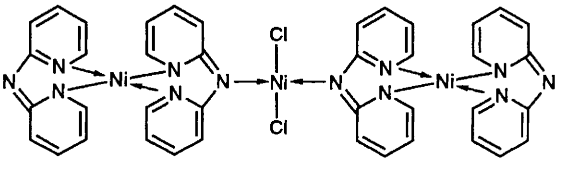
Crystal Structure and Electronic Properties of Tetrakis[μ_3-bis(2-pyridyl)amido]dichlorotrinickel(II)–Water–Acetone (1/0.23/0.5)*

Sujittra Aduldecha and Brian Hathaway
Chemistry Department, University College, Cork, Ireland

The crystal structure of $[Ni_3(bipyam-H)_4Cl_2]\cdot 0.23H_2O\cdot 0.5(CH_3)_2CO$ **1** [bipyam−H = bis(2-pyridyl)-amide] has been determined using X-ray diffractometer data; $C_{41.5}H_{35.5}Cl_2N_{12}Ni_3O_{0.75}$, monoclinic, space group $C2/c$, with $a = 37.525(7)$, $b = 16.237(3)$, $c = 22.550(6)$ Å, $\beta = 110.12(2)$, $Z = 12$; 5778 measured and 5519 unique reflections gave a final R value of 0.051. The structure involves two independent $Ni_3(bipyam-H)_4Cl_2$ units, (1) and (2) [(1) occupies a general position and (2) is on a C_2 axis], one non-co-ordinated water molecule [site occupation factor (s.o.f.) 0.23], and one acetone molecule (s.o.f. 0.5). The $Ni_3N_{12}Cl_2$ chromophores of (1) and (2) involve a nearly linear Ni_3 unit, mean Ni–Ni–Ni angle 178.4(1)°, terminated by the two chloride anions. The four separate bipyam−H ligands act as tridentate ligands, involving co-ordination to three separate nickel(II) ions with Ni–Ni distances 2.443(1) (twice) and 2.431(1) Å for units (1) and (2), respectively. If the Ni–Ni separations are ignored the central Ni atom in both units involves a four-co-ordinate rhombic coplanar NiN_4 chromophore, generated by the four central amido nitrogens of the bipyam−H ligands. The two terminal Ni atoms involve a square-based pyramidal NiN_4Cl chromophore, involving the four pyridine nitrogens of the bipyam−H ligands and an axial Cl atom. A dihedral angle of *ca.* 54° is involved between the planes of the individual pyridine rings of each bipyam−H ligand and results in a spiral configuration in the $Ni_3(bipyam-H)_4Cl_2$ unit. The room-temperature magnetic moment μ_{eff} of compound **1** is 2.46, consistent with a diamagnetic central NiN_4 chromophore and two paramagnetic terminal NiN_4Cl chromophores. The electronic spectrum involves a low-energy peak at 6500 cm^{-1}, an intense peak at 17 700 cm^{-1}, and a low-intensity shoulder at 10 800 cm^{-1}, consistent with the two nickel(II) stereochemistries present.

The original preparation[1] of $[Ni_3(bipyam-H)_4Cl_2]$ [bipyam − H = bis(2-pyridyl)amide] reported the correct stoichiometry and suggested the structure shown in **I**, involving a tetrahedral central NiN_2Cl_2 chromophore and two terminal rhombic square coplanar NiN_4 chromophores. This suggested structure contrasts with the general inability of the $[Ni^{II}(chelate)_2]^{2+}$ cations to form a coplanar stereochemistry, the reported electronic reflectance spectra, and the recently reported structure[2] of $[Cu_3(bipyam-H)_4Cl_2]$. For this reason the preparation has been repeated and the structure determined by X-ray diffraction.



I

Experimental

Preparation.—A slurry of $[Ni(bipyam)_2X_2]$ (X = Cl or Br) or $[Ni(bipyam)_3][SCN]_2$ (0.47 g, 1.00 mmol) in naphthalene (*ca.* 3 g, 23.31 mmol) was heated to 185 °C, with constant stirring. Sodium butoxide (0.023 g, 1.00 mmol of sodium metal in 20 cm^3 of dry butanol) was slowly added with constant stirring and a deep red solution resulted. The slurry was further heated to reflux to facilitate complete removal of the butanol, the naphthalene was removed under vacuum, and the product was recrystallised from acetone–benzene (1:1). Dark red-purple hexagonal-shaped crystals were obtained (*ca.* 0.2 g). The elemental analyses of the products are shown in Table 1.

Table 1 Elemental analysis of the products **1**–**3**

Complex	Analysis (%)* C	H	N	Ni	X
1 $[Ni_3(bipyam-H)_4Cl_2]\cdot$ $0.23H_2O\cdot 0.5(CH_3)_2CO$	51.80 (51.85)	3.85 (3.70)	17.30 (17.50)	17.00 (18.35)	7.60 (7.40)
2 $[Ni_3(bipyam-H)_4Br_2]$	48.95 (47.25)	3.75 (3.15)	16.10 (16.55)	17.35 (17.35)	15.90 (15.75)
3 $[Ni_3(bipyam-H)_4$-$(NCS)_2]\cdot C_{10}H_8\cdot CH_3OH$	56.65 (56.15)	3.90 (3.90)	17.50 (17.30)	15.45 (15.55)	4.95 (5.65)

* Calculated values in parentheses. X = Cl, Br or S for **1**, **2** or **3** respectively.

Crystal data. $C_{41.5}H_{35.5}Cl_2N_{12}Ni_3O_{0.75}$, $M_r = 961.35$, monoclinic, space group $C2/c$, $a = 37.525(7)$, $b = 16.237(3)$, $c = 22.550(6)$ Å, $\beta = 110.12(2)$, $U = 12\,901.51$ Å^3. D_m(flotation) = 1.507 g cm^{-3}, $Z = 12$, $D_c = 1.483$ g cm^{-3}, $F(000) = 6078$.

