cis- and *trans*-Dichloro Chelate Complexes of Niobium(IV): Synthesis and Structure of *trans*-Dichloro[*NN'*-ethylenebis(acetylacetonylideneiminato)(2−)]niobium(IV) and *cis*-Dichloro{7,16-dihydro-6,8,15,17-tetramethyldibenzo[*b*,*i*][1,4,8,11]tetra-azacyclotetradecinato(2−)}niobium(IV)–Acetonitrile (1/2)†

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The reaction of the sodium or potassium salts of H_2acen [H_2acen = *NN*-ethylenebis(acetylacetonylideneimine)] with $NbCl_4$·2thf (thf = tetrahydrofuran) led to *trans*-[Nb(acen)Cl_2] (**1**), while reaction with the lithium salt of H_2L (H_2L = 7,16-dihydro-6,8,15,17-tetramethydibenzo[*b*,*i*][1,4,8,11]tetra-azacyclotetradecine) gave *cis*-[Nb(L)Cl_2] (**2**). Both compounds are paramagnetic [$\mu_{eff.}$ = 1.80 at 292 K (**1**), 1.94 B.M. at 293 K (**2**)] and contain a single unpaired electron. The structures of (**1**) and (**2**) have been established by *X*-ray diffraction methods. In complex (**1**), the acen ligand displays the usual square-planar geometry and the two chlorine atoms are *trans* [Cl–Nb–Cl, 178.5(1) and 178.6(1)° for the two independent molecules in the structure]. In complex (**2**) the macrocycle L has the usual saddle-shaped conformation with the two chlorines *cis* [Cl–Nb–Cl, 81.8(1)°]. Regardless of the isomeric arrangement the Nb–Cl distances are very close in the two complexes [Nb–Cl(av.), 2.434(4) (**1**); 2.452(2) (**2**) Å].

Niobium has an extensive organometallic chemistry,[1] but an extremely limited co-ordination chemistry with polydentate acyclic and macrocyclic ligands.[2] However, various studies on porphyrin derivatives have been reported.[3] Moreover, ancillary ligands used in the organometallic chemistry of niobium are mainly limited to cyclopentadienyls and phosphines.[4] In this context we wish to establish a synthetic approach to easily accessible niobium compounds which can serve as a source of electron-rich complexes and organometallic derivatives.

A class of ancillary ligands different from those mentioned above has the potential use of stabilizing a wide range of oxidation states and organometallic functionalities, although their use in the chemistry of early transition metals is so far very limited. Polydentate acyclic and macrocyclic ligands can be used to this purpose.[4] A few examples have appeared in which quadridentate acyclic and macrocyclic Schiff-base ligands led to the stabilization of titanium–,[5] vanadium–,[6] and zirconium–carbon[7] bonds. A further aspect to be considered for those metals normally requiring six-co-ordination is that a quadridentate ligand can impose either a *cis* or a *trans* arrangement of the two potential co-ordination sites or functionalities left. The mutual arrangement may be crucial for the reactivity at the metal site. This paper deals with the synthesis and structural determination of a *cis*-dichloro and a *trans*-dichloro niobium bonded to a quadridentate ligand. Both compounds are promising starting materials for producing niobium organometallic derivatives and complexes in a low oxidation state.

Experimental

All syntheses were carried out under an atmosphere of purified nitrogen. Solvents were purified and dried by standard methods. Infrared spectra were recorded using a Perkin-Elmer 883 instrument and magnetic measurements made using a Faraday balance. The compounds 7,16-dihydro-6,8,15,17-tetramethyldibenzo[*b*,*i*][1,4,8,11]tetra-azacyclotetradecine (H_2L)[8,9] and $NbCl_4$·2thf (thf = tetrahydrofuran)[10] were prepared by published procedures.

