Syntheses of New {Tetrakis(1-pyrazolyl)borato}samarium(III) Complexes and Their Temperature-Dependent Exchange Motions of All Pyrazolyl Groups

Masayoshi Onishi,* Hitoshi Yamaguchi, Hirokazu Shimotsuma, Katsuma Hiraki, Junko Nagaoka, and Hiroyuki Kawano†
Department of Applied Chemistry, Faculty of Engineering, Nagasaki University, Bunkyo-machi, Nagasaki 852-8521
†*Graduate School of Marine Science and Engineering, Nagasaki University, Bunkyo-machi, Nagasaki 852-8521*

(Received February 10, 1999; CL-990089)

As the first unambiguous syntheses and characterization of the {tetrakis(1-pyrazolyl)borato}lanthanide(III) complexes, stable eight-coordinate (β-ketoenolato)samariums $[Sm\{\eta^3\text{-}B(pz)_4\}_2(\beta\text{-ketoenolato})]$ (pz= 1-pyrazolyl group) were prepared, and novel stereochemically non-rigid temperature-dependent motions of the $B(pz)_4$ ligands were observed on their solution-state ^{1}H-NMR spectra, showing the spectroscopic equivalence of coordinated and uncoordinated pyrazolyl groups at high temperatures.

Beneficial characteristics of bis(pentamethylcyclopentadienyl) (Cp^*_2) supporting ligation have been realized in the rapid growth of lanthanide chemistry during the last two decades.[1] As one comparable class to the uninegative cyclopentadienyls with 6e-donative facial coordination, there are η^3-polypyrazolylborate ligands, formulated as $[BR(pz)_3]^-$ (pz= 1-pyrazolyl group). The polypyrazolylborate ligands, especially tetrakis(1-pyrazolyl)borate $[B(pz)_4]^-$ with a more widely delocalized π-conjugated system, have been shown to confer considerable stability on a variety of ruthenium and some other transition-metal organometallic complexes, and incentive for studies on these transition-metal complexes was derived also from some successful modification of electronic and steric properties of the ligands upon their proper substituent introduction.[2] Concerning lanthanide(III) ions, the complexes of $[M\{BR(pz)_3\}_2Cl(L)_n]$ (L, monodentate neutral ligands), which are regarded as typical precursors to the polypyrazolylborate lanthanide(III) chemistry, have been prepared and studied fairly well,[3] but seemed to be limited to the $BH(pz)_3$ series. The corresponding $B(pz)_4$ complexes have not been isolated so far from the reactions with lanthanide(III) chlorides $MCl_3{\cdot}6H_2O$.[4] In this study, the potassium salt $K[B(pz)_4]$ was allowed to react with samarium(III) triflate $Sm(OTf)_3$,[5] and subsequent treatments with sodium β-ketoenolates gave the stable complexes of $[Sm\{B(pz)_4\}_2(\beta\text{-ketoenolato})]$,[6] for the first unambiguous syntheses and characterization of {tetrakis(1-pyrazolyl)-borato}lanthanide(III) complexes. Moreover, novel stereochemically non-rigid temperature-dependent motions of the $B(pz)_4$ also were found in these complexes, on the basis of solution-state ^{1}H-NMR spectroscopy.

The triflate $Sm(OTf)_3$ in THF was treated with twofold moles of the $K[B(pz)_4]$ salt to afford white microcrystals, probably assignable to $Sm(Bpz_4)_2(OTf)(H_2O)_n$. Decomposition of the salt was not observed. Their subsequent reactions were performed with some sodium β-ketoenolates, involving those of pentane-2,4-dionate (Na[acac]), salicylaldehydate (Na[sal]), 2,2,6,6-tetramethylheptane-3,5-dionate, and 3-methylpentane-2,4-dionate, and in high yields the $[Sm\{B(pz)_4\}_2(\beta\text{-ketoenolato})]$ complexes were isolated.[7]

X-ray structural analysis was carried out for colorless prismatic crystals of $[Sm\{B(pz)_4\}_2(sal)]$, and confirmed its monomeric eight-coordinate structure with two η^3-$B(pz)_4$ chelates, free from conceivable water-molecule coordination (Figure 1).[8] The Sm-N coordinate-bond lengths ranged from 2.523 to 2.602 Å, with an average of 2.561 Å. Furthermore, the complex was found to involve two nearly planar faces of O(1)-N(3)-N(9)-N(13) and O(2)-N(1)-N(5)-N(11), and the dihedral angle between these two faces was only 1.21°. Accordingly, the coordination structure of the complex in the solid state was best described as a distorted square-antiprismatic geometry.

