Synthesis, structure and characterisation of [Ni(bipy)₃][NaAl(ox)₃]: (bipy = 2,2′-bipyridine, ox = oxalate)

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The compound [Ni(bipy)₃][NaAl(ox)₃], where ox^{2-} is the oxalate dianion and bipy is 2,2′-bipyridine, was obtained by mixing of $K_2[Ni(ox)_2(H_2O)_2]\cdot 4H_2O$ and [H₂bipy]Cl₂ in silica hydrogel at room temperature. The complex, which incorporates Na and Al from the silica gel, was characterised by Fourier-transform IR spectroscopy, energy-dispersive X-ray analysis, thermogravimetric techniques and single-crystal X-ray diffraction. It crystallises in the cubic system, space group $P2_13$, with $a = 15.518(2)$ Å, $U = 3736.9(8)$ Å³ and $Z = 4$. The crystal structure consists of a chiral, three-dimensional polymeric network of Al^{3+} and Na^+ bridged by bis(bidentate oxalate) ligands, $[NaAl(ox)_3]_n^{2n-}$, with the $[Ni(bipy)_3]^{2+}$ cations inserted in the anionic network cavities. The cations and anionic network are held together by means of electrostatic forces and weak C–H $\cdots$ O hydrogen bonds.

The design of one- to three-dimensional compounds is a challenge for co-ordination chemists because of the difficulty of synthesising and obtaining single crystals suitable for structural characterisation, but extensively investigated in view of the applications that these systems have in fields ranging from industry to biomedicine. In this context there is much interest in oxalate (ox) as a bridging unit for polynuclear complexes and extended molecular assemblies,[1–3] not only owing to their potential magnetostructural properties but also due to the fact that polynuclear oxalate systems are excellent candidates to improve our still very limited understanding of the way that molecules and ions are organised in the solid state to form materials with given physical and chemical properties.[4] In the present paper, within our general research on the solid-state chemistry of oxalate–nickel(II)–amine systems,[5] we report the synthesis, chemical characterisation and crystal structure of the compound [Ni(bipy)₃][NaAl(ox)₃] (bipy = 2,2′-bipyridine). This compound was obtained by a diffusion silica hydrogel method and shows a chiral, three-dimensional polymeric structure, which is a rare case in inorganic chemistry. Recently, Decurtins and co-workers[2] have been published the crystal structures of analogous [M(bipy)₃][M′M″(ox)₃] compounds, suggesting that $[M^{II}(bipy)_3]^{2+}$ templates seem to induce the crystallisation of basically enantiomerically pure single crystals.

Results and Discussion

Synthesis and characterisation

During our studies of the nickel(II)–oxalate–amine system all attempts to obtain the binuclear compound [{Ni(bipy)₂}₂(μ-ox)]Cl₂ from aqueous solutions containing nickel(II) chloride hexahydrate, potassium oxalate dihydrate and 2,2′-bipyridine in different molar ratios led to a highly insoluble blue polycrystalline powder[6] (Found: C, 56.10; H, 3.65; N, 12.40; Ni, 13.10%). The IR spectrum exhibited the characteristic features of the chelating oxalate and 2,2′-bipyridine ligands and the elemental analysis was in accord with the formula [{Ni(bipy)₂}₂(μ-ox)]Cl₂ (C₄₂H₃₂Cl₂N₈Ni₂O₄ requires C, 56.0; H, 3.60; N, 12.45; Ni, 13.05%). In order to get single crystals of this compound suitable for X-ray analysis we decided to employ the well known diffusion silica hydrogel technique.[7] This method led to the formation of several nice red tetrahedral crystals both at the gel–solution interface and in the gel. The most relevant features of the IR spectra of the compound

