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Mixed Pyrazolylborate–β-Diketonate–Ln(III) Complexes*

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Previous work from our laboratories established that $Ln(HBpz_3)_3$ Ln (lanthanide) = Dy–Lu; pz = pyrazolyl complexes represent a unique class of solution rigid lanthanide compounds [1]. It was shown that the solution structure closely approximates that determined in the solid state for the Yb member [2] and which is based on a bicapped-trigonal prismatic (BCTP) coordination geometry. The eight-coordinate environment of the metal center is provided by two tridentate and one bidentate $HBpz_3$ moieties. Since most other eight-coordinate metal complexes are highly non-rigid [3] it was deemed important to determine whether the $Ln(HBpz_3)_3$ complexes were unique among the $Ln(HBpz_3)_2$ (bidentate-chelate) type complexes or that solution rigid behavior was a common feature of this class of compounds.

We report here the synthesis and solution behavior of $Ln(HBpz_3)_2$(β-diketonate) complexes.

Experimental

The preparation and handling of the compounds were carried out under an atmosphere of purified nitrogen using standard Schlenk techniques in conjunction with a double vacuum manifold. All solvents were dried and distilled just prior to use.

The β-diketones, 2,2,6,6-tetramethyl-3,5-heptanedione (dpmH) and 3-trifluoroacetyl-D-camphor (tfacH) were purchased from Aldrich Chemical Co. and distilled prior to use. $LnCl_3$ (Ln = Lu, Yb) and $K(HBpz_3)$ were prepared by published procedures [4, 5]. The complexes $Ln(HBpz_3)_2Cl\cdot THF$ (THF = tetrahydrofuran) were prepared following the published procedure for Er [6] by reacting equimolar quantities of $LnCl_3$ and $KHBpz_3$ in THF. The potassium salts of the β-diketones were obtained by KH deprotonation in THF. Filtration, followed by removal of the solvent under vacuum gave the pure Kdpm and Ktfac, yield 84–95%.

NMR spectra were recorded on a Bruker WP-400 (^1H and ^{13}C) spectrometer. Mass spectra were obtained from an AEI MS12 mass spectrometer in conjunction with a Data General Nova 3 computer. Elemental analyses were performed by the analytical services laboratory of the chemistry department.

Preparation of the Complexes

All four complexes were prepared by the same general procedure which is outlined below.

Approximately 1.0 g (~1.5 mmol) of $Ln(HBpz_3)_2Cl\cdot THF$ was dissolved in 30 cm^3 of THF. To the clear solution was added an equimolar amount of the potassium β-diketonate dissolved in 10 cm^3 of THF. The solution, which quickly turned cloudy, was stirred at room temperature for 4 h. The solvent was removed under vacuum and the solid residue dried. The solid mixture was transferred to an extraction thimble and was extracted with 150 cm^3 of hexane under vacuum at 50 °C for 5 h. The hexane solution was concentrated and put into a freezer (−10 °C) overnight. The resultant white solid was collected and dried under vacuum. The yields ranged from 50 to 72%.

$Lu(HBpz_3)_2(dpm)$, **1a**. *Anal.* Calc. for $C_{29}H_{39}B_2N_{12}O_2Lu$: C, 44.36; H, 5.01; N, 21.40. Found: C, 44.69; H, 4.84; N, 21.87%.

$Yb(HBpz_3)_2(dpm)$, **1b**. *Anal.* Calc. for $C_{29}H_{39}B_2N_{12}O_2Yb$: C, 44.52; H, 5.02; N, 21.48. Found: C, 44.46; H, 5.17; N, 21.21%.

$Lu(HBpz_3)_2(tfac)$, **2a**. *Anal.* Calc. for $C_{30}H_{34}B_2F_3N_{12}O_2Lu$: C, 42.48; H, 4.04; N, 19.81. Found: C, 41.39; H, 4.21; N, 18.85%.

$Yb(HBpz_3)_2(tfac)$, **2b**. *Anal.* Calc. for $C_{30}H_{34}B_2F_3N_{12}O_2Yb$: C, 42.63; H, 4.05; N, 19.86. Found: C, 42.51; H, 3.95; N, 19.94%.

