Synthesis, structures and characterisations of truly homoleptic acetonitrile Ln^{3+} complexes in solid state and in solution†

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Electronic supplementary information

IUPAC recommendations for NMR chemical shift measurements

In 2001 IUPAC recommended a unified scale for reporting the NMR chemical shifts of all nuclei relative to the ^{1}H resonance of tetramethylsilane (TMS). The unified scale is designed to provide a precise ratio, Ξ, of the resonance frequency of a given nuclide to that of the primary reference, the ^{1}H resonance of TMS in dilute solution (volume fraction, φ < 1 %) in chloroform. Thus, the chemical shifts of the X nuclei can be determined on the unified (TMS based) scale just by measuring the resonance frequency of the sample and using a predetermined reference frequency for the nuclide in question. Therefore, only one (sample) tube is required and no reference substance needs to be added. The predetermined reference frequency is obtained by measuring the proton resonance of TMS under similar condition to the sample (with the same lock compound) in a single experiment for the spectrometer being used. Then, the frequency of the usual secondary reference for the nucleus X can be calculated using the predetermined value of TMS, Eq. S-1:

$$\nu_{X,ref} = \left(\nu_{TMS}\Xi_{ref}\right)/100 \qquad \text{S-1}$$

$\nu_{X,ref}$: resonance frequency of a given nuclei (X) with respect to TMS
ν_{TMS}: proton resonance frequency of TMS
Ξ_{ref}: frequency ratio between the secondary reference frequency and that of the ^{1}H in TMS

The chemical shift of a given X nuclei in the sample can be easily derived from Eq. S- 2:

$$\delta_{X,sample} = \frac{\nu_{X,sample} - \nu_{X,ref}}{\nu_{X,ref}} 10^6 \qquad \text{S-2}$$

$\nu_{X,sample}$: resonance frequency of a given nuclei (X) in the sample
$\delta_{X,sample}$: chemical shift of a given nuclei (X) in the sample with respect to TMS (in ppm)

If the lock substance in the sample solution is not the same as that of the reference solution, a lock correction must be applied, Eq. S-3:

$$\delta_{X,sample} = \delta_{X,observed} + \left(\delta^{lock}_{sample} - \delta^{lock}_{reference}\right) \qquad \text{S-3}$$

Table S1. NMR properties of selected nuclei.

nucleus	spin I	natural abundance (%)	Ξ (%)	γ (10^7 rad s^{-1} T^{-1})	reference compound
^{1}H	1/2	99.989	100	26.75	CH_3Si
^{13}C	1/2	1.07	25.145	6.73	CH_3Si
^{14}N	1	99.63	7.226	1.93	CCl_3F
^{19}F	1/2	100	94.094	25.16	CH_3NO_2
^{27}Al	5/2	100	26.057	6.98	$Al(NO_3)_3$

Table S2 Crystallographic details of the partial structure determinations for $[Nd(CH_3CN)_9][Al(pftb)_4]_3 \cdot 4CH_2Cl_2$ (**1**$\cdot 4CH_2Cl_2$), $[Gd(CH_3CN)_9][Al(pftb)_4]_3 \cdot 3CH_2Cl_2$ (**3**$\cdot 3CH_2Cl_2$), and $[Dy(CH_3CN)_9][Al(pftb)_4]_3 \cdot 3CH_2Cl_2 \cdot CH_3CN$ (**4**$\cdot 3CH_2Cl_2 \cdot CH_3CN$).

