^{171}Yb CP MAS NMR spectroscopy

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A series of ytterbium(II) cyclopentadienyl derivatives are studied by high-resolution solid-state ^{171}Yb CP MAS (cross-polarisation magic angle spinning) NMR spectroscopy; the principal components of the chemical shift tensors have been determined from spinning sideband analysis.

Since the first solution-state NMR observation of the spin 1/2 nucleus ^{171}Yb by us[1] the number of observed ^{171}Yb chemical shifts has reached over 200, with a corresponding chemical shift dispersion of some 3000 ppm {from *ca.* δ +2500 to −500, with respect to [Yb(η-C$_5$Me$_5$)$_2$(thf)$_2$]}, and coupling constants which have been reported for ^{171}Yb to ^{1}H,[2–5] ^{13}C,[6,7] ^{14}N,[1] ^{29}Si,[8] ^{31}P,[9,5] $^{117/119}$Sn,[10] and ^{125}Te.[11] Large temperature dependences for both chemical shifts and linewidths have been observed in many solution-state studies. It is evident that in these studies the interpretation of the solution-state behaviour of ytterbium(II) complexes is complicated by equilibria between, for example, complexes with varying degree of solvation, monomer–dimer equilibria, reversible salt addition reactions or reactions with the solvent itself. Additionally, in common with other heavy metals, ^{171}Yb shifts depend on concentration, solvent and/or temperature. Typical temperature dependences are between +2 and −0.5 δ K^{-1}. Though for many organometallic ytterbium(II) compounds molecular solid-state structures have been determined the extrapolation of such data for these compounds to the solution state is often tenuous.

Solid-state ^{171}Yb NMR data provides a means of both elucidating the structural relationship between the solution and solid state and of course in facilitating the characterisation of the many ytterbium(II) compounds that are noncrystalline instead of the few that are. To date three wide-line solid-state studies of the ^{171}Yb nucleus have been reported.[12–14] More recently, the static and magic angle spinning spectra of RbYbI$_3$ have also been published.[15] The advantages of CP with respect to increased sensitivity and faster acquisition rates are well documented.[16] We now report the study of a series of ytterbium(II) derivatives by high-resolution solid-state ^{171}Yb CP MAS NMR spectroscopy. [Yb(η-C$_5$Me$_5$)$_2$(OEt$_2$)] was prepared[17] from the reaction of Na(C$_5$Me$_5$) with YbI$_2$ in Et$_2$O and was the precursor for the other solvates [Yb(η-C$_5$Me$_5$)$_2$(thf)$_2$] and [Yb(η-C$_5$Me$_5$)$_2$(py)$_2$].† All spectra were obtained using cross-polarisation, dipolar decoupling from ^{1}H and magic angle spinning.‡ Spectra were acquired using either a single or variable contact cross-polarisation sequence.§ The cross-polarisation contact time, 9 ms, was optimised for [Yb(η-C$_5$Me$_5$)$_2$(thf)$_2$]. Chemical shifts were referenced to the absolute resonance frequency of ^{171}Yb in a thf solution of [Yb(η-C$_5$Me$_5$)$_2$(thf)$_2$].

Examining the ^{171}Yb NMR data in Table 1 reveals that: (*i*) with the exception of [Yb(η-C$_5$Me$_5$)$_2$(py)$_2$], the isotropic chemical shifts are in general in good agreement with the solution data thereby providing strong support for the retention of very similar structures in solution; (*ii*) the addition of the O-centred Lewis bases to [Yb(η-C$_5$Me$_5$)$_2$] (which exhibits two magnetically inequivalent Yb atoms within the unit cell, Fig. 1) results in a high frequency shift of some 40–60 ppm; (*iii*) the difference between solid- and solution-state ^{171}Yb NMR chemical shifts for [Yb(η-C$_5$Me$_5$)$_2$(py)$_2$], some 160 ppm, is too large to be explained by magnetic susceptibility changes alone. This high frequency shift is, we propose, due to a solution equilibrium between the bis- and tris-pyridine adducts. Support for this conclusion also derives from the large temperature dependence (1.46 δ K^{-1}) of the ^{171}Yb resonance displayed by pyridine solutions of [Yb(η-C$_5$Me$_5$)$_2$]; (*iv*) the principal values of the σ-tensors were obtained by analysis of the spinning sidebands by the Herzfeld and Berger method.[18] The largest variation is seen is the σ_{33} values. The range of values for Δ_Δ and Δ_s¶ are moderately large but not sufficiently so as to prevent the routine observation of ^{171}Yb CP MAS spectra, particularly at fields lower than 9.5 T. In conclusion we anticipate that, by analogy with solution-state ^{171}Yb NMR spectroscopy, CP MAS ^{171}Yb NMR spectroscopy will become a frequently employed tool in the characterisation of ytterbium(II) complexes.||

