

Syntheses and structures of some homoleptic acetonitrile lanthanoid(III) complexes

Glen B. Deacon,^{*a} Bernd Görtler,^b Peter C. Junk,^{ac} Enno Lork,^b Rüdiger Mews,^{*b} Jan Petersen^b and Boris Zemva^d

^a Department of Chemistry, Monash University, Clayton, Vic 3168, Australia.

E-mail: Glen.B.Deacon@sci.monash.edu.au

^b Institut für Anorganische und Physikalische Chemie, der Universität Bremen, Leobener Straße NW2, Postfach 330440, D-28334, Bremen, Germany.

E-mail: Mews@chemie.uni-bremen.de

^c Department of Chemistry, James Cook University, Townsville, Queensland 4811, Australia

^d Department of Inorganic Chemistry and Technology, "Jozef Stefan" Institute, Jamova 39, 1000 Ljubljana, Slovenia

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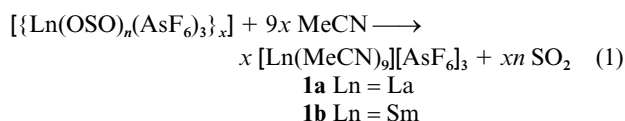
From the reaction of $[\{\text{Ln}(\text{SO}_2)_n(\text{AsF}_6)_3\}_x]$ (Ln = La or Sm) with acetonitrile the complexes $[\text{Ln}(\text{MeCN})_9][\text{AsF}_6]_3$ have been prepared. The crystal structures of $[\text{Ln}(\text{MeCN})_9][\text{AsF}_6]_3 \cdot n\text{MeCN}$ (Ln = La, $n = 1$; Ln = Sm, $n = 3$) show a nine-co-ordinate lanthanoid with a tricapped trigonal prismatic arrangement of N donor atoms. By reaction of LnCl_3 with AlCl_3 in acetonitrile the complexes $[\text{Ln}(\text{MeCN})_9][\text{AlCl}_4]_3$ (Ln = Pr, $n = 9$; Ln = Yb, $n = 8$) have been synthesized, and they have also been prepared very simply by the reaction of the lanthanoid metal, AlCl_3 , and C_2Cl_6 in acetonitrile. The crystal structure of $[\text{Pr}(\text{MeCN})_9][\text{AlCl}_4]_3 \cdot \text{MeCN}$ shows nine-co-ordinate praseodymium also with a tricapped trigonal prismatic arrangement of N donor atoms, whilst $[\text{Yb}(\text{MeCN})_8][\text{AlCl}_4]_3$ has square dodecahedral YbN_8 eight-co-ordination.

Homoleptic lanthanoid complexes $[\text{Ln}(\text{L})_n]^{3+}$ with labile uncharged ligands (e.g. L = MeCN) are valuable synthetic precursors under non-aqueous conditions. They are also Lewis acids and may therefore have valuable catalytic properties (e.g. refs. 1–3). The selection of the counter ion is also critical, as it may compete with the ligands for co-ordination sites, see e.g. $[\{\text{Eu}(\text{MeCN})_3(\text{BF}_4)_3\}_n]$ and its dissociation into $[\text{Eu}(\text{MeCN})_n(\text{BF}_4)_2]^+ + \text{BF}_4^-$ in MeCN,⁴ or it may compete with an incoming ligand during a ligand exchange reaction. Relatively little is known of structures of $[\text{Ln}(\text{MeCN})_n\text{X}_3]$ complexes^{4,5} with a high acetonitrile content ($n > 6$). It appears that replacement of the competitively co-ordinating BF_4^- by AlCl_4^- enables increased acetonitrile co-ordination. Shen and co-workers⁶ have prepared a series formulated as $[\text{Ln}(\text{MeCN})_9][\text{AlCl}_4]_3 \cdot \text{MeCN}$ (Ln = La, Pr, Nd, Sm, Eu, Gd, Tb, Ho or Yb) independent of lanthanoid ion size, on the basis of analytical data and a crystal structure for Ln = Sm. We now report the syntheses and crystal structures of $[\text{Ln}(\text{MeCN})_9][\text{AsF}_6]_3 \cdot n\text{MeCN}$ (Ln = La or Sm), where the anion is a weaker ligand than AlCl_4^- or BF_4^- . Since lanthanoid co-ordination numbers frequently vary with the cation size, we have also determined crystal structures of $[\text{Ln}(\text{MeCN})_n][\text{AlCl}_4]_3 \cdot m\text{MeCN}$ complexes for elements (Pr, Yb) near the ends of the lanthanoid series, and introduce a new synthesis of these compounds from the lanthanoid element.