concern the occurrence of chelating oxalate and 2,2′-bipyridine ligands, but, surprisingly, the elemental analysis showed a C:H:N ratio which was not in agreement with the formula [{Ni(bipy)₂}₂(μ-ox)]Cl₂. When examined by energy-dispersive X-ray analysis the surface of the red tetrahedral crystals appeared to contain Al, Na, Ni and Si, but a scan carried out inside some cut crystals revealed that Si was not present and only Al, Na and Ni appeared in constant concentration all over the cut. The above results, together with metal atomic absorption measurements, were consistent with the formula [Ni(bipy)₃][NaAl(ox)₃]. Atomic absorption measurements of the starting materials gave very small amounts of sodium and no evidence of aluminium. Analysis of the sodium silicate used for the gel preparation showed that aluminium was a contaminant. So that, without doubt, we can conclude that the aluminium and sodium were incorporated from the silica hydrogel used as crystallisation material. This type of gel has been extensively employed[8] in the preparation of a wide variety of inorganic, organic and macrobiological compounds due to its high stability but, as far as we are aware, the incorporation of one of its components in the final product structure, as in our case, has never been previously reported. All our attempts to obtain the compound, in aqueous solution, directly from oxalate–bipyridine–nickel(II)–aluminium oxide systems were unsuccessful.

Crystal structure of [Ni(bipy)₃][NaAl(ox)₃]

The asymmetric unit of the compound contains a complete oxalate ligand, three metal atoms, lying on three-fold axes, and the complete bipy ligand. The compound crystallises in the cubic system as does [Fe(bipy)₃][Fe₂(ox)₃][2a] and the crystal networks are quite similar, although the latter shows a higher symmetry. The oxalate dianion, as a bis(bidentate) ligand, repeatedly bridges the sodium and aluminium ions in all the three dimensions, which finally leads to a three-dimensional polymeric $[NaAl(ox)_3]_n^{2n-}$ network, with a helical architecture (Fig. 1). Two pillars of tris-chelated $[Ni(bipy)_3]^{2+}$ cations occupy the large vacancies in the anionic framework. The tris(oxalato)metal units exhibit D_3 point symmetry and the same holds for the tris(bipyridine)nickel(II) cations. Fig. 2 shows a thermal ellipsoid plot of the Na^+ and Al^{3+} co-ordination through the μ-oxalate ligands. Selected bond lengths and angles are given in Table 1.

The Al(ox)₃ unit has a near-octahedral geometry with a

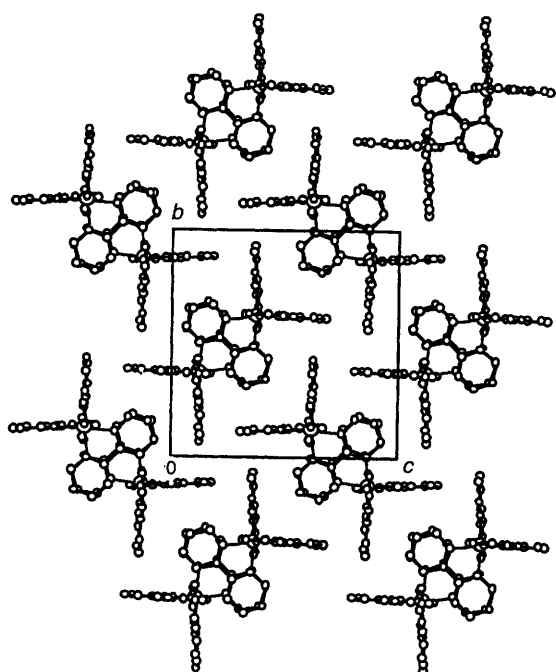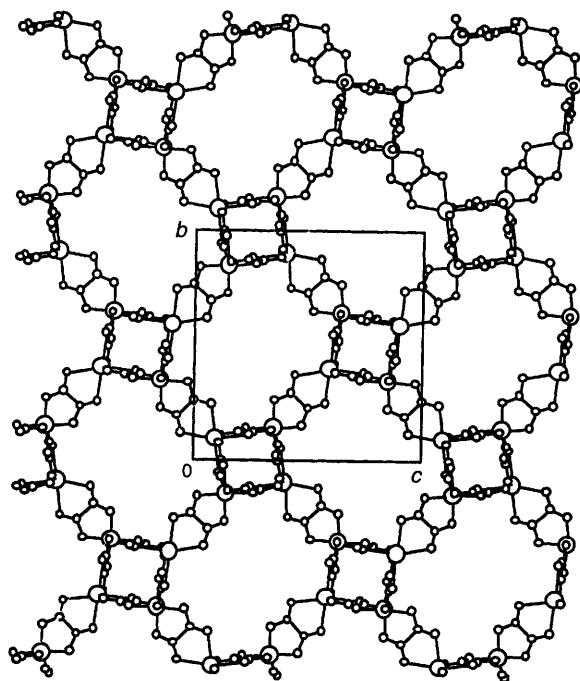**Fig. 1** Projections of the $[NaAl(ox)_3]_n^{2n-}$ network (top) in comparison with the $[Ni(bipy)_3]^{2+}$ counter ions (bottom)