	1$\cdot 4CH_2Cl_2$	**3**$\cdot 3CH_2Cl_2$	**4**$\cdot 3CH_2Cl_2 \cdot CH_3CN$
Empirical formula	$C_{70}H_{35}Al_3Cl_8F_{108}N_9O_{12}Nd$	$C_{69}H_{33}Al_3Cl_6F_{108}N_9O_{12}Gd$	$C_{71}H_{36}Al_3Cl_6F_{108}N_{10}O_{12}Dy$
Fw	3754.85	3682.81	3729.11
crystal size [mm]	0.98 x 0.32 x 0.14	0.49 x 0.23 x 0.21	0.61 x 0.26 x 0.23
crystal system	orthorhombic	orthorhombic	orthorhombic
space group	$Pna2_1$	$Pna2_1$	$Pna2_1$
a [Å]	28.308(10)	28.3168(18)	28.161(5)
b [Å]	29.321(9)	29.3210(16)	29.301(5)
c [Å]	15.203(3)	15.1241(10)	15.2811(16)
α [°]	90	90	90
β [°]	90	90	90
γ [°]	90	90	90
V [nm^3]	12.619(6)	12.557(2)	12.609(3)
Z	4	4	4
ρ_{calc} [Mg m^{-3}]	1.976	1.006	1.908
μ [mm^{-1}]	0.817	0.448	0.953
abs. correction	none	none	none
F (000)	7284	3680	7012
index range	$-29 \leq h \leq 29$	$-38 \leq h \leq 38$	$-32 \leq h \leq 32$
	$-29 \leq k \leq 30$	$-39 \leq k \leq 39$	$-34 \leq k \leq 34$
	$-15 \leq l \leq 15$	$-17 \leq l \leq 17$	$-17 \leq l \leq 17$
Max 2θ	21.51	29.16	24.51
T [K]	100(2)	100(2)	100(2)
diffractometer type	Bruker APEX II	Bruker APEX II	Bruker APEX II
unique reflns. [$I > 2\sigma(I)$]	7603	7377	13586
Data / restraints / parameters	7603 / 592 / 331	7737 / 454 / 193	13586 / 537 / 295
GOOF	1.274	0.770	1.527
final R1 [$I > 2\sigma(I)$]	0.1578	0.1106	0.1561
final wR2	0.3834	0.2683	0.4095
largest residual peak [e Å^{-3}]	2.168	1.574	2.315
largest residual hole [e Å^{-3}]	-0.910	-1.558	-1.407

Table S3 Comparison of the IR and Raman spectra of **1**, **2**, **3**, **4** and **5** with those of free CH_3CN and of the $[Al(pftb)_4]^-$ anion in $[NEt_4][Al(pftb)_4]$ and $Li[Al(pftb)_4]$. Bands assigned to the $[Ln(CH_3CN)_n]^{3+}$ cations are marked in bold (vw = very weak, w = weak, mw = medium weak, m = medium, ms = medium strong, s = strong, vs = very strong, sh = shoulder).

1		**2**		**3**		**4**		**5**		$[Al(pftb)_4]^-$ in $[NEt_4][Al(pftb)_4]$[40]		$[Al(pftb)_4]^-$ in $Li[Al(pftb)_4]$[40]		CH_3CN		assignment
IR	Raman	IR	Raman	IR	Raman	IR	Raman	IR	Raman	IR	Raman	IR	Raman	IR	Raman	
-	233 (w)	-	234 (w)	-	236 (w)	-	233 (w)	-	235 (w)	228 (w)	234 (w)	-	234 (mw)	-	-	C-C-
289 (w)	288 (w)	283 (w)	288 (w)	283 (w)	291 (w)	287 (w)	287 (w)	289 (w)	291 (w)	285 (mw)	289 (w)	289 (w)	297 (w)	-	-	C–C
315 (m)	323 (w)	315 (w)	322 (m)	315 (w)	324 (ms)	315 (m)	323 (w)	315 (m)	324 (m)	316 (m)	323 (ms)	-	316 (w)	-	-	C–C, Al–O
327 (w)	-	-	-	-	-	331 (vw)	-	328 (w)	-	331 (w)	-	326 (w)	327 (m)	-	-	C–C, C–F, Al–O
355 (vw)	-	-	-	-	-	-	-	**355 (vw)**	-	-	-	-	-	-	**383 (mw)**	**C-C-N**
-	368 (w)	-	368 (w)	-	370 (w)	368 (w)	368 (w)	370 (w)	370 (w)	367 (mw)	368 (w)	369 (w)	363 (w)	-	-	C–C, C–F, Al–O
376 (w)	-	376 (w)	-	376 (w)	-	380 (w)	-	375 (w)	-	377 (mw)	-	-	390 (w)	-	-	C–C, C–O
399 (m)	408 (w)	-	409 (mw)	404 (w)	417 (m)	417 (vw)	414 (w)	407 (w)	418 (m)	-	-	-	-	-	-	C-C-N
447 (ms)	-	447 (m)	-	447 (mw)	-	449 (ms)	-	448 (ms)	-	446 (ms)	-	-	-	-	-	C–C, C–O
-	-	-	-	-	-	-	-	-	-	-	-	464 (m)	-		-	-
537 (ms)	538 (w)	537 (mw)	538 (m)	537 (w)	540 (w)	537 (ms)	539 (w)	537 (ms)	549 (w)	537 (m)	538 (w)	539 (m)	539 (mw)	-	-	C–C, C–O
-	-	-	-	-	-	-	-	-	-	-	-	546 (mw)	-	-	-	-
561 (ms)	562 (w)	561 (w)	561 (mw)	561 (vw)	563 (w)	561 (ms)	562 (w)	561 (ms)	563 (w)	562 (mw)	563 (w)	562 (mw)	-	-	-	Al–O, C–C
572 (m)	572 (sh, w)	572 (vw, sh)	572 (sh, w)	572 (vw, sh)	571 (sh, w)	572 (mw)	572 (sh, w)	572 (m)	572 (sh, w)	571 (w)	-	572+582 (m)	573 (mw)	-	-	Al–O, C-–C