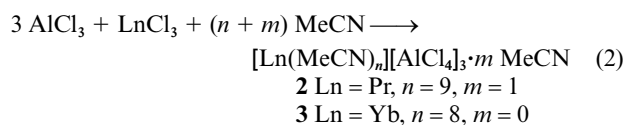
Results and discussion

Syntheses of $[\text{Ln}(\text{MeCN})_n][\text{MX}_m]_3$ complexes

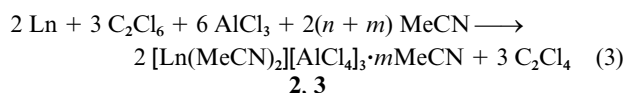
The preparations of $[\text{Ln}(\text{MeCN})_9][\text{AsF}_6]_3$ (Ln = La or Sm) take advantage of the lability of the SO_2 and AsF_6 ligands of the recently prepared $[\{\text{Ln}(\text{OSO})_n(\text{AsF}_6)_3\}_x]$ complexes⁷ with displacement of SO_2 and splitting of the Ln–F–As–F–Ln bridges being effected at room temperature, eqn. (1). Bulk samples



dried under vacuum had analyses consistent with the formulation $[\text{Ln}(\text{MeCN})_9][\text{AsF}_6]_3$, but single crystals grown from acetonitrile had the compositions $[\text{La}(\text{MeCN})_9][\text{AsF}_6]_3 \cdot \text{MeCN}$ and $[\text{Sm}(\text{MeCN})_9][\text{AsF}_6]_3 \cdot 3\text{MeCN}$ (below) and contain very labile acetonitrile of crystallization. Homoleptic cationic complexes were also obtained with the tetrachloroaluminate(III) counter ion. Thus $[\text{Pr}(\text{MeCN})_9][\text{AlCl}_4]_3 \cdot \text{MeCN}$ **2** and $[\text{Yb}(\text{MeCN})_8][\text{AlCl}_4]_3$ **3** were obtained by reaction of LnCl_3 with AlCl_3 in acetonitrile [eqn. (2)]. The complexes **2** and **3** were



more conveniently prepared in a one-pot reaction between the lanthanoid metal, hexachloroethane and aluminum trichloride in acetonitrile under ultrasonication [eqn. (3)]. This reaction



was based on the successful synthesis of $\text{LnCl}_3(\text{thf})_n$ (thf = tetrahydrofuran) complexes by ultrasonication of lanthanoid elements and C_2Cl_6 in thf.⁸ Whilst the composition of **2** agreed with that reported by Shen and co-workers,⁶ that of **3** contrasts the reported (based on analyses) $[\text{Yb}(\text{MeCN})_9][\text{AlCl}_4]_3 \cdot \text{MeCN}$.⁶ In the present case the composition of the bulk solid (which was

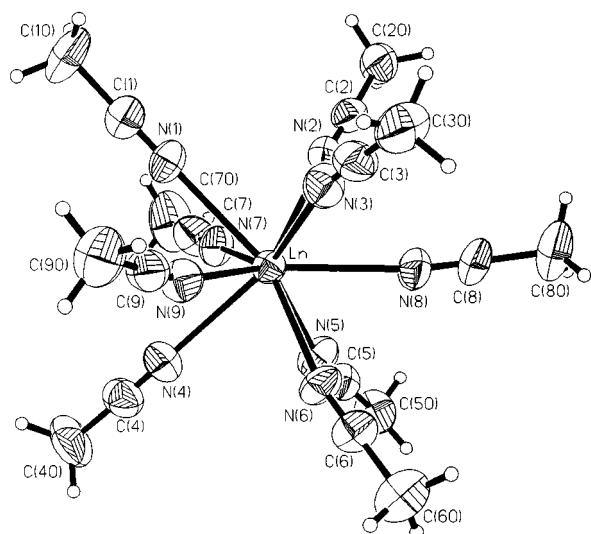


Fig. 1 Crystal structure of the cation of complexes **1a**, **1b** and **2** (showing **1a**).