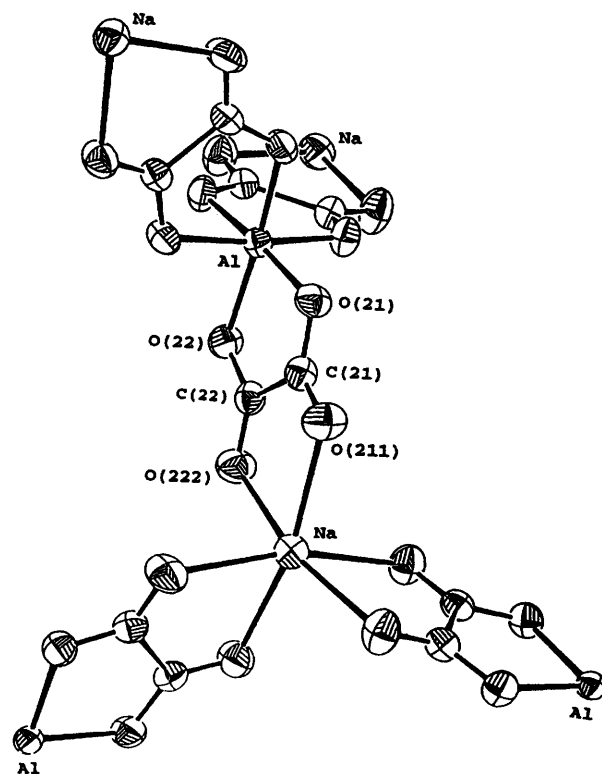**Fig. 2** Thermal ellipsoid plot (50% probability level) with the labelling scheme of the Na^+ and Al^{3+} co-ordination through the μ-oxalate ligands in the three-dimensional anionic network

oxalate ligand bite O–Al–O angle of 84.6°. The distortion from perfect octahedral geometry can be expressed[9] by a twist angle φ of the octahedron staggered triangles (60° for a perfect octahedron) and the ratio s/h which describes the degree of compression or elongation of the octahedron (ideal value 1.22). The values of $\varphi = 56°$ and $s/h = 1.18$ for the present structure correspond to a very slightly twisted and elongated octahedron the distortion of which is induced by the formation of the three-dimensional framework. The Al–O bond distances (mean 1.905 Å) and the oxalate bite angle compare well with those reported in the literature for other tris(oxalato)aluminium compounds.[10,11] The Na^+ ion is also surrounded, in a distorted octahedral fashion, by six oxygen atoms from the oxalate ligands with an average Na–O distance of 2.38 Å, though the smaller bite angle (72.9°), which is a consequence of the longer Na–O bonds, results in a smaller twist angle of 53°. These values are

comparable with published ones.[11] Although, the oxalate bond lengths are normal[12] it is interesting that the weaker sodium–oxalate interactions result in short C–O bond lengths as compared to the aluminium-co-ordinated C–O bonds. The oxalate ligand is approximately planar and the Al and Na atoms lie 0.118 and 0.059 Å out of this plane, respectively, leading to a nearly planar Na–ox–Al fragment with the equatorial planes of the two MO_6 chromophores tilted 9.6° each to other. The Al $\cdots$ Na distance (5.544 Å) is comparable with those found for isolated dimeric copper(II) and nickel(II) complexes (5.1–5.6 Å).[5d,12]

