.** Nitrate complexes were synthesized as follows: Lanthanum(III) nitrate or praseodymium(III) nitrate hydrate (1.2 mmol) and 2,6-diacetylpyridine (1.2 mmol) were dissolved in methanol (20 $cm^3$). To this solution was added a methanolic solution (10 $cm^3$) of 1,3-diamino-2-propanol (1.2 mmol) with stirring. After the mixture was refluxed for 2—3 h with stirring, the precipitate thus formed was filtered, washed with methanol, then with diethyl ether, and dried in the open air.

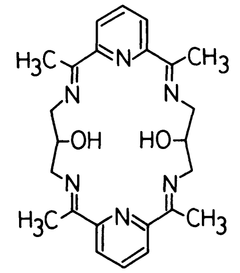

Fig. 1. Chemical structure of $H_2$ apdapy.

Thiocyanate complexes were prepared as follows: Potassium thiocyanate(33 mmol) was added with stirring to a methanolic solution(50 $cm^3$) of lanthanoid chloride hydrate (10 mmol) (Ln=La, Pr, Nd, Sm, or Eu). Potassium chloride precipitated was removed by filtration and washed with methanol (50 $cm^3$). The filtrate and the washings were combined, and to this solution was added 2,6-diacetylpyridine(10 mmol) and then a methanolic solution (25 $cm^3$) of 1,3-diamino-2-propanol (10 mmol) with stirring. After the mixture was refluxed with stirring for 2—3 h, the precipitate thus obtained was filtered, washed with methanol, then with diethyl ether, and dried in the open air.

Results of elemental analyses for the complexes are given in Table 1.

**Measurements.** Infrared spectra were measured with a JASCO IR-G Spectrometer on KBr disks. Magnetic measurements were carried out by the Gouy method at room temperature. The apparatus was calibrated by the use of $HgCo(NCS)_4$. $^{13}$C NMR spectra were recorded on a JEOL FX-100 Spectrometer in dimethylsulfoxide-$d_6$ (DMSO-$d_6$) at 30 °C.

## Results and Discussion

Analytical results summarized in Table 1 demonstrate the composition of the complexes obtained to be $Ln_2(apdapy)(NO_3)_4(H_2O)_5$(Ln=La or Pr) for the nitrate complexes and $Ln_2(apdapy)(NCS)_4(H_2O)_4$ (Ln=La, Pr, Nd, Sm, or Eu) for the thiocyanate complexes, respectively, where the hydroxyl groups of the ligand are presumed to be deprotonated. Infrared spectra of both the nitrate and thiocyanate complexes are essentially similar to each other, except for the IR bands associated with the anions ($NO_3^-$, $NCS^-$). For both types of the complexes, the in-plane ring deformation band due to the coordination of pyridine nitrogen is observed at 630—640 $cm^{-1}$.[1,17] Absorption in the region of 1630—1645 $cm^{-1}$ is attributable to the C=N stretching mode. As described in a previous paper,[17] azomethine nitrogen is probably coordinated to the metal, since Schiff bases of the present type are thermally stabilized only when the azomethine nitrogen is coordinated to a metal ion.[18] In fact, it was impossible to isolate $H_2$apdapy in the metal free state, as was the case of 1,3-bis(2-pyridylmethyleneamino)-2-prop-

Table 1. Analytical and Magnetic Data of Complexes

| | Found(%) (Calcd(%)[a]) | | | | $\mu_{eff}$ |
|---|---|---|---|---|---|
| | Ln | C | H | N | (B.M.) |
| Nitrate complex | | | | | |
| La | 26.38<br>(26.50) | 27.70<br>(27.49) | 3.77<br>(3.65) | 13.05<br>(13.36) | dia. |
| Pr | 27.23<br>(26.78) | 26.65<br>(27.39) | 3.43<br>(3.64) | 12.91<br>(13.31) | 3.42 |
| Thiocyanate complex | | | | | |
| La | 27.08<br>(27.38) | 32.98<br>(33.14) | 3.28<br>(3.58) | 12.93<br>(13.80) | dia. |
| Pr | 27.33<br>(27.66) | 32.81<br>(33.01) | 3.41<br>(3.56) | 12.91<br>(13.75) | 3.43 |
| Nd | 28.41<br>(28.13) | 33.18<br>(32.80) | 3.34<br>(3.54) | 13.08<br>(13.66) | 3.49 |
| Sm | 28.85<br>(28.98) | 32.82<br>(32.41) | 3.14<br>(3.50) | 13.22<br>(13.50) | 1.60 |
| Eu | 29.18<br>(29.20) | 33.08<br>(32.31) | 3.28<br>(3.49) | 12.85<br>(13.46) | 3.41 |

a) Values for $Ln_2(apdapy)(NO_3)_4(H_2O)_5$ or $Ln_2(apdapy)(NCS)_4(H_2O)_4$.

