Functionalizable Schiff Base Complexes of Lanthanum. Synthesis and Crystal Structures of $[La_2L_4(thf)_2(\mu\text{-}Cl)_2]$ and $[La(L')_2(HL')Cl]$ [HL = *N*-(2,4,6-trimethylphenyl)salicylideneimine, HL′ = *N*-(2-dimethylaminoethyl)-salicylideneimine, and thf = tetrahydrofuran]†

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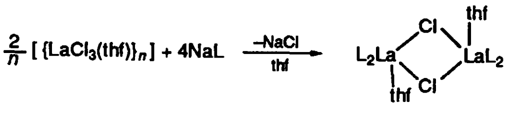
The reaction of $[\{LaCl_3(thf)\}_n]$ (thf = tetrahydrofuran) under anhydrous conditions with the sodium salt of a bi- or tri-dentate Schiff base derived from salicylaldehyde and 2,4,6-trimethylaniline [HL = *N*-(2,4,6-trimethylphenyl)salicylideneimine] or *N*,*N*-dimethylethylenediamine [HL′ = *N*-(2-dimethylaminoethyl)salicylideneimine] led to the isolation of the corresponding monochloro derivatives, $[La_2L_4(thf)_2(\mu\text{-}Cl)_2]$ and $[La(L')_2(HL')Cl]$. Their structures have been elucidated by *X*-ray crystallography.

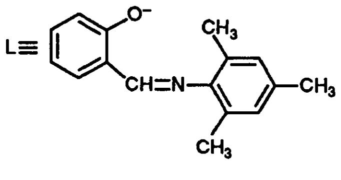
Some of the characteristics of lanthanide Schiff base complexes have received little attention, as evident from the recent and comprehensive reviews.[1,2] In particular, syntheses in non-aqueous solution, leading to functionalizable compounds that can be used in reactivity studies, have been disregarded. Recently, the organometallic chemistry of the lanthanides has developed extensively, but has been confined to cyclopentadienyl and alkoxo ancillary ligands.[3] Schiff bases can provide as good a, or sometimes better, structurally and electronically flexible co-ordination environment. This parallels some of the developments of the early transition metals, for which the starting materials[4] and organic derivatization[5] have been reported.

A prerequisite is the use of anhydrous chlorides and bulky ligands to ensure solubility in organic solvents.[1,2] This paper describes the synthesis of a mono- and a di-nuclear Schiff base complex of lanthanum and their structure determinations.



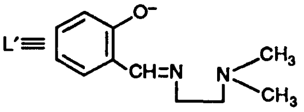
(1)

(1)



$$\frac{1}{n}[\{LaCl_3(thf)\}_n] + 2NaL' \xrightarrow{-NaCl} \xrightarrow{+HL'} [La(L')_2(HL')Cl] \quad (2)$$

(2)



Results and Discussion

Anhydrous $LaCl_3$ was converted into the crystalline tetrahydrofuran (thf) derivative $[\{LaCl_3(thf)\}_n]$ by a lengthy extraction with thf. It was then treated with the sodium salt of a bi- or tri-dentate Schiff base according to reactions (1) and (2).

Reaction (1), carried out in thf, gave a mixture of (1) and NaCl. The stoicheiometry should be strictly controlled in order to avoid the complete substitution of the chlorides by three Schiff bases. Complex (1) was isolated from the mixture by extracting it with thf for 1 week. The structure of (1) was solved by an *X*-ray structure analysis (see later). Reaction (2), carried out in thf, gave complex (2) independently of the stoicheiometric ratio used. However, using the stoicheiometry required by the product gave a yield of 70% (see Experimental section). Extraction with thf for 1 week gave the compound free of NaCl.