As far as the $[Ni(bipy)_3]^{2+}$ cation is concerned, the Ni–N bond distances and the small bite N–Ni–N angle [78.9(1)°] are similar to those found for the compound $[Ni(ox)(bipy)_2]$.[5b] The bond lengths and angles of the bipy ligand are comparable to those previously reported.[13] The individual pyridine rings of the bipy ligand are planar and the dihedral angle between them is only 0.9(1)°.

The cohesion of the crystal lattice is ensured by electrostatic interactions and several weak C–H $\cdots$ O contacts involving the C(3), C(5), C(9) and C(12) atoms of the bipy ligand as hydrogen donors and all the oxygen atoms of the oxalate as acceptors (Table 2). The C $\cdots$ O distances involving the C(3) and C(9) atoms are the shortest ones due to the inductive effect of neutral nitrogen atoms which decrease the electron density of immediately adjacent CH groups (C_α atoms) and enhance the facility with which they participate in hydrogen bonds.[14] The importance of C–H $\cdots$ O hydrogen bonds has long been known to spectroscopists and crystallographers, but definitive evidence for their structural significance was given only a few years ago.[15]

In compounds containing π systems it is quite common to find non-covalent interactions. In our case, an examination of the relative geometric positions of the planar bipy and oxalate ligands in the crystal structure shows no particular stacking, although the planes are nearly coplanar (tilt angle 7°). Similarly, although two bipy ligands of adjacent $[Ni(bipy)_3]^{2+}$ cations

are parallel stacked, no face-to-face π interactions are present due to the large interplanar distance (shortest Ni $\cdots$ Ni distance 9.50 Å). However, a C–H $\cdots$ π-ring interaction [16] has been observed in which the H(41) atom is directed towards the centre of one pyridine ring belonging to an adjacent bipy (H $\cdots$ centroid of the ring distance 3.44 Å, C–H $\cdots$ ring plane angle 158° and dihedral angle between the bipy ligands 89°). These T-type interactions are common in compounds like benzene, where they are more significant than parallel ones, or in protein structures.[17]

An important feature of the present compound is its chirality, since there exist very few examples as yet of inorganic compounds with chiral structures based on three-dimensional three-connected nets. As found for similar $[MM'(ox)_3]_n^{2n-}$ networks,[2] the two $M(ox)_3$ units show the same Λ configuration which produces a non-planar helical three-dimensional net. Networks with a Δ–Λ alternating chirality of the $M(ox)_3$ units generate a two-dimensional honeycombed layered structure.[2b,3] The tris-chelating cationic subunits also

have a Λ configuration. The homochirality and the helical shape of the cation enable it to fit into the cavities of the helical anionic network. A search of potential accessible solvent areas in the structure revealed that there are no favourable empty spaces between the cations and the surrounding anion network, but there are four empty spaces per unit cell, centred on a three-fold axis and surrounded by $[Ni(bipy)_3]^{2+}$ cations. The cations are assembled in a specific and highly symmetrical manner such that in all three directions a pairing of parallel aligned, adjacent bipyridine ligands occurs. Three of these pairs together, perpendicularly oriented to each other and connected by the above-mentioned C–H $\cdots$ π interaction, form well cubic shaped vacancies which would be large enough (ca. 80 Å^3) to encapsulate small molecules. In our case, it is not surprising that no water molecule has been incorporated into the empty cavities because of the hydrophobic environment of these cavities. However, recently, in the crystal structure of analogous compounds containing $[M^{III}(bipy)_3]^{3+}$ cations the accumulation of positive charge from the tripositive cations results in an attractive Coulomb force strong enough to encapsulate in the cubic holes an additional anionic species per formula unit, which is needed to establish the charge balance.[2e]