Synthesis of [Nb(acen)Cl_2] (**1**).—*NN'*-Ethylenebis(acetylacetonylideneimine) (H_2acen) (8.90 g, 39.7 mmol) was dissolved in thf (300 cm^3) and then treated with NaH (1.90 g, 79.2 mmol). The suspension was stirred for 1 h, refluxed overnight, and $NbCl_4$·2thf (15.0 g, 39.6 mmol) added. The resulting red-purple suspension was refluxed for 2 h. NaCl was removed by extracting the solid with thf (yield *ca.* 60%) (Found: C, 37.55; H, 4.75; N, 7.20. $C_{12}H_{18}Cl_2N_2NbO_2$ requires C, 37.30; H, 4.65; N, 7.25%); $\mu_{eff.}$ = 1.80 B.M. at 292 K. The same reaction can be carried out using KH to form the potassium salt of the ligand.

Synthesis of [Nb(L)Cl_2] (**2**).—A thf solution of H_2L (26.18 g, 76.0 mmol) was slowly treated with an Et_2O solution (1.60 mol dm^{-3}, 95 mmol) of methyl-lithium. The Et_2O was evaporated, and to the resulting red solution $NbCl_4$·2thf (28.84 g, 76.0 mmol) was added. A red-brown crystalline solid suddenly formed and the suspension was stirred overnight. The solid was dried *in vacuo* (yield *ca.* 73%) (Found: C, 53.80; H, 5.15; Cl, 12.10; N, 9.45. $C_{22}H_{22}Cl_2N_4Nb·C_4H_8O$ requires C, 54.00; H, 5.20; Cl, 12.25; N, 9.70%); $\mu_{eff.}$ 1.94 B.M. at 293 K. Crystals suitable for *X*-ray analysis were obtained by recrystallizing the solid from MeCN. They contain acetonitrile of crystallization (Found: C, 53.10; H, 4.95; Cl, 12.25; N, 14.60. $C_{22}H_{22}Cl_2N_4Nb·2CH_3CN$ requires C, 53.05; H, 4.75; Cl, 12.05; N, 14.30%).

X-*Ray Structure Determination of* [Nb(acen)Cl_2] (**1**) *and* [Nb(L)Cl_2]·2MeCN (**2**).—The crystals selected for study were mounted in glass capillaries and sealed under nitrogen. Data were collected at room temperature on a single-crystal four-circle diffractometer. Crystal data and details of the parameters

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

Non-S.I. unit employed: B.M. = 9.275 × 10^{-24} J T^{-1}.

Table 1. Experimental data for the *X*-ray diffraction studies of $[Nb(acen)Cl_2]$ (**1**) and $[Nb(L)Cl_2]\cdot 2MeCN$ (**2**)[a]

Complex	(**1**)	(**2**)
Formula	$C_{12}H_{18}Cl_2N_2NbO_2$	$C_{22}H_{22}Cl_2N_4Nb\cdot 2CH_3CN$
M	386.1	588.4
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
Cell parameters at 295 K[b]		
a/Å	7.965(1)	12.339(3)
b/Å	14.422(2)	14.128(3)
c/Å	28.030(6)	9.015(2)
α/°	90	106.52(3)
β/°	101.55(2)	91.63(3)
γ/°	90	111.45(3)
U/Å^3	3 155(1)	1 386.8(7)
Z	8	2
D/g cm^{-3}	1.626	1.409
$F(000)$	1 560	602
Crystal size/mm	0.10 × 0.34 × 0.72	0.20 × 0.36 × 0.50
μ/cm^{-1}	10.7	6.35
2θ range/°	6—47	6—52
Reflections measured	$+h\ k\ l$	$\pm h\ \pm k\ l$
Unique total data	4 638	5 488
Criterion for 'observed'	$I > 3\sigma(I)$	$I > 3\sigma(I)$
Unique observed data (n.o.)	2 362	4 122
No. of variables (n.v.)	343	315
Overdetermination ratio (n.o./n.v.)	6.9	13.1
Max. shift/error ratio on last cycle	0.3	0.2
$R\ (=\Sigma\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\Sigma\lvert F_o\rvert)$	0.044	0.035
$R'\ (=\Sigma w^{\frac{1}{2}}\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\Sigma w^{\frac{1}{2}}\lvert F_o\rvert)$	0.042	—
Goodness of fit $\{=[\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/(\text{n.o.} - \text{n.v.})]^{\frac{1}{2}}\}$	1.41	—

