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An Octahedral Aluminium(III) Complex as a Three-Fold node for Supramolecular Heterometallic Self-Assemblies: Solution and Solid State Chemistry

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The new ditopic ligand Al**L**$_3$ (**L**=3-(pyridin-4-ylmethyl)acetylacetonate) has been prepared. The crystal structure of the aluminium(III) complex Al**L**$_3$.H$_2$O is reported and shows three pendant pyridyl groups available for bridging metal ions. With square planar ions (Cu(II), Pd(II)) the formation of a symmetric cage complex $[M_6(AlL_3)_8]^{12+}$ is proposed. With Co(NCS)$_2$ an extended structure $[\{Co(NCS)_2\}(AlL_3)(OH_2)]_n$ is found. Factors favouring cage or extended structures are briefly discussed.

Introduction

The use of weak interactions in supramolecular chemistry has yielded a great number of structures with varying sizes and shapes in recent years. The greatest challenge for synthetic chemists is to tune and control these interactions to lead to the desired product. Coordination-driven self-assembly processes harness the directionality and reversibility of metal-ligand interactions to allow the formation of the thermodynamically favoured product.[1] Some pioneers obtained remarkable structures with various nuclearities by tuning the symmetries of both metal centres and ligands.

The synthesis of hollow metal clusters using coordination chemistry has become a subject of considerable interest with significant contributions from several groups such as those of Fujita,[2, 3] Raymond,[4, 5] Stang,[6, 7] and Nitschke.[8, 9] The resulting capsules have been studied for host guest properties [9-13] and as potential catalysts or reaction flasks.[14, 15]

Various strategies have been developed towards the synthesis of these closed systems.[6, 16] Fujita has employed square planar Pd(II) as a coordination centre and shown that varying the angle between the coordination vectors of a bridged bis(4-pyridyl) ligand allows control of nuclearity.[2] Many workers have used approaches based on generating Platonic or Archimedean solids,[17] where symmetry considerations are important. As an example we may consider the case of fivefold symmetry: it is impossible to generate a tiling using pentagons, and an assembly of pentagons must lead to a closed shape as in C_{60}: this has been shown by Scheer[18] and ourselves [19, 20] with pentagonal ligands, and by Müller[21-23] for giant polyoxometallates, and five-fold symmetry is also observed in the assembly of biological capsules.[24]

A major problem in self-assembly of capsules is to ensure the formation of a closed surface in three dimensions rather than an extended surface in two dimensions. Pentagonal symmetry is one solution to this, but nature uses another symmetry-based approach in the iron-storage protein ferritin[25] which combines four-fold and three-fold axes to give a closed capsule with 432 symmetry; as Raymond remarked,[26] such a combination must give rise to an octahedral symmetry. Fujita,[27] Shionoya[28] and Batten[29, 30] have generated octahedral structures using ligands with threefold symmetry to link square planar four coordinate metal ions.

Our objective in this work was to generate an octahedral system by placing three-fold and four-fold axes at the required angle of 55° but more particularly to avoid the initial synthesis of a threefold symmetric ligand. We sought to generate both three-fold and four-fold axes by coordination reactions, thereby combining 38 components into one molecule.

To generate the fourfold axis we chose the square planar ions Cu(II) and Pd(II), and to obtain a 3-fold axis, a tris-chelate complex of an octahedral metal was an obvious choice. The ligand which is to bridge between the square planar and octahedral sites must do so selectively: the bidentate site should bind selectively the octahedral ion and the monodentate ligand which binds the square planar metal ion should have low

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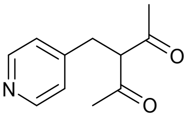
affinity for the octahedral ion. The two interactions must be orthogonal.[31] This selectivity is particularly important if labile metal ions such as Cu(II) and Al(III) are used. Acetylacetonate is a hard ligand which forms stable species with hard metal ions such as Al(III) or Fe(III) and it is readily derivatised.[32] A pyridyl group has strong affinity for Cu(II) and Pd(II) but less for the harder metal ions. A combination of anionic oxygen chelates and pyridyl donors has also been used for selective orthogonal complexation by Shionoya[33]. Studies of models suggested the ligand **L**H in which the pyridyl ligand is connected at the 4- position by a methylene bridge to the 3-position of the acetyl acetone (Scheme 1).


LH

Scheme 1

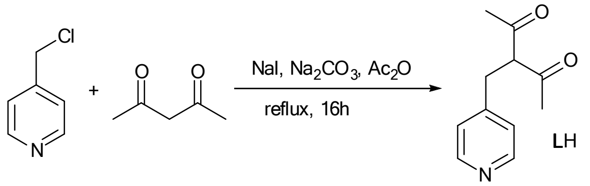
Models indicated that in the complex [Al**L**$_3$] the coordination vector of the pyridyl group would be correctly oriented with respect to the threefold axis.