Crystal Structure Determination of $[Ni_3(bipyam-H)_4Cl_2]$ **1**.—The unit-cell data (25 reflections, θ 3–25°) and the intensities were collected on a Philips PW 1100 diffractometer with graphite-monochromatised Mo-Kα radiation, λ = 0.710 69 Å. Reflections with 3.0 < θ 25° in one quadrant were examined in the ω–2θ scan mode, with a constant scan speed of 0.05° s^{-1} and

---

* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Table 2 Fractional atomic coordinates with estimated standard deviations (e.s.d.s) in parentheses for $[Ni_3(bipyam-H)_4Cl_2]\cdot0.23H_2O\cdot0.50(CH_3)_2CO$ **1**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ni(2)	0.277 50(2)	0.607 34(6)	0.365 36(4)	N(9)	0.416 3(1)	0.538 3(3)	0.464 3(3)
Ni(1)	0.332 48(2)	0.530 43(5)	0.432 68(4)	N(10)	0.254 8(1)	0.487 9(3)	0.346 0(3)
Ni(3)	0.387 36(2)	0.455 96(6)	0.502 86(4)	C(31)	0.216 5(2)	0.478 1(5)	0.322 7(4)
Cl(1)	0.439 67(5)	0.384 67(13)	0.569 88(10)	C(32)	0.199 2(2)	0.402 2(5)	0.310 5(4)
Cl(2)	0.226 21(5)	0.685 14(13)	0.301 30(10)	C(33)	0.221 3(2)	0.332 8(5)	0.319 8(4)
Ni(5)	0.037 60(3)	0.484 57(6)	0.181 13(5)	C(34)	0.260 7(2)	0.341 4(5)	0.344 9(4)
Ni(4)	0.000 0	0.482 79(8)	0.250 00	C(35)	0.277 2(2)	0.420 2(4)	0.356 8(3)
Cl(3)	0.073 98(6)	0.487 31(15)	0.115 97(12)	N(11)	0.315 3(1)	0.434 6(3)	0.383 4(3)
N(1)	0.261 7(1)	0.605 8(3)	0.446 3(3)	C(36)	0.341 7(2)	0.382 1(4)	0.374 6(3)
C(1)	0.235 6(2)	0.658 5(4)	0.453 4(4)	C(37)	0.335 3(2)	0.334 1(5)	0.320 5(4)
C(2)	0.225 9(2)	0.662 7(5)	0.506 3(4)	C(38)	0.365 2(2)	0.287 5(5)	0.314 5(4)
C(3)	0.245 1(2)	0.612 4(5)	0.557 3(4)	C(39)	0.399 8(2)	0.286 8(6)	0.362 8(4)
C(4)	0.271 9(2)	0.557 5(5)	0.552 0(4)	C(40)	0.404 8(2)	0.334 8(5)	0.414 8(4)
C(5)	0.279 0(2)	0.552 5(4)	0.493 8(3)	N(12)	0.376 5(1)	0.381 2(3)	0.421 7(3)
N(2)	0.304 8(1)	0.499 7(3)	0.484 5(3)	N(13)	−0.011 0(2)	0.428 2(4)	0.117 5(3)
C(6)	0.310 9(2)	0.423 0(4)	0.513 1(3)	C(41)	−0.007 9(2)	0.379 4(5)	0.071 7(4)
C(7)	0.282 0(2)	0.376 4(4)	0.524 0(3)	C(42)	−0.037 9(3)	0.336 5(5)	0.032 2(4)
C(8)	0.289 9(2)	0.300 2(5)	0.551 1(4)	C(43)	−0.073 1(3)	0.342 4(5)	0.040 6(4)
C(9)	0.326 9(2)	0.267 7(5)	0.565 7(4)	C(44)	−0.076 4(2)	0.391 8(5)	0.087 7(4)
C(10)	0.353 6(2)	0.315 3(4)	0.552 0(3)	C(45)	−0.044 5(2)	0.435 0(5)	0.126 0(3)
N(3)	0.346 2(2)	0.390 4(3)	0.526 7(3)	N(14)	−0.044 3(1)	0.482 0(4)	0.178 2(3)
N(4)	0.314 8(1)	0.707 6(3)	0.397 4(3)	C(46)	−0.076 2(2)	0.522 8(5)	0.179 8(3)
C(11)	0.311 5(2)	0.774 5(5)	0.360 6(4)	C(47)	−0.103 7(2)	0.554 2(4)	0.125 5(4)
C(12)	0.338 4(3)	0.836 9(5)	0.376 1(4)	C(48)	−0.134 2(2)	0.597 2(5)	0.131 4(5)
C(13)	0.368 5(2)	0.832 2(5)	0.431 5(4)	C(49)	−0.135 9(2)	0.611 4(5)	0.189 6(5)
C(14)	0.372 5(2)	0.763 9(5)	0.468 8(4)	C(50)	−0.107 3(2)	0.581 2(5)	0.242 5(5)
C(15)	0.344 9(2)	0.700 5(4)	0.450 5(3)	N(15)	−0.078 1(2)	0.536 1(4)	0.237 6(3)
N(5)	0.349 3(1)	0.626 5(3)	0.482 0(3)	N(16)	0.010 5(2)	0.597 4(4)	0.154 7(3)
C(16)	0.367 4(2)	0.620 3(4)	0.545 2(3)	C(51)	0.003 3(2)	0.629 8(5)	0.096 0(4)
C(17)	0.366 0(2)	0.682 9(5)	0.588 4(3)	C(52)	−0.014 9(3)	0.703 1(6)	0.076 4(4)
C(18)	0.383 4(2)	0.670 7(6)	0.652 0(4)	C(53)	−0.027 1(2)	0.745 4(5)	0.117 8(4)
C(19)	0.401 5(2)	0.596 4(6)	0.674 2(4)	C(54)	−0.022 2(2)	0.715 2(5)	0.177 6(4)
C(20)	0.401 6(2)	0.537 5(5)	0.630 2(4)	C(55)	−0.003 2(2)	0.639 5(5)	0.195 2(4)
N(6)	0.385 7(1)	0.548 3(3)	0.567 4(3)	N(18)	0.054 1(2)	0.368 3(3)	0.223 2(3)
N(7)	0.304 2(2)	0.586 9(3)	0.299 2(3)	C(61)	0.088 4(2)	0.335 9(5)	0.227 6(4)
C(21)	0.283 9(2)	0.593 7(5)	0.237 4(3)	C(62)	0.101 9(2)	0.263 2(5)	0.257 9(4)
C(22)	0.298 7(2)	0.584 5(5)	0.191 5(4)	C(63)	0.078 8(2)	0.218 9(5)	0.283 6(4)
C(23)	0.337 3(3)	0.565 9(5)	0.207 9(4)	C(64)	0.044 5(2)	0.251 2(5)	0.281 4(4)
C(24)	0.358 4(2)	0.558 2(5)	0.270 4(4)	C(65)	0.032 5(2)	0.326 8(4)	0.250 3(3)
C(25)	0.341 7(2)	0.570 2(4)	0.316 6(4)	N(17)	0.000 0	0.598 0(5)	0.250 0
N(8)	0.360 7(1)	0.560 7(3)	0.380 9(3)	N(19)	0.000 0	0.365 6(5)	0.250 0
C(26)	0.398 9(2)	0.578 1(4)	0.409 3(4)	O(1)	0.524 9(9)	0.523 1(19)	0.203 8(14)
C(27)	0.418 7(2)	0.635 9(5)	0.385 2(4)	C(66)	0.185 1(5)	0.402 2(10)	0.582 8(8)
C(28)	0.455 9(2)	0.649 1(5)	0.417 3(4)	C(67)	0.168 5(6)	0.450 7(11)	0.533 6(9)
C(29)	0.474 4(2)	0.608 5(5)	0.474 6(4)	C(68)	0.170 8(6)	0.405 6(13)	0.629 5(9)
C(30)	0.453 3(2)	0.555 4(5)	0.496 4(4)	O(2)	0.210 4(4)	0.359 9(10)	0.587 9(7)

