Novel Tetra- and Hexa-dentate Ligands from 6,6′-Dicyano-2,2′-bipyridine†

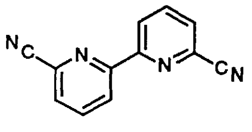
Paul N. W. Baxter,[a] **Joseph A. Connor,***[,a] **W. Bernd Schweizer**[b] **and John D. Wallis**[a]
[a] *Chemical Laboratory, University of Kent, Canterbury, Kent CT2 7NH, UK*
[b] *Organic Chemistry Laboratory, Swiss Federal Institute of Technology, ETH-Zentrum, CH-8092, Zürich, Switzerland*

A simple, direct route from 2,2′-bipyridine to 6,6′-dicyano-2,2′-bipyridine and its conversion to the 6,6′-dithiocarboxamide and various novel tetra- and hexa-dentate ligands such as the 6,6′-bis(4-methylthiazol-2-yl) and 6,6′-bis[4-(2-pyridyl)thiazol-2-yl] derivatives have been established. Diaqua[6,6′-bis(4-methylthiazol-2-yl)-2,2′-bipyridine]zinc(II) bis(trifluoromethanesulfonate) has been prepared and its crystal structure determined. The tetra-heterocyclic ligand is planar, binding through two bipyridine nitrogen atoms and, more weakly, through two thiazolyl nitrogen atoms to zinc(II) which is in a distorted octahedral environment.

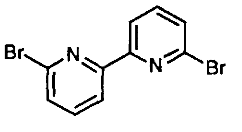
The incorporation of 6,6′-disubstituted 2,2′-bipyridines and 2,2′:6′,2″-terpyridines in macrocyclic[1] and multidentate[2] ligands has resulted in a variety of new metal complex types which display unique physicochemical properties. Two of the most notable examples are the helicates, which exhibit features such as self-assembly based on molecular recognition events,[3] and systems which incorporate molecular links and knots.[4] As part of our exploration of the chemistry of various dicyano-2,2′-bipyridines,[5] we decided to exploit the extensive synthetic utility of the cyano groups in 6,6′-dicyano-2,2′-bipyridine (L^1) in order to obtain polyfunctional ligands which are difficult to synthesise by other routes. We now report a simple route to L^1, and its conversion to some derivatives which are potential polydentate co-ordinating ligands. An example of the co-ordination complexes which have been prepared is provided by the product of the reaction of 6,6′-bis(4-methylthiazol-2-yl)-2,2′-bipyridine with zinc(II) trifluoromethanesulfonate (triflate). The structure of the zinc(II) complex has been determined by X-ray diffraction.

Results and Discussion

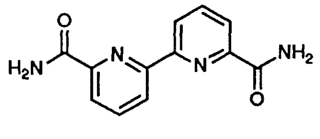
The only report[6] of the synthesis of L^1 describes the reaction between 6,6′-dibromo-2,2′-bipyridine (L^2) and copper(I) cyanide in biphenyl solution at high temperature (above 200 °C). The yield of L^1 was not reported. As a result of an improved description[7] for the preparation of L^2 from 2,6-dibromopyridine, we reinvestigated the above-mentioned method for preparing L^1. We find that optimal yields of 81–90% (based on L^2) of L^1 can be obtained on cyanation of L^2 by CuCN in pyridine solution at 180–185 °C, followed by release of L^1 by treatment of its copper(II) complex with concentrated aqueous KCN. The copper complex must be destroyed as rapidly as possible at room temperature in order to minimise hydrolysis which produces 6,6′-dicarboxamido-2,2′-bipyridine (L^3). A much simpler route to L^1 makes use of a modification of the Reissert reaction.[8] A precipitate of L^1 rapidly develops when an aqueous solution of 2,2′-bipyridine *N*,*N*′-dioxide[9] (L^4) and KCN is treated with a solution of benzoyl chloride in tetrahydrofuran (thf) and when *N*,*N*′-dimethyl-2,2′-bipyridinium sulfate is treated with aqueous KCN. The yield of L^1 by these routes is in the range 40–56%. This method has the significant advantages of low cost and ease of access of the



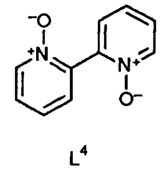
L^1



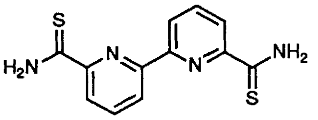
L^2



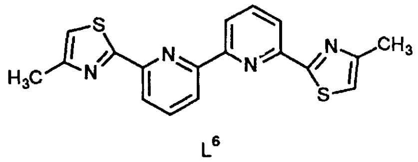
L^3



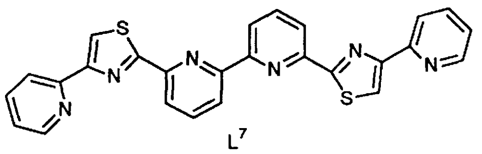
L^4



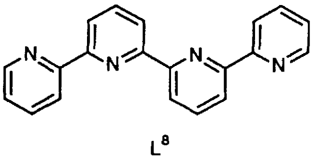
L^5



L^6



L^7



L^8

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.
Non-SI unit employed: Tor ≈ 133 Pa.

