60. Complexes of 2,2′,2″-Nitrilotriphenol

Part 3

Crystal and Molecular Structures of Three Aluminium Complexes

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Crystal and molecular structures of three Al(III) complexes of the tripod ligand 2,2′,2″-nitrilotriphenolate (**I**) are presented. They all show 5-coordinate Al in approximately trigonal bipyramidal geometry, with an external nucleophile X occupying the second axial position. X is OH^- in $[Al(\mathbf{I})(OH)]^-[Hquin]^+$ (quin = quinuclidine), N in [Al(**I**)(py)] (py = pyridine), and one of the O-atoms of a second molecule in the dimeric $[(Al(\mathbf{I}))_2]$. Correlated variations in the axial bond lengths of the trigonal bipyramid are observed: $[(Al(\mathbf{I}))_2]$: $Al-N_{int.} = 2.094$ Å, $Al-O_{ext.} = 1.850$ Å; [Al(**I**)(py)]: $Al-N_{int.} = 2.153$ Å, $Al-N_{ext.} = 1.992$ Å; $[Al(\mathbf{I})(OH)]^-$: $Al-N_{int.} = 2.278$ Å, $Al-O_{ext.} = 1.765$ Å. They are interpreted in terms of a dissociative reaction path at the Al(III) centre.

Introduction. – In [1] and [2], we have reported on structure and reactivity of three B(III) complexes with 2,2′,2″-nitrilotriphenolate (**I**), namely [B(**I**)] and its pyridine and quinuclidine adducts. Analogous complexes of **I** with Al(III) were also studied in order to see whether – for a given environment – this second-row ion behaves like its first-row homologue B(III) or like its second-row neighbour Si(IV). Al(III) complexes of **I** have first been described by *Frye et al.* [3], who report on the complex [Al(**I**)] and its adduct with i-PrOH. Analogous adducts with pyridine [Al(**I**)(py)] and with diazabicyclooctane ($[[Al(\mathbf{I})]_2dabco]$) have been prepared by *Hauser* [4]. The complexes are generally obtained by reacting solutions of 2,2′,2″-nitrilotriphenol (**I**·3 H) with aluminium tris(isopropoxylate) ($[Al(i\text{-}PrO)_3]$) in an appropriate solvent in the presence of an additional nucleophile *(Eqn. 1)*.

$$\begin{tikzcd} \mathbf{I}\cdot 3\,H + [Al(i\text{-}PrO)_3] \arrow[r] & {[Al(\mathbf{I})] + 3\ i\text{-}PrOH} \arrow[d, "\text{Nucleophile}"] \\ & {[Al(\mathbf{I})(\text{Nucleophile})]} \end{tikzcd} \qquad (1)$$

In the absence of a sufficiently strong nucleophile, a molecule of i-PrOH is retained in the product, which may, however, be expelled by heating, as shown below for the analogous case of pyridine. The thermolysis product is a complex of formal composition [Al(I)].

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Experimental. – *General.* All chemicals were purchased from *Fluka*, if not indicated otherwise.

(2,2',2"-Nitrilotriphenoxy)pyridinealuminium ([Al(**I**)(py)]). A soln. of 1.00 g (3.4 mmol) of **I**·3 H in 10 ml of dry, hot pyridine was added to a soln. of 0.70 g (3.4 mmol) of [Al(i-PrO)$_3$] in 10 ml of dry, hot benzene. After refluxing for 5 min, the resulting mixture was allowed to cool down to r.t., and the white precipitate was filtered, washed with a little pyridine and dried *in vacuo:* 1.2 g (88%). [Al(**I**)(py)] lost pyridine upon heating above 110° *(Fig. 1)*; the residue was identified as [(Al(**I**))$_2$] by IR and showed no m.p. below 300°. [Al(**I**)(py)]: IR: 3120*vw*, 3100*vw*, 3080*w* (sh), 3060*w*, 3030*w*, 3010*vw*, 1620*m*, 1600*s*, 1495*vs*, 1475*s* (sh), 1450*s*, 1305*vs*, 1290*s*, 1270*m*, 1255*m*, 1220*s*, 1190*m*, 1165*w*, 1155*m*, 1145*m*, 1120*m*, 1110*m*, 1075*s*, 1055*m*, 1035*m* (sh), 1030*m*, 1020*w*, 960*w*, 950*w*, 940*w*, 920*m*, 860*s*, 840*vs*, 765*s* (sh), 760*vs*, 750*s*, 725*vs*, 700*s*, 675*m*, 660*m*, 615*m*, 560*m*, 550*m* (sh), 445*m*, 430*w*, 405*s*, 350*m*. Anal. calc. for $C_{23}H_{17}AlN_2O_3$ (396.40): C 69.69, H 4.33, N 7.07; found[3]): C 68.38, H 4.41, N 6.93.

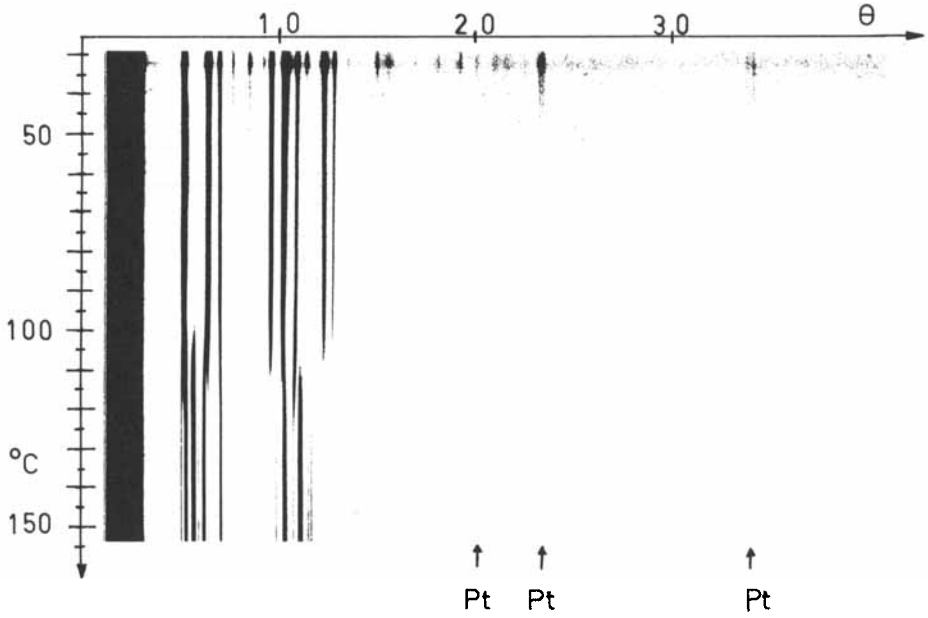

Fig. 1. *Powder diagram of [Al(*I*)(py)] as a function of temperature.* Pyridine is lost at *ca.* 110°.

Single crystals of [Al(**I**)(py)] suitable for X-ray studies were obtained as follows: 100 mg of [Al(**I**)(py)] were dissolved in *ca.* 2 ml of dry, boiling pyridine. This soln. was cooled slowly (–10°/day) to ambient temperature. After a week, crystals of sufficient size could be isolated and dried as described above.