We report here our studies on the chemistry of ligand **L** with different metal ions. While this work was in progress two related studies have appeared: Wu[34] used the octahedral aluminium complex of the ligand 4-pyridyl-butane-1,3-dione with Pd(II) as a square planar centre, and Nitschke[35] used an octahedral iron(II) complex of a Schiff base derivatised with a 4-pyridyl group to bind Pd(II). Both groups reported the formation of cages.

Results and Discussion

Synthesis of metalloligand AlL$_3$

The ditopic ligand **L**H is accessible by a one pot reaction of 4-chloromethylpyridine with pentane-2,4-dione in acetone in presence of sodium iodide and sodium carbonate (Scheme 2).[36] The ligand is isolated after column chromatography as brown oil in 74% yield.



Scheme 2. Synthesis of **L**H

Reaction of the ditopic ligand with $Al(NO_3)_2{\cdot}9H_2O$ gives the neutral metalloligand Al**L**$_3$.H$_2$O as a white crystalline powder under basic conditions in water. The ^{1}H-NMR spectrum shows only one set of peaks, confirming the coordination of aluminium by the absence of keto-enol tautomerism. Slow evaporation of a water solution gave X-ray quality crystals. The product crystallises in the non-centrosymmetric space group *C*2. The crystal structure of the complex was determined and shows aluminium coordinated by three ligands, in a bidentate fashion through the acetylacetonate moiety in a pseudo-octahedral geometry (Figure 1). Al · · · O distances are in the range 1.877 – 1.910 Å and Al-O-Al angles are 88.10-92.90°, in agreement with expected values for acetylacetonate complexes of aluminium(III).[37] The water molecule acts as a hydrogen bond donor to two pyridyl groups from neighbouring complexes. No π-π interactions were observed. The structure confirmed the favourable orientation of the pyridyl moieties predicted from the modelling studies.

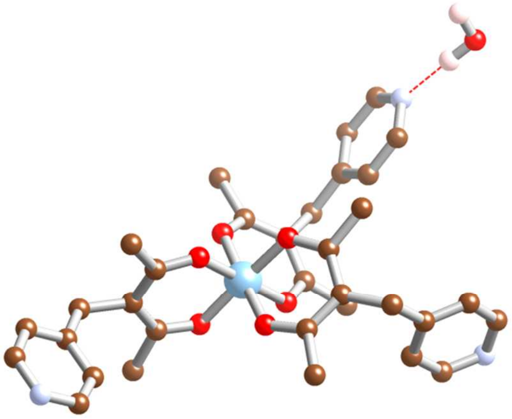


Figure 1. View of Al**L**$_3$ with 50% thermal ellipsoids. Hydrogen atoms and solvent are omitted for clarity (key: C brown, O red, N blue, Al sky blue).

Complexation by [Al(L)$_3$] in solution.

Our first studies in solution were carried out using copper (II) as a square planar node. Its high affinity for nitrogen-containing ligands and its lability should allow the system to give the generally thermodynamically favoured product. Coordination of pyridines to copper centres causes a significant shift in the copper d-d band so that spectrophotometric titrations are appropriate to follow the formation of self-assembled species in solution Copper(II) perchlorate was used because of the weakly-coordinating nature of the perchlorate anion and for solubility reasons, the titration was carried out in acetonitrile. The addition of copper to the solution of [Al**L**$_3$] results in the growth of a new band with λ_{max}= 582 nm.(Figure S1) For the complex $[Cu(py)_4]^{2+}$ (py = pyridine) in acetonitrile, λ_{max} =584 nm. Free copper(II) absorbs only very weakly at this wavelength, so this observation supports the complexation of copper by the pyridyl moieties.

The plot of the absorbance at five different wavelengths as a function of the Cu:Al ratio shows a clear end point at a ratio of 0.75 (Figure 2). A less marked change in gradient is visible around 0.25.

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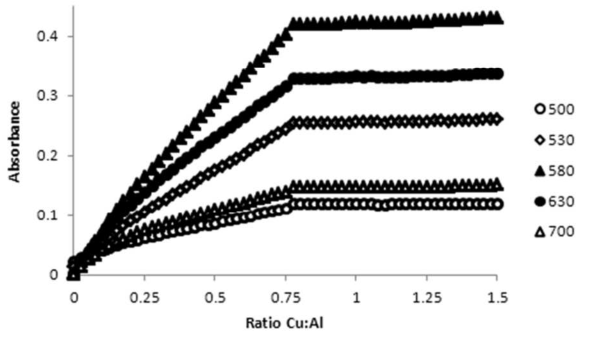

Figure 2. Plot of absorbance against copper to aluminium ratio for the titration of 10^{-2}M [AlL_3] with $Cu(ClO_4)_2$ $5.0\cdot10^{-2}$M in acetonitrile. The wavelengths (in nm) are distinguished by different markers.

Another method to follow the formation of charged species in solution is conductimetry. This technique is well established in coordination chemistry[38] but has been used less frequently in supramolecular chemistry.[39, 40] Conductimetric titrations were carried out in acetonitrile with concentrations of [Al$\mathbf{L}_3$] between $1\cdot10^{-3}$ and $6\cdot10^{-2}$ M and [$Cu(ClO_4)_2$] between $3.4\cdot10^{-4}$ and $2\cdot10^{-2}$ M. A typical conductimetric curve is shown in Figure 3.