Thermal analysis

The thermal behaviour of the present compound has been studied in synthetic air and argon atmospheres (Table 3). The TG and DTA curves for both atmospheres are shown in Fig. 3. As for other oxalato-complexes,[18] the thermal stability does not show a significant dependence on the nature of the environmental gas. In the oxidative atmosphere an exothermic abrupt mass loss takes place in the range 340–440 °C attributable to cation pyrolysis and breakdown of the anionic network. In the argon atmosphere the thermal degradation starts with an endothermic peak between 330 and 455 °C in which the biggest mass loss takes place. This step is followed by a progressive mass loss, without clear peaks in the DTG and DTA curves, up to 730 °C after which there is no further weight loss on the TG curve.

The final residues are affected by the surrounding atmosphere. The mass loss observed in air atmosphere (Δm = 81.40%) is that expected for a final residue of NiO, Na$_2$O and Al$_2$O$_3$ in a ratio 2:1:1. In the argon atmosphere the experimental mass loss (Δm = 82.89%) is consistent with the formation of metallic nickel, Na$_2$O and Al$_2$O$_3$. The X-ray powder diffractograms of the final residues exhibit peaks due to

Table 1 Bond distances (Å) and angles (°) for compound [Ni(bipy)$_3$][NaAl(ox)$_3$]

$[NaAl(ox)_3]_n^{2n-}$ network

Al–O(21)	1.895(2)	C(21)–O(21)	1.281(3)
Al–O(22)	1.915(2)	C(22)–O(22)	1.275(3)
Na–O(211)	2.397(3)	C(21)–O(211)	1.226(3)
Na–O(222)	2.358(3)	C(22)–O(222)	1.223(3)
		C(21)–C(22)	1.564(4)
O(21)–Al–O(22)	84.6(1)	Al–O(21)–C(21)	114.9(2)
O(21)–Al–O(21^I)	92.9(1)	Al–O(22)–C(22)	114.1(2)
O(21)–Al–O(22^I)	173.2(1)	Na–O(211)–C(21)	112.0(2)
O(22)–Al–O(22^I)	89.2(1)	Na–O(222)–C(22)	113.1(2)
O(22)–Al–O(21^I)	93.6(1)	O(21)–C(21)–O(211)	126.7(3)
O(211)–Na–O(222)	72.9(1)	O(21)–C(21)–C(22)	112.6(2)
O(211)–Na–O(211^{II})	104.4(1)	C(22)–C(21)–O(211)	120.7(2)
O(211)–Na–O(222^{II})	163.4(1)	C(21)–C(22)–O(222)	121.2(2)
O(222)–Na–O(222^{II})	90.7(1)	O(22)–C(22)–C(21)	113.5(2)
O(222)–Na–O(211^{II})	92.1(1)	O(22)–C(22)–O(222)	125.4(2)

$[Ni(bipy)_3]^{2+}$ cation

Ni–N(2)	2.089(2)	C(5)–C(6)	1.380(6)
Ni–N(8)	2.088(2)	C(7)–N(8)	1.348(4)
C(1)–N(2)	1.350(4)	C(7)–C(12)	1.398(4)
C(1)–C(6)	1.403(4)	N(8)–C(9)	1.336(4)
C(1)–C(7)	1.484(4)	C(9)–C(10)	1.396(4)
N(2)–C(3)	1.344(4)	C(10)–C(11)	1.365(8)
C(3)–C(4)	1.389(5)	C(11)–C(12)	1.395(6)
C(4)–C(5)	1.375(7)		