starting materials, simplicity of the direct conversion and ease of isolation of the product which minimises side-reactions. When the same procedure is applied to 4,4′-dimethyl-, 4,4′-di(*tert*-butyl)- and to 5,5′-dimethyl-2,2′-bipyridine *N*,*N*′-dioxides, the corresponding 6,6′-dinitriles are also obtained in satisfactory yield. The yield of 6,6′-dicyano-4,4′-dimethyl-2,2′-bipyridine was found to be highly dependent on reaction conditions, therefore the optimised combination of reagents for the preparation of this compound is recorded in the Experimental section.

Treatment of L^1 in methanol with, first, ammonia gas and then with hydrogen sulfide leads to the 6,6′-bis(thiocarboxamide) (L^5) a yellow crystalline solid (yield 88–90%). Thiazole-functionalised 2,2′-bipyridines can then be readily prepared upon reaction of L^5 with excess of α-halogenoacetyl compounds in thf solution. Thus, reaction of L^5 with excess of 1-chloropropan-2-one produces 6,6′-bis(4-methylthiazol-2-yl)-2,2′-bipyridine (L^6) a potentially tetradentate ligand. Reaction with α-bromoacetylpyridine produces 6,6′-bis[4-(2-pyridyl)-thiazol-2-yl]-2,2′-bipyridine (L^7) a potentially hexadentate ligand. As one example of the co-ordination compounds which can be prepared, reaction of L^6 with zinc trifluoromethanesulfonate in acetonitrile solution gave colourless prisms of the complex $[ZnL^6(H_2O)_2][CF_3SO_3]_2$ the crystal structure of which was determined by X-ray diffraction.

The molecular and crystal structure of $[ZnL^6(H_2O)_2][CF_3SO_3]_2$ are illustrated in Figs. 1 and 2. Bond lengths and angles are given in Table 1, and fractional atomic coordinates in Table 2. The tetradentate ligand is almost planar and arranged in the form of a horseshoe around the zinc ion with all four nitrogen atoms directed towards the cation. The three bite angles at zinc are very similar [72.8(2)–74.2(2)°]. The zinc ion lies very close to the best plane through the non-hydrogen atoms of the ligand [deviation: 0.006(1) Å towards O(1)]. The co-ordination of the metal is completed by two pseudo-axial water molecules, arranged so that the O–Zn–O angle is 151.8(2)°, and the Zn–O bonds lie above and below the mouth of the horseshoe ligand. Hydrogen bonds between the co-ordinated water ligands and trifluoromethanesulfonate ions form an infinite array in the lattice (H···O 1.9–2.0 Å, O–H···O 168–178°). The two Zn–OH_2 distances are slightly, but significantly, different [2.066(3), 2.022(4) Å]; both are well within the normal Zn–OH_2 distance[10] (2.097 Å). The zinc ion lies closer to the pyridine nitrogens N(2) and N(3) (average bond length 2.154 Å) than to the thiazole nitrogens N(1) and N(4) (average bond length 2.269 Å). All of these Zn–N bonds, but particularly the latter, are longer than standard average values[10] [*e.g.* Zn–N (bipyridine) 2.088 Å; Zn–N (imidazole) 2.084 Å]. From this it would appear that the zinc is stabilised principally by the two water molecules and by the bipyridine nitrogen atoms in a distorted octahedral environment.

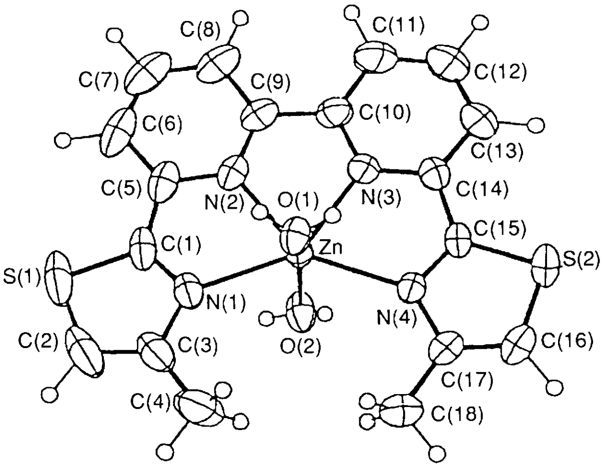


Fig. 1 View of $[ZnL^6(H_2O)_2][CF_3SO_3]_2$ with anisotropic thermal parameters drawn at the 50% probability level (ORTEP II)