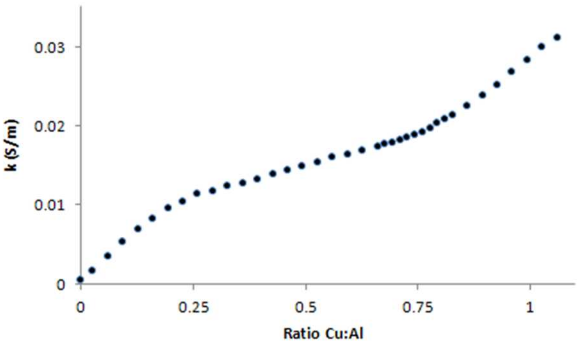

Figure 3. Plot of conductivity *vs* copper to aluminium ratio ([AlL_3]= $3\cdot10^{-3}$ M, [$Cu(ClO_4)_2$]= $2\cdot10^{-3}$M). Two inflection points are visible at Cu/Al=0.25 and 0.75.

There are now two inflections in the curve, the first around 0.25 which is much clearer than for the spectrophotometric titration, and the second at 0.75 Cu:Al ratio.

The results of the conductimetric and spectroscopic titrations are consistent with successive formation of species with Cu:Al ratios of 1:4 and 3:4. The first would be a complex $[Cu(Al\mathbf{L}_3)_4]^{2+}$ with one pyridyl from each metalloligand binding to the copper to give the $Cu(py)_4$ chromophore shown by the spectra. The second species shows a Cu:Al ratio of 3:4 and also contains a $Cu(py)_4$ chromophore. This ratio implies that all the pyridyl groups are bound to Cu(II). Inspection of models shows that the pyridyl groups of the [Al$\mathbf{L}_3$] ligand are too far apart to act as chelate to one metal ion, and so the metalloligand must either be monodentate as in $[Cu(Al\mathbf{L}_3)_4]^{2+}$ or bridging. We can think of no structure for a 3:4 ratio which satisfies these conditions, but the octahedral complex $[Cu_6(Al\mathbf{L}_3)_8]^{12+}$ with eight triply bridging metalloligands and six square planar copper(II) tetrapyridyl units is consistent with the stoichiometry and the electronic spectra. A model structure (prepared using Scigress[41]) for the complex $[Cu_6(Al\mathbf{L}_3)_8]^{12+}$ is shown in Figure 4.

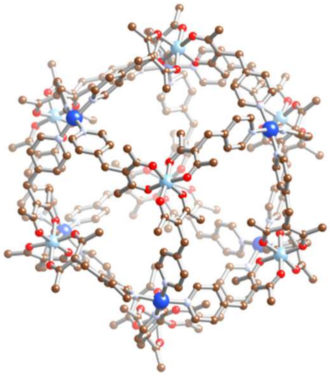

Figure 4. Model of the complex $[Cu_6(Al\mathbf{L}_3)_8]^{12+}$ looking along the threefold axis.

This is consistent with the conductivity data. At the beginning of the titration the conductivity rises as more $[Cu(Al\mathbf{L}_3)_4]^{2+}$ is formed, but beyond 0.25 equivalents, $[Cu_6(Al\mathbf{L}_3)_8]^{12+}$ is formed. The size of this highly charged ion reduces its mobility and so the rise in conductivity is less. After 0.75 equivalents the excess copper added is not complexed and the conductivity again rises rapidly. Attempts to characterise the cage by ESI-MS in acetonitrile or methanol showed only fragments of the proposed structure.

The paramagnetic nature of the copper(II) ion precludes NMR studies, but according to the argument presented in the introduction it should be possible to use palladium(II) in place of copper, at the cost of slower kinetics. Figure 5 shows the ^{1}H NMR spectra of the ligand before and after addition of palladium nitrate in stoichiometry corresponding to Pd_6Al_8. Although some heating is required to reach equilibrium, the final system shows significant downfield shifts of the pyridyl protons, consistent with their coordination to Pd(II). The methyl groups of the acetylacetone moiety shift little but are broadened, consistent with the fact that they are no longer equivalent, one being directed to the inside of the cage, the other to the outside. If substoichiometric quantities of palladium were used the spectrum showed a mixture of free ligand and palladium complex. If excess of palladium was used, the spectrum was unchanged. These observations agree with the formation of $[Pd_6(Al\mathbf{L}_3)_8]^{12+}$.

If palladium(II) acetate was used instead of nitrate the peaks were better defined but complete coordination could not be achieved. Even after several days of heating, only approximately 60% of the pyridine moieties were coordinated to a metal centre.

