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Synthesis and Characterization of Barium(II) Macrobicyclic Complexes and Related Compounds

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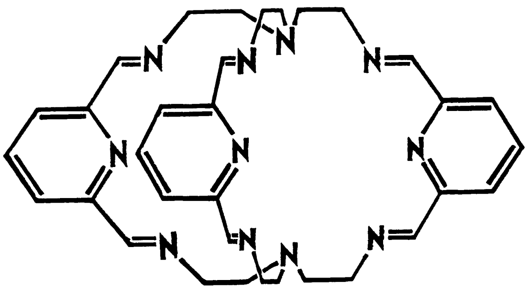
New mononuclear metal-cage complexes of a macrobicyclic ligand, pytren (metal = Ba(II), K(I), and Cs(I) and pytren = 1,4,12,15,18,26,31,39,42,43,44-undeca-azapentacyclo-$[13.13.13.1^{6,10}.1^{20,24}.1^{33,37}]$tetratetraconta-4,6(42),7,9,11,18,20(43),21,23,25,31,33(44),34,36,38-pentadecaene), were prepared and characterized including the crystal structure analysis of $[Ba(pytren)](B(C_6H_5)_4)_2$.

The chemical and physical properties of cage complexes have received considerable attention.[1] We have been studying the properties of 18-membered macrocycle complexes of lanthanides, which were prepared by template reactions of 2,6-pyridinedicarboxaldehyde (pda) and diamines.[2] It might be expected that cage complexes are obtained using tripod-type amines instead of the diamines in the reaction. Indeed, the synthesis of the ligand pytren, and binuclear pytren complexes containing two Cu^+ or two Ag^+ ions were reported by Jazwinski et al.[3] Several macrobicyclic complexes, the structures of which are similar to that of pytren, have recently been reported,[4] however, all of the metal complexes contains two metal ions in their large cavity. In this communication, the structure of the cage complex of pytren containing one barium(II) ion located at the center of the ligand is reported for the first time. We compare some properties of the Ba complex with the corresponding K(I), Cs(I) complexes and the ligand itself.



pytren

Ba-cage complexes were prepared as follows. To a methanolic solution of BaI_2 (1.0 mmol in 50 mL) were added tren (2.0 mmol) and pda (3.0 mmol). The solution was stirred at 45 °C for 1.5 h. Resulting yellow crystals, $[Ba(pytren)]I_2\cdot6H_2O$ (**1a**), were filtered off and recrystallized from hot methanol (52%).[5] The $[Ba(pytren)](ClO_4)_2\cdot H_2O$ (**1b**) and $[Ba(pytren)](B(C_6H_5)_4)_2$ (**1c**) could be isolated in a similar manner.[6] These crystals are somewhat light sensitive.

Yellow crystals of **1c** were suitable for X-ray analysis.[7] The structure of the complex is shown in Fig. 1. The complex has a crystallographical C_2 axis through the N(C2) atom in a pyridine ring and the central barium ion. The complex cation also has an approximate trigonal symmetry. Three N atoms in the pyridine rings and six N atoms of the imino groups co-ordinate to the barium ion. The Ba-N bond lengths for the imino groups (2.93 - 2.95 Å) are slightly shorter than those for the pyridine groups (2.985 Å). The lone pairs of the two tertiary N atoms at the center of the tren moieties are directed toward the central barium ion, but the Ba-N distance (3.85 Å) is too long for co-ordination. The ^{13}C-NMR spectrum of the Ba(pytren) complex shows only six peaks although the ligand contains