a variable scan width of (0.7 + 0.1 tan θ)°. With an acceptance criterion of $I > 2.5\ \sigma(I)$, 5778 observed reflections were collected, (h −42 to 40, k 0–18, l 0–27) and yielded 5519 unique reflections. Lorentz and polarisation corrections were applied but no correction was made for absorption [μ(Mo-$K\alpha$) = 14.78 cm^{-1}].

The structure was solved by the SHELX 86 direct methods[3] and Fourier difference techniques, SHELX 76,[4] and refined by blocked-matrix least-squares analysis, $\Sigma w|F_o - F_c|^2$, with the initial $w = 1/\sigma^2(F_o)$, and anisotropic thermal parameters for 85 non-hydrogen atoms. The positions of the H atoms were calculated geometrically and 'floated' on the adjacent carbon or oxygen atom positions, assuming C–H and O–H distances of 1.08 Å and a fixed thermal factor of 0.07 $Å^2$. The data converged when the maximum shift/e.s.d. was < 0.08, with a final refined weighting scheme, $w = k[\sigma^2(F_o) + g(F_o)^2]^{-1}$, where $k = 0.82$ and $g = 0.0018$, to yield $R = 0.051$ and $R' = 0.056$. The maximum and minimum residual electron densities were 0.79 and −0.51 e $Å^{-3}$, respectively. Complex neutral atom scattering factors were employed and those for Ni were taken from ref. 5. All calculations were carried out with SHELX 76,[4] SHELX 86,[3] XANADU,[6] CHEM-X,[7] and PUBTAB,[8] on the mainframe IBM 4341 and VAX 11/780 computers at University College, Cork.

The final atomic coordinates are given in Table 2 and selected bond lengths and bond angles in Table 3. Fig. 1 illustrates the local molecular structures of the two independent units and the atomic numbering scheme used.

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

The X-ray data collection on crystals of $[Ni_3(bipyam-H)_4(NCS)_2]$ **3** was attempted, but the crystals were unstable in the X-ray beam and decomposed during the data collection.

Spectroscopic Measurement.—Infrared spectra were recorded on a Mattson Polaris Fourier-Transform IR10410 spectrometer in the range 4000–500 cm^{-1} using the KBr disc technique, diffuse reflectance spectra in the range 4000–25 000 cm^{-1} on polycrystalline samples using a Beckman DK-2A spectrometer. The room-temperature magnetic moment was measured on a Gouy balance, using $[Ni(en)_3][S_2O_3]$ (en = ethylenediamine) as a standard.

Table 3 Selected bond lengths (Å) and angles (°) with e.s.d.s in parentheses

Unit (1)		Unit (2)	
Ni(1)–Ni(2)	2.443(1)	Ni(4)–Ni(5)	2.431(1)
Ni(2)–Ni(3)	2.443(1)	Ni(4)–Cl(3)	2.325(3)
Ni(1)–Cl(1)	2.340(2)	Ni(4)–N(13)	2.102(5)
Ni(3)–Cl(2)	2.331(2)	Ni(4)–N(16)	2.080(6)
Ni(1)–N(1)	2.105(7)	Ni(4)–N(18)	2.108(6)
Ni(1)–N(4)	2.107(5)	Ni(4')–N(15)	2.110(5)
Ni(1)–N(7)	2.090(7)	Ni(5)–N(14)	1.881(5)
Ni(1)–N(10)	2.103(6)	Ni(5)–N(17)	1.870(8)
Ni(2)–N(2)	1.879(6)	Ni(5)–N(19)	1.902(8)
Ni(2)–N(5)	1.893(5)		
Ni(2)–N(8)	1.892(7)		
Ni(2)–N(11)	1.893(5)		
Ni(3)–N(3)	2.092(7)		
Ni(3)–N(6)	2.106(6)		
Ni(3)–N(9)	2.090(7)		
Ni(3)–N(12)	2.116(6)		
Ni(1)–Ni(2)–Ni(3)	178.2(1)	Ni(4)–Ni(5)–Ni(4')	178.6(1)
N(1)–Ni(1)–Cl(1)	97.2(2)	N(13)–Ni(4)–Cl(3)	97.9(2)
N(4)–Ni(1)–Cl(1)	95.9(1)	N(16)–Ni(4)–Cl(3)	97.9(2)
N(7)–Ni(1)–Cl(1)	98.0(2)	N(18)–Ni(4)–Cl(3)	99.0(2)
N(10)–Ni(1)–Cl(1)	100.4(1)	C(46)–N(14)–C(45)	122.0(5)
N(3)–Ni(3)–Cl(2)	96.5(2)	C(55)–N(17)–C(55')	121.2(5)
N(6)–Ni(3)–Cl(2)	97.1(2)	C(65)–N(19)–C(65')	125.3(5)
N(9)–Ni(3)–Cl(2)	98.4(2)		
N(12)–Ni(3)–Cl(2)	98.3(2)		
C(6)–N(2)–C(5)	120.4(7)		
C(16)–N(5)–C(15)	122.3(6)		
C(26)–N(8)–C(25)	122.7(7)		
C(36)–N(11)–C(35)	122.0(6)		