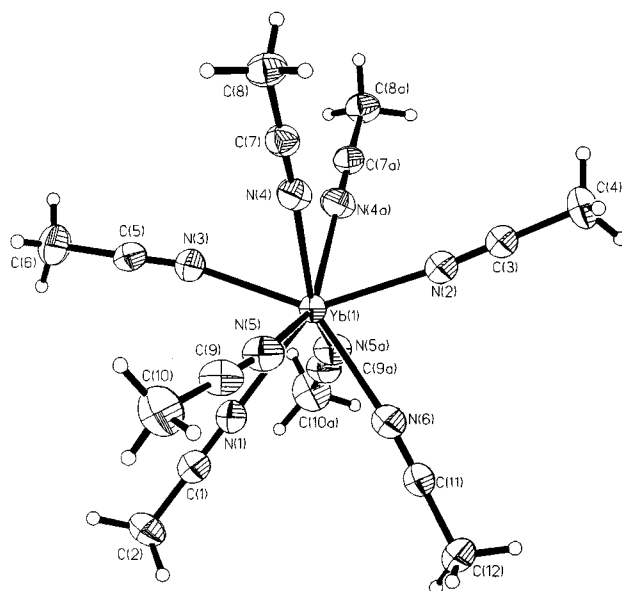


Fig. 2 Crystal structure of the cation of complex **3**.

washed with MeCN) was in agreement with that of the single crystals (which were not dried), hence it appears unlikely that a complex or solvate with more than 8 MeCN per ytterbium can be authenticated. In other cases, it is evident that variations in the washing and drying procedure are likely to affect the composition of the isolated solid. Changes in the number of co-ordinated MeCN ligands may require quite vigorous heating, as it requires replacement of co-ordinated MeCN by AsF_6^- or AlCl_4^- , both of which are very weak ligands, though known to co-ordinate to Ln^{3+} , e.g. in $[\{\text{Ln}(\text{OSO})_n(\text{AsF}_6)_3\}_x]^{7-}$ and $[\text{Ln}(\text{arene})(\text{AlCl}_4)_3]^{9-}$. An attempted simplification of reaction (3) by treating metals Yb and Al with C_2Cl_6 in acetonitrile failed owing to the lack of reactivity of aluminium. The new syntheses (1) and (3) appear to have general potential in the synthesis of homoleptic lanthanoid(III) complexes with neutral ligands and this is being explored.

The nine-co-ordinate (see below) complexes, **1a**, **1b** and **2**, and eight-co-ordinate **3** have similar intense $\nu(\text{CN})$ stretching absorptions[†] at higher frequencies than the free MeCN value (2250 cm^{-1}) as expected on co-ordination.¹⁰ The far-infrared spectra of **2** and **3** showed a strong band at $500\text{--}480\text{ cm}^{-1}$ attributable¹¹ to $\nu_{\text{asym}}(\text{Al-Cl})$ of AlCl_4^- , whilst intense absorption of the AsF_6^- salts at ca. 700 cm^{-1} is assigned to $\nu_{\text{asym}}(\text{As-F})$.¹¹

Crystal structures

A general structure for the cations of complexes **1a**, **1b** and **2** is displayed in Fig. 1 and that for the cation of **3** in Fig. 2. Selected bond distances and angles are given in Table 1.

In complexes **1a**, **1b** and **2** the homoleptic lanthanoid cations are nine-co-ordinate with the N-donor atoms in a tricapped trigonal prismatic array (best fit polyhedron¹²), two views of which are shown in Fig. 3. The cation of **1b** is very similar to that of $[\text{Sm}(\text{MeCN})_9][\text{AlCl}_4]_3 \cdot \text{MeCN}$ **4** with the largest difference being in the Sm-N-C angles {compare **1b** (Table 1) and **4** [164.1(6)–176.9(7), average 170.3°]; hence the cation structure is essentially unaffected by the anion. In addition, **2** are isostructural with **4**. For **1b** and **2** the Ln-N distances show little variation ($\leq 0.035\text{ \AA}$), with no significant difference between bonds to the capping (cap) and prismatic (pr) donor atoms. With **1a** there is a range of 0.075 \AA for La-N_{cap} , but smaller variations in La-N_{pr} , whilst $\langle \text{La-N}_{\text{cap}} \rangle \approx \langle \text{La-N}_{\text{pr}} \rangle$. Wide variation is observed between Ln-O_{cap} and Ln-O_{pr} ($\Delta = 10\text{ pm}$) for