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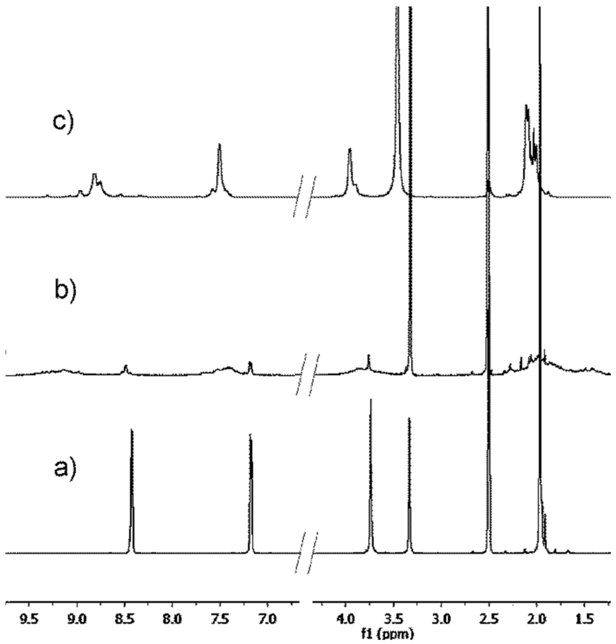


Figure 5. a) Spectrum of the Al**L**$_3$ in d$_6$-DMSO; b) and c) Spectra of a mixture containing 8 eq. of Al**L**$_3$ and 6 eq. of Pd(NO$_3$)$_2$ in d$_6$-DMSO. b) immediately after mixing. c) after 40 hours of heating at 80°C. Peaks at 2.50 and 3.33 ppm are due to solvent and water respectively.

DOSY-NMR has established itself as a useful tool for supramolecular chemistry.[42-44] The three quite well-resolved peaks due to the pyridine protons and the CH$_2$ group were used in metalloligand and the final product (Table S1). For the metalloligand, diffusion coefficient D measured was $2.26(9)\cdot10^{-10}\mathrm{m^2s^{-1}}$. For Al**L**$_3$ with 0.75 equivalents of Pd^{II}, all three peaks gave similar values for the coefficient D, an average of $7.60(3)\cdot10^{-11}\mathrm{m^2s^{-1}}$. The drop by a factor of three of the diffusion coefficient is substantial and most likely due to an increase in size of the species in solution. Even if the interpretation of DOSY-NMR results is nontrivial, the shape of the product can be assumed in a first approximation as spherical and one may use the Stokes-Einstein equation[45] to obtain hydrodynamic radius of the pseudo-spherical product. With a value of $1.99\cdot10^{-3}\mathrm{kg\cdot s\cdot m^{-2}}$ for the viscosity of DMSO at 25°C, a radius of 14.5Å is obtained. The modelled structure in figure 4 fits just inside a sphere of radius 15 Å.

We attempted to follow the formation of the cage by UV-visible spectroscopy, but the spectral changes were rather small since the spectra of Pd(II), Al**L**$_3$ and the final complex overlap. The slow kinetics require the measurements to be made in batches, and the resulting data were of low quality, but a poorly resolved endpoint was observed around a Al**L**$_3$: Pd(II) ratio of 1.2. ESI-MS was again unsuccessful.

Solid state structures

All efforts to crystallise a salt of $[\mathrm{Cu_6(Al\mathbf{L}_3)_8}]^{12+}$ were unsuccessful. If one uses monovalent anions such as nitrate or perchlorate, 12 anions need to be packed around the structure. Attempts using more highly charged anions such as $[\mathrm{SiW_{12}O_{40}}]^{4-}$ merely gave intractable precipitates. We reasoned that it might be easier to crystallise a neutral species, and, following Batten et al.[30] who used octahedral ions with two *trans*- anionic ligands as a four-fold node, reacted Al**L**$_3$ with Co(NCS)$_2$. The resulting solution gave an NMR spectrum with very broad signals that could not be interpreted, but standing allowed us to obtain crystals of quality suitable for X-ray crystallography. Attempts to dry the crystals under vacuum for elemental analysis led to decomposition, the crystals changing from pink to blue.

The crystal structure of the product obtained showed it to be $[\{\mathrm{Co(NCS)_2}\}(\mathrm{Al\mathbf{L}_3})(\mathrm{H_2O})]$ with a Co: Al ratio of 1:1. It forms an extended structure composed of tapes of composition $[\{\mathrm{Co(NCS)_2}\}(\mathrm{Al\mathbf{L}_3})_2]_n$ in which Al**L**$_3$ units bridge cobalt ions along the crystallographic *a* axis (Figure 6). The cobalt ions show the desired *trans*-Co(py)$_4$(NCS)$_2$ configuration.

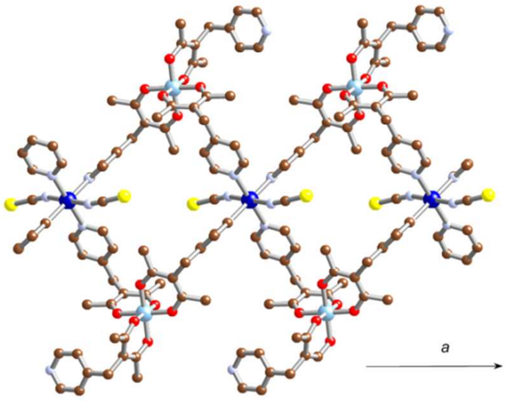


Figure 6. $[\{\mathrm{Co(NCS)_2}\}(\mathrm{Al\mathbf{L}_3})_2]_n$ tapes in $[\{\mathrm{Co(NCS)_2}\}(\mathrm{Al\mathbf{L}_3})(\mathrm{H_2O})]$.