Results and Discussion

Crystal Structure.—The crystal structure of compound **1** involves two independent [Ni_3(bipyam$-$H)$_4$$Cl_2$] units, (1) and (2), one water molecule [site occupation factor (s.o.f.) 0.23], and one acetone molecule (s.o.f. 0.5) in the asymmetric unit. Unit (1) is situated in a general position, $Z = 8$, whereas unit (2) is situated on a two-fold axis, $Z = 4$. Both units involve almost linear Ni_3 groups, bond angles 178.2(1) and 178.6(1)°, for units (1) and (2), respectively, with the two Cl^- atoms co-ordinated to the two terminal Ni atoms. For unit (2) the central Ni(5) atom and two of the *trans* amido nitrogen atoms (from the four independent bipyam$-$H ligands) are situated on a C_2 axis. In (1) the three nickel(II) ions are bridged by the central deprotonated amido nitrogen atoms and two pyridine nitrogen atoms of the four bipyam$-$H ligands, with two equal Ni–Ni distances of 2.443(1) Å for (1), and a Ni–Ni distance of 2.431(1) Å for (2), respectively. If the Ni–Ni separations are ignored, the central Ni atoms in both units are four-co-ordinate, rhombic coplanar, involving the four independent deprotonated nitrogen atoms of the bipyam$-$H ligands. The mean Ni–N distances of 1.889(7) and 1.884(6) Å, of the central NiN_4 environment in units (1) and (2), respectively, are consistent with the Ni–N distance, *ca.* 1.90 Å, usually found in the low-spin square coplanar nickel(II) systems.[9] The terminal Ni atoms in both units are five-co-ordinate with a square-based pyramidal geometry, to give a NiN_4Cl chromophore, again with a slight rhombic component. The basal plane consists of the four terminal pyridine nitrogen atoms of the four independent bipyam$-$H ligands, mean Ni–N 2.101(7) and 2.100(7) Å, for units (1) and (2), respectively. These distances are significantly longer than those of the central NiN_4 environments, 1.889(7) and 1.884(6) Å, but again consistent with equatorial Ni–N distances 2.0–2.1 Å in square-pyramidal nickel(II) complexes.[10] The axial co-ordination sites are occupied by the chloride anions, mean Ni–Cl 2.335(3) and 2.325(3) Å. The Ni–Cl distances are also consistent with those normally found in square-based pyramidal nickel(II) structures,[11,12] 2.33 Å in chloro(3,7-diazanonane-1,9-diamine)nickel(II) chloride, and are within the range of 2.25–2.45 Å in different nickel co-ordination geometries.[10] The Ni atoms are displaced out of the N_4 planes, *ca.* 0.28 Å, towards the terminal chloride atoms and result in mean N–Ni–Cl angles of 97.73 and 98.27° for units (1) and (2), respectively.

The bipyam$-$H ligands act as tridentate nitrogen chelate ligands, Fig. 2(*a*), compared with the normal bidentate function of the bipyam or bipyam$-$H ligands previously reported[2,13,14] and a single example of it occurring as a monodentate ligand,[15] in [W(CO)$_5$(bipyam)]. There are no unusual bond lengths or angles in the bipyam$-$H ligands.[2,14,16,17] Each tridentate ligand is non-planar, with an average dihedral angle between the planes of the two pyridine rings of 53.88 and 55.79° for units (1) and (2), respectively, and results in a spiral structure for the trimer, Fig.1. Fig. 2(*b*) shows the molecular structure viewed down the Ni(1)–Ni(2)–Ni(3) direction and gives a better impression of this spiral structure. This arises mainly from the interaction between the two ring hydrogen atoms, for example, H(4) and H(7), of the coplanar tridentate bipyam$-$H ligand, Fig. 2(*a*).

The basic stereochemistries of the terminal NiN_4Cl chromophores of unit (1) are not significantly different. There is a slightly larger tetrahedral twist in the Ni(1) chromophore [root mean square deviation (r.m.s.d.) of the basal plane 0.0119 Å] than in those of the Ni(2) and the Ni(3) chromophores (r.m.s.d. of the basal plane 0.0072 and 0.0061 Å, respectively). These are significantly different from those of the terminal NiN_4Cl chromophores in unit (2) (r.m.s.d. of the basal plane 0.69 Å). This arises due to the slightly greater twist of the two pyridine rings in unit (2), av. 55.8°, than that in unit (1), av. 53.88°, and results in the bigger N–Ni–Cl angle, av. 98.27°, than that of unit (1), av. 97.73°. In addition, the two terminal nickel atoms in unit (1) lie 0.2873 and 0.2765 Å, respectively, above the planes defined by the four nitrogen atoms, while that of unit (2) is only 0.0348 Å above the basal plane. However, this difference in the deviation of the nickel atoms from the basal plane is not reflected in significant differences in the axial Ni–Cl bond distances, namely 2.340(2) and 2.331(2), and 2.325(3) Å for the terminal Ni(1), Ni(3); and Ni(4) atoms in the NiN_4Cl chromophores of units (1) and (2), respectively.

The structure of compound **1** is significantly different from that originally proposed,[1] namely **I**.