The molecular structure of (1) is shown in Figure 1(*a*). The two portions of the dimer [denoted by (*a*) and (*b*)] are related by a pseudo centre of symmetry. The mean values quoted in Figure 1 are calculated between the corresponding pseudo-centrosymmetric values. Each lanthanum is seven-co-ordinate; the co-ordination includes two bridging chlorines,[6] the oxygen and nitrogen atoms from two bidentate Schiff base ligands, and the oxygen atom from a thf molecule. The co-ordination polyhedron is rather irregular, but can be viewed as a distorted monocapped trigonal prism [see Figure 1(*b*)]. The two prisms in the dimer are sharing the Cl(1)–Cl(2) edge. The La–O, La–N and La–Cl bond distances fall in the normal range for complexes in which the metal has the same co-ordination number.[6,7] The structural parameters related to the Schiff base ligands are in the usual range.[8]

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† Di-μ-chloro-bis{tetrahydrofuranbis[*N*-(2,4,6-trimethylphenyl)salicylideneiminato]lanthanum(III)} and chlorobis[*N*-(2-dimethylaminoethyl)salicylideneiminato][*N*-(2-dimethylaminoethyl)salicylideneimine]lanthanum(III).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

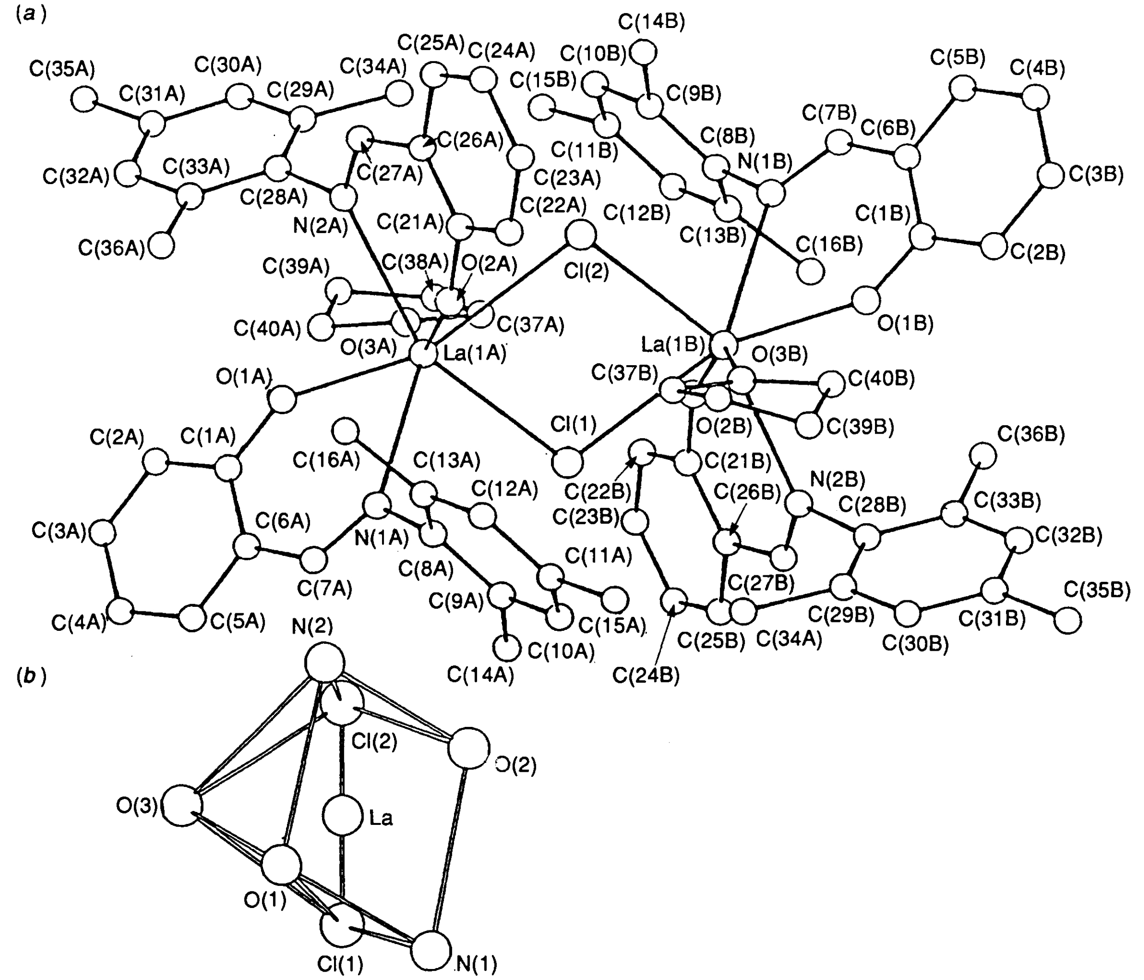

Figure 1. A view of the dimer (*a*) and the metal co-ordination polyhedron (*b*) in complex (**1**). Bond distances (Å): La(1A)–Cl(1), 2.865(5); La(1A)–Cl(2), 2.996(6); La(1A)–O(1A), 2.295(11); La(1A)–O(2A), 2.259(11); La(1A)–O(3A), 2.588(15); La(1A)–N(1A), 2.788(18); La(1A)–N(2A), 2.659(16); La(1B)–Cl(1), 2.987(6); La(1B)–Cl(2), 2.845(5); La(1B)–O(1B), 2.301(18); La(1B)–O(2B), 2.284(12); La(1B)–O(3B), 2.636(14); La(1B)–N(1B), 2.786(20); La(1B)–N(2B), 2.716(17). Bond angles (°): O(2A)–La(1A)–N(2A), 68.8(5); O(1A)–La(1A)–N(1A), 67.0(5); Cl(1)–La(1A)–Cl(2), 73.0(2); O(2B)–La(1B)–N(2B), 68.8(5); O(1B)–La(1B)–N(1B), 67.3(6); Cl(1)–La(1B)–Cl(2), 73.5(2); La(1A)–Cl(1)–La(2), 106.6(2); La(1A)–Cl(2)–La(2), 106.9(2)