*Bis[µ-(2,2',2"-nitrilotriphenoxy-*O*)]dialuminium* ([(Al(**I**))$_2$]). This compound was obtained by high vacuum sublimation of [Al(**I**)(py)] at 400°/0.05 Torr. The pyridine is lost and the product obtained in near quant. yield as well formed, yellowish crystals. IR: 3080*w*, 3040*w*, 1600*s*, 1500*vs*, 1485*vs*, 1470*s* (sh), 1300*vs*, 1290*s*, 1270*s*, 1260*vs*, 1190*m*, 1185*m* (sh), 1175*m*, 1155*m*, 1150*m*, 1110*s*, 1040*m* (sh), 1035*m*, 980*w*, 970*w*, 950*m*, 920*m*, 915*w* (sh), 870*vs*, 855*vs*, 845*vs*, 780*s*, 770*vs*, 760*vs*, 755*vs*, 745*s* (sh), 740*m*, 730*s*, 720*s*, 685*m*, 675*m*, 625*s*, 570*m*, 550*w*, 500*w*, 490*w*, 430*s*, 420*m*, 370*w*, 360*w*, 320*w*, 305*w*, 280*w*. Anal. calc. for $(C_{18}H_{12}AlNO_3)_2$ (2 · 341.24): C 63.36, H 3.54, N 4.10; found: C 67.79, H 4.07, N 4.36[4]).

Quinuclidinium Hydroxo(2,2',2"-nitrilotriphenoxy)aluminate ([Al(**I**)(OH)]$^-$[Hquin]$^+$). To prepare a crystalline quinuclidine adduct, 1.00 g of quinuclidine (quin) was added to a soln. of 1.00 g (3.4 mmol) of **I**·3 H and 0.70 g (3.4 mmol) of Al(i-PrO)$_3$ in 10 ml of dimethylsulfoxide (DMSO) at 100°, dried previously over activated 4-Å molecular

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[3]) Mean of 2 determinations.

[4]) The unsatisfactory analysis is possibly due to pyrolytic decomposition during the sublimation (yellowish color). As no simple method for further purification was available (recrystallization from solvents in which the compound is soluble leads to adducts), the well developed crystals were directly used for the X-ray structure determination.

sieves. The clear soln. was cooled (−20°/day) to r.t. in a stoppered flask. After 4 days, well developed crystals were isolated, washed with Et_2O and dried *in vacuo* for a short time: 0.80 g of $[Al(\mathbf{I})(OH)]^-[Hquin]^+$. IR: 3440*s*, 3070*w*, 3030*w*, 3010*w*, 2970*w* (sh), 2960*w*, 2890*w*, 1600*s*, 1495*vs*, 1480*vs* (sh), 1470*s*, 1410*w*, 1390*w*, 1370*w*, 1310*vs*, 1295*vs*, 1265*s*, 1250*m*, 1240*s*, 1225*m*, 1210*m*, 1170*m*, 1155*w*, 1150*m*, 1110*m*, 1105*m* (sh), 1040*w* (sh), 1030*m*, 975*m*, 945*w*, 935*w*, 920*m*, 865*s*, 840*s*, 810*w*, 800*w*, 760*vs*, 750*s*, 705*s*, 690*s*, 675*m* (sh), 640*m*, 615*s*, 575*w* (sh), 565*m*, 495*m*, 480*w*, 425*s*. Anal. calc. for $C_{27}H_{33}O_5N_2SAl$ (548.56)[5]: C 59.12, H 6.06, N 5.11; found: C 61.47, H 6.22, N 5.12[6].

X-Ray Data Collection. Preliminary investigations by precession photography. Determination of cell parameters and intensity measurements on an automated *CAD 4* diffractometer *(Enraf Nonius)* λ = 0.71067 Å; bisecting geometry, ω or $\omega/2\theta$ scan techniques; first and last sixth of each scan for background correction. *Table 1* summarizes crystal data, data collection, and structure analysis for all three compounds; *Lorentz* and polarization corrections, direct methods (MULTAN 77 [5]); weighted least-squares refinements using XRAY 72 [6] program system, weighting scheme of *Seiler* and *Dunitz* [7], real and imaginary scattering factors for neutral atoms [8], all atoms refined; C, N, O, S and Al anisotropically.

Table 1. *Crystal Data and Parameters Used in Data Collections and Structure Determinations*

	$[(Al(\mathbf{I}))_2]$	$[Al(\mathbf{I})(py)]$	$[Al(\mathbf{I})(OH)]^-$
Formula	$(C_{18}H_{12}AlNO_3)_2$	$C_{23}H_{17}AlN_2O_3$	$C_{27}H_{33}AlN_2O_5$
Space group	monoclinic, $P2_1/b$	monoclinic, $C2_1$[a]	monoclinic, $P2_1/n$
a [Å]	8.972(2)	10.584(4)	8.921(4)
b [Å]	17.814(4)	15.560(4)	9.761(3)
c [Å]	18.776(17)	35.283(8)	32.402(13)
α [°]	74.23(4)	90.0	90.0
β [°]	90.0	90.0	90.0
γ [°]	90.0	89.36(3)	69.09(3)
V [Å^3]	2888.0	5810.2	2635.5
Z	8	12	4
Crystal size [mm]	0.2·0.2·0.2	0.3·0.3·0.1	0.2·0.2·0.3
θ_{max} [°]	25	25	25
Scan type	$\omega/2\theta$	ω	ω
Total scan angle/reflection [°]	1.5	1.5	1.5
Max. measuring time/reflection [s]	60	90	90
No. of independent reflections	5073	5189	4640
No. of reflections used in refinements	3484 ($> \sigma_F$)	3632 ($> \sigma_F$)	3469 ($> \sigma_F$)
No. of variables	512	938[b]	414
Final R_w[c]	0.033	0.035	0.051
Weighting, A[c]	7.5	0	0

[a] The C-centered cell was chosen rather than the primitive $P2_1$ for its proximity to the orthorhombic space group $Cmc2_1$. The structure is, however, definitely not orthorhombic.

[b] Block diagonal refinement.

[c] $w = 1/\sigma^2(F)\cdot\exp(2\cdot A\cdot(\sin\theta/\lambda)^2)$.

Results and Discussion. – Atomic numbering schemes are given in *Fig. 2*. Positional and equivalent isotropic displacement parameters are given in *Tables 2, 3,* and *4*. Anisotropic displacement parameters are available [1]. Molecular structures and packings are illustrated in *Figs. 3, 4,* and *5*. Where appropriate, bond distances and angles are averaged over the independent molecules and with respect to non-crystallographic symmetry (mirror plane or 3-fold axis). Values for the tricycloundecane cages are reported in *Table 5*.

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[5] The compound obtained analyzed as $[Al(\mathbf{I})(OH)]^-[Hquin]^+$ with 1 molecule of DMSO (see X-ray structure).

[6] Either the drying procedure was inefficient, and there was still enough H_2O in the DMSO solvent to produce hydrolysis, or H_2O leaked into the reaction flask during crystallization.

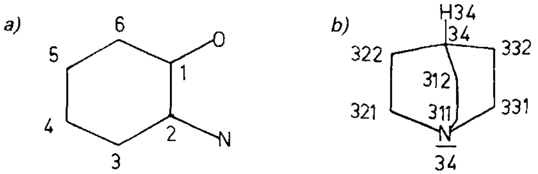

Fig. 2. *Atom numbering scheme for the three structures* $[(Al(\mathbf{I}))_2]$*,* $[Al(\mathbf{I})(py)]$*, and* $[Al(\mathbf{I})(OH)]^-$ $[Hquin]^+\cdot$*DMSO. a)* Systematic numbering of the Al(**I**) fragment: where there is more than one independent molecule in the unit cell, the first digit after the atom symbol refers to the molecule number; the second digit refers to the ring number within the frame of **I**, and the third digit to the atom within the ring, as indicated. *b)* Labelling of the quinuclidine fragment; the labelling of the pyridine fragment is seen from the ORTEP drawing.