The mass spectrum of each compound showed the parent ion with prominent fragment due to the loss of the β-diketonate ligand. The ^1H and ^{13}C NMR data on the complexes are collected in Table I.

Results and Discussion

Simple metathesis between $Ln(HBpz_3)_2Cl\cdot THF$ and the appropriate β-diketonate gives the mixed complexes in a straightforward fashion, eqn. 1. The white crystalline products are thermally stable and

$$Ln(HBpz_3)_2Cl\cdot THF + K(\beta\text{-diketonate}) \xrightarrow{THF} Ln(HBpz_3)_2(\beta\text{-diketonate}) \qquad (1)$$

dpm Ln = Lu, **1a**; Yb, **1b**
tfac Lu, **2a**; Yb, **2b**

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TABLE I. ^1H and ^{13}C NMR Spectra of $Ln(HBpz_3)_2$(β-diketonate) Complexes

Complex	H_3	H_4	H_5	Other resonances
Lu(dmp), **1a**	7.01(d)	6.04(t)	7.71(d)	6.01(s, C*H*), 0.94(s, C*Me*$_3$)
Yb(dmp), **1b**	15.6(br)	4.2(s)	4.7(s)	3.0(br, B*H*), –17.9(s, C*Me*$_3$), –53.8(s, C*H*)
Lu(tfac), **2a**	7.04(dd) 7.08(dd)	7.05(m)	7.69(d) 7.73(d)	4.5 and 4.8(br, B*H*), 6.97(t, C*H*), 2.15, 1.70, 1.55, 1.26(m, C*H*$_2$), 0.97, 0.96, 0.79(s, Me)
Yb(tfac), **2b**	27.0(br) 21.5(br)	5.57(s) 2.64(s)	or 6.09(s) 6.53(s)	2.0 and –4.5(br, B*H*), –20.7(s, C*H*), –7.0, –11.2, –14.5, –22.4(s, C*H*$_2$), 6.2, –6.1, –8.9(s, Me)
	C_3	C_4	C_5	Other resonances
Lu(dmp), **1c**	141.83	104.06	134.88	200.75(*C*(O)), 93.08(*C*H), 41.08(*C*Me$_3$), 28.05(C*Me*$_3$)
Yb(dmp), **1b**	144.14	99.55	132.52	41.18(*C*(O)), –121.23(*C*H), 7.16(*C*Me$_3$), 3.42(C*Me*$_3$)
Lu(tfac), **2a**	141.98 141.31	104.51 104.26	135.38	210.15 and 115.67(*C*(O)), 20.57(q, CF$_3$), 58.43, 51.09, 48.37, 30.68, 28.33, 20.53, 19.38, 9.52, 1.23(tfac carbons)
Yb(tfac), **2b**	150(br)	134.73 130.97	or 102.76 101.96	120.7 and 24.7 (*C*(O)), 92.5(q, CF$_3$), 41.9, 33.9, 17–8 (unresolved peaks) and 1.1(tfac carbons)

sufficiently volatile to record the mass spectrum which, in all cases, exhibits well defined parent molecular ion. Major fragmentation is due to the loss of the β-diketonate ligand. The materials are moderately hygroscopic, especially in solution and are best handled under an inert atmosphere.

Figures 1 and 2 show the ^1H and ^{13}C NMR spectra of the $Yb(HBpz_3)_2$(dpm) and $Lu(HBpz_3)_2$(tfac) complexes respectively. The NMR data for these and the other two compounds are collected in Table I. It is clear from the simple NMR spectra that, contrary to $Ln(HBpz_3)_3$, complexes **1** and **2** are fluxional in solution. The activation energy for the rearrangement must be very small since even at –110 °C the low temperature limiting spectrum could not be obtained.