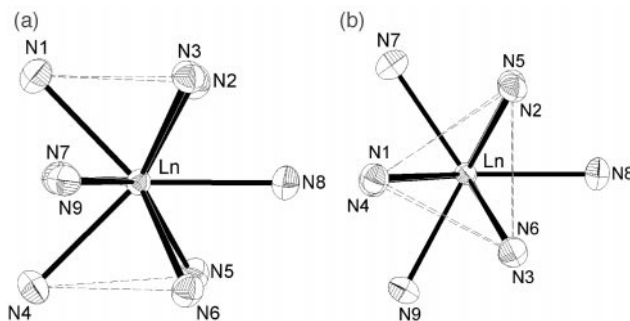


Fig. 3 The co-ordination sphere (a) parallel to the plane of the capping atoms N6N7N8 in complexes **1a**, **1b** and **2** (showing **2**), (b) showing a projection of the N-donor atoms onto the N7N8N9 plane.

trigonal prismatic $[\text{Ln}(\text{H}_2\text{O})_9]^{3+}$, and there is dependence on the counter ion owing to variations in hydrogen bonding.¹³ Subtraction of the ionic radii¹⁴ for nine-co-ordinate Ln^{3+} from $\langle \text{Ln-N} \rangle$ for **1a**, **1b**, **2** and **4** gives 1.41, 1.40, 1.41 and 1.41 \AA for the nitrogen “ionic radii” respectively. These distances correspond to similarly derived values (1.37–1.41 \AA) for a range of heteroleptic ytterbium(III) acetonitrile complexes,^{5c} and lie between values for 11-co-ordinate $[\text{LnCp}_3(\text{RCN})_2]$ ($\text{R} = \text{Me}$ or Et)¹⁵ (1.44–1.47 \AA) and ten-co-ordinate $[\text{LnCp}_3(\text{MeCN})]^{16}$ (1.35–1.38 \AA) organometallic derivatives. (Presumably in the last two cases, there is markedly increased steric repulsion on addition of the second nitrile ligand.) Rather longer values (1.50–1.54 \AA) are derived from $\langle \text{Ln-N} \rangle$ of $[\text{LnCl}_3(\text{H}_2\text{O})_2(\text{MeCN})_2]$ ($\text{Ln} = \text{Y}$ or Er).^{5a,b} Given the sterically undemanding ligands, the reasons for this lengthening are not obvious. Interestingly, the ammonia “nitrogen radius” derived from $\langle \text{La-N} \rangle$ of $[\text{La}(\text{NH}_3)_9][\text{Cu}(\text{S}_4)_2]^{17}$ is 1.50 \AA , and NH_3 and nitriles are considered to have the same steric co-ordination numbers.¹⁸ However, in homoleptic $[\text{Ln}(\text{L})_9]^{3+}$ ($\text{L} = \text{MeCN}$ or NH_3) complexes, the nitrile is significantly more strongly bound, as indicated by their “nitrogen radii” (1.41 and 1.50 \AA respectively). Ligand geometries and Ln-N-C angles show no unusual features apart from the variation in the angles with anion for **2** and **4**.

Complex **3** (Fig. 2) has dodecahedral eight-co-ordination for ytterbium and the donor atom polyhedron is as shown in Fig. 4. The range for Yb-N (0.055 \AA) lies between that (0.075 \AA) for **1a** and those of **1b**, **2** and **4**. Subtraction of the ionic radius for eight-co-ordinate Yb^{3+} (0.985 \AA)¹⁴ from $\langle \text{Yb-N} \rangle$ gives 1.41 \AA in

[†] There may be significant contribution to the intensity of one band from the combination $\delta_{\text{sym}}(\text{CH}_3) + \nu_{\text{sym}}(\text{C-C})$.¹⁰

Table 1 Selected bond distances (Å) and angles (°) for complexes **1a**, **1b**, **2** and **3**