Table 2. $^{13}C$ NMR Spectral Data of Complexes

| Complex | Chemical shift (ppm) | | | | | |
|---|---|---|---|---|---|---|
| | Azomethine carbon[a] | Pyridine carbon[a] | Thiocyanate carbon | Methine carbon | Methylene carbon | Methyl carbon |
| $La_2(apdapy)(NO_3)_4(H_2O)_5$ | 168.55, 166.67<br>167.56 | 154.87, 125.76<br>141.67, 125.23 | — | 75.68<br>74.39 | 60.00, 58.42<br>59.24 | 16.50, 16.03<br>16.26, 15.85 |
| $La_2(apdapy)(NCS)_4(H_2O)_4$ | 169.67, 168.44<br>168.79, 167.32 | 154.76, 141.49<br>154.64, 125.99<br>154.35, 125.46<br>141.90 | 131.10 | 75.85<br>74.50 | 59.83, 58.95<br>59.24, 58.77 | 16.97, 16.38<br>16.50, 16.09 |
| $Ba(H_2apdapy)(ClO_4)_2(H_2O)_2$[b] | 165.86 | 155.05, 123.88<br>139.67 | — | 68.69 | 57.47 | 16.09 |

a) Ref. 8 and 22. b) Values measured in this work in order to compare with the present La complexes.

anol.[17]

For the nitrate complexes, the bands assignable to bidentate nitrate ion appear at 1450, 1300, 1030—1035, and 815 cm$^{-1}$.[19] The frequencies of the nitrate bands are very similar to those of hexaazamacrocyclic lanthanum(III) complex, in which all the nitrate ions are revealed to be bidentate.[6] Based on this fact, it may be concluded that all of the nitrate ions of $Ln_2(apdapy)(NO_3)_4(H_2O)_5$ function as bidentate ligands. This is also supported by the splitting of the combination bands in the 1700—1800 cm$^{-1}$ region;[20] the separation for the La and Pr complexes is 25 and 29 cm$^{-1}$, respectively.

For the thiocyanate complexes, a sharp singlet band appears at 2050 cm$^{-1}$, suggesting that the thiocyanate ions are coordinated to the metal at the nitrogen.[21]

Magnetic moments of the complexes at room temperature are common for the tervalent lanthanoid ions and no significant magnetic interaction was inferred between a pair of metal ions, for the reason that 4f-electrons are shielded by outer-shell electrons.

It seems that the binuclear structure of the macrocycle is maintained even in solutions because each complex gave no precipitate when treated with KOH in DMSO or DMSO-$H_2O$.[6]

The $^{13}C$ NMR spectral data of $La_2(apdapy)(NO_3)_4(H_2O)_5$ and $La_2(apdapy)(NCS)_4(H_2O)_4$ in DMSO-$d_6$ are summarized in Table 2. These complexes give no signal at about 200 ppm, whereas the signal due to carbonyl carbon is observed at 198.68 or 200.09 ppm for the DMSO-$d_6$ solution of 2,6-diacetylpyridine or of lanthanum(III) nitrate and 2,6-diacetylpyridine, respectively, suggesting that apdapy does not dissociate into its components in DMSO. Signals due to the methine carbon atoms of the La complex shift downfield compared with those of complex reported by Fenton et al.,[14] implying that the hydroxyl groups are deprotonated and coordinated to the metal. Furthermore, it is seen that each signal for the La complexes is composed of two or more components. This fact suggests that (1) the symmetry of the binuclear structure is low or (2) the complex is a mixture of some geometrical isomers. All efforts to obtain single crystals of the lanthanoid complexes suitable for X-ray analysis are in vain at this moment.

Though the detailed structure of the complexes is still unknown, it is evident from the above discussion that the lanthanoid ions function as the template for the 2:2 condensation of 2,6-diacetylpyridine and 1,3-diamino-2-propanol to form binucleating macrocycle $H_2$apdapy.

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