There are several plausible mechanisms that could account for the pyrazolyl group exchange in these molecules. However the appearance of two sets of averaged $HBpz_3$ NMR signals in compounds **2** rules out mechanisms which allow for symmetrization of the two $HBpz_3$ moieties, since they are clearly distinct at all temperatures in these inherently asymmetric compounds. Thus tfac ligand dissociation or dechelation with the formation of a seven-coordinate intermediate are ruled out as being responsible for the non-rigidity of these compounds. Other possibilities are best considered by reference to the molecular structure of the complexes. A schematic view of **1b**, as determined by X-ray crystallography [7], is shown in Fig. 3 and it is assumed that the

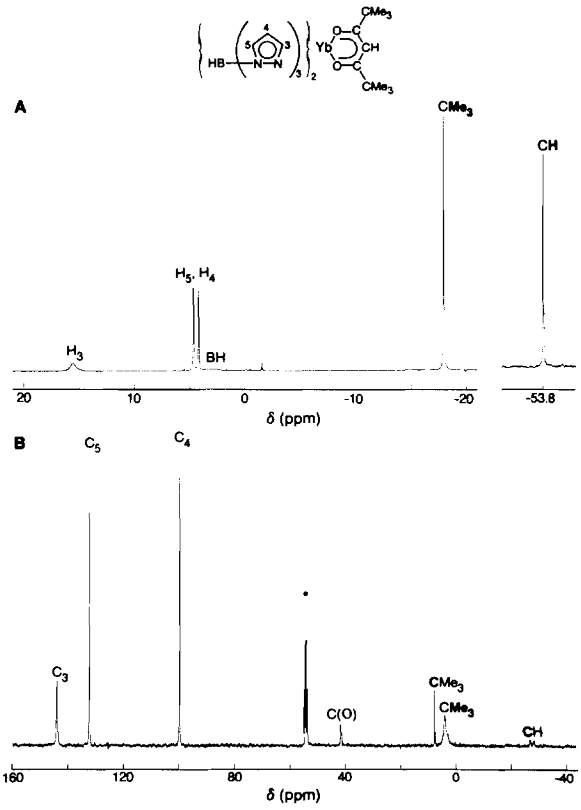


Fig. 1. ^1H (A) and ^{13}C (B) NMR spectra of $Yb(HBpz_3)_2$(dpm), **1b**, in CD_2Cl_2 at 25 °C.

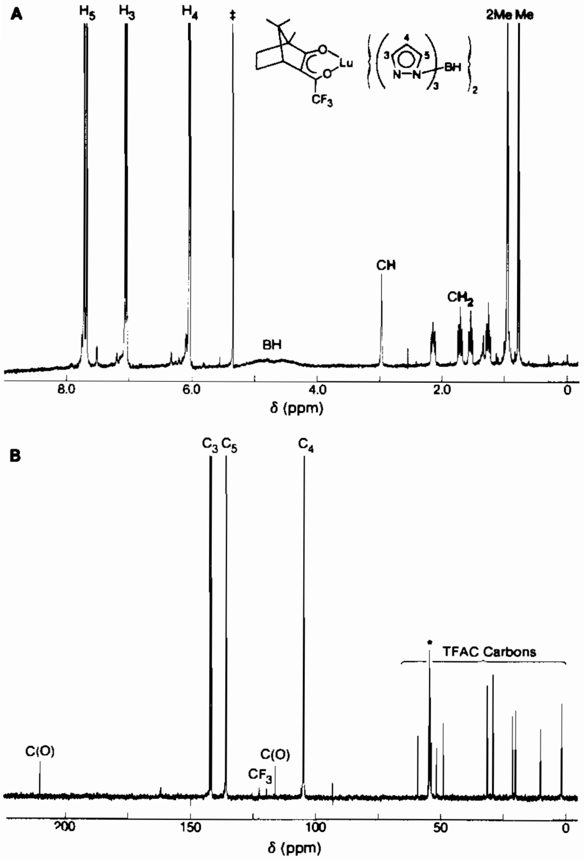


Fig. 2. ^1H (A) and ^{13}C (B) NMR spectra of $Lu(HBpz_3)_2$-(tfac), **2a**, in CD_2Cl_2 at 25 °C.

other complexes conform to this type of coordination geometry as well.