These tapes are then linked together to give a two-dimensional structure by Co(NCS)$_2$(OH$_2$)$_2$ units bound to the third, uncoordinated pyridines of the Al**L**$_3$ in $[\{\mathrm{Co(NCS)_2}\}(\mathrm{Al\mathbf{L}_3})_2]_n$ on neighbouring tapes (Figure 7). Both cobalt ions lie on crystallographic centres of inversion.

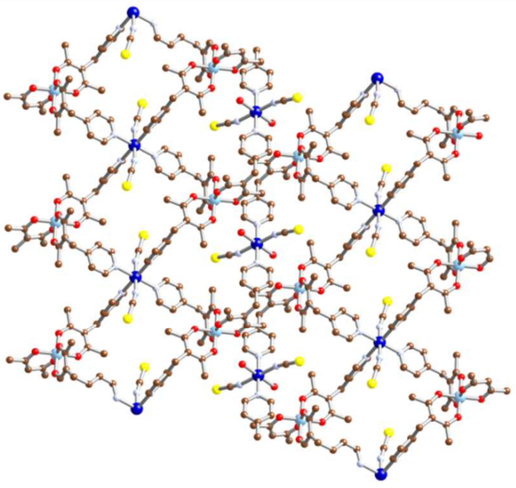


Figure 7. The tapes in figure 6 run vertically and are linked by Co(NCS)$_2$(OH$_2$)$_2$ units which lie between the tapes.

The geometry around aluminium is slightly deformed octahedral. Al - O distances are in the range 1.857 – 1.885 Å and O-Al-O angles are 86.2-93.5°. All cobalt atoms are pseudo-octahedral. Co - N distances round the four-fold cobalt are 2.160-2.199 Å for pyridines and 2.080 Å for thiocyanates. N-Co-N angles are in the range 87.3-92.7°. For the other cobalt atom, Co-N distances are 2.160 Å for pyridines, 2.070 Å for thiocyanates and 2.109 Å for oxygen from water. *Cis*-bond angles are 89.6-90.5° a little closer to the perfect octahedron than for aluminium. The hydrogens of the coordinated water molecule hydrogen bond to acetylacetone oxygens. We suppose that the change in colour observed when the crystals are dried under vacuum results from the loss of the coordinated water leading to a coloured tetrahedral cobalt(II) centre.

Crystals were also obtained the same way with copper(II) chloride instead of cobalt(II) thiocyanate but data were weak. Only a poorly resolved structure could be obtained, showing a similar structure in which half the copper are square pyramidal with four pyridines lying in a plane with a chloride on an axial position and the other half is square planar with two pyridines and two chlorides in a *trans*- coordination.

Experimental Section:

General: All reagents were purchased from Acros, Aldrich or Fluka and used without further purification. All ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 spectrometer at 400 MHz (^{1}H) or 101 MHz (^{13}C) at ambient temperature and shifts are given with respect to TMS. Deuterated solvents were purchased from Cambridge Isotopic Laboratories Inc. Electronic spectra in the UV/Vis region were recorded at 298 K with a Perkin-Elmer Lambda 900 spectrometer using quartz cells of 1 cm path length. A Perkin-Elmer Spectrum One instrument was employed for IR spectra. Electrospray mass spectra were obtained by the Mass Spectroscopy Laboratory, University of Geneva. Low resolution spectra were obtained on an Applied Biosystems Sciex API 150EX instrument. Elemental analyses were performed at Geneva University on a Vario Micro Cube apparatus under a helium atmosphere. Spectrophotometric titrations in the UV range were recorded in solution with a TIDAS spectrophotometer interfaced to a PC and using a probe of 1.0 cm path length. Titrations were carried out at 25°C using a Metrohm burette with a 5 mL syringe and were performed by the addition of 0.1 mL aliquots. All spectrophotometric spectra were acquired in acetonitrile for solubility reasons. The concentration of [$\mathrm{Al}\mathbf{L}_3$] was 10^{-2} M and $5\cdot10^{-2}$ M for $Cu(ClO_4)_2$. Conductimetric measurements were performed on a Metrohm 644 Conductometer equipped with a Metrohm conductimetric cell (constant = 0.82 cm^{-1}) at ambient temperature. All measurements were performed in acetonitrile for solubility reasons. Concentrations of $\mathrm{Al}\mathbf{L}_3$ were between $3\cdot10^{-2}$ and $5\cdot10^{-4}$ [mol/L] and those of $Cu(ClO_4)_2$ between $2\cdot10^{-2}$ and $3.4\cdot10^{-4}$ [mol/L]. The additions of copper(II) perchlorate to the $\mathrm{Al}\mathbf{L}_3$ solution were of 1 mL (0.5 mL around equivalent point). After each addition, the measured value was reported after a delay of 20 minutes.