[a] Details common to both determinations: diffractometer, Philips PW 1100; diffraction geometry, equatorial; scan type, $\omega/2\theta$; scan speed, 0.100° s^{-1}; scan width, 1.40°; radiation, graphite-monochromatized Mo-K_α (λ = 0.7107 Å). [b] Unit-cell parameters were obtained by least-squares analysis of the setting angles of 35 carefully centred reflections chosen from diverse regions of reciprocal space.

Table 2. Fractional atomic co-ordinates (× 10^4) for $[Nb(acen)Cl_2]$ (**1**)

	Molecule A			Molecule B		
Atom	X/a	Y/b	Z/c	X/a	Y/b	Z/c
Nb	−2 237(1)	3 069(1)	2 538(1)	−2 522(1)	2 402(1)	4 935(1)
Cl(1)	−5 112(3)	2 820(2)	2 056(1)	−1 458(4)	997(2)	4 614(1)
Cl(2)	670(3)	3 299(2)	3 003(1)	−3 643(3)	3 777(2)	5 254(1)
O(1)	−1 415(8)	2 203(4)	2 106(2)	−1 172(8)	3 182(4)	4 592(2)
O(2)	−2 370(7)	4 365(4)	2 349(2)	−4 807(7)	2 106(5)	4 584(2)
N(1)	−2 397(8)	1 830(5)	2 956(2)	−220(9)	2 425(5)	5 496(2)
N(2)	−3 416(8)	3 577(5)	3 121(2)	−3 236(10)	1 570(5)	5 503(2)
C(1)	−928(12)	970(7)	1 584(3)	501(13)	4 312(7)	4 301(4)
C(2)	−1 408(11)	1 311(6)	2 040(3)	228(11)	3 683(6)	4 694(3)
C(3)	−1 776(10)	710(6)	2 380(3)	1 320(10)	3 574(7)	5 122(3)
C(4)	−2 159(10)	964(5)	2 840(3)	1 163(11)	2 937(6)	5 498(3)
C(5)	−2 200(12)	171(6)	3 184(3)	2 670(11)	2 870(9)	5 912(3)
C(6)	−2 712(12)	2 047(6)	3 450(3)	−211(13)	1 730(7)	5 878(3)
C(7)	−3 869(12)	2 848(6)	3 432(3)	−1 987(14)	1 576(8)	5 967(3)
C(8)	−4 863(12)	4 636(7)	3 604(3)	−5 031(13)	585(7)	5 912(3)
C(9)	−3 937(11)	4 427(6)	3 197(3)	−4 693(13)	1 126(6)	5 480(3)
C(10)	−3 649(11)	5 195(6)	2 901(3)	−6 076(12)	1 121(7)	5 063(4)
C(11)	−2 954(10)	5 147(6)	2 487(3)	−6 113(11)	1 602(7)	4 648(3)
C(12)	−2 788(12)	5 976(6)	2 182(4)	−7 602(11)	1 646(8)	4 232(3)

associated with data collection are given in Table 1. The reduced cells quoted were obtained with use of TRACER.[11] For intensities and background the 'three-point' technique was used. The structure amplitudes were obtained after the usual Lorentz and polarization corrections[12] and the absolute scale was established by the Wilson method.[13] The crystal quality was tested by ψ scans showing that crystal absorption effects could be neglected. The function minimized during the least-squares refinement was $\Sigma w\lvert\Delta F\rvert^2$. Weights were applied according to the scheme $w = k/[\sigma^2(F_o) + \lvert g\rvert(F_o)^2]$ for complex (**1**). At the end of the refinement the values for k and g were 1.2950 and 0.000 265 respectively. For complex (**2**) unit weights were applied leading to better agreement analyses and indices. Anomalous scattering corrections were included in all structure factor calculations.[14a] Scattering factors for neutral atoms were taken from ref. 14(*b*) for the non-hydrogen atoms and from ref. 15 for the hydrogen atoms. Among the low-angle reflections no correction for secondary extinction was deemed necessary.