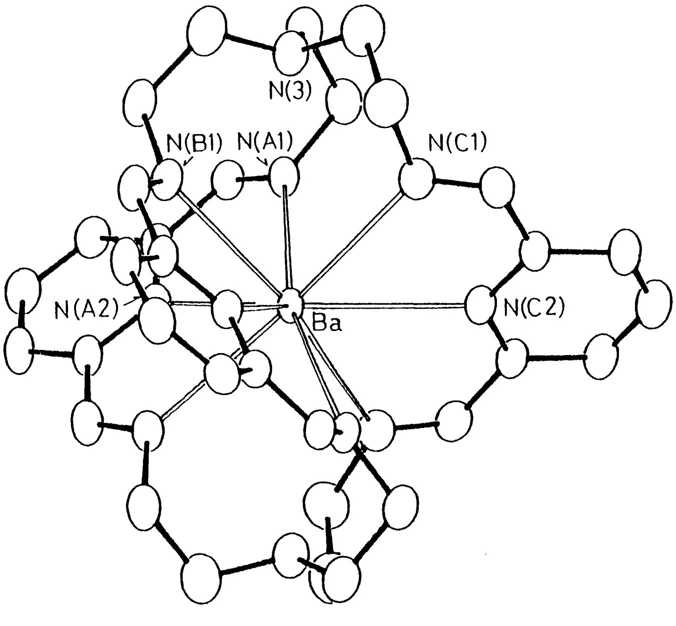


Fig. 1. ORTEP drawing of $[Ba(pytren)]^{2+}$ complex; selected bond lengths(Å) and angles(°): Ba-N(A1) 2.949 (6); Ba-N(A2) 2.985(5); Ba-N(B1) 2.938 (7); Ba-N(C1) 2.930(7); Ba-N(C2) 2.985 (7); Ba····N(3) 3.851(9); N(A1)-Ba-N(A2) 55.2(2); N(A2)-Ba-N(C2) 121.7(1); N(C2)-Ba····N(3) 89.9(1); N(C1)-Ba-N(C2) 55.4(1).

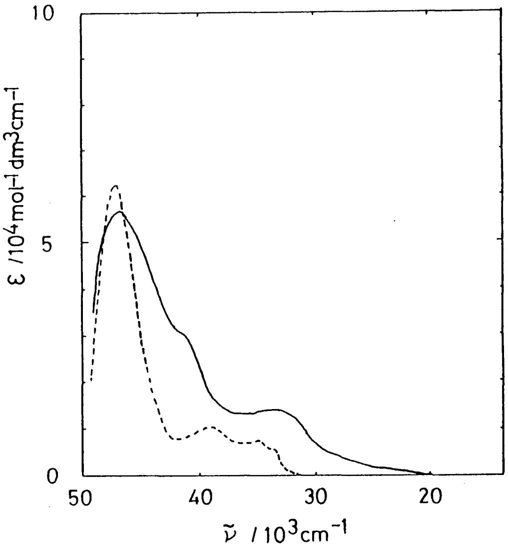


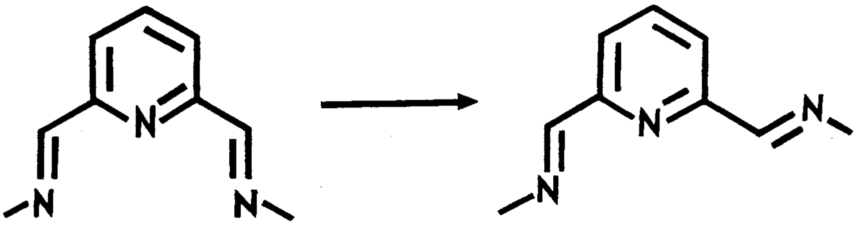
Fig. 2. Absorption spectra of $[Ba(pytren)]^{2+}$ (———) and $[Cs(pytren)]^{+}$ (----------) in MeOH. The absorption spectra of $[K(pytren)]^{+}$ and pytren are superimposable with that of $[Cs(pytren)]^{+}$.

33 carbon atoms.[8)] The fact indicates that the complex has a **D**$_3$ symmetry in solution. The electronic absorption spectrum of the Ba complex **1** shows three bands in UV region (Fig. 2). These bands are assigned to the singlet π-π^* transitions of the π-conjugated chromophore ($C=N-C_5H_3N-C=N$).[2)]

Besides the Ba(II) complex, compounds, K(pytren)I$\cdot 2C_2H_5OH$ (**2**) and Cs(pytren)I (**3**) were also prepared using MI salts (M = K or Cs) by similar procedures as the synthesis of **1a**.[9)] The yields were lower than that of **1a**. The ligand, pytren, were prepared by the reaction of tren with pda in the absence of metal ions: Tren and pda (1.0 mmol and 1.5 mmol, respectively) were dissolved in methanol (20 mL) and heated for 3 h at 40 °C. The solution was concentrated under reduced pressure. The syrup obtained was dissolved in a minimum amount of dimethyl sulfoxide. Colorless crystals of pytren (**4**) were deposited on standing (yield 28%).[10)]

The IR spectra of the ligand **4** as well as all the metal complexes show C=N stretching vibrations (1635-1638 cm^{-1}) and no C=O band. Each of the ^{13}C NMR spectra of the ligand and the complexes (M = K and Cs) shows also six peaks. These spectral results indicate that the macrobicyclic pytren complexes are formed as well as the template synthesis of the Ba complex.