	Ln = La 1a	Sm 1b	Pr 2	Yb 3
Ln–N(1)	2.648(7)	2.545(5)	2.590(3)	2.422(4)
Ln–N(2)	2.636(5)	2.530(5)	2.583(3)	2.378(5)
Ln–N(3)	2.616(6)	2.545(5)	2.595(4)	2.367(5)
Ln–N(4)	2.653(7)	2.521(5)	2.603(3)	2.411(3)
Ln–N(5)	2.616(4)	2.510(5)	2.584(3)	2.391(4)
Ln–N(6)	2.635(8)	2.537(5)	2.599(3)	2.388(5)
Ln–N(7)	2.575(9)	2.543(5)	2.591(3)	
Ln–N(8)	2.629(9)	2.546(5)	2.581(3)	
Ln–N(9)	2.650(5)	2.530(5)	2.594(3)	
N(1)–Ln–N(2)	73.88(19)	72.6(2)	77.86(10)	144.9(2)
N(1)–Ln–N(3)	79.5(3)	70.2(2)	73.00(13)	71.4(2)
N(1)–Ln–N(4)	88.9(2)	96.7(2)	90.92(12)	130.4(1)
N(1)–Ln–N(5)	139.2(2)	140.6(2)	136.97(11)	72.02(8)
N(1)–Ln–N(6)	140.48(18)	140.9(2)	137.81(9)	72.1(2)
N(1)–Ln–N(7)	70.9(3)	67.9(2)	68.30(11)	
N(1)–Ln–N(8)	134.52(19)	130.2(2)	134.07(12)	
N(1)–Ln–N(9)	68.1(2)	72.5(2)	67.86(9)	
N(2)–Ln–N(3)	77.1(2)	73.2(2)	76.99(11)	143.7(2)
N(2)–Ln–N(4)	137.0(2)	138.4(2)	139.82(11)	74.6(1)
N(2)–Ln–N(5)	94.71(16)	90.9(2)	82.40(11)	100.71(9)
N(2)–Ln–N(6)	136.7(1)	139.7(2)	138.19(11)	72.8(2)
N(2)–Ln–N(7)	67.7(2)	71.5(2)	69.72(11)	
N(2)–Ln–N(8)	67.7(2)	67.7(2)	69.18(10)	
N(2)–Ln–N(9)	131.45(15)	134.7(2)	136.54(12)	
N(3)–Ln–N(4)	138.95(18)	142.1(2)	136.57(10)	76.7(1)
N(3)–Ln–N(5)	137.1(3)	139.7(2)	138.19(11)	90.65(9)
N(3)–Ln–N(6)	84.4(3)	95.7(2)	92.24(13)	143.5(2)
N(3)–Ln–N(7)	138.8(2)	131.2(2)	132.96(11)	
N(3)–Ln–N(8)	69.2(2)	70.5(2)	69.14(11)	
N(3)–Ln–N(9)	67.41(19)	68.4(2)	68.19(13)	
N(4)–Ln–N(5)	72.92(19)	71.9(2)	80.12(11)	71.4(1)
N(4)–Ln–N(6)	80.0(3)	71.8(2)	72.82(13)	129.6(1)
N(4)–Ln–N(7)	69.5(2)	67.34(15)	70.28(11)	
N(4)–Ln–N(8)	136.13(19)	132.9(2)	134.74(11)	
N(4)–Ln–N(9)	71.71(17)	73.7(2)	68.38(13)	
N(5)–Ln–N(6)	73.1(1)	72.6(2)	79.46(11)	78.14(9)
N(5)–Ln–N(7)	68.6(3)	73.1(2)	69.06(11)	
N(5)–Ln–N(8)	68.8(2)	69.2(2)	69.62(11)	
N(5)–Ln–N(9)	133.84(16)	134.2(2)	141.05(12)	
N(6)–Ln–N(7)	136.3(3)	132.8(2)	134.60(12)	
N(6)–Ln–N(8)	69.2(2)	72.1(2)	69.23(11)	
N(6)–Ln–N(9)	72.4(2)	68.4(2)	69.96(9)	
N(7)–Ln–N(8)	113.5(3)	122.6(2)	124.22(11)	
N(7)–Ln–N(9)	122.9(3)	119.1(2)	117.60(12)	
N(8)–Ln–N(9)	123.6(2)	118.3(2)	118.13(12)	
				N(4)–Yb–N(4') 74.7(2)
				N(4)–Yb–N(5') 145.7(1)
				N(5)–Yb–N(5') 141.5(2)
N–C range	1.091(14)–1.154(15)	1.117(7)–1.158(8)	1.125(4)–1.138(5)	1.141(5)–1.19(5)
mean	1.115	1.13	1.13	1.13
Ln–N–C range	165.0(5)–178.1(9)	154.8(6)–169.7(5)	164.3(3)–175.6(3)	163.4(3)–179.6(4)
mean	170.1	163.0	170.0	172.5
N–C–C range	177.5(12)–179.9(12)	175.4(7)–179.4(7)	178.7(5)–179.5(5)	178.6(5)–179.9(5)
mean	178.4	177.5	179.2	179.5