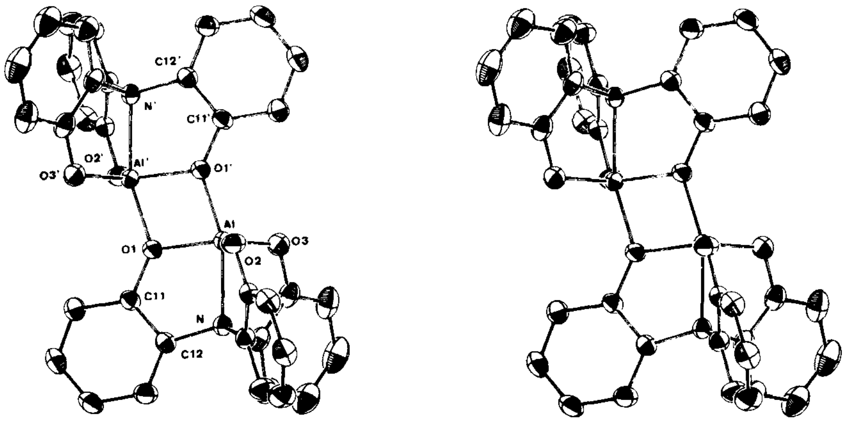

Fig. 3. *Stereoscopic drawing of the* $[(Al(\mathbf{I}))_2]$ *molecule*

The X-ray analysis of the supposed quinuclidine adduct, which crystallizes with a molecule of H_2O, unambiguously shows a coordinated O-atom in apical position. This forms a relatively short H-bridge to the quinuclidine N-atom (O(1)···N(34): 2.658(3) Å; O(1)–H(1): 1.460(28) Å; H(1)–N(34): 1.208(28) Å). As the H-atom was localized closer to the N-atom than to the O-atom, the latter must be regarded as deprotonated, and hence the compound can be formulated as $[Al(\mathbf{I})(OH)]^-[Hquin]^+$, with a coordinated OH group.

In all three compounds the Al(**I**) fragment has a tricyclo[3.3.3.0]undecane structure with a central N→Al dative bond. The Al(III) ion is 5-coordinate, in an approximately trigonal-bipyramidal environment, in which the 3 donor O-atoms of the ligand **I** occupy the equatorial and the N-atom of **I** one of the two axial positions. The remaining *apical* position is occupied by an external nucleophile (OH^-, pyridine or an O-atom of a second Al(**I**) unit). This behaviour contrasts with that of B(III), which is at most 4-coordinate in a similar environment, and where 5-coordination occurs only as a transition state in bimolecular nucleophilic substitution; this transition state lies several kcal·mol^{-1} above the ground state [1] [2].

The length of the central N→Al dative bond varies with the nature of the apical ligand (*Table 5*): it is shortest in $[(Al(\mathbf{I}))_2]$, where the apical ligand is a poor donor (a 3-coordinate O-atom), and longest in $[Al(\mathbf{I})(OH)]^-$, with an OH group in apical position.

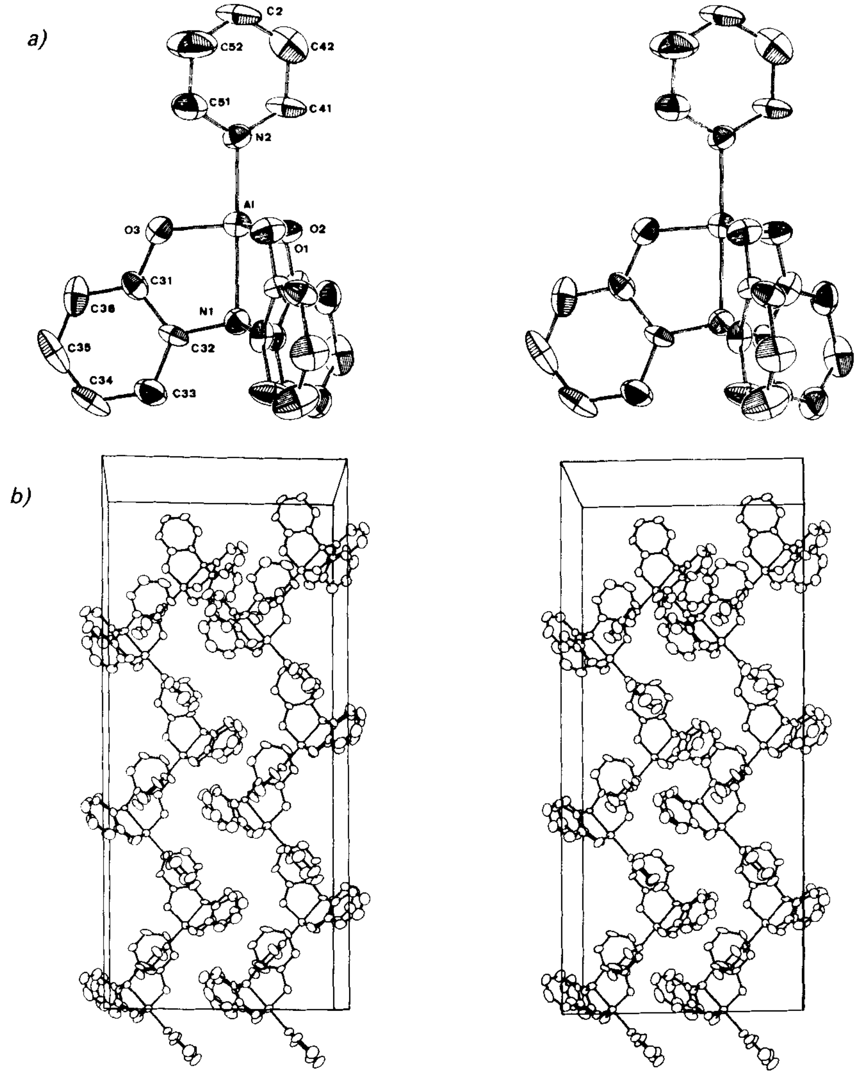

Fig. 4. *Stereoscopic drawings of the [Al(**1**)(py)] molecule. a)* View perpendicular to the molecular axis; *b)* packing diagram of the centered unit cell.

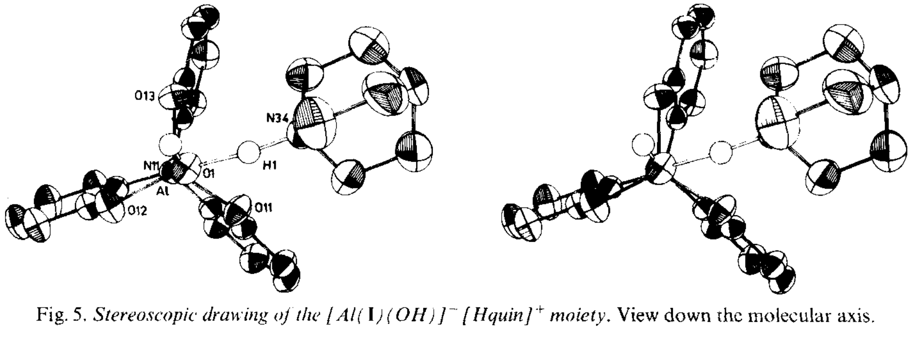

Fig. 5. *Stereoscopic drawing of the [Al(**1**)(OH)]$^-$ [Hquin]$^+$ moiety.* View down the molecular axis.