Synthesis of 3-(pyridin-4-ylmethyl)acetylacetone (**L**H)**:** **L**H was synthesized by a nucleophilic substitution of acetylacetone by 4-iodomethylpyridine which is formed in situ from 4-chloromethylpyridine by a Finkelstein reaction. Acetylacetone (3.051 g, 314 μL, 30.5 mmol) was dissolved in dry acetone (30 mL). NaI (0.914 g, 6.1 mmol) and K_2CO_3 (4.213 g, 30.5 mmol) were added. The mixture was stirred at room temperature for 2 h. Then 4-chlorometylpyridine (1.000 g, 6.1 mmol) was added and the solution was heated to reflux and stirred overnight. Water was then added and the solution extracted with diethyl ether (3x50 mL). The organic layer was dried over $MgSO_4$, followed by removal of the solvent under reduced pressure. The crude product was purified by column chromatography (silica, EtOAc/CH_2Cl_2 4:1). The product is obtained as a yellow oil in 79 % yield. ES-HRMS *m/z* calcd : 192.1019 ; found : 192.1019 $[M+H]^+$; ^{1}H NMR ($CDCl_3$, 400 MHz) : δ (ppm) ketone : 1.98 (s, 6H), 3.09 (d, *J* = 7.4 Hz, 2H), 3.98 (1H), 7.05 (d, *J* = 5.3 Hz, 2H), 8.46 (d, *J* = 5.3 Hz, 2H). enol : 2.00 (s, 6H), 3.61 (s, 2H), 7.05 (d, *J* = 5.3 Hz, 2H), 8.46 (d, *J* = 5.3 Hz, 2H). ketone / enol : 1/3; ^{13}C NMR ($CDCl_3$, 400 MHz) : δ (ppm) ketone : 29.53 (CH_3), 32.22 (CH_2), 68.75 (CH), 122.71 (CH_{pyr}), 149.1 (C_{pyr}), 149.92 (CH_{pyr}), 202.42 (C=O). enol : 23.08 (CH_3), 32.83 (CH_2), 106.72 (CH), 123.77 (CH_{pyr}), 147.2 (C_{pyr}), 149.92 (CH_{pyr}), 192.03 (C=O) ; IR (cm^{-1}) : 3024 (w), 1725 (m), 1699 (s), 1598 (s), 1413 (s), 1357 (s), 1252 (m), 1150 (m), 993(m), 941 (m), 804 (m), 480 (m).

Synthesis of $\mathrm{Al}\mathbf{L}_3$**:** Ligand **L**H (100 mg, 0.52 mmol) was dissolved in water (5 mL). Sodium acetate (300 mg, 3.66mmol) was added and once all the solid was dissolved, $Al(NO_3)_3\cdot9H_2O$ (65 mg, 0.17 mmol) was added. The white precipitate was filtered and washed with cold water. Slow evaporation of the filtrate gave transparent crystals suitable for X-ray diffraction. ES-HRMS for $[\mathrm{Al}(\mathbf{L})_2]^+$ *m/z* calcd : 407.1546 ; found : 407.1547 ; ^{1}H NMR (400 MHz, DMSO) δ : 8.43 (6H, d, 4.0 Hz), 7.18 (6H, d, 4.0 Hz), 3.74 (6H, s), 1.96 (18 H, s) ; IR (cm^{-1}) : 3264 (w), 1575 (s), 1469 (s), 1366 (s), 1310 (s), 1176 (m), 1002 (m), 941 (m), 761 (m), 725 (m), 593 (m), 493 (m) ; Elemental analysis calculated for $\mathrm{Al}\mathbf{L}_3\cdot H_2O$ (%) : C: 64.38, H: 6.22, N: 6.83. Found %: C: 64.47, H: 5.90, N: 6.64.

Synthesis and crystallisation of $[(\mathrm{Al}\mathbf{L}_3)\{Co(NCS)_2\}(H_2O)]_n$**:** A solution of $\mathrm{Al}\mathbf{L}_3$ (10 mg, 0.016 mmol) in CH_2Cl_2 (3 mL) was placed in a test tube and a mixture of CH_2Cl_2/MeOH (1:1, v:v) was layered on the top. A solution of $Co(NCS)_2$ (2.1 mg, 0.012 mol) in MeOH was carefully layered on the top of the two solutions and the tube was sealed. After two weeks of diffusion, light pink crystals suitable for X-ray diffraction studies were obtained.

Conclusions

We have shown that the ligand **L** may readily prepared in good yield, and, when bound to aluminium(III), can act as a three-fold bridging ligand. An advantage of the derivatisation at the 3-position of the acetylacetonate is that there is no mixture of *mer*- and *fac*- isomers. However the flexibility of the ligand does not constrain it to adopt three-fold symmetry as shown in the structure of [{Co(NCS)$_2$}(Al**L**$_3$)(OH$_2$)]$_n$.