Table 3. Fractional atomic co-ordinates (× 10^4) for $[Nb(L)Cl_2]\cdot 2MeCN$ (**2**)*

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Nb	3 624.2(3)	1 690.9(3)	2 723.8(4)	C(13)	478(4)	−244(4)	−1 806(5)
Cl(1)	2 369(1)	655(1)	4 230(1)	C(14)	1 404(4)	742(4)	−1 236(5)
Cl(2)	2 494(1)	2 813(1)	3 596(1)	C(15)	2 393(3)	846(3)	−304(4)
N(1)	5 070(2)	3 169(2)	3 056(3)	C(16)	3 854(3)	2 619(3)	−130(4)
N(2)	5 112(2)	1 530(2)	3 697(3)	C(17)	4 802(4)	3 550(3)	696(4)
N(3)	3 417(2)	182(2)	1 131(3)	C(18)	5 421(3)	3 818(3)	2 179(4)
N(4)	3 368(3)	1 817(2)	462(3)	C(19)	6 731(4)	943(4)	4 095(5)
C(1)	5 652(3)	3 418(3)	4 591(4)	C(20)	3 529(4)	−1 591(3)	−106(5)
C(2)	6 055(3)	4 408(3)	5 760(5)	C(21)	3 447(4)	2 527(4)	−1 788(5)
C(3)	6 536(4)	4 512(3)	7 236(5)	C(22)	6 525(4)	4 816(3)	2 682(5)
C(4)	6 585(4)	3 623(4)	7 557(4)	C(1S)	31(6)	1 941(6)	5 787(8)
C(5)	6 142(3)	2 624(3)	6 425(4)	N(1SA)	669(13)	3 318(11)	8 627(18)
C(6)	5 663(3)	2 515(3)	4 926(4)	C(2SA)	303(13)	2 704(12)	7 393(18)
C(7)	5 541(3)	765(3)	3 328(4)	N(1SB)	−535(20)	2 884(17)	8 267(26)
C(8)	4 948(3)	−201(3)	2 155(4)	C(2SB)	−357(25)	2 358(22)	6 954(34)
C(9)	3 940(3)	−497(3)	1 103(4)	N(2S)	8 579(8)	3 537(7)	3 625(12)
C(10)	2 408(3)	−55(3)	67(4)	C(5S)	9 405(8)	3 949(7)	3 113(12)
C(11)	1 437(4)	−1 022(3)	−463(5)	C(4S)	10 424(9)	4 462(8)	2 499(13)
C(12)	488(4)	−1 112(4)	−1 422(5)				

* Site occupation factors for disordered atoms: 0.6 for N(1SA) and C(2SA); 0.4 for N(1SB) and C(2SB).

Table 4. Selected bond distances (Å) and angles (°) for $[Nb(acen)Cl_2]$ (**1**)

	Molecule			Molecule	
	A	B		A	B
Nb–Cl(1)	2.441(3)	2.437(4)	Nb–O(2)	1.940(6)	1.935(5)
Nb–Cl(2)	2.442(3)	2.418(3)	Nb–N(1)	2.155(7)	2.164(6)
Nb–O(1)	1.942(7)	1.939(7)	Nb–N(2)	2.169(7)	2.159(7)
Cl(1)–Nb–Cl(2)	178.5(1)	178.6(1)	N(2)–Nb–O(2)	82.7(3)	83.8(3)
N(1)–Nb–N(2)	77.8(2)	77.4(2)	N(1)–Nb–O(2)	160.3(3)	161.2(3)
O(1)–Nb–O(2)	117.1(3)	115.7(3)	N(2)–Nb–O(1)	159.7(3)	160.4(3)
N(1)–Nb–O(1)	82.5(3)	83.0(3)			

Table 5. Selected bond distances (Å) and angles (°) for $[Nb(L)Cl_2]\cdot$ 2MeCN (**2**)