Table 4 continued Comparison of the IR and Raman spectra of 1, 2, 3, 4 and 5 with those of free CH_3CN and of the $[Al(pftb)_4]^-$ anion in $[NEt_4][Al(pftb)_4]$ and $Li[Al(pftb)_4]$. Bands assigned to the $[Ln(CH_3CN)_n]^{3+}$ cations are marked in bold (vw = very weak, w = weak, mw = medium weak, m = medium, ms = medium strong, s = strong, vs = very strong, sh = shoulder).

1		**2**		**3**		**4**		**5**		$[Al(pftb)_4]^-$ in $[NEt_4][Al(pftb)_4]$[40]		$[Al(pftb)_4]^-$ in $Li[Al(pftb)_4]$[40]		CH_3CN		assignment
IR	Raman	IR	Raman	IR	Raman	IR	Raman	IR	Raman	IR	Raman	IR	Raman	IR	Raman	
727 (ms)	-	727 (s)	-	727 (ms)	-	727 (ms)	-	727 (ms)	-	727 (s)	-	726 (s)	730 (s)	-	-	C–C, C–O
-	746 (ms)	-	746 (s)	-	748 (s)	-	746 (ms)	-	748 (ms)	-	747 (ms)	740 (ms)	745 (s)	-	-	-
755 (vw)	-	756 (vw)	-	756 (vw)	-	756 (vw)	-	756 (vw)	-	756 (mw)	-	756+760 (m)	-	-	-	C–C, C–O
-	798 (ms)	-	797 (s)	-	799 (s)	-	798 (ms)	-	799 (ms)	-	798 (s)	798 (m)	801 (w)	-	-	-
832 (mw)	-	832 (w)	-	833 (w)	-	832 (w)	-	832 (mw)	-	833 (m)	834 (w)	844 (ms)	843 (w)	-	-	Al–O, C–C
-	-	-	-	-	-	-	-	-	-	-	-	863 (ms)	-	-	-	Al–O, C–C
933 (vw)	**936 (vw)**	**935 (w)**	**938 (w)**	**934 (vw)**	**942 (w)**	**937 (vw)**	**938 (vw)**	-	**942 (w)**	-	-	936 (ms)	-	**918 (wv)**	**922 (m)**	**C-C**
-	-	-	-	-	-	-	-	-		-	-	964 (vs)	-	-	-	C-C
972 (vs)	978 (w)	972 (vs)	973 (vw)	972 (vs)	977 (vw)	972 (vs)	-	972 (vs)	977 (w)	973 (s)	978 (mw)	976 (vs)	978 (w)	-	-	C–C, C–F
-	-	-	-	-	-	-	-	-	-	-	-	-	-	**1039 (w)**		**H-C-N**
-	-	-	1135 (vw)	-	-	-	-	-	-	-	1139 (mw)	-	1113 (w)	-	-	C–C, C–F
1168 (m)	-	1170 (ms)	-	1171 (m)	-	1171 (m)	-	-	-	-	1173 (mw)	1184 (ms)	1171 (w)	-	-	C–C, C–F
1218 (vs)	-	1216 (vs)	1218 (vw)	1218 (vs)	-	1217 (vs)	-	1217 (vs)	-	1217 (vs)	-	1225 (vs)	1214 (mw)	-	-	C–C, C–F