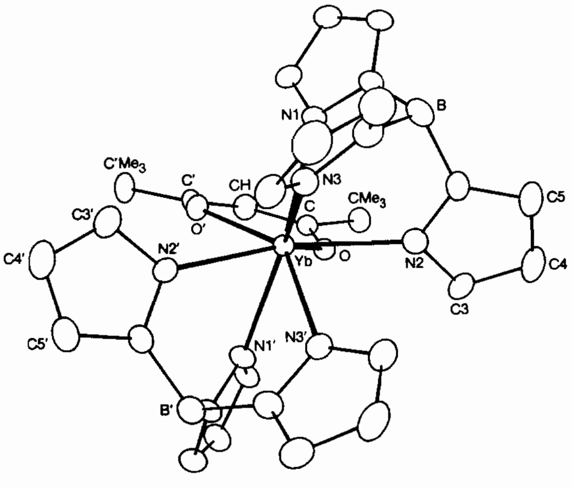
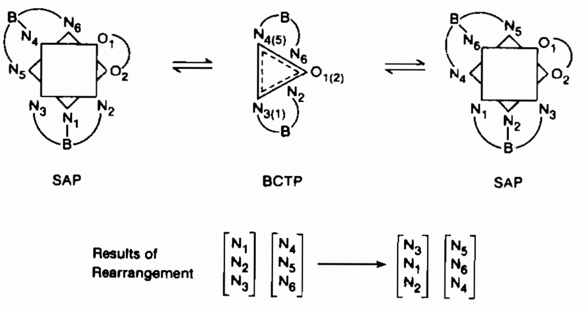


Fig. 3. Perspective view of $Yb(HBpz_3)_2(dpm)$ looking down the approximate molecular C_2 (Yb–CH) axis of symmetry. Primed positions are intended to indicate related atoms under idealized C_2 symmetry.

Although it may not be immediately obvious from the view shown, which emphasizes the approximate C_2 symmetry of **1b**, analysis of the shape parameters [8] clearly indicates that the coordination geometry is best described as square-antiprismatic, SAP. The change in coordination geometry between $Ln(HBpz_3)_3$, BCTP, and $Ln(HBpz_3)_2$(β-diketonate), SAP, has profound influence on the respective solution behavior.

Focussing on the structure shown in Fig. 3, it is easy to see that simple $HBpz_3$ group rotation about the Ln–B axis would accomplish the exchange of pyrazolyl ligands required for the appearance of the simple NMR spectra. Although such trigonal twist type motion of the $HBpz_3$ moiety has been identified before in transition metal pyrazolylborate complexes [9], the barriers for rotation were sufficiently high to give well defined low temperature limiting NMR spectra. Furthermore, were this process responsible for the dynamic behavior of complexes **1** and **2** it is not readily apparent why such movement would not cause equilibration of the pyrazolyl groups of the tridentate $HBpz_3$ ligands in the related $Ln(HBpz_3)_3$ compounds. For these reasons we favor an exchange process which involves interchange between different eight-coordinate geometrical forms. Due to the small energy difference between these forms such a process is commonly very facile [3]. The interchange between two SAP forms via a BCTP intermediate is particularly well suited for compounds **1** and **2** and is shown in Scheme 1. It is clear that the SAP $\leftrightarrows$ BCTP isomerization is accompanied by $HBpz_3$ group rotation and easily accounts for the equilibration between the three pyrazolyl rings of individual $HBpz_3$ ligands. The C_2 symmetry of **1** and the asymmetric nature of **2** ensures that one and two averaged $HBpz_3$ moieties are expected for the respective molecules, in full accord with the NMR observation.

In conclusion, it appears that solution rigid behavior is not a common feature of $Ln(HBpz_3)_2$ (bidentate-chelate) type compounds but it may be a unique property of BCTP–$Ln(HBpz_3)_3$ complexes. Indeed it is interesting to note that even with $Ln(HBpz_3)_3$ complexes we have detected a minor



Scheme 1. Pyrazolyl group exchange in SAP $Yb(HBpz_3)_2$-(β-diketonate) via BCTP intermediate.

isomeric component to which the SAP form was tentatively assigned and which also shows non-rigid solution behavior [10].

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