Table 2. *Positional and Displacement Parameters* ($100 \cdot U_{eq}$ or $100 \cdot U_{iso}$) *for [(Al(***I***))$_2$]*
(e.s.d. in terms of least significant digit)

Atom	x	y	z	U_{eq}
1st Molecule				
Al(1)	0.40450(7)	0.05399(3)	0.44912(3)	2.4(1)
N(1)	0.28107(19)	0.02075(9)	0.36838(9)	2.4(1)
O(11)	0.48811(18)	0.12441(9)	0.37688(9)	3.5(1)
O(12)	0.23563(17)	0.07626(9)	0.48554(8)	3.1(1)
O(13)	0.46475(17)	−0.04928(8)	0.47365(8)	2.9(1)
C(111)	0.4604(2)	0.1168(1)	0.3083(1)	3.2(1)
C(112)	0.3576(2)	0.0612(1)	0.2996(1)	2.8(1)
C(113)	0.3293(3)	0.0494(1)	0.2308(1)	4.0(1)
C(114)	0.4022(4)	0.0953(2)	0.1696(1)	5.0(2)
C(115)	0.5020(3)	0.1512(2)	0.1775(2)	5.3(2)
C(116)	0.5340(3)	0.1621(2)	0.2462(2)	4.4(1)
C(121)	0.1171(2)	0.0794(1)	0.4399(1)	2.6(1)
C(122)	0.1337(2)	0.0535(1)	0.3766(1)	2.5(1)
C(123)	0.0179(3)	0.0592(1)	0.3269(1)	3.5(1)
C(124)	−0.1172(3)	0.0896(2)	0.3406(2)	4.0(1)
C(125)	−0.1352(2)	0.1139(1)	0.4042(1)	3.7(1)
C(126)	−0.0197(3)	0.1090(1)	0.4537(1)	3.3(1)
C(131)	0.3812(2)	−0.0989(1)	0.4452(1)	2.6(1)
C(132)	0.2832(2)	−0.0650(1)	0.3887(1)	2.5(1)
C(133)	0.1898(3)	−0.1111(1)	0.3601(1)	3.3(1)
C(134)	0.1956(3)	−0.1915(1)	0.3881(1)	3.7(1)
C(135)	0.2924(3)	−0.2249(1)	0.4449(1)	3.6(1)
C(136)	0.3869(3)	−0.1792(1)	0.4741(1)	3.2(1)
2nd Molecule				
Al(2)	0.58821(7)	−0.05592(4)	0.05284(3)	2.5(1)
N(2)	0.49181(20)	−0.14546(10)	0.13671(9)	2.6(1)
O(21)	0.39294(16)	−0.02908(9)	0.02909(8)	3.1(1)
O(22)	0.66729(18)	−0.2027(9)	0.12176(9)	3.5(1)
O(23)	0.67607(20)	−0.12818(10)	0.02202(9)	4.0(1)
C(211)	0.2865(2)	−0.0638(1)	0.0798(1)	2.7(1)
C(212)	0.3325(2)	−0.1267(1)	0.1368(1)	2.6(1)
C(213)	0.2299(3)	−0.1638(1)	0.1894(1)	3.6(1)
C(214)	0.0838(3)	−0.1375(2)	0.1842(1)	4.2(1)
C(215)	0.0405(3)	−0.0740(2)	0.1278(1)	4.0(1)
C(216)	0.1420(2)	−0.0363(1)	0.0752(1)	3.4(1)
C(221)	0.6564(2)	−0.0690(1)	0.1907(1)	3.0(1)
C(222)	0.5722(2)	−0.1370(1)	0.2025(1)	2.9(1)
C(223)	0.5679(3)	−0.1902(1)	0.2715(1)	4.0(1)
C(224)	0.6448(3)	−0.1740(2)	0.3296(1)	4.9(2)
C(225)	0.7234(3)	−0.1050(2)	0.3192(1)	5.0(2)
C(226)	0.7304(3)	−0.0529(2)	0.2500(1)	4.2(1)
C(231)	0.6296(3)	−0.2020(1)	0.0542(1)	3.7(1)
C(232)	0.5296(3)	−0.2156(1)	0.1134(1)	3.1(1)
C(233)	0.4744(3)	−0.2894(1)	0.1453(1)	4.2(1)
C(234)	0.5226(4)	−0.3507(2)	0.1188(2)	5.8(2)
C(235)	0.6241(4)	−0.3381(2)	0.0622(2)	6.3(2)
C(236)	0.6768(4)	−0.2645(2)	0.0290(2)	5.4(2)

Table 2 (cont.)

Atom	x	y	z	U_{iso}
H(113)	0.255(4)	0.006(2)	0.229(2)	5.4(8)
H(114)	0.378(4)	0.086(2)	0.121(2)	5.7(9)
H(115)	0.554(4)	0.183(2)	0.135(2)	5.6(9)
H(116)	0.601(3)	0.201(2)	0.252(2)	5.3(8)
H(123)	0.031(3)	0.044(2)	0.283(2)	4.5(8)
H(124)	−0.196(3)	0.095(2)	0.304(2)	5.0(8)
H(125)	−0.228(3)	0.134(2)	0.413(1)	4.8(8)
H(126)	−0.027(3)	0.127(2)	0.495(2)	4.5(8)
H(133)	0.119(3)	−0.087(2)	0.324(1)	4.0(7)
H(134)	0.130(3)	−0.224(2)	0.367(1)	4.0(7)
H(135)	0.292(3)	−0.281(2)	0.466(1)	3.9(7)
H(136)	0.454(3)	−0.202(2)	0.514(1)	3.6(7)
H(213)	0.261(4)	−0.207(2)	0.229(2)	5.1(8)
H(214)	0.010(3)	−0.162(2)	0.221(2)	5.5(8)
H(215)	−0.058(3)	−0.055(2)	0.124(2)	4.4(8)
H(216)	0.120(3)	0.010(2)	0.035(2)	4.7(7)
H(223)	0.512(3)	−0.236(2)	0.279(1)	4.4(7)
H(224)	0.643(3)	−0.208(2)	0.376(2)	5.2(8)
H(225)	0.777(4)	−0.092(2)	0.360(2)	6.9(10)
H(226)	0.782(3)	−0.003(2)	0.241(2)	5.3(8)
H(233)	0.402(3)	−0.296(2)	0.181(2)	5.3(8)
H(234)	0.483(4)	−0.405(2)	0.141(2)	7.0(10)
H(235)	0.655(4)	−0.381(2)	0.044(2)	8.9(12)
H(236)	0.747(4)	−0.253(2)	−0.010(2)	5.9(9)

Table 3. *Positional and Displacement Parameters* (100 · U_{eq} or 100 · U_{iso}) *for [Al(**1**)(py)]* (e.s.d. in terms of least significant digit)