Structural Comparison with Other Relevant Complexes.—The structures of the two chloride and bromide copper(II) trimers,[2] [Cu_3(bipyam$-$H)$_4$$X_2$] (X = Cl or Br), are essentially isostructural with **1**, with two terminal square-based pyramidal MN_4X chromophores and a central square coplanar MN_4 chromophore. These copper trimers also involve nearly linear Cu_3 units, with comparable Cu(2)–Cu(1)–Cu(2') angles of 178.12 and 178.51° for the chloride and bromide, respectively, but with significantly longer mean Cu–Cu separations of 2.471(1) and 2.468(1) Å respectively. Each tridentate bipyam$-$H ligand co-ordinates to all three copper atoms with an average dihedral twist of the two pyridine rings of *ca.* 48°, in both copper trimers, significantly smaller than that in the nickel trimer, *ca.* 55°. The mean Cu–Cl distance of 2.46 Å is significantly longer than the mean Ni–Cl distance of *ca.* 2.33 Å in the nickel trimer, consistent with the usual elongation of the axial Cu–X distance, normally found in square-based pyramidal copper(II) structures.[13] The mean Cu–Cu separations of 2.471 and 2.468 Å for the chloride and bromide trimers, respectively, are slightly longer than the corresponding mean Ni–Ni trimer distances of 2.443 and 2.431 Å, however both distances are shorter than the corresponding distances in the metals, 2.56 and 2.49 Å, for copper and nickel, respectively.

The tridentate co-ordination of bipyam$-$H has also been observed in the copper(I) polymer [{Cu_2(bipyam$-$H)$_2$}$_n$], **II**,[14] while bidentate co-ordination of bipyam$-$H has been

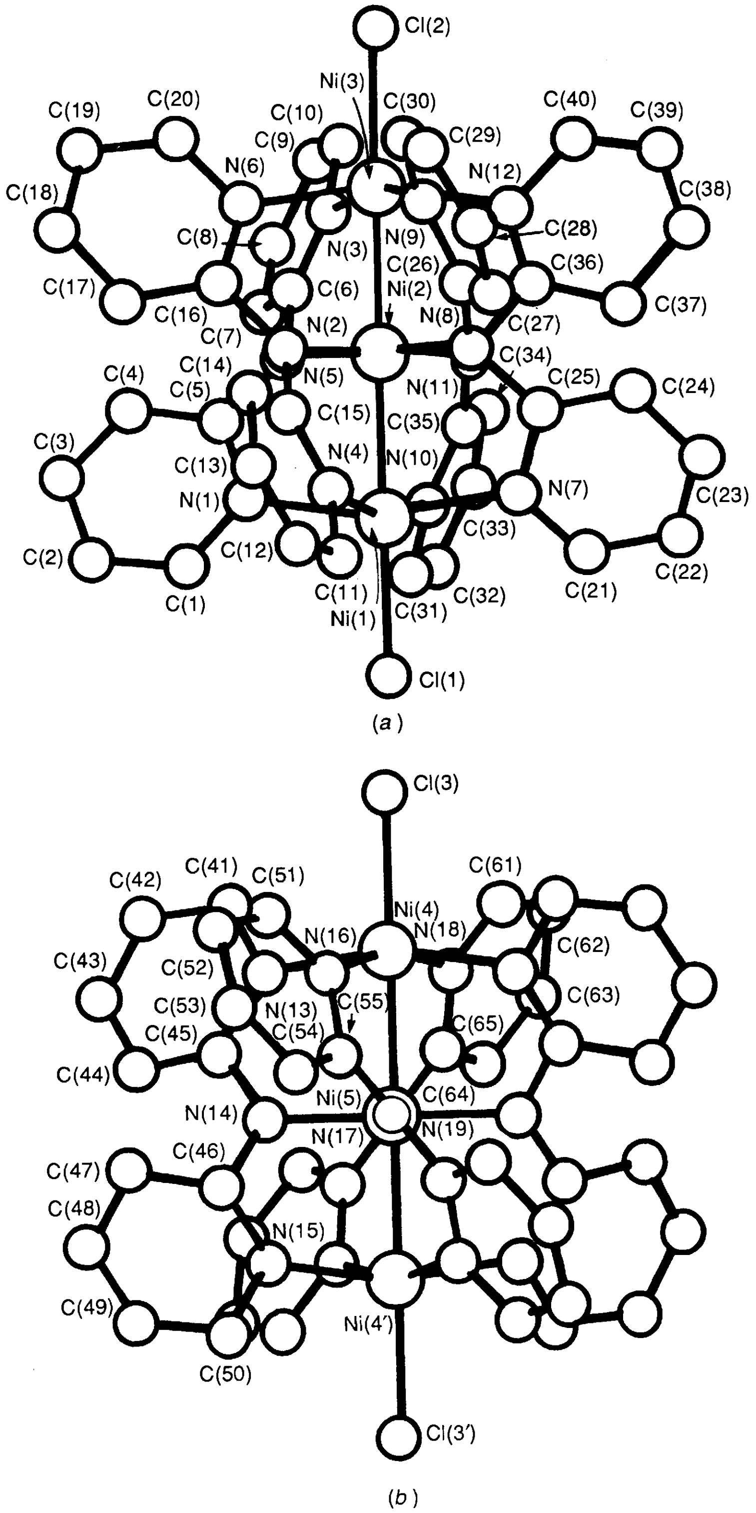
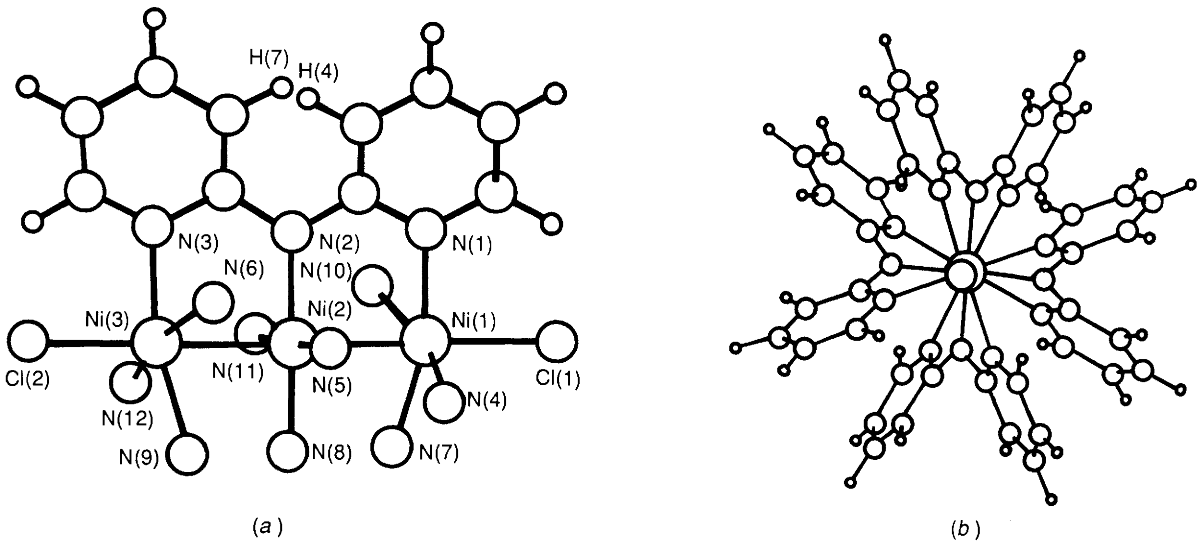