agreement with values for **1a**, **1b**, **2** and **4**. This value is less than the 1.48–1.50 Å derived from ⟨Yb–N⟩ of [Yb(NH₃)₈][Cu(S₄)₂] \cdot *n*NH₃ (*n* = 1 or 2)¹⁷ and maintains the same relative size relationship between ⟨Ln–NCMe⟩ and ⟨Ln–NH₃⟩ distances as observed in the corresponding [Ln(L)₉]³⁺ (L = MeCN or NH₃) complexes (above). There are no exceptional features shown by the ligand geometries or the Yb–N–C angles, though ⟨Yb–N–C⟩ is marginally larger (>2°) than those of **1a**, **1b**, **2** and **4**. Anion ligand geometries for all structures conform to those reported for AsF₆[−] and AlCl₄[−], e.g. for [Ag(12-crown-4)₂][AsF₆]¹⁹ and [Al(MeCN)₅Cl][AlCl₄] \cdot MeCN.²⁰

The lanthanoid contraction asserts itself in [Ln(MeCN)_{*n*}]³⁺ complexes with a reduction in co-ordination number from *n* = 9 for Ln = La, Pr or Sm to *n* = 8 for Yb. This parallels the behaviour for [Ln(NH₃)_{*n*}]³⁺ as so far established, where *n* = 9 for La and 8 for Yb.¹⁷

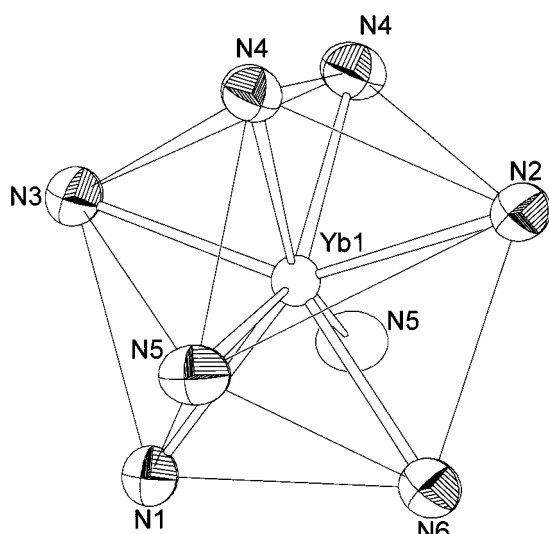
Experimental

The complexes [M(SO₂)_{*n*}(AsF₆)₃]_{*n*} were prepared according to the reported method,⁷ hexachloroethane and anhydrous aluminium chloride were purchased from Aldrich Chemical Co. and the aluminium chloride was freshly sublimed prior to use. Anhydrous ytterbium chloride was from Cerac Incorporated, Milwaukee, WI and used without further purification. Lanthanoid metals were from Rhone-Poulenc, Arizona. Acetonitrile was freshly distilled from calcium hydride prior to use. The lanthanoid complexes are moisture-sensitive and all preparations were conducted under an inert atmosphere (purified N₂ or Ar) involving conventional glove-box and Schlenk techniques. Microanalyses were performed by CMAS, Melbourne, Australia and by Microanalytical Laboratory Beller, Göttingen, Germany. Praseodymium was analysed by standard EDTA

Table 2 Crystal data and structure refinement for complexes **1a**, **1b**, **2** and **3**