Nb–Cl(1)	2.445(2)	Nb–N(2)	2.126(3)
Nb–Cl(2)	2.459(2)	Nb–N(3)	2.124(3)
Nb–N(1)	2.127(3)	Nb–N(4)	2.122(3)
Cl(1)–Nb–Cl(2)	81.8(1)	N(3)–Nb–N(4)	74.4(1)
N(1)–Nb–N(2)	74.0(1)	N(2)–Nb–N(3)	81.3(1)
N(1)–Nb–N(4)	82.0(1)	N(2)–Nb–N(4)	125.5(2)
N(1)–Nb–N(3)	125.8(1)		

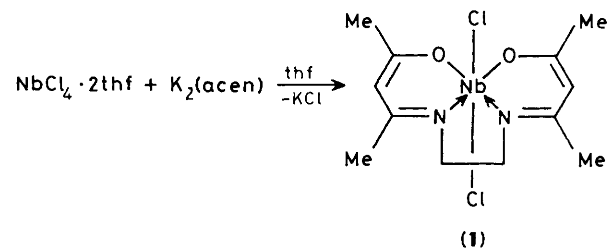
The structures were solved by the heavy-atom method starting from three-dimensional Patterson maps. Refinement was first carried out isotropically, then anisotropically for the non-hydrogen atoms, by blocked full-matrix least-squares. Solution and refinement were based on the observed reflections. For complex (**2**) the *X*-ray analysis revealed the presence of two MeCN molecules of crystallization. One was found to be disordered over two positions sharing the methyl carbon [C(1S)]. The disordered atoms were isotropically refined with site occupation factors of 0.6 for N(1SA) and C(2SA) and 0.4 for N(1SB) and C(2SB). All hydrogen atoms except those of the MeCN molecules were located in difference maps and introduced in the subsequent refinement as fixed contributors with isotropic thermal parameters fixed at 0.08 Å^2 for both compounds. The final difference maps showed no unusual features, with no significant peaks above the general background.

Data reduction, structure solution, and refinement were carried out on a GOULD 32/77 computer using SHELX 76.[12]

Final atomic co-ordinates are listed in Tables 2 and 3. Selected bond distances and angles are listed in Tables 4 and 5. Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, remaining bond distances and angles.

Results and Discussion

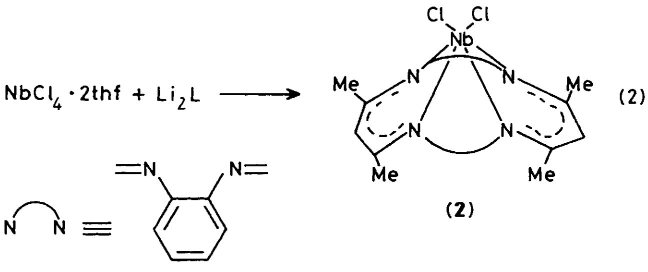
Reacting the sodium or potassium salt of *N,N'*-ethylenebis(acetylacetonylideneimine), $Na_2(acen)$ or $K_2(acen)$, with an equimolar amount of $NbCl_4\cdot 2thf$, produces a red-violet solution; after removal of the alkali metal chloride, complex (**1**) crystallized (yield *ca.* 60%) [equation (1)].



(1)

(**1**)

Reaction (2) was carried out following the same procedure and using Li_2L [H_2L = 7,16-dihydro-6,8,15,17-tetramethyldibenzo[*b,i*][1,4,8,11]tetra-azacyclotetradecine]. Complex (**2**) was obtained as a red-brown crystalline solid, $[Nb(L)Cl_2]\cdot$thf, in *ca.* 73% yield. Crystals suitable for *X*-ray analysis were