It is noteworthy that some physical properties of the Ba complexes **1a**-**1c** are different from those of the other complex **2**, **3**, and the ligand **4**: Although **1a**-**1c** were isolated as yellow crystals, **2**-**4** are colorless in the solid state. The absorption spectra of **2** and **3** in solution are superimposable with that of **4**, but the spectrum of **1** is different from those of **2**-**4** as shown in Fig. 2. The IR spectra of **2**-**4** are indistinguishable from each other. However, the IR spectra of **1a**-**1c** are different from those of **2**-**4** and simpler than those of **2**-**4**, although the locations of the main IR bands are similar to those of **2**-**4**. Bell and Guzzo[11)] proposed a conformational change of 2,6-diiminopyridine moiety in a 18-membered macrocycle which is prepared by the template reaction of pda with o-phenylenediamine. Our results suggest that a similar conformational change of the 2,6-diiminopyridine group occurs in the pytren ligand as shown in the scheme. The results show that the conformation of the



Scheme 1. Conformational change of 2,6-diiminopyridine group.

pytren ligand, which exists without metal or in the K or Cs complex, is more unsymmetrical than that of the [Ba(pytren)]$^{2+}$ complex. Further studies are in progress.

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References

1) L. L. Martin, R. L. Martin, K. S. Murray, and A. M. Sargeson, Inorg. Chem., **29**, 1387 (1990); J. Hunter, J. Nelson, C. Harding, M. McCann, and V. Mckee, J. Chem. Soc., Chem. Commun., **1990**, 1148; S. Grammenudi and F. Vogtle, Angew. Chem., Int. Ed. Engl., **25**, 1122 (1986).

2) T. Tsubomura, K. Yasaku, and M. Morita, Inorg. Chem., **31**, 447 (1992).

3) J. Jazwinski, J.-M. Lehn, D. Lilienbaum, R. Ziessel, J. Guilhem, and C. Pascard, J. Chem. Soc., Chem. Commun., **1987**, 1691; D. MocDowell and J. Nelson, Tetrahedron Lett., **29**, 385 (1988).

4) R. Menif, J. Reibenspies, and A. E. Martell, Inorg. Chem., **30**, 3446 (1991); M. G. B. Drew, D. Mars, J. Hunter, and J. Nelson, J. Chem. Soc., Dalton Trans., **1992**, 11.

5) **1**: Anal. Found: C, 36.55; H, 4.74; N, 13.94%. Calcd for $BaC_{33}H_{51}N_{11}O_6I_2$: C, 36.40; H, 4.72; N, 14.14%.

6) **2**: Anal. Found: C, 41.74; H, 4.38; N, 16.37%. Calcd for $BaC_{33}H_{41}N_{11}O_9Cl_2$: C, 41.99; H, 4.38; N, 16.32%. **3**: Anal. Found: C, 71.11; H, 6.19; N, 11.37%. Calcd for $BaC_{81}H_{79}N_{11}B_2$ C, 71.55; H, 5.83; N, 11.28%.

7) Crystal Data: $[Ba(C_{33}H_{39}N_{11})](B(C_6H_5)_4)_2$, M = 1365.47, monoclinic, C2/c, a = 28.04(1), b = 15.310(4), c = 20.850(9) Å, β = 128.67(7)° ; V = 6989(2) Å^3, Z = 4, D_c = 1.298 g cm^{-1}, Mo-Kα(λ = 0.71073 Å) radiation on RIGAKU AFC-4 diffractometer; scan speed 8°/min, number of reflections used in the analysis: 6101 with $I > 3\sigma(I)$. The structure was solved by a heavy-metal method. The positional and anisotropic thermal parameters of all non-hydrogen atoms and the positional and isotropic thermal parameters were refined. R = 0.061 and R_w = 0.067.

8) ^{13}CNMR data for $[Ba(pytren)](ClO_4)_2$ (CD_3CN 23 °C): δ 167.3, 154.4, 141.8, 130.0, 64.9, and 59.8.

9) **2**: Anal. Found: C, 52.69; H, 5.88; N, 18.39%. Calcd. for $KC_{37}H_{51}N_{11}O_{12}I$: C, 52.42; H, 6.06; N, 18.17%. **3**: Anal. Found: C, 46.87; H, 4.78; N, 17.87%. Calcd for $CsC_{33}H_{39}N_{11}I$: C, 46.66; H, 4.63; N, 18.14%.

10) **4**: Anal. Found: C, 67.33; H, 6.87; N, 26.34%. Calcd for $C_{33}H_{39}N_{11}$: C, 67.21; H, 6.35; N, 26.13%.

11) T. W. Bell and F. Guzzo, J. Chem. Soc., Chem. Commun., **1986**, 769.

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