Table 4 continued Comparison of the IR and Raman spectra of **1**, **2**, **3**, **4** and **5** with those of free CH_3CN and of of the $[Al(pftb)_4]^-$ anion in $[NEt_4][Al(pftb)_4]$ and $Li[Al(pftb)_4]$. Bands assigned to the $[Ln(CH_3CN)_n]^{3+}$ cations are marked in bold (vw = very weak, w = weak, mw = medium weak, m = medium, ms = medium strong, s = strong, vs = very strong, sh = shoulder).

1		**2**		**3**		**4**		**5**		$[Al(pftb)_4]^-$ in $[NEt_4][Al(pftb)_4]$[40]		$[Al(pftb)_4]^-$ in $Li[Al(pftb)_4]$[40]		CH_3CN		assignment
IR	Raman	IR	Raman	IR	Raman	IR	Raman	IR	Raman	IR	Raman	IR	Raman	IR	Raman	
1244 (vs)	1245 (w)	1244 (vs)	1244 (w)	1245 (vs)	-	1245 (vs)	-	1245 (s)	-	1240 (s)	1235 (mw)	1243 (s)	1250 (mw)	-	-	C–C, C–F
-	-	-	-	-	-	-	-	-	-	1245 (s)	-	-	-	-	-	C–C, C–F
1275 (s)	1274 (w)	1275 (s)	1273 (w)	1275 (s)	1276 (w)	1275 (vs)	1271 (mw)	1275 (s)	1276 (w)	1274 (vs)	1274 (mw)	1270 (s)	1281 (mw)	-	-	C–C, C–F
1299 (ms)	-	1299 (ms)	1307 (w)	1299 (ms)	1308 (w)	1299 (s)	1308 (w)	1299 (ms)	1308 (w)	1298 (s)	1300 (m)	1297 (s)	-	-	-	C–C, C–F
1353 (m)	-	1353 (m)	-	1353 (m)	-	1353 (m)	-	1353 (m)	-	1353 (ms)	-	1353 (ms)	1337 (mw)	-	-	C–C, C–F
-	**1377 (m)**	**1377 (vw)**	**1377 (m)**	-	**1379 (m)**	**1376 (vw)**	**1377 (m)**	-	**1379 (m)**	-	-	-	-	**1376 (ms)**	**1377 (w)**	**H-C-H, H-C-N**
-	-	-	**1416 (vw)**	-	**1420 (vw)**	-		-	**1420 (vw)**	-	-	-	-	**1444 (ms)**	**1448 (w)**	**H-C-H**
2281 (m)	**2284 (vs)**	**2283 (m)**	**2285 (vs)**	**2283 (mw)**	**2290 (vs)**	**2284 (m)**	**2286 (vs)**	**2286 (m)**	**2290 (vs)**	**-**	-	-	-	**2253 (vs)**	**2255 (s)**	**C-N**
2310 (w)	**2312 (ms)**	**2311 (w)**	**2313 (s)**	**2312 (vw)**	**2318 (s)**	**2313 (w)**	**2314 (ms)**	**2314 (w)**	**2318 (ms)**	**-**	-	-	-	**2292 (mw)**	**2295 (w)**	**C-N**
2955 (vw)	**2956 (s)**	**2956 (vw)**	**2956 (vs)**	**2955 (vw)**	**2957 (vs)**	**2955 (vw)**	**2955 (w)**	**2955 (vw)**	-	**-**	-	-	-	**2945 (vw)**	**2945 (vs)**	**C-H**
-	**3022 (mw)**	-	**3021 (w)**	-	**3023 (mw)**		**3024 (vs)**	-	**3023 (vs)**	-	-	-	-	**3002 (vw)**	**3004 (w)**	**C-H**