Table 1. Details of X-ray crystal structure determinations

Compound	Al**L**$_3$·H$_2$O	[(Al**L**$_3$){Co(NCS)$_2$ (H$_2$O)]n
Empirical formula	$C_{33}H_{38}AlN_3O_7$	$C_{35}H_{38}AlCoN_5O_7S_2$
Formula weight	615.66	790.73
Temperature K	293	180
Radiation	Mo	Cu
Crystal system	monoclinic	triclinic
Space group	*C*2	*P*-1
a Å	21.656(6)	11.5825(9)
b Å	8.050(5)	11.6170(7)
c Å	21.087(8)	16.3471(13)
α /°	90	76.488(7)
β/°	117.959(8)	75.077(7)
γ/°	90	81.263(6)
Volume, Å^3	3247(3)	2056.7(3)
Z	4	2
ρ_{calc} mg/mm^3	1.259	1.277
μ/mm^{-1}	0.113	4.835
F(000)	1304.0	822.0
2Θ range for data collection	10.13 to 51.46°	5.72 to 117.86°
Reflections collected	21705	10784
Independent reflections	6051[Rint = 0.055]	5874[Rint = 0.0439]
Data/restraints/parameters	6051/1/407	5874/0/470
Goodness-of-fit on F2	1.067	1.033
Final R indexes [I>=2σ (I)]	R1 = 0.0469, wR2 = 0.1132	R1 = 0.0809, wR2 = 0.2123
Final R indexes [all data]	R1 = 0.0575, wR2 = 0.1214	R1 = 0.1233, wR2 = 0.2582
Absolute structure (Flack) parameter	0.2(3)	

Conclusions

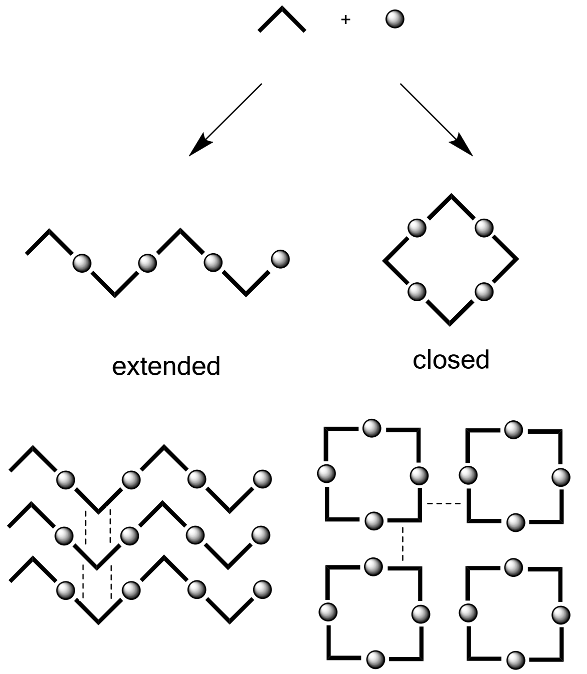
We have shown that the ligand **L** may readily prepared in good yield, and, when bound to aluminium(III), can act as a three-fold bridging ligand. An advantage of the derivatisation at the 3-position of the acetylacetonate is that there is no mixture of *mer*- and *fac*- isomers. However the flexibility of the ligand does not constrain it to adopt three-fold symmetry as shown in the structure of [{Co(NCS)$_2$}(Al**L**$_3$)(OH$_2$)]$_n$.

When Al**L**$_3$ reacts with a M(II) ion the pyridyl group binds to the divalent metal. In none of the systems that we have studied did we observe decomplexation of the acetylacetone group from the aluminium showing the orthogonality of the two binding centres.

In solution M(II) ions (M = Cu, Pd) appear to form cages [M$_6$(Al**L**$_3$)$_8$]$^{12+}$. The stoichiometry was established by UV-visible and NMR titrations and conductivity, and the Cu(II) visible spectra and NMR of the proton systems are consisted with the proposed model structure. The conductivity and DOSY measurements are consistent with a high molecular weight species.

When the Cu(II) ions were replaced with an octahedral ion with two anionic ligands, Co(NCS)$_2$, a cage structure was not observed even though the putative complex [Co$_6$(NCS)$_{12}$(Al**L**$_3$)$_8$] would not seem to suffer from any particular structural hindrance. The extended solid structure [{Co(NCS)$_2$}(Al**L**$_3$)(OH$_2$)]$_n$ was formed preferentially. The ligand Al**L**$_3$ is no longer able to satisfy fully the coordination requirements of the cobalt ions which are completed by water. The ligand Al**L**$_3$ adopts a conformation wherein the three-fold symmetry is missing, so that the symmetry constraints arising from the simultaneous presence of three- and fold-fold axes are no longer present and an extended form can grow.

The factors which determine the choice between an extended and a discrete assembly are not frequently discussed. As an example we show in Scheme 3 the possibilities for the combination of a linearly coordinating cation with a 90° bent bridging ligand.