N(2)–Ni–N(8)	78.9(1)	N(2)–C(3)–C(4)	122.4(3)
N(2)–Ni–N(2^I)	94.4(1)	C(3)–C(4)–C(5)	118.3(3)
N(2)–Ni–N(8^I)	170.9(1)	C(4)–C(5)–C(6)	120.3(3)
N(8)–Ni–N(8^I)	95.1(1)	C(1)–C(6)–C(5)	118.8(3)
N(8)–Ni–N(2^I)	92.3(1)	C(1)–C(7)–N(8)	116.0(2)
Ni–N(2)–C(1)	115.0(2)	C(1)–C(7)–C(12)	122.6(3)
Ni–N(2)–C(3)	125.6(2)	N(8)–C(7)–C(12)	121.3(3)
Ni–N(8)–C(7)	114.7(2)	C(7)–N(8)–C(9)	119.7(2)
Ni–N(8)–C(9)	125.6(2)	N(8)–C(9)–C(10)	121.6(4)
N(2)–C(1)–C(6)	121.0(3)	C(9)–C(10)–C(11)	119.2(4)
N(2)–C(1)–C(7)	115.3(2)	C(10)–C(11)–C(12)	119.8(3)
C(6)–C(1)–C(7)	123.7(3)	C(7)–C(12)–C(11)	118.4(4)
C(1)–N(2)–C(3)	119.3(2)		

Symmetry relations: I $-z + \frac{1}{2}$, $1 - x$, $y - \frac{1}{2}$; II $-z + \frac{1}{2}$, $1 - x$, $y - \frac{1}{2}$.

Table 3 Thermoanalytical data for the decomposition of [Ni(bipy)$_3$]-[NaAl(ox)$_3$] in synthetic air and argon atmospheres

Step	$\Delta T/°C$	Δm (%)
Synthetic air		
1	340–440(–)^a	81.40
Argon		
1	330–455(–)	76.42
2	455–730^b	6.47
	330–730	82.89

^{a} Endothermic (–) process. ^{b} Progressive mass loss without clear peaks in DTG and/or DTA curves.

Table 2 Hydrogen-bonding system for [Ni(bipy)$_3$][NaAl(ox)$_3$]

	C–H/Å	C $\cdots$ O/Å	H $\cdots$ O/Å	C–H $\cdots$ O/°
C(3)–H(31) $\cdots$ O(211^I)	0.94(5)	3.202(4)	2.51(5)	130(4)
C(5)–H(51) $\cdots$ O(222^{II})	0.90(6)	3.443(5)	2.59(6)	159(5)
C(9)–H(91) $\cdots$ O(21^{III})	1.05(6)	3.303(4)	2.63(6)	131(4)
C(12)–H(121) $\cdots$ O(22^{IV})	1.05(6)	3.441(4)	2.56(6)	141(4)

Symmetry relations: I $-x + \frac{1}{2}$, $-y + 1$, $z - \frac{1}{2}$; II $x + \frac{1}{2}$, $-y + \frac{3}{2}$, $-z$; III $-y$, $z + \frac{1}{2}$, $-x + \frac{1}{2}$; IV z, $x + 1$, $y - 1$.