Fig. 1 The local molecular structures of the two independent units of $[Ni_3(bipyam-H)_4Cl_2]$ **1** and the atom numbering system used; (*a*) unit (1) and (*b*) unit (2)

characterised in mononuclear complexes, of copper(II),[2,14,16,17] palladium(II)[18] and ruthenium(II).[19]

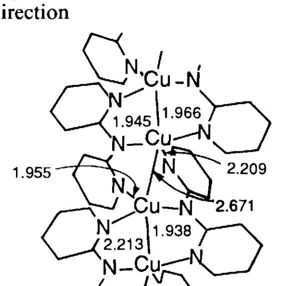
The mean nickel–nickel separation of 2.437 Å for both trimer units compares well with those found in dimeric nickel(II) complexes,[20–22] 2.38–2.56 Å, for which metal–metal interaction has been suggested. This distance is significantly shorter than that, in a linear trinuclear nickel(II) complex $[\{Ni(acac)_2\}_3]$ (acac = acetylacetonate)[23] (2.88 and 2.89 Å) **III**. The closest structural similarity to the nickel trimer is found in the dimers of the 1,8-naphthyridine (napy) ligand, involving an average nickel oxidation state of 1.5, namely $[Ni_2(napy)_4Br_2]BPh_4$, **IV**,[24] with a Ni–Ni separation of 2.415 Å and an angle of twist of 25.1°, between axes of the two NiN_4Br chromophores.

Infrared Spectrum.—The infrared spectrum of compound **1** is dominated by that of the tridentate bipyam – H ligand. The N–H stretching bands in the 3300–3400 cm^{-1} region are, as expected, completely absent and the highest-energy pyridine-ring vibration shows a significant shift to 1600 cm^{-1}, compared

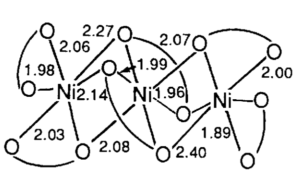


(*a*) (*b*)

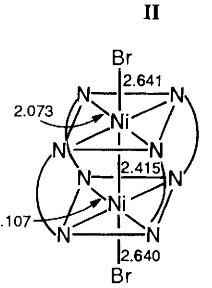
Fig. 2 The molecular structure of compound **1**: (*a*) a schematic view of the $Ni_3N_{12}Cl_2$ chromophore, (*b*) the view down the Ni(1)–Ni(2)–Ni(3) direction



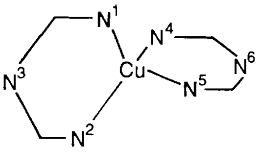
II



III



IV



V

Distances in Å

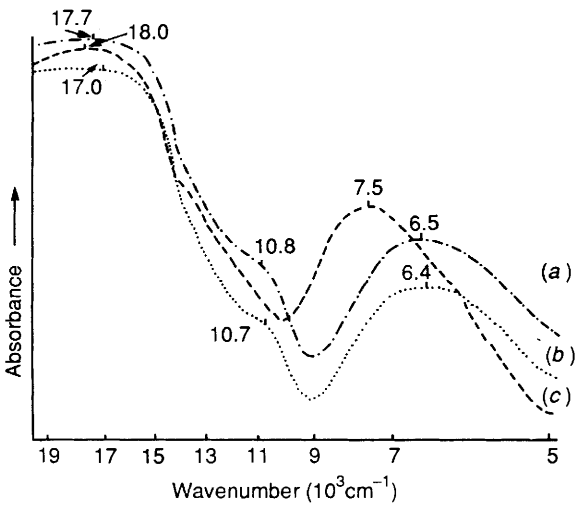


Fig. 3 Electronic reflectance spectra of (*a*) $[Ni_3(bipyam-H)_4Cl_2]$, (*b*) $[Ni_3(bipyam-H)_4Br_2]$, and (*c*) $[Ni_3(bipyam-H)_4(NCS)_2]$

with the spectrum of the normal bipyam ligand, namely 1650 cm^{-1} for $[Ni(bipyam)_2Cl_2]$. This is consistent with the typical IR features[1,2,17] of the bipyam – H system. The infrared spectrum of the trimer compares well with that of the copper(II) trimers[2] and with that of $[\{Cu^I_2(bipyam-H)_2\}_n]$,[14] **II**, involving the tridentate bipyam – H ligand, but is slightly different from that of $[Cu^{II}(bipyam-H)_2]$,[17,25] **V**, in which the bipyam – H shows a bidentate co-ordination. The infrared spectrum of the trimer exhibits new bands at 1360 and 1310 cm^{-1}, which are not present for **V** and may be attributed to vibrations of the co-ordinated bridging amido nitrogen group. These may be used to distinguish the bi- and tri-dentate co-ordination[2,17,26] of the bipyam – H ligand. An additional strong band occurs for **1** at 1710 cm^{-1}, due to the C=O stretch of the acetone[9] in the complex.