Atom	x	y	z	U_{eq}
1st Molecule				
Al(1)	0.0481(2)	0.3291(1)	0.0000(–)	3.2(1)
N(1)	0.0695(5)	0.4201(4)	0.0453(2)	3.3(4)
O(11)	0.0522(5)	0.2513(3)	0.0354(1)	3.9(4)
O(12)	0.1883(5)	0.3729(3)	−0.0184(1)	5.0(4)
O(13)	−0.0916(4)	0.3859(3)	−0.0101(1)	3.9(4)
C(111)	0.0650(6)	0.2771(4)	0.0724(2)	3.3(5)
C(112)	0.0734(6)	0.3637(5)	0.0797(2)	3.3(5)
C(113)	0.0851(8)	0.3928(5)	0.1167(2)	6.0(7)
C(114)	0.0882(9)	0.3341(6)	0.1452(2)	7.2(7)
C(115)	0.0777(8)	0.2477(5)	0.1376(2)	5.8(6)
C(116)	0.0699(7)	0.2171(5)	0.1009(2)	4.4(6)
C(121)	0.2431(6)	0.4351(4)	0.0026(2)	3.8(5)
C(122)	0.1864(6)	0.4613(4)	0.0362(2)	3.1(5)
C(123)	0.2403(6)	0.5282(5)	0.0566(2)	4.8(6)
C(124)	0.3489(8)	0.5659(5)	0.0450(3)	5.9(7)
C(125)	0.4049(7)	0.5395(5)	0.0110(3)	6.2(7)
C(126)	0.3522(7)	0.4773(6)	−0.0093(2)	5.9(7)
C(131)	−0.1206(7)	0.4537(5)	0.0112(2)	3.5(5)
C(132)	−0.0428(6)	0.4738(4)	0.0418(2)	2.7(5)
C(133)	−0.0668(7)	0.5466(5)	0.0637(2)	5.1(6)
C(134)	−0.1718(7)	0.5965(5)	0.0560(3)	5.0(6)
C(135)	−0.2484(7)	0.5786(5)	0.0260(3)	5.3(6)
C(136)	−0.2231(7)	0.5077(5)	0.0038(2)	4.4(6)

Table 3 (cont.)

Atom	x	y	z	U_{eq}
1st Molecule				
N(12)	0.0292(6)	0.2466(4)	–0.0425(2)	4.0(4)
C(11)	0.1297(8)	0.2123(6)	–0.0587(3)	7.1(7)
C(12)	0.1179(9)	0.1479(6)	–0.0862(3)	8.8(9)
C(13)	0.0030(9)	0.1259(6)	–0.0977(3)	8.0(8)
C(14)	–0.0974(8)	0.1565(6)	–0.0793(3)	7.2(7)
C(15)	–0.0864(7)	0.2195(5)	–0.0524(2)	5.0(6)

Atom	x	y	z	U_{iso}[a])
H(113)	0.078(5)	0.452(4)	0.125(2)	7.0
H(114)	0.089(6)	0.360(4)	0.172(2)	8.0
H(115)	0.085(5)	0.204(4)	0.157(2)	8.0
H(116)	0.064(5)	0.164(4)	0.097(2)	7.0
H(123)	0.190(5)	0.546(4)	0.079(2)	7.0
H(124)	0.372(6)	0.608(4)	0.058(2)	8.0
H(125)	0.479(6)	0.571(4)	0.005(2)	8.0
H(126)	0.384(6)	0.449(4)	–0.030(2)	7.0
H(133)	–0.016(5)	0.565(4)	0.079(2)	7.0
H(134)	–0.200(5)	0.642(4)	0.077(2)	8.0
H(135)	–0.340(6)	0.608(4)	0.022(2)	8.0
H(136)	–0.287(6)	0.496(4)	–0.009(2)	7.0
H(11)	0.206(6)	0.220(4)	–0.050(2)	8.0
H(12)	0.191(6)	0.125(4)	–0.096(2)	8.0
H(13)	–0.006(6)	0.086(4)	–0.113(2)	8.0
H(14)	–0.181(6)	0.141(4)	–0.084(2)	8.0
H(15)	–0.153(6)	0.248(4)	–0.038(2)	8.0

Atom	x	y	z	U_{eq}
2nd Molecule				
Al(2)	–0.0634(2)	0.3335(1)	0.66566(8)	3.3(1)
N(21)	–0.0425(5)	0.4234(4)	0.7114(2)	3.8(4)
O(21)	–0.0814(4)	0.2554(3)	0.7021(1)	3.7(3)
O(22)	–0.1951(4)	0.3970(3)	0.6520(1)	4.0(3)
O(23)	0.0896(4)	0.3662(3)	0.6528(1)	4.5(4)
C(211)	–0.0604(7)	0.2805(4)	0.7381(2)	3.1(5)
C(212)	–0.0361(6)	0.3665(5)	0.7443(2)	3.2(5)
C(213)	–0.0078(7)	0.3930(5)	0.7808(2)	4.4(6)
C(214)	–0.0019(8)	0.3372(5)	0.8104(2)	7.4(7)
C(215)	–0.0291(8)	0.2506(5)	0.8035(2)	6.1(7)
C(216)	–0.0591(8)	0.2222(5)	0.7675(2)	4.9(6)
C(221)	–0.2328(6)	0.4574(4)	0.6773(2)	3.6(5)
C(222)	–0.1594(7)	0.4725(4)	0.7095(2)	3.2(5)
C(223)	–0.2015(7)	0.5314(5)	0.7359(2)	4.7(6)
C(224)	–0.3146(8)	0.5779(5)	0.7300(2)	5.6(7)
C(225)	–0.3824(8)	0.5652(5)	0.6976(3)	6.1(7)
C(226)	–0.3435(7)	0.5036(5)	0.6715(2)	4.8(6)
C(231)	0.1295(6)	0.4380(4)	0.6702(2)	3.7(5)
C(232)	0.0715(6)	0.4711(5)	0.7023(2)	3.6(5)
C(233)	0.1097(8)	0.5443(5)	0.7194(2)	5.3(6)
C(234)	0.2141(8)	0.5864(5)	0.7052(3)	6.5(7)
C(235)	0.2758(7)	0.5539(5)	0.6748(3)	6.3(7)
C(236)	0.2373(7)	0.4815(5)	0.6571(2)	4.9(6)
N(22)	–0.0772(5)	0.2503(4)	0.6234(2)	3.6(4)

Table 3 (cont.)