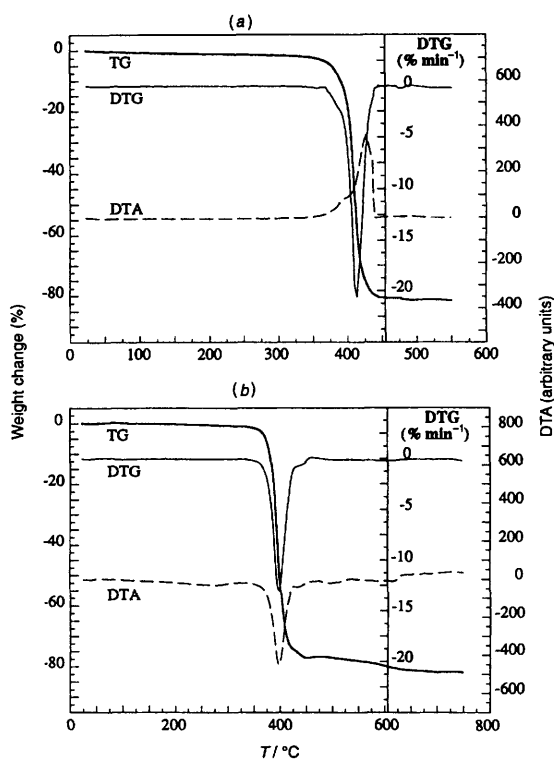**Fig. 3** Thermal decomposition of [Ni(bipy)₃][NaAl(ox)₃] in synthetic air (a) and argon atmospheres (b)

nickel(II) oxide (ASTM 4-0835) for the air atmosphere and metallic nickel (ASTM 4-0850) for the argon atmosphere, but no peaks due to sodium and aluminium compounds have been identified probably owing to the amorphous state of their oxides. However, the presence of both elements has been confirmed by X-ray fluorescence analysis.

Experimental

Materials

All chemicals were Merck analytical grade reagents used as obtained. The complex $K_2[Ni(ox)_2(H_2O)_2]\cdot 4H_2O$ was prepared according to the method described in previous papers[5a,c] and the purity checked by elemental analysis. Sodium silicate (density $1.37\ g\ cm^{-3}$) (Merck) was diluted with water to obtain a solution of density $1.06\ g\ cm^{-3}$.

Physical techniques

Microanalyses of carbon, nitrogen and hydrogen were performed on a Perkin-Elmer CHN-2400 analyser. Dispersive X-ray analysis was carried out by a QX-2000 analytical link incorporated in a DSM 950 digital scanning microscope. Density was measured by flotation in a mixture of CCl_4–$CHBr_3$. The infrared spectrum was recorded on a Nicolet FT-IR 740 spectrometer for KBr pellets in the 4000–$400\ cm^{-1}$ region. A Setaram TAG 24 S16 thermobalance was used to obtain the thermogravimetric analysis (TG, DTG) and differential thermal analysis (DTA) curves, simultaneously, in synthetic air and argon atmospheres with a heating rate of $5\ ^{\circ}C\ min^{-1}$. All thermal decompositions were recorded in a dynamic atmosphere with a flow rate of $50\ cm^3\ min^{-1}$. X-Ray powder diffraction patterns of the microcrystalline final products of the thermal decompositions were recorded at room temperature with a Philips PW 1710 instrument equipped with graphite-monochromated Cu-Kα radiation, and compared with those obtained from the ASTM powder diffraction files of the Joint Committee on Powder Diffraction Standards, JCPDS.[19] X-Ray fluorescence analysis was performed on a Philips PW 1480 spectrometer.

Preparation of [Ni(bipy)₃][NaAl(ox)₃]