Lanthanum is eight-co-ordinate in complex (**2**), as revealed by the *X*-ray structure analysis. The co-ordination involves a chlorine atom, the oxygen and nitrogen atoms of two tridentate Schiff base ligands, and the oxygen atom of a protonated Schiff base acting as a monodentate ligand [Figure 2(*a*)]. The co-ordination geometry is highly irregular, but can be viewed as a distorted bicapped trigonal prism [see Figure 2(*b*)]. The main structural features are: (*i*) the La–O bond distances involving the tridentate Schiff base ligands [mean 2.432(2) Å] are significantly shorter than those involving the monodentate one [2.483(4) Å] and are very close to those observed in complex (**1**) in spite of the different lanthanum co-ordination number;[6,9] (*ii*) the O(2) oxygen atom of the protonated Schiff base is strongly hydrogen bonded to the N(3) iminic nitrogen: O(2)–N(3), 2.698(9); O(2)–H[O(2)], 0.93; H[O(2)] ··· N(3), 2.02 Å; O(2)–H[O(2)] ··· N(3), 128°; (*iii*) the La–N bond distances fall in a large range, 2.669(6)—2.872(7) Å, the longest bonds involving the aminic nitrogen; (*iv*) all the other structural parameters are in the usual range.[6,8,9]

Experimental

All the reactions were carried out under an atmosphere of purified nitrogen. Solvents were dried and distilled before use by standard methods. The Schiff bases (HL and HL′) were synthesized from the corresponding amine and salicylaldehyde in the presence of a catalytic amount of sulphuric acid followed by azeotropic distillation of water using benzene. The ^1H n.m.r. spectra were recorded with a Bruker AC 200 instrument.

Preparation of [{LaCl$_3$(thf)}$_n$].—The compound LaCl$_3$·7H$_2$O (50.0 g, 138 mmol) was refluxed in SOCl$_2$ (350 cm^3) for 2 d. The resulting solid was washed with n-hexane and toluene several times, and then extracted with thf for 6 weeks. A white microcrystalline solid formed (39.0 g) which was dried *in vacuo* (Found: C, 14.90; H, 2.65; Cl, 33.80; La, 43.65. C$_4$H$_8$Cl$_3$LaO requires C, 15.15; H, 2.50; Cl, 33.50; La, 43.80%).