Magnetic Properties.—The observed room-temperature magnetic moment μ_{eff} of compound **1** is 2.46 per paramagnetic nickel(II) ion (or 3.5 per trimer), significantly less than the normal value of 2.83 for the free nickel(II) ion. This corresponds in **1** to the presence of two unpaired electron spins on the two terminal nickel ions and no unpaired electron spins on the central Ni. The lower value of the observed magnetic moment of the trimer is consistent with the mixed stereochemistry of the square-based pyramidal/square coplanar/square-based pyramidal system and also shows that the square-based pyramidal environments of two terminal nickel(II) ions involve high-spin species.[9] This value is slightly less than the previously observed value[1] of 2.64 per paramagnetic nickel(II) ion or 3.7 per trimer. However, it compares well with μ_{eff} values (all per Ni^{II}) for the mixed stereochemistries (diamagnetic–paramagnetic) of nickel(II) complexes: square coplanar–square pyramidal,[27,28] 2.3–2.4; square coplanar–tetrahedral,[29] 2.7; and square coplanar–octahedral,[30,31] 2.20–2.58

Electronic Spectra.—The crystals of compound **1** are dark reddish purple. The observed electronic reflectance spectrum, Fig. 3, shows two main peaks at *ca.* 17 700 and 6500 cm^{-1}, and an unresolved shoulder at *ca.* 10 800 cm^{-1}. It is dominated by the intense band of 17 000 cm^{-1}, which is the normal band found for low-spin complexes of square coplanar nickel(II) complexes.[9,32,33] This band probably arises from the $^1A_{1g} \longrightarrow {}^1A_{2g}$ transition for the diamagnetic rhombic coplanar nickel(II) ion in D_{2h} symmetry, and corresponds with the central rhombic coplanar NiN_4 chromophore of the trimer. This compares well with that of other diamagnetic rhombic coplanar $Ni^{II}N_4$ chromophores,[9] such as the single absorption band at about

18 600 cm^{-1} for the [Ni(Hdmg)$_2$] complex[33] (Hdmg = dimethylglyoximate). The rather broad low-energy band at *ca.* 6500 cm^{-1} is consistent with the two high-spin square-based pyramidal NiN$_4$Cl chromophores, and arises from the unresolved $^3B_1 \rightarrow {}^3E,{}^3A({}^3T_{2g})$ transitions of the nickel(II) ion, in approximately C_{4v} symmetry. The low-energy shoulder on the intense peak at 17 700 cm^{-1}, at approximately 10 800 cm^{-1}, is then assigned as one of the components of the $^3B_1 \rightarrow {}^3E,{}^3A({}^3T_{1g})$ transitions, in C_{4v} symmetry, with the higher-energy component masked by the tail of the more intense band of 17 700 cm^{-1}.

Proposed Structures of [Ni$_3$(bipyam − H)$_4$X$_2$], (X = Br, **2**; *or* NCS, **3**).—The microanalysis of compounds **2** and **3**, Table 1, suggest the same trimer stoichiometry as in **1**, with the Br$^-$ and NCS$^-$ anions, respectively, replacing the terminally co-ordinated Cl$^-$ ligands of **1**. This is supported by a comparison of the electronic reflectance spectra, Fig. 3. The spectra of both trimers compare well with that of the chloride, suggesting a central four-co-ordinate square-coplanar NiN$_4$ environment and two terminal five-co-ordinate square-based pyramidal NiN$_4$X chromophores, within the trimers. The observed energies of the reflectance specta, increase in the order $-NCS^- \gg Cl^- > Br^-$ corresponding with the position of these ligands in the spectrochemical series.[32] The magnetic moments of the bromide and thiocyanate trimers were not determined owing to the small quantity of the complexes obtained. The infrared spectra of the trimers **1** and **2** are almost superimposable, while that of **3** has the extra bands of the ν(C≡N), and ν(C–S) vibrations at 2080 and 820 cm^{-1}, respectively, for the thiocyanate group present.[34] This suggests that the bipyam − H ligand with tridentate co-ordination is involved in all three nickel(II) trimers. The relatively high ν(C–S) streching frequency at *ca.* 820 cm^{-1} suggests Ni–N co-ordination in **3**.[34] The value of the ν(C=N) stretching frequency is also consistent with this.

[Ni(bipyam − H)$_2$] **4**.—An attempt was made to reprepare complex **4**, by the method in the original paper[1] and by other possible methods corresponding to those of the [Cu(bipyam − H)$_2$] complex, as follows. (*a*) Deprotonation of [Ni(bipyam)$_2$X$_2$] (X = Cl, Br or I) or [Ni(bipyam)$_3$]X$_2$ (X = BF$_4$ and CH$_3$CO$_2$) by sodium butoxide, NaOH, or KOH, in dry butanol.[1] (*b*) Refluxing Ni(OH)$_2$ with bipyam in benzene.[17,35] (*c*) Refluxing nickel metal with bipyam under CO$_2$-free air in ethanol, methanol, water, acetonitrile, butanol or benzene.[36] (*d*) Nickel or copper metal reduction of [Ni(bipyam)$_2$X$_2$] (X = Cl, Br or I) or [Ni(bipyam)$_3$]X$_2$ (X = BF$_4$ or CH$_3$CO$_2$) in the presence of extra bipyam in acetonitrile, ethanol, methanol, water or benzene.[36,37] (*e*) By adding a previously prepared Na(bipyam − H) solution (addition of sodium metal to a solution of bipyam in rigorously anhydrous dimethoxymethane, acetonitrile, or benzene) to a dimethoxymethane (acetonitrile or benzene) solution of [Ni(bipyam)$_3$]X$_2$ (X = BF$_4$ or CH$_3$CO$_2$),[19] even under reflux. (*f*) The corresponding hydroxylamine hydrochloride reduction[38] of [Ni(bipyam)$_2$Cl$_2$] and [Ni(bipyam)$_3$]X$_2$ (X = BF$_4$, CH$_3$CO$_2$ or NO$_2$). (*g*) Refluxing [Ni$_3$(bipyam − H)$_4$Cl$_2$] with sodium butoxide in butanol.[1]

All the above procedures failed to yield any clear evidence for complex **4** in a pure crystalline form. The products seem to be a mixture of **4**, Ni(OH)$_2$, and polymeric hydroxide–dipyridylamine complexes. Attempts to purify and recrystallise the product were frustrated by its insolubility in nearly all solvents. Although this product is soluble in and thus can be separated by using pyridine as the solvent, it is cleaved quite readily by the action of pyridine and, presumably, other complexing solvents.