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Table 1 ^{171}Yb NMR data for the Yb(η-C$_5$Me$_5$)$_2$ complexes

Compound	δ_{soln}	δ_{iso}	$\omega_{1/2}$/Hz	Δ_Δ/ppm	Δs/ppm	η	Tensor elements/ppm
[Yb(η-C$_5$Me$_5$)$_2$]$_n$	−33 (toluene)	34	170	916	629	0.95	σ_{11} −644 ± 4
							σ_{22} −50 ± 5
							σ_{33} 595 ± 7
	−33	−36	170	898	722	0.85	σ_{11} −562 ± 3
							σ_{22} −14 ± 1
							σ_{33} 686 ± 2
[Yb(η-C$_5$Me$_5$)$_2$(thf)$_2$]	0 (thf)	24	300	465	365	0.7	σ_{11} −334 ± 3
							σ_{22} −79 ± 2
							σ_{33} 341 ± 1
[Yb(η-C$_5$Me$_5$)$_2$(OEt$_2$)]	26 (OEt$_2$)	23	300	854	511	0.8	σ_{11} −592 ± 2
							σ_{22} 34 ± 1
							σ_{33} 488 ± 2
[Yb(η-C$_5$Me$_5$)$_2$(py)$_2$]	949 (py)	782	1000	774	403	0.56	σ_{11} −1298 ± 2
							σ_{22} −669 ± 2
							σ_{33} −379 ± 2

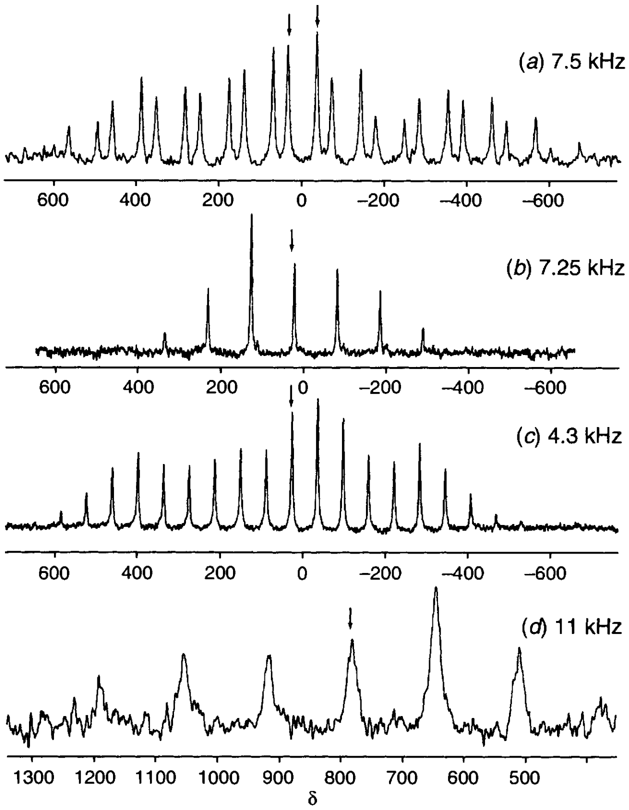

Fig. 1 The CP MAS spectra, of (*a*) {Yb(η-$C_5Me_5)_2\}_n$, (*b*) [Yb(η-$C_5Me_5)_2$(thf)$_2$], (*c*) [Yb(η-$C_5Me_5)_2(OEt_2)$] and (*d*) [Yb(η-$C_5Me_5)_2$(py)$_2$] (arrows indicate δ_{iso})

Footnotes

† In a typical experiment [Yb(η-$C_5Me_5)_2(OEt_2)$] was dissolved in toluene, followed by the addition of an excess of pyridine which resulted in the immediate precipitation of a dark green crystalline solid. After stirring for 1 h, the solvent was removed under dynamic vacuum and the dark green crystalline solid washed with pentane.

The base-free compound, [Yb(η-$C_5Me_5)_2$], is best prepared *via* repeated sublimations of the ether solvate.

‡ Samples were ground in a glove box operating at < 1 ppm H_2O and < 1 ppm O_2 and packed into zirconia rotors with Kel-F end caps and spun with N_2. NMR experiments were performed on a Bruker DMX-400 spectrometer (89 mm wide-bore magnet) with a 4 mm variable-temperature double-bearing probe. The irradiation and detection frequencies were 400.13 and 70.02 MHz for ^{1}H and ^{171}Yb respectively.

§ At spin rates in excess of 8 KHz a variable amplitude (triangular ramp ±30%) CP contact pulse was employed.

¶ Where $\Delta_{\Delta} = \sigma_{11} - [(\sigma_{22} + \sigma_{33})/2]$ and $\Delta s = (\sigma_{33} - \sigma_{iso})$.

|| *Note added at proof:* Recently the authors have been made aware of another simultaneous ^{171}Yb CP MAS study.[19]

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