Synthesis of [La$_2$L$_4$(thf)$_2$(μ-Cl)$_2$] (**1**).—The Schiff base HL (5.35 g, 22.3 mmol) was dissolved in thf (180 cm^3) and NaH (0.54 g, 22.4 mmol) was added. The solution was refluxed for 2 h and then filtered to remove a small amount of solid. The compound [{LaCl$_3$(thf)}$_n$] (3.56 g, 11.23 mmol) was added. The suspension obtained was refluxed for 2 d and then extracted for 1 week with thf in order to remove NaCl. The extracted solution, cooled to 0 °C gave yellow crystals of (**1**) (70%). Two weakly bonded thf molecules of crystallization were lost on

Table 1. Fractional atomic co-ordinates (× 10^4) with estimated standard deviations in parentheses for complex (**1**)*

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
La(1A)	710(1)	3 773(1)	2 754(1)	C(11A)	3 280(8)	4 759(6)	1 643(6)
La(1B)	−631(1)	5 707(1)	2 365(1)	C(12A)	3 564(8)	4 367(6)	2 140(6)
Cl(1)	−174(4)	4 593(3)	1 791(2)	C(13A)	3 001(8)	3 921(6)	2 226(6)
Cl(2)	230(4)	4 888(3)	3 322(2)	C(21A)	2 572(8)	4 315(7)	3 861(5)
O(1A)	595(8)	2 745(5)	2 534(6)	C(22A)	3 252(8)	4 730(7)	3 918(5)
O(2A)	2 051(8)	4 128(6)	3 301(6)	C(23A)	3 789(8)	4 915(7)	4 491(5)
O(3A)	−872(9)	3 501(6)	2 698(6)	C(24A)	3 647(8)	4 685(7)	5 005(5)
N(1A)	1 552(9)	3 435(7)	1 941(7)	C(25A)	2 967(8)	4 271(7)	4 948(5)
N(2A)	1 187(10)	3 377(7)	3 890(7)	C(26A)	2 430(8)	4 086(7)	4 376(5)
O(1B)	−537(11)	6 743(8)	2 559(7)	C(27A)	1 804(16)	3 604(11)	4 375(11)
O(2B)	−1 984(8)	5 323(6)	1 839(6)	C(28A)	703(7)	2 888(5)	4 046(5)
O(3B)	973(8)	5 977(8)	2 402(7)	C(29A)	−5(7)	3 016(5)	4 240(5)
N(1B)	−1 494(10)	6 055(8)	3 163(7)	C(30A)	−507(7)	2 538(5)	4 347(5)
N(2B)	−1 153(10)	6 067(7)	1 190(7)	C(31A)	−301(7)	1 932(5)	4 260(5)
C(14A)	990(13)	4 172(11)	812(9)	C(32A)	407(7)	1 804(5)	4 067(5)
C(15A)	3 926(16)	5 256(12)	1 569(13)	C(33A)	910(7)	2 282(5)	3 959(5)
C(16A)	3 313(13)	3 444(10)	2 758(9)	C(1B)	−493(10)	7 180(7)	2 952(6)
C(34A)	−296(15)	3 679(10)	4 308(11)	C(2B)	−58(10)	7 723(7)	2 917(6)
C(35A)	−840(15)	1 427(10)	4 387(11)	C(3B)	49(10)	8 177(7)	3 355(6)
C(36A)	1 719(14)	2 133(11)	3 810(12)	C(4B)	−279(10)	8 086(7)	3 829(6)
C(37A)	−1 608(13)	3 963(12)	2 573(12)	C(5B)	−714(10)	7 543(7)	3 864(6)
C(38A)	−2 403(16)	3 535(16)	2 563(15)	C(6B)	−821(10)	7 090(7)	3 426(6)
C(39A)	−2 126(16)	2 920(11)	2 690(16)	C(7B)	−1 380(14)	6 572(11)	3 480(10)
C(40A)	−1 218(15)	2 852(10)	2 663(11)	C(8B)	−2 107(8)	5 622(6)	3 264(6)
C(14B)	−977(14)	5 324(12)	4 285(9)	C(9B)	−1 867(8)	5 232(6)	3 764(6)
C(15B)	−3 959(16)	4 276(11)	3 456(12)	C(10B)	−2 467(8)	4 807(6)	3 839(6)
C(16B)	−3 245(14)	6 072(12)	2 326(10)	C(11B)	−3 306(8)	4 772(6)	3 414(6)
C(34B)	334(15)	5 738(12)	780(10)	C(12B)	−3 546(8)	5 161(6)	2 914(6)
C(35B)	769(18)	8 077(13)	568(11)	C(13B)	−2 947(8)	5 587(6)	2 839(6)
C(36B)	−1 722(15)	7 320(11)	1 283(11)	C(21B)	−2 546(8)	5 177(7)	1 295(5)
C(37B)	1 704(15)	5 561(11)	2 521(12)	C(22B)	−3 244(8)	4 791(7)	1 271(5)
C(38B)	2 480(16)	5 955(13)	2 581(13)	C(23B)	−3 848(8)	4 626(7)	714(5)
C(39B)	2 160(16)	6 546(13)	2 278(12)	C(24B)	−3 754(8)	4 845(7)	180(5)
C(40B)	1 270(15)	6 635(11)	2 375(10)	C(25B)	−3 056(8)	5 231(7)	204(5)
C(1S)	8 811(22)	3 097(18)	885(16)	C(26B)	−2 452(8)	5 397(7)	761(5)
C(2S)	8 109(26)	3 571(16)	515(19)	C(27B)	−1 785(14)	5 850(9)	733(9)
C(3S)	7 304(21)	3 262(17)	521(19)	C(28B)	−680(9)	6 568(6)	1 012(6)
O(1S)	7502(17)	2 621(13)	543(14)	C(29B)	33(9)	6 439(6)	824(6)
C(4S)	8 372(21)	2 495(17)	814(17)	C(30B)	505(9)	6 918(6)	684(6)
C(1A)	566(9)	2 318(6)	2 116(5)	C(31B)	264(9)	7 524(6)	733(6)
C(2A)	130(9)	1 771(6)	2 136(5)	C(32B)	−449(9)	7 653(6)	921(6)
C(3A)	23(9)	1 331(6)	1 685(5)	C(33B)	−921(9)	7 175(6)	1 061(6)
C(4A)	352(9)	1 439(6)	1 215(5)	C(5S)	3 406(51)	2 028(33)	782(34)
C(5A)	788(9)	1 986(6)	1 195(5)	C(6S)	3 687(32)	1 366(25)	944(21)
C(6A)	895(9)	2 426(6)	1 646(5)	C(7S)	3 146(39)	968(27)	564(27)
C(7A)	1 433(12)	2 940(9)	1 605(8)	C(8S)	2 805(39)	1 352(28)	−6(26)
C(8A)	2 153(8)	3 866(6)	1 816(6)	C(9S)	2 595(36)	2 007(25)	295(24)
C(9A)	1 869(8)	4 258(6)	1 319(6)	C(10S)	2 804(51)	1 803(35)	918(32)
C(10A)	2 432(8)	4 704(6)	1 232(6)	C(11S)	2 271(48)	1 396(37)	312(35)