Table S5. ^{19}F-NMR data measured on $[Nd(CH_3CN)_9][Al(OC(CF_3)_3)_4]_3$ **1** at 376 MHz, 25°C in CH_3CN (5 mm NMR tubes).

Sample	[Ln] (mmol kg^{-1})	[anion]/[Ln]	$\Delta\nu_{1/2}$ (Hz)	$1/T_{2obs}$ (s^{-1})
$[Nd(CH_3CN)_9][Al(OC(CF_3)_3)_4]_3$ **1**	16.00	3	6.3	20
		6	8.0	25
		9	6.3	20

Table S6. ^{19}F-NMR data measured on $Eu(CH_3CN)_3(CF_3SO_3)_2$ and $[Eu(CH_3CN)_9][Al(OC(CF_3)_3)_4]_2$ **2a** at 376 MHz, 25°C in CH_3CN (5 mm NMR tubes).

Sample	[Ln] (mmol kg^{-1})	[anion]/[Ln]	$\Delta\nu_{1/2}$ (Hz)	$1/T_{2obs}$ (s^{-1})
$Eu(CH_3CN)_3(CF_3SO_3)_2$	9.43	3	316	991
		6	282	887
		9	253	795
$[Eu(CH_3CN)_9][Al(OC(CF_3)_3)_4]_2$ **2a**	10.08	3	11.4	36
		6	11.3	36
		9	10.4	33

Table S7. ^{19}F-NMR data measured on $Gd(CH_3CN)_3(CF_3SO_3)_3$ and $[Gd(CH_3CN)_9][Al(OC(CF_3)_3)_4]_3$ **3** at 376 MHz, 25°C in CH_3CN (5 mm NMR tubes).

Sample	[Ln] (mmol kg^{-1})	[anion]/[Ln]	$\Delta\nu_{1/2}$ (Hz)	$1/T_{2obs}$ (s^{-1})
$Gd(CH_3CN)_3(CF_3SO_3)_3$	12.51	3	817	2568
		6	497	1561
		9	385	1210
$[Gd(CH_3CN)_9][Al(OC(CF_3)_3)_4]_3$ **3**	13.37	3	46	143
		6	51	159
		9	53	167
	8.56	3	45	140
		6	50	158
		9	45	142
	1.35	3	26	82

Table S8. ^{19}F-NMR data measured on $[Dy(CH_3CN)_9][Al(OC(CF_3)_3)_4]_3$ **4** at 376 MHz, 25°C in CH_3CN (5 mm NMR tubes).

Sample	[Ln] (mmol kg^{-1})	[anion]/[Ln]	$\Delta\nu_{1/2}$ (Hz)	$1/T_{2obs}$ (s^{-1})
$[Dy(CH_3CN)_9][Al(OC(CF_3)_3)_4]_3$ **4**	78.20	3	6.9	22
	44.67	3	6.9	22
		6	6.5	20
		9	8.5	27
	27.87	3	5.7	18

Table S9. ^{19}F-NMR data measured on $[Tm(CH_3CN)_8][Al(OC(CF_3)_3)_4]_3$ **5** at 376 MHz, 25°C in CH_3CN (5 mm NMR tubes).

Sample	[Ln] (mmol kg^{-1})	[anion]/[Ln]	$\Delta\nu_{1/2}$ (Hz)	$1/T_{2obs}$ (s^{-1})
$[Tm(CH_3CN)_8][Al(OC(CF_3)_3)_4]_3$ **5**	130	3	6.8	21
	70.72	3	5.9	18
		6	8.0	25
		9	8.2	26
	18.11	3	4.8	15