Atom	x	y	z	U_{eq}
2nd Molecule				
C(21)	−0.1880(7)	0.2314(5)	0.6073(3)	5.7(6)
C(22)	−0.1969(8)	0.1714(6)	0.5793(3)	8.3(8)
C(23)	−0.0895(9)	0.1283(6)	0.5686(3)	8.1(8)
C(24)	0.0210(8)	0.1474(6)	0.5837(3)	7.0(7)
C(25)	0.0255(7)	0.2077(5)	0.6116(3)	5.9(6)

Atom	x	y	z	U_{iso}[a])
H(213)	0.017(6)	0.454(4)	0.786(2)	7.0
H(214)	0.013(6)	0.359(4)	0.835(2)	8.0
H(215)	−0.031(6)	0.219(4)	0.821(2)	8.0
H(216)	−0.082(6)	0.164(4)	0.766(2)	7.0
H(223)	−0.157(6)	0.542(4)	0.754(2)	7.0
H(224)	−0.337(6)	0.619(4)	0.742(2)	8.0
H(225)	−0.443(6)	0.597(4)	0.694(2)	8.0
H(226)	−0.390(5)	0.499(4)	0.654(2)	7.0
H(233)	0.062(6)	0.565(4)	0.739(2)	7.0
H(234)	0.238(6)	0.644(4)	0.719(2)	8.0
H(235)	0.353(6)	0.586(4)	0.663(2)	8.0
H(236)	0.280(5)	0.457(4)	0.642(2)	7.0
H(21)	−0.259(6)	0.265(4)	0.614(2)	8.0
H(22)	−0.272(6)	0.164(4)	0.569(2)	8.0
H(23)	−0.078(6)	0.079(4)	0.547(2)	8.0
H(24)	0.108(6)	0.119(4)	0.574(2)	8.0
H(25)	0.103(5)	0.216(4)	0.620(2)	8.0

Atom	x	y	z	U_{eq}
3rd Molecule				
Al(3)	0.0069(2)	0.3343(2)	0.33247(7)	3.1(1)
N(31)	−0.0201(5)	0.4242(4)	0.3786(2)	3.1(4)
O(31)	0.0104(4)	0.2554(3)	0.3684(1)	4.2(4)
O(32)	0.1439(4)	0.3935(3)	0.3227(1)	3.7(3)
O(33)	−0.1383(5)	0.3744(3)	0.3146(2)	5.0(4)
C(311)	−0.0143(7)	0.2813(5)	0.4048(2)	3.5(5)
C(312)	−0.0322(6)	0.3704(4)	0.4113(2)	2.8(5)
C(313)	−0.0549(7)	0.3975(5)	0.4478(2)	4.5(6)
C(314)	−0.0605(8)	0.3396(5)	0.4771(2)	6.0(6)
C(315)	−0.0425(8)	0.2532(5)	0.4700(2)	6.1(7)
C(316)	−0.0186(7)	0.2254(5)	0.4347(2)	4.4(6)
C(321)	0.1735(7)	0.4595(4)	0.3456(2)	3.2(5)
C(322)	0.0931(6)	0.4784(5)	0.3761(2)	3.3(5)
C(323)	0.1202(7)	0.5419(5)	0.4009(2)	4.6(6)
C(324)	0.2266(8)	0.5898(5)	0.3963(3)	6.0(7)
C(325)	0.3068(7)	0.5736(5)	0.3647(3)	5.9(7)
C(326)	0.2780(7)	0.5073(5)	0.3405(2)	4.4(6)
C(331)	−0.1909(7)	0.4397(5)	0.3334(2)	4.4(5)
C(332)	−0.1376(7)	0.4699(5)	0.3671(2)	3.3(5)
C(333)	−0.1905(7)	0.5394(5)	0.3866(2)	4.0(6)
C(334)	−0.2975(7)	0.5804(5)	0.3715(3)	5.5(7)
C(335)	−0.3506(7)	0.5490(5)	0.3390(2)	5.1(6)
C(336)	−0.2980(7)	0.4835(5)	0.3207(2)	5.1(6)
N(32)	0.0313(5)	0.2492(3)	0.2902(2)	3.5(4)

Table 3 (cont.)

Atom	x	y	z	U_{eq}
3rd Molecule				
C(31)	–0.0692(7)	0.2084(6)	0.2754(3)	5.9(7)
C(32)	–0.0505(9)	0.1453(6)	0.2476(3)	7.3(8)
C(33)	0.0678(9)	0.1272(6)	0.2356(3)	7.1(8)
C(34)	0.1680(8)	0.1693(6)	0.2502(3)	6.2(7)
C(35)	0.1473(7)	0.2326(5)	0.2771(2)	5.0(6)

Atom	x	y	z	U_{iso}[a])
H(313)	–0.060(6)	0.460(4)	0.453(2)	7.0
H(314)	–0.085(6)	0.368(4)	0.503(2)	8.0
H(315)	–0.042(6)	0.212(4)	0.487(2)	8.0
H(316)	–0.002(6)	0.170(4)	0.432(2)	7.0
H(323)	0.071(6)	0.562(4)	0.419(2)	7.0
H(324)	0.236(6)	0.635(4)	0.412(2)	8.0
H(325)	0.386(6)	0.601(4)	0.360(2)	8.0
H(326)	0.329(6)	0.496(4)	0.325(2)	7.0
H(333)	–0.154(6)	0.555(4)	0.405(2)	7.0
H(334)	–0.322(6)	0.625(4)	0.383(2)	8.0
H(335)	–0.418(6)	0.574(4)	0.333(2)	8.0
H(336)	–0.332(6)	0.458(4)	0.304(2)	7.0
H(31)	–0.153(6)	0.232(4)	0.281(2)	8.0
H(32)	–0.129(6)	0.132(4)	0.239(2)	8.0
H(33)	0.077(6)	0.082(4)	0.217(2)	8.0
H(34)	0.256(6)	0.159(4)	0.242(2)	8.0
H(35)	0.216(6)	0.260(5)	0.290(2)	8.0

[a]) The temperature factors of the H-atoms were not refined.

Table 4. *Positional and Displacement Parameters* (100 · U_{eq} or 100 · U_{iso}) *for [Al(**1**)(OH)]$^-$ [Hquin]$^+$ · DMSO.* E.s.d. in terms of least significant digit.

Atom	x	y	z	U_{eq}
Al(1)	0.6539(1)	0.9432(1)	0.06801(3)	4.0(1)
O(1)	0.6911(2)	1.0337(2)	0.02418(6)	4.0(1)
O(11)	0.5268(2)	0.8596(2)	0.04382(6)	4.1(1)
O(12)	0.8587(2)	0.8369(2)	0.07775(6)	4.3(1)
O(13)	0.5583(3)	1.0887(2)	0.10266(6)	4.8(1)
N(11)	0.6192(3)	0.8072(3)	0.12180(7)	3.1(2)
C(111)	0.5042(4)	0.7425(3)	0.06137(10)	3.5(2)
C(112)	0.5513(4)	0.7079(3)	0.10246(10)	3.2(2)
C(113)	0.5364(4)	0.5853(4)	0.12065(10)	4.3(2)
C(114)	0.4749(5)	0.4979(4)	0.09802(12)	5.4(3)
C(115)	0.4249(4)	0.5348(4)	0.05797(12)	5.1(3)
C(116)	0.4377(4)	0.6566(4)	0.03946(10)	4.3(2)
C(121)	0.9004(4)	0.7578(3)	0.11249(9)	3.6(2)
C(122)	0.7819(4)	0.7370(3)	0.13750(9)	3.5(2)
C(123)	0.8220(4)	0.6557(4)	0.17364(10)	4.6(2)
C(124)	0.9822(5)	0.5955(4)	0.18483(11)	5.5(3)
C(125)	1.1004(5)	0.6145(4)	0.16091(12)	5.4(3)
C(126)	1.0598(4)	0.6962(4)	0.12489(10)	4.6(2)
C(131)	0.4901(4)	1.0627(4)	0.13715(9)	4.0(2)
C(132)	0.5115(4)	0.9193(4)	0.14863(9)	3.3(2)
C(133)	0.4355(4)	0.8918(4)	0.18288(11)	4.9(2)

Table 4 (cont.)