	1a	1b	2	3
Empirical formula	C ₂₀ H ₃₀ As ₃ F ₁₈ LaN ₁₀	C ₂₄ H ₃₆ As ₃ F ₁₈ N ₁₂ Sm	C ₂₀ H ₃₀ Al ₃ Cl ₁₂ N ₁₀ Pr	C ₁₆ H ₂₄ Al ₃ Cl ₁₂ N ₈ Yb
<i>M</i>	1116.21	1209.76	1057.79	1013.82
<i>T</i> /K	173(2)	173(2)	173(2)	173(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁	<i>P</i> <i>n</i> <i>m</i>
<i>a</i> /Å	12.6740(10)	12.098(2)	13.0970(10)	25.281(4)
<i>b</i> /Å	20.534(2)	16.5100(10)	13.2510(10)	15.536(2)
<i>c</i> /Å	16.3120(10)	23.949(3)	14.2070(10)	10.370(2)
β /°	103.590(10)	103.950(10)	108.491(1)	
<i>U</i> /Å ³ , <i>Z</i>	4126.3(6), 4	4642.4(10), 4	2338.3(3), 2	4073.0(11), 4
<i>D_c</i> /Mg m ⁻³	1.797	1.731	1.502	1.644
μ /mm ⁻¹	3.532	3.491	1.811	3.170
Crystal size/mm	0.9 × 0.45 × 0.4	0.8 × 0.3 × 0.1	0.6 × 0.5 × 0.5	0.6 × 0.5 × 0.3
Reflections collected	10468	13029	12319	6094
<i>R</i> (int)	0.0464	0.0508	0.0339	0.0330
Data, restraints, parameters	5126, 198, 588	10544, 0, 573	10520, 1, 427	4848, 0, 212
Absorption correction	DIFABS	Semiempirical	—	DIFABS
<i>R</i> 1 [<i>I</i> > 2σ(<i>I</i>)]	0.0391	0.0419	0.0310	0.0340
<i>wR</i> 2 (all data)	0.0879	0.0949	0.0733	0.0788
Absolute structure parameter			0.257(8) ^a	
Largest difference peak, hole/e Å ⁻³	0.440, -0.489	0.783, -0.700	1.119, -0.912	1.415, -0.669
Variata	<i>b</i>	<i>c</i>	<i>a</i>	

Details in common: graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å); ω -2 θ scans; Siemens P4 diffractometer; refinement based on F^2 ; $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$. Programs used: SHELX 97,²² SHELXTL,²³ DIAMOND²⁴ and DIFABS.²⁵ ^a The inverted structure gave 0.73(1), so the structure was refined as a racemic twin. ^b Two of the three AsF₆ anions are disordered and were built from two slightly displaced octahedra. These two octahedra were assigned to an ideal geometry. ^c One AsF₆ anion is disordered and therefore it was refined as two octahedra with one common F-As-F axis.

**Fig. 4** The dodecahedral co-ordination sphere in complex **3**.

titration with addition of a 5% aqueous solution of sulfosalicylic acid to mask Al.²¹

Preparations

[M(MeCN)₉][AsF₆]₃, general method. Into a glass tube fitted with a Teflon valve was placed [M(SO₂)₃(AsF₆)₃] (1–2 mmol). Onto this, 20 ml of SO₂ (as solvent) and a tenfold excess of MeCN (90–180 mmol) were condensed from a vacuum line. The reaction mixture was warmed to ambient temperature and stirred for 6 h. Then the solvent and excess of the ligand were removed under vacuum (2–3 h, ambient temperature). The products remained behind in quantitative yield. Suitable crystals for structure analysis were obtained by slow diffusion of diethyl ether into solutions of the salts in MeCN at -30 °C.

[La(MeCN)₉][AsF₆]₃, **1a:** from [La(SO₂)₃(AsF₆)₃] (1.26 g, 1.4 mmol), colourless (1.53 g, 100%), mp 103 °C (decomp.) (Found: C, 20.6; H, 2.6; F, 31.4. C₁₈H₂₇As₃F₁₈LaN₃ requires C, 20.8; H, 2.6; F, 31.8%). Infrared (Nujol-Kel F, $\tilde{\nu}/\text{cm}^{-1}$): 3017w, 2950w, 2312s, 2282s, 1412m, 1371m, 1039m, 935m, 750w, 698vs, 666m

and 536w. Single crystals obtained as described above had the composition [La(MeCN)₉][AsF₆]₃·MeCN.