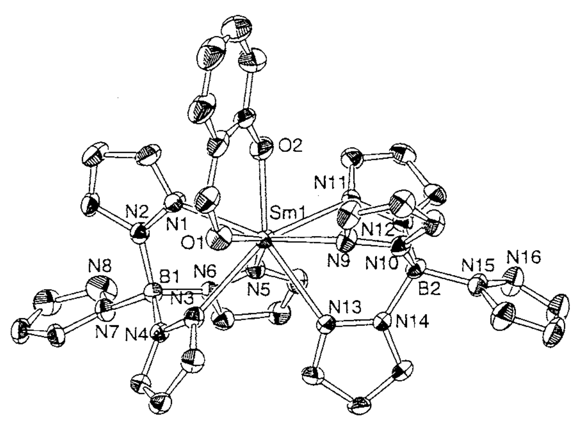

Figure 1. ORTEP view of $[Sm\{B(pz)_4\}_2(sal)]$ showing 30% probability thermal ellipsoids and atom labels for only important atoms. Selected distances (Å) and angles (deg); Sm(1)-O(1) 2.411(5), Sm(1)-O(2) 2.278(5), Sm(1)--B(1) 3.741(8), Sm(1)--B(2) 3.725(8), Sm(1)-N(1,3,5)$_{av}$ 2.562, Sm(1)-N(9,11,13)$_{av}$ 2.560, O(1)-Sm(1)-O(2) 73.0(2), B(1)--Sm(1)--B(2) 128.6(2).

On the ^{1}H-NMR spectra of $[Sm\{B(pz)_4\}_2(\beta\text{-ketoenolato})]$ in the present study, β-ketoenolato protons showed sharp signal patterns satisfactorily,[9] whereas each of the $B(pz)_4$ ligands gave two or three significantly broad signals at room temperature. Observation of variable-temperature ^{1}H-NMR revealed stereochemically non-rigid temperature-dependent motions of the ligands. As one example, at -80 °C, two $B(pz)_4$ ligands in $[Sm\{B(pz)_4\}_2(acac)]$ exhibited three NMR signals at δ 2.78, 5.64, and 9.08 for six spectroscopically equivalent coordinated pyrazolyl groups, and three ones at δ 6.70, 8.43, and 8.52 for two uncoordinated groups. On the other hand at 100 °C, the $B(pz)_4$ ligands gave three signals at δ 5.38, 5.90, and 8.34 for eight pyrazolyl groups, indicating spectroscopical equivalence of the four pyrazolyl groups in the respective $B(pz)_4$ ligands, due to fast exchange between coordinated and uncoordinated groups.[10] In spite of the η^3-coordination-favoring chelate frame of ligating $B(pz)_4$ ligands, strengthened also by the electrostatic attraction of the negative charge on boron atoms with samariums, each of the Sm-N coordinate bonds was found to be still weak, enough to bring about dissociation of one coordinated pyrazolyl groups, i.e. formation of short-lived η^2-$B(pz)_4$ transients, probably followed by inversion of the six-membered Sm-(N-N)$_2$-B ring and further by coordination of the previously uncoordinated pyrazolyl group.