Atom	x	y	z	U_{eq}
C(134)	0.3396(5)	1.0063(5)	0.20659(11)	6.2(3)
C(135)	0.3199(5)	1.1474(4)	0.19675(12)	6.2(3)
C(136)	0.3941(5)	1.1760(4)	1.16257(12)	5.7(2)
N(34)	0.8853(3)	0.8507(3)	-0.03002(8)	4.6(2)
C(311)	0.8019(5)	0.7478(5)	-0.03954(14)	7.3(3)
C(312)	0.8960(5)	0.6368(5)	-0.07184(14)	8.4(3)
C(321)	0.9000(6)	0.9309(5)	-0.06796(13)	8.0(3)
C(322)	0.9961(6)	0.8223(5)	-0.10016(13)	8.8(4)
C(331)	1.0490(5)	0.7703(5)	-0.01332(12)	7.0(3)
C(332)	1.1469(5)	0.6583(5)	-0.04422(14)	8.5(3)
C(34)	1.0461(5)	0.6656(5)	-0.08313(12)	7.2(3)

Atom	x	y	z	U_{iso}[a])
H(113)	0.560(4)	0.563(3)	0.1485(9)	7.0
H(114)	0.467(4)	0.412(3)	0.1094(9)	8.0
H(115)	0.377(4)	0.472(3)	0.0411(9)	8.0
H(116)	0.402(4)	0.678(3)	0.0091(8)	7.0
H(123)	0.728(4)	0.645(3)	0.1906(9)	7.0
H(124)	1.009(4)	0.536(3)	0.2092(9)	8.0
H(125)	1.216(4)	0.578(3)	0.1705(9)	8.0
H(126)	1.146(4)	0.716(3)	0.1096(9)	7.0
H(133)	0.451(4)	0.792(3)	0.1899(9)	7.0
H(134)	0.286(4)	0.984(3)	0.2304(9)	8.0
H(135)	0.249(4)	1.236(3)	0.2119(9)	8.0
H(136)	0.375(4)	1.270(3)	0.1559(9)	7.0
H(311)	0.810(4)	0.691(3)	-0.0108(9)	8.0
H(312)	0.700(4)	0.822(3)	-0.0541(9)	8.0
H(313)	0.947(4)	0.533(3)	-0.0544(9)	8.0
H(314)	0.844(4)	0.676(3)	-0.1015(9)	8.0
H(321)	0.776(4)	0.972(3)	-0.0772(9)	8.0
H(322)	0.945(4)	1.011(3)	-0.0559(9)	8.0
H(323)	0.934(4)	0.823(3)	-0.1239(9)	8.0
H(324)	1.112(4)	0.834(3)	-0.1045(9)	8.0
H(331)	1.086(4)	0.859(3)	-0.0141(9)	8.0
H(332)	1.022(4)	0.718(3)	0.0123(9)	8.0
H(333)	1.221(4)	0.710(3)	-0.0582(9)	8.0
H(334)	1.145(4)	0.565(3)	-0.0312(9)	8.0
H(34)	1.097(4)	0.595(3)	-0.1044(9)	8.0
H(1)	0.802(4)	0.942(3)	-0.0064(9)	8.0
H(2)	0.625(4)	1.069(3)	0.0091(9)	8.0

Atom	*PP*	x	y	z	$U_{eq\ or\ iso}$
Disordered DMSO molecule					
S(1)	0.5	0.3301(4)	0.5952(6)	0.25404(9)	11.5(4)
S(2)	0.5	0.4182(6)	0.5945(6)	0.27442(15)	15.6(4)
C(1)	0.5	0.3132(13)	0.7455(11)	0.2982(3)	10.4(3)
C(2)	0.5	0.4185(13)	0.4751(12)	0.3033(3)	12.4(4)
C(3)	0.5	0.2292(22)	0.6986(19)	0.2723(5)	22.6(7)
C(4)	0.5	0.2991(15)	0.4879(13)	0.2753(4)	14.1(4)
O(3)	1.0	0.4819(5)	0.5762(4)	0.23219(9)	11.5(3)

[a]) The temperature factors of the H-atoms were not refined.

Table 5. *Geometries of the Tricycloundecane Frameworks of [(Al(**I**))$_2$], [Al(**I**)(py)], and [Al(**I**)(OH)]$^-$[Hquin]$^+$·DMSO.* Bond lengths in Å, bond angles and torsion angles in °[a])[b]).

	[(Al(**I**))$_2$]		[Al(**I**)(py)]	[Al(**I**)(OH)]
	[c])	[d])		
Al–N(1)	2.094(18)		2.153(6)	2.278(3)
N(1)–C(12)	1.471(12)	1.469(8)	1.461(9)	1.457(4)
C(12)–C(11)	1.392(16)	1.390(11)	1.393(10)	1.399(5)
C(11)–O(1)	1.355(6)	1.372(18)	1.350(9)	1.345(4)
O(1)–Al	1.745(18)	1.846(19)	1.762(5)	1.782(2)
Al–O(1′)	1.850(4)			
Al–N(2)			1.992(6)	
Al–OH				1.765(2)
C(12)–N(1)–C(22)	114.8(2)		115.1(5)	115.2(2)
Al–N(1)–C(12)	102.1(2)	106.2(2)	103.0(4)	102.8(2)
N(1)–C(12)–C(11)	114.2(2)	114.9(2)	114.7(6)	114.1(3)
N(1)–C(12)–C(13)	125.3(2)	124.6(2)	125.2(6)	125.3(3)
C(12)–C(11)–O(1)	119.4(2)	116.7(2)	119.2(6)	119.7(3)
C(16)–C(11)–O(1)	120.8(2)	123.3(2)	121.9(6)	121.7(3)
C(11)–O(1)–Al	114.7(2)	116.8(1)	117.2(4)	120.2(2)
O(1)–Al–N(1)	87.7(1)	83.1(1)	85.3(2)	81.1(1)
O(1)–Al–O(1′)	101.7(1)	77.7(1)		
O(1)–Al–N(2)			94.7(3)	
O(1)–Al–OH				99.0(1)
N(1)–Al–O(1′)	160.8(1)			
N(1)–Al–N(2)			178.8(3)	
N(1)–Al–OH				174.9(1)
O(1)–Al–O(2)	119.6(1)		119.4(3)	117.6(1)
Al–O(1′)–Al′	102.3(1)			
Al···Al′	2.877(42)			
Al–N(1)–C(12)–C(11)	–11.0	–8.3	–3.7	–9.7
N(1)–C(12)–C(11)–O(1)	4.0	–1.9	0.2	1.5
C(12)–C(11)–O(1)–Al	7.7	13.3	4.6	11.3
C(11)–O(1)–Al–N(1)	–11.4	–14.1	–5.2	–12.9
O(1)–Al–N(1)–C(12)	12.2	11.9	4.8	12.0
O(1)–Al–N(2)–C(41)			(29.8)[e])	

[a]) E.s.d. in terms of least significant digit; the e.s.d. of multiple determinations were estimated as the arithmetic mean of the individual e.s.d. of all contributors.

[b]) E.s.d. of torsion angles are in the order of 1.0°.

[c]) Nonbridging chelate rings (1 and 2).

[d]) Bridging chelate ring (3).

[e]) The smallest of the six torsion angles between an O–Al and a pyridine N–C bond.

[Al(**I**)(py)] with a pyridine N-atom as apical ligand atom, lies between. There is concomitant variation of some of the other geometric parameters of the tricycloundecane cage, *e.g.* the planarity of the AlO$_3$ fragment, as indicated by the N–Al–O and average O–Al–O angles.