* Site occupation factors for the disordered atoms: 1.0000 for the pivot atom of thf solvate, C(9S), and $\frac{2}{3}$ for C(5S), C(6S), C(7S), C(8S), C(10S), and C(11S).

drying the solid *in vacuo* (Found: C, 60.00; H, 5.70; Cl, 4.85; N, 3.75. $C_{72}H_{80}Cl_2La_2N_4O_6$ requires C, 59.80; H, 5.55; Cl, 4.90; N, 3.85%). Proton n.m.r. in CD_2Cl_2: δ 7.91 (s, 1 H), 6.75 (m, 4 H), 2.27 (s, 3 H), 1.88 (s, 6 H), and 1.82 (m, 4 H).

Synthesis of $[La(L')_2(HL')Cl]$ (**2**).—To a thf (100 cm^3) solution of the Schiff base HL′ (2.24 g, 11.65 mmol) NaH (0.28 g, 11.63 mmol) was added and the evolution of H_2 was observed. The suspension was refluxed for 8 h. Then HL′ (1.12 g, 5.82 mmol) was added, followed by $[\{LaCl_3(thf)\}_n]$ (1.84 g, 5.79 mmol). The suspension was refluxed for 4 d and then extracted for 1 week with thf. Complex (**2**) is very soluble in thf and it crystallized as a yellow solid (69%) upon concentration to 50 cm^3 and addition of n-hexane (100 cm^3). Complex (**2**) can form in different yields independently of the La–L′ and L′–NaH ratios. The best synthesis is that reported above (Found: C, 52.80; H, 6.15; Cl, 4.85; N, 11.10. $C_{33}H_{46}ClLaN_6O_3$ requires C, 52.85; H, 6.15; Cl, 4.75; N, 11.20%). With low yields of (**2**) we were unable to characterise any other compound. Proton n.m.r. in CD_2Cl_2: δ 12.90 (br s, 1 H), 8.15 (s, 2 H), 8.03 (s, 1 H), 7.17 (br s, 6 H), 6.50 and 6.46 (br s, 6 H), 2.33 [a large multiplet (24 H) with two distinct singlets at δ 2.40 and 2.26].