Copyright © 1999 The Chemical Society of Japan

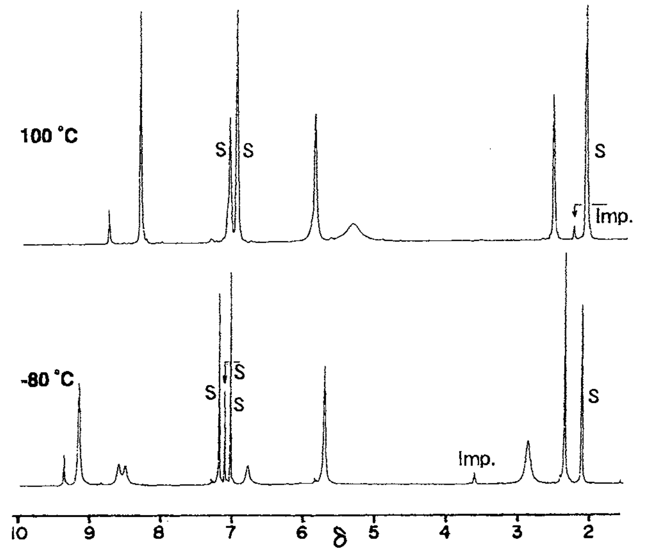

Figure 2. ^{1}H-NMR of [Sm{B(pz)$_4$}$_2$(acac)] in C$_6$D$_5$CD$_3$. S, solvent; Imp., impurity.

In summary, we prepared the {tetrakis(1-pyrazolyl)borato}lanthanides(III) of [Sm{B(pz)$_4$}$_2$(β-ketoenolato)], which showed novel stereochemically non-rigid temperature-dependent motions of the B(pz)$_4$ ligands on their ^{1}H-NMR spectra, involving the fast exchange of coordinated and uncoordinated pyrazolyl groups at high temperatures.

We appreciate Prof. Y. Kawasaki (Osaka Institute of Technology) for his fruitful discussions.

References and Notes

1 C. J. Schaverien, *Adv. Organomet. Chem.*, **36**, 283 (1994); T. J. Marks and R. D. Ernst, in "Comprehensive Organometallic Chemistry," ed by G. Wilkinson, Pergamon, Oxford (1982), Vol. **3**, Chap. 21, p.173; P. L. Watson and G. W. Parshall, *Acc. Chem. Res.*, **18**, 51 (1985); P. L. Watson, *J. Am. Chem. Soc.*, **104**, 337 (1982); P. L. Watson, *J. Chem. Soc., Chem. Commun.*, **1983**, 276; G. Jeske, L. E. Schock, P. N. Swepston, H. Schumann, and T. J. Marks, *J. Am. Chem. Soc.*, **107**, 8103 (1985).

2 S. Trofimenko, *Chem. Rev.*, **93**, 943 (1993); A. Shaver, in "Comprehensive Coordination Chemistry," ed by G. Wilkinson, Pergamon, Oxford (1987), Vol. **2**, Chap. 13.6, p. 245.

3 D. L. Reger, S. J. Knox, J. A. Lindeman, and L. Lebioda, *Inorg. Chem.*, **29**, 416 (1990); D. L. Reger, J. A. Lindeman, and L. Lebioda, *Inorg. Chim. Acta*, **139**, 71 (1987); M. Onishi, N. Nagaoka, K. Hiraki, and K. Itoh, *J. Alloys and Compds.*, **236**, 6 (1996).

4 Separations and characterization of the products obtained are under way in these laboratories, from the reactions of the chlorides with twofold moles of the K[B(pz)$_4$] salt. Using the salt in large quantities, the complexes [M{B(pz)$_4$}$_3$], assinable to [M{η^3-B(pz)$_4$}$_2${η^2-B(pz)$_4$}] presently, have been prepared. See a brief description in the following literature also; K. W. Bagnall, A. C. Tempest, J. Takats, and A. P. Masino, *Inorg. Nucl. Chem. Lett.*, **12**, 555 (1976).

5 S-Y. Liu, G. H. Maunder, A. Sella, M. Stevenson, and D. A. Tocher, *Inorg. Chem.*, **35**, 76 (1996); M. E. M. Hamidi and J. -L. Pascal, *Polyhedron*, **13**, 1787 (1994).

6 Mixed-ligand chelate extraction of trivalent lanthanoid ions into benzene with polypyrazolylborates BH$_n$(pz)$_{4-n}$ (n= 0, 1) and β-diketone has been described. H. Kokusen, Y. Sohrin, H. Hasegawa, S. Kihara, and M. Matsui, *Bull. Chem. Soc. Jpn.*, **68**, 172 (1995). As for preparations and characterization of [Sm{BH(pz)$_3$}$_2$(β-ketoenolato)], see the following; R. G. Lawrence, C. J. Jones, and R. A. Kresinski, *J. Chem. Soc., Dalton Trans.*, **1996**, 501; M. A. J. Moss and C. J. Jones, *Polyhedron*, **9**, 697 (1990); M. A. J. Moss, C. J. Jones, and A. J. Edwards, *J. Chem. Soc., Dalton Trans.*, **1989**, 1393; M. Onishi, K. Itoh, K. Hiraki, R. Oda, and K. Aoki, *Inorg. Chim. Acta*, **277**, 8 (1998).

