April, 1986] © *1986 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn., 59, 1273—1274 (1986)* 1273

Synthesis and Characterization of Lanthanoid Complexes with 1,3-Bis(2-pyridylmethyleneamino)-2-propanol

Masatomi SAKAMOTO
Department of Industrial Chemistry, Faculty of Engineering, Ehime University, Bunkyo-cho, Matsuyama 790

(Received December 2, 1985)

Synopsis. Lanthanoid complexes of a general formula $[Ln(appy)(NO_3)_2]H_2O$ (Ln=La, Pr, Nd, Eu, or Gd) have been synthesized with 1,3-bis(2-pyridylmethyleneamino)-2-propanol (Happy). The complexes were characterized to be mononuclear and of nine-coordination in solid state with quinquedentate appy$^-$ and two bidentate NO_3^- ions. On dissolution in dimethyl sulfoxide, the complexes were shown to dissociate into $[Ln(appy)(dmso)_n]^{2+}$ based on ^{13}C-NMR spectra and molar conductance measurements.

Many mononuclear lanthanoid complexes have been obtained and structurally characterized.[1] On the other hand, less attention has been paid to binuclear lanthanoid complexes, in spite of much interest in physicochemical properties such as spin-exchange interaction and quantum efficiency of luminescence in condensed systems of f-block elements.[2]

Recently, Schiff base derived from 1,3-diamino-2-propanol and a carbonyl compound such as salicylaldehyde or 2,4-pentanedione was shown to form binuclear copper(II) complexes bridged by the deprotonated alcoholic oxygen of the Schiff base.[3] X-Ray crystallographic analyses for the complexes revealed the Cu–Cu distance to be considerably long (≈3.5 Å), suggesting that the Schiff bases can also function as binucleating ligands toward lanthanoid(III) ions of a large ionic radius.

In this study, lanthanoid complexes (Ln=La, Pr, Nd, Eu, or Gd) of 1,3-bis(2-pyridylmethyleneamino)-2-propanol (the 1:2 condensation product of 1,3-diamino-2-propanol and 2-pyridinecarbaldehyde, abbreviated as Happy hereafter) have been synthesized and characterized, to see the complexing behavior of Happy toward lanthanoid(III) ions.

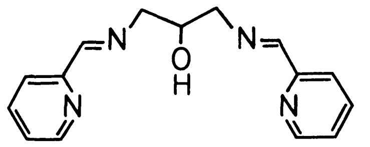

Fig. 1. Chemical structure of Happy.

Experimental

Preparation of Complexes. The metal nitrate (2 mmol) and 2-pyridinecarbaldehyde (2 mmol) were dissolved in methanol (20 cm^3). To this solution was added dropwise a methanolic solution (10 cm^3) of 1,3-diamino-2-propanol (1 mmol) under stirring at room temperature. The precipitate thus formed was filtered, washed with methanol and then with diethyl ether, and dried in vacuo. The yield based on the diamino alcohol was 30—50%.

Elemental analyses for the complexes are given in Table 1.

Measurements. Infrared spectra were measured with a JASCO IR-G spectrometer on KBr disks or nujol mulls. Electric conductivity measurements were carried out with a YOKOGAWA HEWLETT·PACKARD LCZ meter Model 4276A in dimethyl sulfoxide (DMSO) at 25 °C. Magnetic measurements were carried out by the Gouy method at room temperature. The apparatus was calibrated by the use of $Hg[Co(NCS)_4]$. ^{13}C-NMR spectra were recorded on a JEOL FX-100 spectrometer in DMSO-d_6 at 30 °C.

Results and Discussion

Analytical results demonstrated the stoichiometry of the complexes obtained to be $Ln(appy)(NO_3)_2H_2O$ (Table 1). It is presumed that the alcoholic group of the ligand is deprotonated and coordinated to the metal.

Infrared spectra of the complexes are essentially similar to each other. The coordination of the pyridine nitrogen to the metal is inferred from its in-plane deformation band located at 630 cm^{-1}.[1,4,5] The intense vibration at 1655 cm^{-1} is attributed to the C=N stretching mode. The azomethine nitrogen is probably coordinated to the metal, since Schiff bases are generally stabilized thermally when coordinated to a metal at the azomethine nitrogen.[6] In fact, it was impossible to isolate Happy in the metal-free state.

Table 1. Analytical, Magnetic, and Molar Conductance Data of Complexes

Complex	Found(%)(Calcd (%)$^{a)}$)				μ_{eff} (B.M.)	$\Lambda_M$$^{b)}$ (S cm^{2}mol^{-1})
	Ln	C	H	N		
La	24.67 (25.34)	32.64 (32.86)	2.85 (3.13)	15.71 (15.32)	dia.	78
Pr	25.93 (25.61)	32.06 (32.74)	2.79 (3.11)	15.22 (15.27)	3.34	77
Nd	26.29 (26.06)	32.32 (32.55)	2.95 (3.10)	15.06 (15.18)	3.31	77
Eu	27.92 (27.07)	31.73 (32.10)	2.79 (3.05)	14.99 (14.97)	3.31	77
Gd	28.43 (27.75)	31.82 (31.80)	2.76 (3.02)	14.86 (14.83)	7.95	76

a) Values for $Ln(appy)(NO_3)_2H_2O$. b) For 10^{-3} mol dm^{-3}.