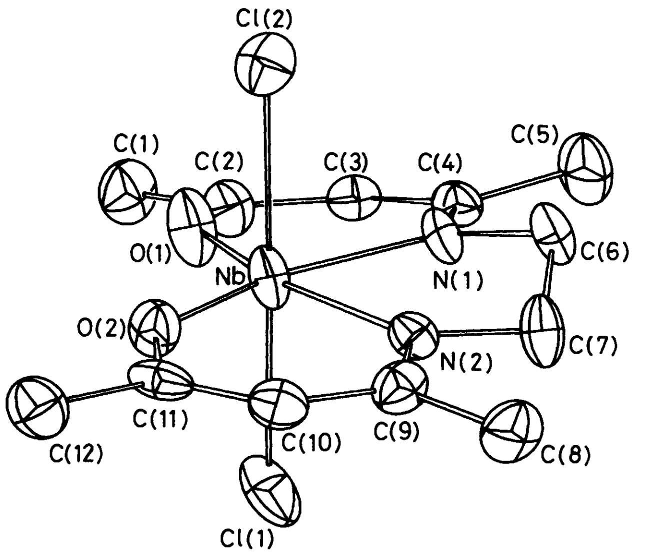


Figure 1. ORTEP plot of [Nb(acen)Cl_2] (**1**) (42% probability ellipsoids)

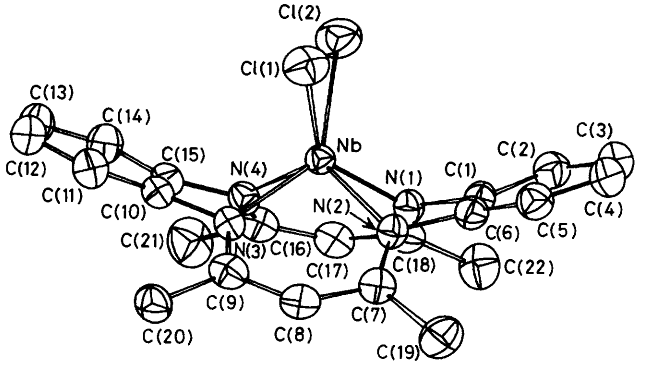


Figure 2. ORTEP plot of [Nb(L)Cl_2]·2MeCN (**2**) (48% probability ellipsoids)

obtained by recrystallizing from acetonitrile, [Nb(L)Cl_2]·2MeCN. Magnetic moments of 1.80 B.M. at 292 K and 1.94 B.M. at 293 K for (**1**) and (**2**) respectively are in agreement with the presence of one unpaired electron in both compounds. They are also air- and moisture-sensitive. The structures of [Nb(acen)Cl_2] (**1**) and [Nb(L)Cl_2]·2MeCN (**2**) have been determined by *X*-ray analysis.

The structures of (**1**) and (**2**) are shown in Figures 1 and 2 while the most significant bond distances and angles within the co-ordination sphere are listed in Tables 4 and 5. In both compounds Nb^{IV} is six-co-ordinate, the MeCN being a lattice solvent in complex (**2**). Since both ligands derive from the condensation of acetylacetone with a diamine there is a significant similarity in some structural parameters within the ligand and the metal co-ordination sphere. The most significant chemical difference, besides the nature of the polydentate ligand, is the arrangement of the two chlorines, which are *trans* in (**1**) [Cl–Nb–Cl, 178.5(1)°] and *cis* in (**2**) [Cl–Nb–Cl, 81.8(1)°].