The compound was obtained in U-tubes using silica hydrogel as crystallisation environment. The gel was prepared at room temperature by adding diluted sodium silicate solution (density $1.06\ g\ cm^{-3}$, $13\ cm^3$) over $1\ mol\ dm^{-3}$ acetic acid ($10\ cm^3$) under continuous mechanical stirring. The mixture was poured into U-tubes and allowed to stand. When the gel was firm an aqueous solution ($20\ cm^3$) of $K_2[Ni(ox)_2(H_2O)_2]\cdot 4H_2O$ (0.32 g, 0.75 mmol) was placed in one arm of a U-tube and an aqueous solution ($20\ cm^3$) of 2,2'-bipyridinium chloride (0.26 g, 1.14 mmol) in the other arm. In the course of a few weeks several red tetrahedral crystals of the compound appeared. All of these crystals showed excellent faces and habits, and they could easily be observed under a microscope without taking them out of the gel. The crystals were isolated from the gel manually, using a needle, washed with water, and dried in air (Found: C, 51.30; H, 2.90; Al, 3.15; N, 10.05; Na, 2.70; Ni, 6.95. $C_{36}H_{24}AlN_6NaNiO_{12}$ requires C, 51.40; H, 2.90; Al, 3.20; N, 10.00; Na, 2.75; Ni, 7.00%). IR (KBr, cm^{-1}): 3100w, 3075w, 2920w, 2850w, 1715 (sh), 1685vs, 1665vs, 1610m, 1605m, 1590m, 1435m, 1465w, 1395s, 1295s, 1015m, 900w, 775s and 490m. Owing to the low yield ($<10\%$ based on Ni), the synthesis was repeated until the required amount of the compound to make thermal measurements and elemental analysis was obtained. Single crystals of the compound were also obtained in test-tubes, adding one of the reactants during the gel preparation and allowing the other one to diffuse through the gel column. Crystal growth occurs both at the gel–solution interface and in the gel.

Crystallography

Crystal data and data collection parameters. $C_{36}H_{24}AlN_6$-$NaNiO_{12}$, $M = 841.30$, cubic, space group $P2_13$ (no. 198), $a = 15.518(2)$ Å, $U = 3736.9(8)$ Å³ (by least-squares refinement on diffractometer angles for 25 well centred reflections, $8 < \theta < 17^{\circ}$), $T = 295(1)$ K, graphite-monochromated Mo-Kα radiation, $\lambda = 0.710\,69$ Å, $Z = 4$, $D_m = 1.48(1)\ g\ cm^{-3}$, $D_c = 1.50\ g\ cm^{-3}$, $F(000) = 1720$, red tetrahedral crystal with $L = 0.76$ mm, μ(Mo-Kα) $= 6.227\ cm^{-1}$; Enraf-Nonius CAD4 four-circle diffractometer, ω–2θ scan mode, data collection range $2 < 2\theta < 70^{\circ}$, $+h$, $+k$, $+l$; two standard reflections showed no significant variation in intensity; corrections were made for Lorentz-polarisation and for absorption (minimum and maximum correction coefficients of 0.922 and 1.098);[20] 8873 reflections measured, 2971 unique ($R_{int} = 0.015$), 1602 of which were considered as observed by applying the condition $I \geqslant 3\sigma(I)$.

Structure solution and refinement. The crystal structure was solved by direct methods[21] and refined anisotropically by full-matrix least-squares methods on F (X-RAY 76).[22] Hydrogen atoms were clearly revealed in a Fourier-difference map and refined with isotropic thermal factors. A conventional weighting scheme was used in the final refinement cycle in order to obtain a flat dependence of $\langle w\Delta^2F\rangle$ vs. $\langle F_o\rangle$ and vs. $\langle \sin \theta/\lambda\rangle$.[23] After the final refinement cycle the agreement factors were $R(F_o) = 0.030$ and $R'(F_o) = 0.032$, 204 variables, $S = 1.46$, $(\Delta/\sigma)_{max} = 0.194$, $(\Delta/\sigma)_{av} = 0.011$, and $\Delta\rho_{max} = 0.75$ e Å⁻³. Atomic scattering factors and anomalous dispersion factors were taken from ref. 24. In order to establish the absolute configuration of the structure an identical refinement procedure was carried out by using the inverse set of coordinates. This converged with R and R' of 0.044 and 0.056, respectively, which are significantly larger than the above values. The correctness of the chosen enantiomer was also confirmed by refining the coefficient of the imaginary component of the anomalous scattering, giving a Rogers η parameter[25] of 1.01(5).

Final geometrical calculations were carried out with the PARST[26] and PLATON[27] programs. Graphical manipul-

ations were produced using the ORTEP utility of the XTAL 3.0 system.[28] All calculations were performed on a Digital Micro VAX 4500 computer.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/198.

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