Acknowledgements

The authors acknowledge the award of a Senior Studentship (to S. A.), help in data collection by Dr. M. McPartlin and Mr. A. Bashall (Department of Applied Chemistry and Life Sciences, Polytechnic of North London), the Computer Bureau, University College, Cork (U.C.C.), for computing facilities, Professor G. M. Sheldrick, Drs. S. Motherwell, K. Henrick and K. Davies, for the use of their programs, and the Microanalysis Section, U.C.C., for analysis.

References

1 T. J. Hurley and M. A. Robinson, *Inorg. Chem.*, 1968, **7**, 33.
2 L.-P. Wu, P. Field, T. Morrissey, C. Murphy, P. Nagle, B. J. Hathaway, C. Simmons and P. Thornton, *J. Chem. Soc., Dalton Trans.*, 1990, 3835.
3 G. M. Sheldrick, SHELX 86, a program for crystal structure solution, University of Cambridge, 1986.
4 G. M. Sheldrick, SHELX 76, a program for crystal structure determination University of Cambridge, 1976.
5 D. T. Cromer and J. T. Waber, *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4, pp. 71, 148 (Present distributor, Kluwer Academic Publishers, Dordrecht).
6 P. Roberts and G. M. Sheldrick, XANADU, a program for the calculation of crystallographic data, University of Cambridge, 1979.
7 E. K. Davies, CHEM-X, a molecular graphics program, Chemical Design Ltd., Oxford, 1980.
8 K. Henrick, PUBTAB, a program to prepare and print crystallographic tables for publication, 1980, Polytechnic of North London.
9 L. Sacconi, F. Mani, and A. Bencini, in *Comprehensive Coordination Chemistry*, eds. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon, Oxford, 1987, vol. 5, section 50.
10 G. J. Long and E. O. Schlemper, *Inorg. Chem.*, 1974, **13**, 279.
11 M. A. Hitchman, *Inorg. Chem.*, 1972, **11**, 2387.
12 J. G. Gibson and E. D. McKenzie, *J. Chem. Soc. A*, 1971, 1029.
13 B. J. Hathaway, in *Comprehensive Coordination Chemistry*, eds. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon, Oxford, 1978, vol. 5, Section 15.5, pp. 533–774.
14 P. Akhter and B. J. Hathaway, unpublished work.
15 B. S. Creavan, C. V. Gallagher, R. A. Howie, C. Long and G. P. McQuillan, 1990, personal communication.
16 M. E. Keniry, Ph.D. Thesis, National University of Ireland, 1988.
17 O. R. Rodig, T. Brueckner, B. K. Hurlburt, R. K. Schlatzer, T. L. Venable and E. Sinn, *J. Chem. Soc., Dalton Trans.*, 1981, 196.
18 J. F. Geldard and F. Lions, *J. Am. Chem. Soc.*, 1962, **84**, 2262.
19 D. E. Morris, Y. Ohsawa, D. P. Segers, M. K. DeArmond and K. W. Hanck, *Inorg. Chem.*, 1983, **23**, 3010.
20 M. Corbett, B. F. Hoskins and N. J. McLead, *Aust. J. Chem.*, 1975, **28**, 2377.
21 R. A. Jones and B. R. Whittlesey, *Inorg. Chem.*, 1986, **25**, 52.
22 S. A. Laneman and G. G. Stanley, *Inorg. Chem.*, 1987, **26**, 1177.
23 M. B. Hursthouse, M. A. Laffey, P. T. Moore, D. B. New, P. R. Raithby and P. Thornton, *J. Chem. Soc., Dalton Trans.*, 1982, 308.
24 R. J. Butcher and E. Sinn, *Inorg. Chem.*, 1979, **16**, 2334.
25 P. Akhter and B. J. Hathaway, *Acta Crystallogr., Sect. C*, in the press.
26 J. H. Thomas and A. R. Martin, *Inorg. Chem.*, 1968, **7**, 33.
27 G. A. Melson, P. T. Greens and R. F. Bryan, *Inorg. Chem.*, 1970, **9**, 1116.
28 G. A. Melson, N. P. Crawford and B. J. Geddes, *Inorg. Chem.*, 1970, **9**, 1123.
29 D. Nicholls, *Complexes and First-Row Transition Elements*, Whitefriars, London, 1974.
30 S. C. Nyburg and J. S. Wood, *Inorg. Chem.*, 1964, **3**, 468.
31 B. T. Kilbourn, H. M. Powell and J. A. C. Darbyshire, *Proc. Chem. Soc.*, 1963, 207.
32 D. Sutton, *Electronic Spectra of Transition Metal Complexes*, McGraw-Hill, London, 1968.
33 A. A. G. Tomlinson, *Coord. Chem. Rev.*, 1981, **37**, 221.
34 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd edn., Wiley, New York, 1978.
35 C. E. Baxter, O. R. Rodig, R. K. Schlatzer and E. Sinn, *Inorg. Chem.*, 1979, **18**, 1918.
36 P. Akhter, Ph.D. Thesis, National University of Ireland, 1989.
37 S. Aduldecha, Ph.D. Thesis, National University of Ireland, 1989.
38 A. A. Schilt and R. C. Taylor, *J. Inorg. Nucl. Chem.*, 1959, **9**, 211.

Received 13*th August* 1990; *Paper* 0/03707I