In the asymmetric unit of (**1**) there are two crystallographically independent [Nb(acen)Cl_2] molecules, denoted A and B, and the values referring to molecule B are given in square brackets. Niobium has a pseudo-octahedral co-ordination with the N_2O_2 set of atoms from the acen ligand in the equatorial plane and two chlorine atoms in the *trans* axial positions (Figure 1). Niobium is almost coplanar with the N_2O_2 set of donor atoms {deviation from N_2O_2 plane 0.028(2) [0.008(2)] Å}. The N_2O_2 group does not lie exactly in a plane and the atoms show small but significant tetrahedral distortions. Molecules A and B do not contain any planar chelating ring. Niobium is displaced by 0.235(2) [0.250(2)] and 0.035(2) [0.070(2)] Å respectively from the planes through O(1),C(2),C(3),C(4),N(1) and O(2),C(11),C(10),C(9),N(2). The mean planes through the six-membered rings form a dihedral angle of 8.4(2)° [2.6(2)°]. The five-membered chelate rings show λ and δ conformations in molecules A and B respectively referred to the co-ordinates of Table 2. Since the space group is centrosymmetric both enantiomeric conformations are present for each molecule in the structure. The other structural parameters within the acen ligand are in the usual range.[16,17] The CH=N unit which is the most affected by the binding to the metal, has similar lengths in complexes (**1**) [average, 1.32(1)] and (**2**) [1.337(6) Å]. Few [M(acen)Cl_2] complexes of the early transition metals have been obtained and structurally characterized; they include those with M = Ti, Zr, Hf, Mo,[18] and V.[17] A *trans* arrangement of the two chlorines was found in all cases except for M = Zr or Hf.[18] This is probably related to the ionic radius of the metal ion. An interesting property of the M(acen) moiety over other similar Schiff-base derivatives is its significantly higher solubility in organic solvents.

The structure of [Nb(L)Cl_2]·2MeCN (**2**) consists of discrete monomeric units where niobium is co-ordinated by the N_4 set of atoms from the ligand and two chlorine atoms which are disposed in a *cis* configuration, *i.e.* at the same side of the perfect plane running through the nitrogen atoms (Figure 2). Niobium is displaced by 0.970(2) Å from that plane towards the chlorines. The NbCl(1)Cl(2) plane is perpendicular to the N_4 plane [dihedral angle 89.0(1)°] and the Cl(1)–Cl(2) line is parallel to the N(3)–N(4) and N(2)–N(1) sides of the basal square plane. Co-ordination of the L results in two five-membered and two six-membered rings. The first two have an envelope conformation with niobium lying 1.275(2) and 1.320(2) Å from the perfect planes through N(1),C(1),C(6),N(2) and N(3),C(10),C(15),N(4) respectively. The six-membered rings are nearer to being planar, with niobium 0.127(1) and 0.190(2) Å from the mean planes through N(2),C(7),C(8),C(9),N(3) and N(4),C(16),C(17),C(18),N(1). This is in agreement with the values of the C–N [average 1.337(4) Å] and C–C [average 1.392(5) Å] distances within them, indicating a high degree of π delocalization. The conformation of the molecule can be described by the bending of its portions with respect to the N_4 plane which forms dihedral angles of 32.5(1), 30.5(1), 17.2(1), and 19.6(1)° respectively with the mean planes through N(2),C(7),C(8),C(9),N(3); N(4),C(16),C(17),C(18),N(1); N(1),C(1)—C(6),N(2); and N(3),C(10)—C(15),N(4). The bending of the six-membered chelate rings is opposite to that of the five-membered rings, the former being bent away from the chlorine atoms, the latter being bent towards them, so that the Nb(L) moiety assumes a saddle-shaped conformation.

The two Nb–Cl distances [Nb–Cl(1), 2.445(2); Nb–Cl(2), 2.459(2) Å] are slightly but significantly different, though there is no apparent reason for this. Their values are very close to those found in (**1**) [2.418(3)—2.442(3) Å]. These distances, which are expected to be equivalent, can be considered to be mainly affected by solid-state effects. The four Nb–N distances are very close [2.122(2)—2.127(3) Å].

The *cis* arrangement of the two chlorine atoms and the conformation of L provide a cavity for the metal. The metal site is located in a cavity that resembles that in [$Nb(\eta^5-C_5H_5)_2Cl_2$].[19] The structure of **(2)** is similar to [M(L)] (M = Ti[20] or Zr[7]). Structural parameters within the ligand L do not differ significantly from those found in complexes containing the same ligand.[7,20,21] Both complexes **(1)** and **(2)** are noteworthy since acen and L are known to stabilize M–C bonds[5–7] and low metal oxidation states.[22] Moreover they provide potential co-ordination sites available for co-ordination or substitution reactions that are *trans* or *cis* to each other, in a similar environment.

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