These findings are consistent with the interpretation that the Al(III) ion is successively 'drawn out' of the **I** cage by more and more nucleophilic apical ligands; the bond between Al and the N-atom of **I** is weakened, as the bond between Al and the external nucleophile is strengthened. The three structures [(Al(**I**))$_2$], [Al(**I**)(py)], and [Al(**I**)(OH)]$^-$ can be regarded as distinct points on a reaction pathway of a nucleophilic ligand substitution reaction at 5-coordinate Al(III) *(Fig. 6a)*. Extrapolation in the direction of short Al–N distances (not observed) suggests that substitution of an apical ligand X by another ligand Y occurs through a 4-coordinate, dissociative intermediate, which then would be able to add another apical ligand *(Eqn. 2)*.

$$[\mathrm{Al}(\mathbf{I})\mathrm{X}] \underset{+\mathrm{X}}{\overset{-\mathrm{X}}{\rightleftharpoons}} [\mathrm{Al}(\mathbf{I})] \underset{-\mathrm{Y}}{\overset{+\mathrm{Y}}{\rightleftharpoons}} [\mathrm{Al}(\mathbf{I})\mathrm{Y}] \tag{2}$$

The energy profile along such a reaction coordinate can be regarded as a flat valley, delimited by relatively steep walls on both sides *(Fig. 6a)* [9] [10]. The minimum energy reaction pathway along the bottom of such a valley is obtained in good approximation by the empirical rule of *conservation of bond order* [9] which states that the bonding, and, therefore, the bond energy lost by breaking (fully or partially) a chemical bond is, as far as possible, recovered by shortening some or all of the remaining bonds. An empirical relation between bond length and bond order has been given by *Pauling* [11] *(Eqn. 3)*,

$$\Delta r = r - r_s = -c \cdot \ln(n) \tag{3}$$

where r is the actual bond length, r_s is the standard single-bond length, n is the bond order, and c is a constant which depends mainly on the type of the reacting central atom.

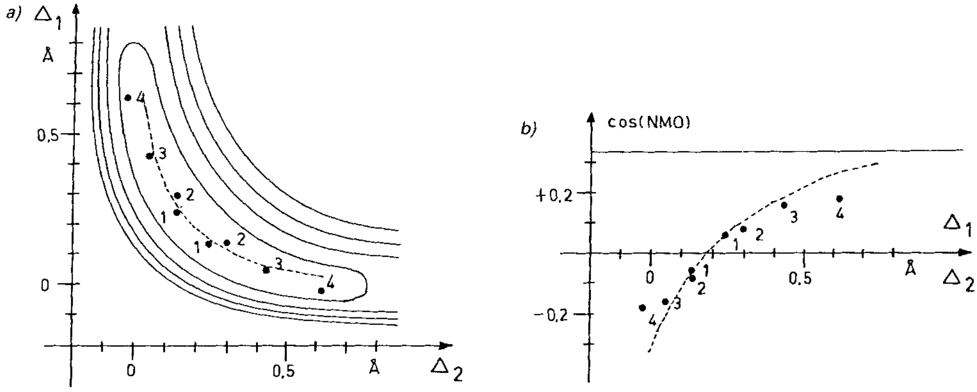

Fig. 6. *Structure correlation of four [M(**I**)X] structures. 1)* [(Al(**I**))$_2$]; *2)* [Al(**I**)(py)]; *3)* [Al(**I**)(OH)]$^-$; *4)* [Si(**I**)(C$_6$H$_5$)] [12] (isoelectronic to [Al(**I**)(py)]). *a)* Bond lengthenings in the axial system N···M···X: Δ_1 plotted against Δ_2 (the dashed line corresponds to $\exp(-\Delta_1/c) + \exp(-\Delta_2/c) = 1$; with $c = 0.27$). *b)* Bond lengthenings Δ_1, Δ_2 plotted against the cosine of the N–M–O angle (the dashed line corresponds to $\Delta = -c \cdot \ln(\frac{1}{2} - \frac{3}{2}\cos\alpha)$; with $c = 0.27$). Energy contours are indicated schematically in drawing *a)*.

Conservation of bond order in the axial system N···Al···X, characterized by r_1 (N–Al), n_1, r_2(Al–X), and n_2, leads to a hyperbolic expression for the curve relating r_1 and r_2 *(Eqn. 4* and *5)*:

$$n_1 + n_2 = \text{const.} \tag{4}$$

$$\exp[-(r_1 - r_s)/c] + \exp[-(r_2 - r_s)/c] = \text{const.} \tag{5}$$

For replacement of one *single* bond by another, the constant is unity. An analogous expression can be derived for the dependency of the bond lengthening Δ on the cosine of the N–M–O angle *(Eqn. 6)*:

$$\Delta = -c \cdot \ln(1/2 - 3/2 \cos \alpha) \qquad (6)$$

(*i.e.* the bond lengthening will be zero for $\alpha = 109.5°$ (tetrahedron) and infinite for $\alpha = 70.5°$ (*Walden* reversed tetrahedron)).

Fig. 6 shows a scatterplot of $\Delta_1 = r_1 - r_s$ *vs.* $\Delta_2 = r_2 - r_s$ (*Table 6*), and of Δ_1, Δ_2 *vs.* the cosine of the N−M−O angles for the three structure [(Al(**I**))$_2$], [Al(**I**)(py)], and [Al(**I**)(OH)]$^-$, as well as a related structure found in the literature, [Si(**I**)(C$_6$H$_5$)] [12]. The resulting curves ($c \approx 0.30$) are similar to those found for Cd [13], Sn [14], and Si [15]. This implies that the systems [M(**I**)X] (M = Al(III), Si(IV)) respond to imposed variations of the apical ligand X mainly by distortion along a dissociative/associative coordinate of the axial 3-center-4-electron system N···M···X. Further kinetic work is needed to elucidate the nature of the postulated 4-coordinate dissociative intermediate [Al(**I**)]. and to obtain a more quantitative idea about the energy variations along the reaction valley.

Table 6. *Structure Correlation of [M(***I***)X] Complexes* (M = Al, Si). $c \approx 0.30$.

Entry	[MIX]	M	X	M−N$_{\text{int.}}$	Δ_1^{a})	M−X$_{\text{ext.}}$	Δ_2^{a})	M−O$_{\text{eq}}$	Δ_{eq}^{a})	N−M−O	cos(NMO)
1	[(Al(**I**))$_2$]	Al	O	2.094	0.24	1.850	0.14	1.778	0.07	86.4	0.06
2	[Al(**I**)(py)]	Al	N	2.153	0.30	1.992	0.14	1.762	0.05	85.5	0.08
3	[Al(**I**)(OH)]$^-$	Al	O	2.278	0.43	1.765	0.05	1.782	0.07	81.0	0.16
4	[Si(**I**)(C$_6$H$_5$)] [13]	Si	C	2.344	0.62	1.852	−0.02	1.639	0.03	79.0	0.18

^{a}) Reduced bond lengths: $\Delta_i = r_i - r_s = d(\text{M–X}) - d°(\text{M–X})$, with d(M−X) = measured bond length M−X, $d°$(M−X) = standard single-bond length [16]; $d°$(Si−C) = 1.87 Å, $d°$(Si−N) = 1.72 Å, $d°$(Si−O) = 1.61 Å, $d°$(Al−N) = 1.85 Å, $d°$(Al−O) = 1.71 Å.

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