The bands due to the nitrate ion appeared at 1450, 1300, 1035, and 815 cm^{-1}. This fact implies that the nitrate ion coordinates to the metal as a bidentate ligand.[7] The nitrate coordination is also supported by the splitting of the combination band in the 1700—1800 cm^{-1} region into two components;[8] the separation of the components for the La, Pr, Nd, Eu, and Gd complexes being 25, 27, 29, 32, and 34 cm^{-1}, respectively. The spectra on nujol mulls showed a broad band at 3500 cm^{-1}, suggesting that the H_2O molecule is not coordinated to the metal in each complex. Room-temperature magnetic moments for the complexes given in Table 1 are quite common for tervalent lanthanoid ions, respectively. Judging from these facts, the $[Ln(appy)(NO_3)_2]H_2O$ complexes are presumably mononuclear and of nine coordination with quinquedentate appy$^-$ and two bidentate NO_3^- ions, though the detailed structure for the complexes is unclear at present.

^{13}C-NMR spectrum of the La complex in DMSO-d_6 exhibited eight singlets at 163.62, 153.76, 149.71, 137.67, 125.76, 122.06, 70.04, and 64.41 ppm. The spectrum of 2-pyridinecarbaldehyde showed the carbonyl carbon signal at more lower field (193.33 ppm). Therefore, any indication of the cleavage of appy$^-$ into its components was not recognized from the spectrum of the La complex. It is likely that the coordination of appy$^-$ to the metal is maintained even in DMSO. The assignments of the signals for the La complex are as follows: 163.62 (azomethine carbon);[9] 153.76—122.06 (pyridine carbons);[9] 70.04 (methine carbon); 64.41 ppm (methylene carbon).

Electrical conductance measurements, on the other hand, revealed the complexes to become electrolytes in DMSO (Table 1). For 1:1 and 1:3 electrolytes, the molar conductances in DMSO are reported to be 37—43[10] and 110 S cm^2 mol^{-1},[11] respectively. Molar conductances for $[Ln(appy)(NO_3)_2]H_2O$ (76—78 S cm^2 mol^{-1}) clearly indicate that they behave as 1:2 electrolytes in DMSO. Evidently the nitrate ions are displaced with the solvent molecules to form $[Ln(appy)(dmso)_n]^{2+}$ species, though the number (n) of the coordinated solvent molecules is unknown.

From the above discussion, it is evident that Happy acts as a quinquedentate ligand toward lanthanoid ions to form 1:1 complexes with these ions. It should be mentioned that the complexing behavior of Happy differs from that of the macrocyclic Schiff base H_2apdapy (Fig. 2) bearing a structural relation to Happy. Recently, this macrocyclic Schiff base was shown to form 1:2 complexes with lanthanoid ions.[12]

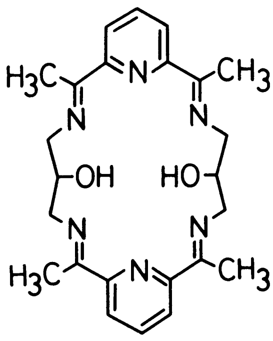

Fig. 2. Chemical structure of H_2apdapy.

The author is greatly thankful to Prof. Dr. Tomitaro Ishimori of Ehime University for his helpful discussion and encouragement throughout this work.

References

1) G. D. Smith, C. N. Caughlan, Mazhar-ul-Haque, and F. A. Hart, *Inorg. Chem.*, **12**, 2654 (1973); J. D. J. Backer-Dirks, C. J. Gray, F. A. Hart, M. B. Hursthouse, and B. C. Schoop, *J. Chem. Soc., Chem. Commun.*, **1979**, 774; K. K. Abid and D. E. Fenton, *J. Chem. Soc., Dalton Trans.*, **1984**, 351.

2) M. Nakamura, H. Ōkawa, S. Kida, and S. Misumi, *Bull. Chem. Soc. Jpn.*, **57**, 3147 (1984).

3) Y. Nishida, M. Takeuchi, K. Takahashi, and S. Kida, *Chem. Lett.*, **1983**, 1815; **1985**, 631.

4) W. Radecka-Paryzek, *Inorg. Chim. Acta*, **45**, L147 (1980); **52**, 261 (1981).

5) K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds," 3rd ed., Wiley-Interscience, New York (1978), pp. 211—213.

6) M. M. Jones, "Ligand Reactivity and Catalysis," Academic Press, New York (1968), Chap. 2.

7) R. B. King and P. R. Heckley, *J. Am. Chem. Soc.*, **96**, 3118 (1974).

8) A. B. P. Lever, E. Mantovani, and B. S. Ramaswany, *Can. J. Chem.*, **49**, 1957 (1971).

9) D. E. Fenton and M. Vidali, *Inorg. Chim. Acta*, **95**, 187 (1984).

10) P. G. Sears, G. R. Lester, and L. R. Dawson, *J. Phys. Chem.*, **60**, 1433 (1956).

11) S. K. Ramalingan and S. Soundararajan, *J. Inorg. Nucl. Chem.*, **29**, 1763 (1967).

12) M. Sakamoto, represented at the 35th Symposium of Coordination Chemistry in Japan, Hiroshima, October 12, 1985.