7 IR and ^{1}H-NMR spectroscopic data of these β-ketoenolato complexes were consistent with their chemical formulation. Concerning IR bands of O,O'-linking β-ketoenolates, see, K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley-Intetscience, New York (1970).

8 Crystal data; (C$_{31}$H$_{29}$B$_2$N$_{16}$O$_2$Sm, M= 829.70); triclinic, space group $P\bar{1}$(No.2), a= 14.035(2), b= 27.143(2), c= 9.485(2) Å, α= 98.975(10)°, β= 91.23(1)°, γ=102.161(8)°, V= 3483.7(8) Å^3, Z= 4, D_{calc}= 1.582 g/cm^3, μ(MoKα)= 17.45 cm^{-1}, Data collected at 296 K with a Rigaku AFC-7S diffractometer (Mo radiation, λ= 0.71069 Å; $2\theta_{\mathrm{max}}$= 55.0°.); R= 0.045 and R_{w}= 0.048 for 10016 observations (I>3.00$\sigma(I)$). Sm(1)-N(1), 2.544(6); Sm(1)-N(3), 2.544(6); Sm(1)-N(5), 2.599(5); Sm(1)-N(9), 2.602(6); Sm(1)-N(11), 2.523(6); Sm(1)-N(13), 2.556(5) Å.

9 NMR signals of acac in [Sm{B(pz)$_4$}$_2$(acac)] (C$_6$D$_5$CD$_3$); δ 2.27 and 9.29 at -80 °C; δ 2.56 and 8.78 at 100 °C.

10 Similar stereochemically non-rigid temperature-dependent dynamics of the ligating B(pz)$_4$ ligands, which induce ^{1}H-NMR spectroscopic equivalence of their coordinated and uncoordinated pyrazolyl groups at high temperatures, have been described to date for some d^8 transition-metal complexes {Pd(II), Pt(II), and Rh(I)} and for a few of [M{B(pz)$_4$}$_2$]-type compounds of Group 14 typical-elements {M= Sn(II) and Pb(II)}. Mutual interchange between η^2 and η^3-coordination modes of the B(pz)$_4$ ligands and inversion of boat-type six-membered M-(N-N)$_2$-B rings in the η^2-species have been regarded as essential key steps, affording the spectroscopic equivalence of the coordinated and uncoordinated pyrazolyl groups. See for example; L. E. Manzer and P. Z. Meakin, *Inorg. Chem.*, **15**, 3117 (1976); M. Cocivera, G. Ferguson, F. J. Lalor, and P. Szczecinski, *Organometallics*, **1**, 1139 (1982); D. L. Reger, S. J. Knox, M. F. Huff, A. Rheingold, and B. S. Haggerty, *Inorg. Chem.*, **30**, 1754 (1991); D. L. Reger, M. F. Huff, A. L. Rheingold, and B. S. Haggerty, *J. Am. Chem. Soc.*, **114**, 579 (1992); M. Onishi, K. Hiraki, M. Shironita, Y. Yamaguchi, and S. Nakagawa, *Bull. Chem. Soc. Jpn.*, **53**, 961 (1980). Furthermore, it is noted that zinc and thallium compounds, [Zn{B(pz)$_4$}$_2$] and [TlR$_2${B(pz)$_4$}] have shown similar NMR spectroscopic equivalence of all four pyrazolyl groups. However, η^3-coordinate bonding character of the B(pz)$_4$ ligands has not been ascertained for these compounds in the solution state even at low temperatures, and accordingly these equivalence seems to be attributable to their ionic bonding-character between the metal atoms and the B(pz)$_4$ ligands. S. Trofimenko, *Acc. Chem. Res.*, **4**, 17 (1971); M. Onishi, K. Hiraki, and S. Nakagawa, *Bull. Chem. Soc. Jpn.*, **53**, 1459 (1980).