Crystal Structure Determinations.—Crystals of (**1**) and (**2**) were sealed in capillaries under nitrogen because of their high sensitivity to moisture.

Crystal data for complex (**1**). $C_{72}H_{80}Cl_2La_2N_4O_6{\cdot}2C_4H_8O$, $M = 1\,558.46$, monoclinic, space group $P2_1/n$, $a = 16.185(2)$, $b = 21.813(2)$, $c = 23.456(2)$ Å, $\beta = 109.40(1)°$, $U = 7\,811(1)$ Å^3, $Z = 4$, $D_c = 1.325$ g cm^{-3}, $F(000) = 800$, Mo-K_α radiation

Table 2. Fractional atomic co-ordinates (× 10^4) with e.s.d.s in parentheses for complex (**2**)*

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
La	2 224.6(2)	2 459.9(6)	1 757.1(2)	C(25)	3 445(3)	3 480(5)	4 622(2)
Cl	1 368(1)	372(2)	2 265(1)	C(26)	3 026(3)	2 850(5)	4 087(2)
O(1)	1 357(3)	2 999(5)	809(3)	C(27)	2 491(5)	1 895(8)	4 237(4)
N(1)	2 203(4)	662(6)	849(3)	C(28)	1 539(5)	155(8)	4 018(5)
N(2)	3 547(4)	688(6)	1 994(3)	C(29)	1 891(7)	−1 088(10)	3 925(6)
C(1)	871(3)	2 493(6)	311(2)	O(3)	3 315(3)	3 259(5)	1 250(3)
C(2)	185(3)	3 176(6)	46(2)	N(5)	2 354(4)	4 984(6)	1 914(3)
C(3)	−336(3)	2 689(6)	−480(2)	N(6)	866(4)	3 600(8)	2 207(4)
C(4)	−170(3)	1 518(6)	−742(2)	C(41)	3 809(3)	4 251(5)	1 216(3)
C(5)	516(3)	835(6)	−477(2)	C(42)	4 515(3)	4 075(5)	915(3)
C(6)	1 036(3)	1 322(6)	50(2)	C(43)	5 035(3)	5 089(5)	841(3)
C(7)	1 707(5)	508(8)	319(4)	C(44)	4 848(3)	6 279(5)	1 068(3)
C(8)	2 799(5)	−373(8)	1 015(4)	C(45)	4 142(3)	6 455(5)	1 369(3)
C(9)	3 607(5)	150(7)	1 334(4)	C(46)	3 622(3)	5 441(5)	1 443(3)
C(10)	3 433(6)	−299(9)	2 469(5)	C(47)	2 896(6)	5 741(8)	1 753(5)
C(11)	4 308(5)	1 400(10)	2 213(5)	C(48)	1 700(6)	5 565(10)	2 232(6)
O(2)	2 732(3)	2 611(6)	2 942(2)	C(49)	886(7)	4 934(10)	1 993(5)
N(3)	2 058(4)	1 179(6)	3 817(4)	C(50)	865(6)	3 503(12)	2 911(5)
N(4)	2 700(5)	−1 302(8)	4 236(5)	C(51)	105(5)	3 002(10)	1 884(5)
C(21)	3 143(3)	3 198(5)	3 452(2)	C(30)	2 636(10)	−1 342(16)	4 947(9)
C(22)	3 679(3)	4 176(5)	3 350(2)	C(31)	3 093(11)	−2 383(21)	4 009(10)
C(23)	4 098(3)	4 806(5)	3 885(2)	C(30′)	3 330(29)	−2 071(40)	4 584(25)
C(24)	3 982(3)	4 458(5)	4 521(2)	C(31′)	2 637(38)	−2 432(69)	3 586(35)

* Site occupation factors for the disordered methyl carbons C(30) and C(31) are 0.78 and 0.22 for the unprimed and primed atoms respectively.