Scheme 3. Interaction between a linearly coordinating cation and a 90° bent ligand. In solution (centre) the closed form is favoured as giving the maximum number of particles. In the solid state (bottom), intermolecular attractions (dashed lines) must also be considered.

Both the closed and the extended form in solution can fully satisfy the coordination requirements of metal and ligand without distortion. Entropy considerations will then favour the closed form as having the lower molecular mass and giving the greater number of particles.

In the solid state however, the entropy of translation is lost and the entropic argument is no longer valid. Furthermore, we must consider the intermolecular interactions between the units. The extended form has more contact with neighbouring

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molecules than the closed form, and consequently will be more stable. For neutral systems such as that studied here, the observation of an extended structure is thus not surprising. We have previously observed a similar effect with a pentagonal system using a pentapyrazoleferrocene ligand bridged by rhodium dicarboxylates[20]. In this case, an initial precipitate analysed correctly for the closed spherical system, but, on standing, an extended form of different composition crystallised where the coordination requirements of the ligand were not fully satisfied.

When the assembly is charged, the closed form will probably be favoured in solution by entropy considerations, and may be further stabilised by high solvation energies as a result of the high charge. Crystallisation then requires assembling a large number of counter ions around the large closed species. In a structure extended in one or two dimensions it is possible to alternate cations and anions at least in one dimension. Large closed species will tend to crystallise in more or less close-packed structures, and the anions thus occupy the interstices between them. If the number of counterions is large then anion-anion distances can become quite short. From a practical point of view, it is often difficult to crystallise these species, as shown by our failure to crystallise $[M_6(Al\mathbf{L}_3)_8]^{12+}$. Self-assembly of large charged species is then in competition with crystallisation of lower charged or neutral species which can compensate the loss of full occupation of coordination sites by increased intermolecular attractions. An example is the crystallisation of $Ag[C_5(CN)_5]$ when models suggested that a caged species $Ag_{30}[C_5(CN)_5]_{12}^{18+}$ would be stable.[46] These factors can explain why self-assembly can give different products in solution and in the solid state.

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Notes and references

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†Electronic Supplementary Information (ESI) available: Spectroscopic titration, DOSY data and hydrogen bonding data. CCDC 981451-981452. For crystallographic data in CIF form see DOI: 10.1039/b000000x/

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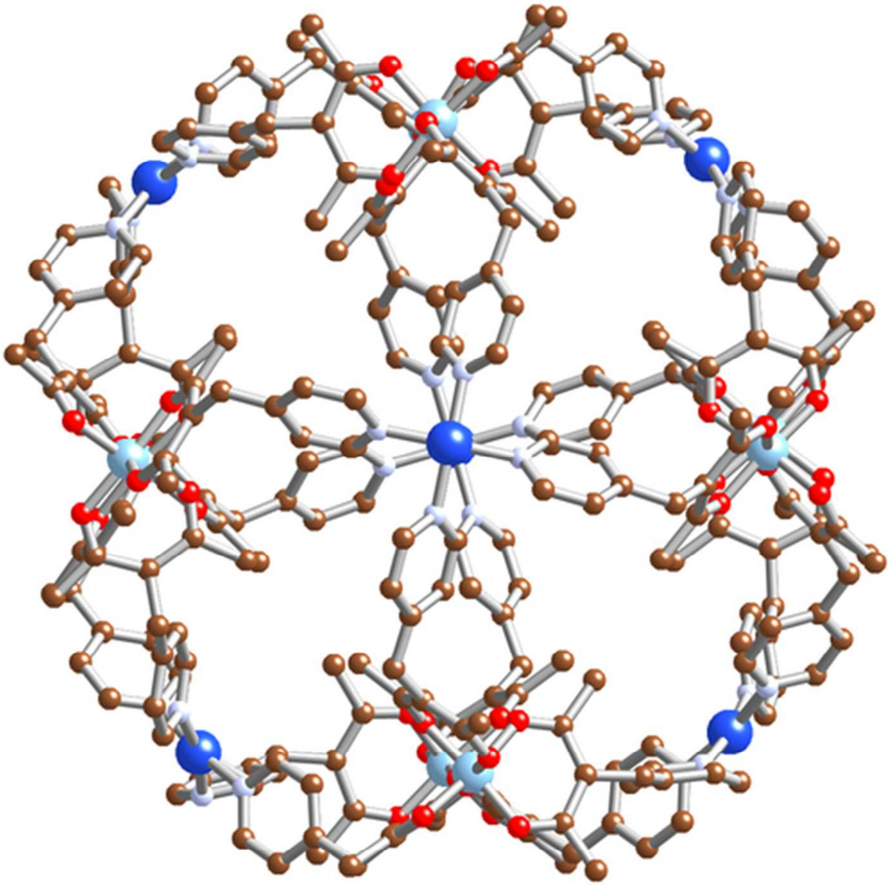

A ligand possessing two orthogonal metal binding sites is designed to bind three-fold and four-fold symmetric metal ions in such a way as to form a cage.

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