[Sm(MeCN)₉][AsF₆]₃, **1b:** from [Sm(SO₂)₃(AsF₆)₃] (1.0 g, 1.1 mmol), faint yellow (1.25 g, 100%), mp 125 °C (decomp.) (Found: C, 19.4; H, 2.6; F, 29.7. C₁₈H₂₇As₃F₁₈N₃Sm requires C, 19.9; H, 2.5; F, 31.4%). Infrared (Nujol-Kel F, $\tilde{\nu}/\text{cm}^{-1}$): 3015w, 2950w, 2314s, 2285s, 1415m (br), 1372m, 1039m, 937m, 786w, 699vs, 667m and 540w. Single crystals obtained as above had the composition [Sm(MeCN)₉][AsF₆]₃·3MeCN.

[Pr(MeCN)₉][AlCl₄]₃·MeCN **2. Method 1.** Aluminium chloride (0.81 g, 6.0 mmol) and PrCl₃ (0.50 g, 2.0 mmol) were placed in a glass vessel fitted with a Teflon valve. Onto these compounds, MeCN (20 ml) was condensed from a vacuum line. The reaction mixture was heated under reflux until a clear solution resulted. After removal of the solvent under vacuum complex **2** remained as a faint green crystalline solid (2.1 g, 100%) (Found: C, 21.6; H, 3.0; Cl, 40.0. C₂₀H₃₀Al₃Cl₁₂N₁₀Pr requires C, 22.7; H, 2.9; Cl, 40.2%). Infrared (Nujol-Kel-F, $\tilde{\nu}/\text{cm}^{-1}$): 3000m, 2935s, 2306s, 2277s, 2251w, 1408m, 1367m, 1036m, 937m and 782w.

Method 2. Acetonitrile (30 ml) was added under N₂ to a mixture of praseodymium chips (0.28 g, 2.0 mmol), AlCl₃ (0.80 g, 6.0 mmol), and C₂Cl₆ (0.76 g, 3.2 mmol). An exothermic reaction occurred after sonication for 3 h, a clear light green solution was obtained and all metal had been consumed. The solvent was removed *in vacuo* to give a quantitative yield of crystalline light green complex **2**, decomp. >300 °C (Found: Pr, 13.1. C₂₀H₃₀Al₃Cl₁₂N₁₀Pr requires Pr, 13.3%). Infrared (Nujol-KBr plates, $\tilde{\nu}/\text{cm}^{-1}$): 2309s, 2281s, 1155m, 1036m, 937m, 782w and 492vs.

[Yb(MeCN)₈][AlCl₄]₃, **3. Method 1.** Acetonitrile (30 ml) was added to a mixture of anhydrous YbCl₃ (0.28 g, 1.0 mmol), and AlCl₃ (0.40 g, 3.0 mmol), resulting in an exothermic reaction and a cloudy mixture. This was stirred overnight, the fine precipitate allowed to settle, and the solution decanted by a cannula. The solvent volume was then reduced *in vacuo* and allowed to stand at -40 °C overnight whereupon colourless crystals of complex **3** deposited (1.5 g, 74%). The infrared spectrum was in agreement with that of the analytically pure product obtained from method 2.

Method 2. Ytterbium metal (0.35 g, 2.0 mmol), AlCl₃ (0.80 g, 6.0 mmol) and hexachloroethane (0.76 g, 3.2 mmol) were placed in a Schlenk flask. Acetonitrile (30 ml) was added and an exothermic reaction took place. The solution turned red and the mixture was then sonicated until all traces of metal had been consumed (*ca.* 12 h). The solution was then decanted by cannula to remove a faint precipitate, which settled, and the solvent volume was reduced *in vacuo* until traces of material began to precipitate. After standing at -40 °C overnight large colourless, prismatic crystals of complex **3** deposited, were collected and washed with cold acetonitrile (1.7 g, 84% based on Yb metal) (Found: C, 19.1; H, 2.6; N, 11.3. C₁₆H₂₄Al₃Cl₁₂N₈Yb requires C, 19.1; H, 2.4; N, 11.1%). Infrared (Nujol–AgCl plates, $\tilde{\nu}/\text{cm}^{-1}$): 2314s, 2285s, 1155w, 1034m, 940m, 792w and 484s.

Crystallography

Details of the crystal data and the structure solutions are given in Table 2. All figures show the atoms at the 50% probability level of the thermal vibration ellipsoids.

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See <http://www.rsc.org/suppdata/dt/1998/3887/> for crystallographic files in .cif format.

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