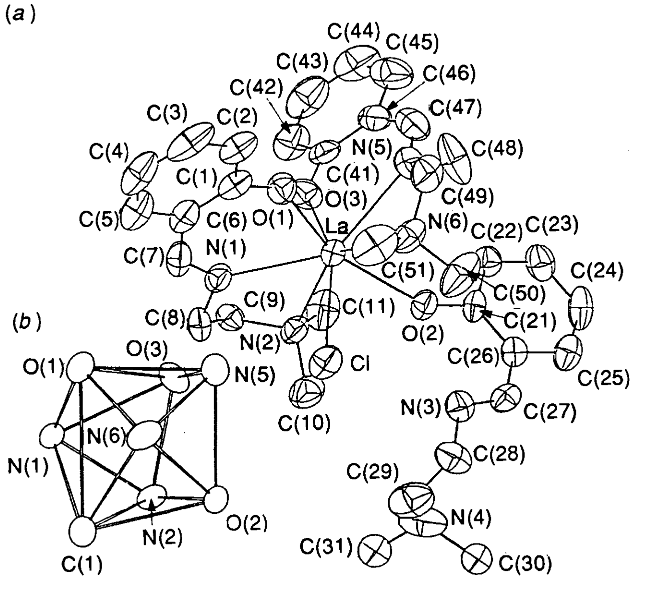

Figure 2. A view of complex (**2**) (*a*) and the metal co-ordination polyhedron (*b*) [disorder affecting the methyl carbons C(30) and C(31) not represented]. Bond distances (Å): La–Cl, 2.892(2); La–O(1), 2.342(6); La–O(2), 2.483(4), La–O(3), 2.342(6); La–N(1), 2.669(6); La–N(2), 2.872(7); La–N(5), 2.706(7); La–N(6), 2.799(8). Bond angles (°): O(1)–La–N(1), 68.8(2); N(1)–La–N(2), 66.1(2); O(3)–La–N(5), 69.0(2); N(5)–La–N(6), 65.5(2)

(λ = 0.710 69 Å), μ(Mo-K_α) = 12.01 cm^{-1}, crystal dimensions 0.29 × 0.37 × 0.40 mm.

The structure was solved by the heavy-atom method (Patterson and Fourier synthesis) and refined by full-matrix least squares. One of the two thf solvent molecules was found to be disordered. Refinement was anisotropic only for the metal atoms, the co-ordinating atoms, the methyl carbons, and the atoms of the non-disordered thf molecules. For 4 845 unique observed structure amplitudes [$I > 3\sigma(I)$, not corrected for absorption] collected at room temperature on a Philips PW 1 110 diffractometer in the range $6 < 2\theta < 47°$ the structure refined to an *R* of 0.089 (*R′* = 0.086). The number of refined parameters was 482. Atomic co-ordinates for (**1**) are listed in Table 1.

Crystal data for complex (**2**). $C_{33}H_{46}ClLaN_6O_3$, *M* = 749.1, monoclinic, space group $P2_1/c$, *a* = 16.454(1), *b* = 10.622(1), *c* = 20.574(2) Å, β = 97.08(1)°, *U* = 3568.4(5) $Å^3$, *Z* = 4, D_c = 1.394 g cm^{-3}, *F*(000) = 384, Mo-K_α radiation (λ = 0.710 69 Å), μ(Mo-K_α) = 13.15 cm^{-1}; crystal dimensions 0.19 × 0.45 × 0.45 mm.

The structure was solved by the heavy-atom method (Patterson and Fourier synthesis) and refined by full-matrix least squares anisotropically for all atoms excepting the methyl carbons C(30) and C(31) which were found to be disordered over two positions. For 2 803 unique observed structure amplitudes [$I > 3\sigma(I)$] collected at room temperature on a Philips PW 1100 diffractometer in the range $6 < 2\theta < 47°$ the structure refined to an *R* value of 0.039 (*R′* = 0.038). The number of refined parameters was 389. Most of the hydrogen atoms were located in a difference Fourier map and introduced as fixed contributors in the final stage of refinement. For both complexes the aromatic rings were refined as regular hexagons. All calculations were carried out using SHELX 76.[10] Atomic co-ordinates for (**2**) are listed in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

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