The ligand 2,2′:6′,2″:6″,2‴-quaterpyridine L^8 binds to cobalt(II),[11] nickel(II)[2] and copper(II)[11] in a similar way in the complexes $[CoL^8(H_2O)_2][NO_3]_2$, $[NiL^8(NCMe)_2][PF_6]_2\cdot MeCN$ and $[CuL^8(H_2O)(NO_3)][NO_3]$. In each case, the terminal pyridine rings are involved in longer metal–nitrogen bonds than the two inner pyridine rings. If the copper(II) complex is excluded from further discussion because of the consequences of a tetragonal distortion, it is apparent that the 'mouth' of the horseshoe is much more open in the zinc(II) complex of L^6 than in either the nickel(II) or the cobalt(II) complexes, Table 3. In all these complexes, the metal ion appears slightly too small for the ligand cavity, so that the metal is not bound centrally. The wider binding cavity of L^6 in $[ZnL^6(H_2O)_2]^{2+}$ appears therefore still not to be wide enough to induce binuclear double helix complex formation such as that observed, for example, in certain sexipyridine complexes.[12] The zinc ion in $[ZnL^6(H_2O)_2]^{2+}$ prefers instead to make a mononuclear six-co-ordinate complex (in the presence of other donor ligands), rather than a helicate. Cations preferring tetrahedral co-ordination geometry or those which involve greater mismatches in size between the bonding cavity of L^6 and the metal ion may perhaps promote the formation of helicate complexes of L^6.

The ligand L^6 in the zinc complex deviates slightly from planarity: one thiazole ring is tilted slightly with reference to the other rings. This reduces intramolecular $CH_3\cdots CH_3$ steric interactions [C(4)···C(18) 3.827(7) Å] and contributes to the significant difference (0.02 Å) in the Zn–N (thiazole) bond

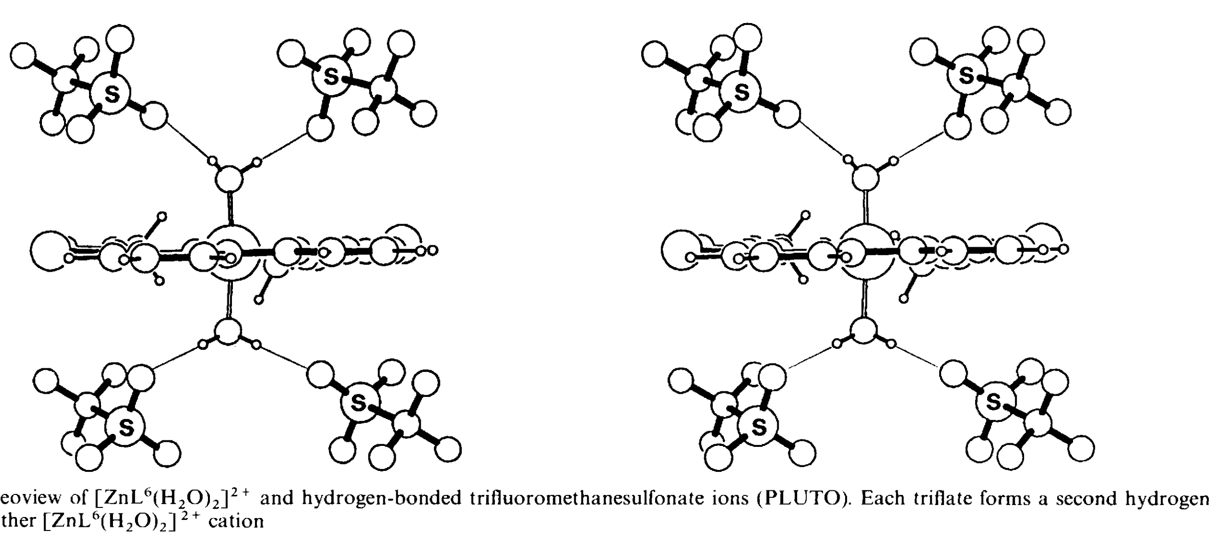


Fig. 2 Stereoview of $[ZnL^6(H_2O)_2]^{2+}$ and hydrogen-bonded trifluoromethanesulfonate ions (PLUTO). Each triflate forms a second hydrogen bond to another $[ZnL^6(H_2O)_2]^{2+}$ cation

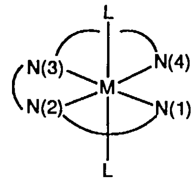
Table 1 Bond lengths (Å) and angles (°) for $[ZnL^6(H_2O)_2][CF_3SO_3]_2$ with estimated standard deviations (e.s.d.s) in parentheses

Cation			
C(1)–C(5)	1.461(9)	C(12)–C(13)	1.37(1)
C(1)–N(1)	1.295(7)	C(13)–C(14)	1.393(8)
C(1)–S(1)	1.708(5)	C(14)–C(15)	1.460(7)
C(2)–C(3)	1.37(1)	C(14)–N(3)	1.336(6)
C(2)–S(1)	1.68(1)	C(15)–N(4)	1.312(6)
C(3)–C(4)	1.47(1)	C(15)–S(2)	1.705(5)
C(3)–N(1)	1.395(7)	C(16)–C(17)	1.345(8)
C(5)–C(6)	1.394(8)	C(16)–S(2)	1.701(6)
C(5)–N(2)	1.337(7)	C(17)–C(18)	1.499(8)
C(6)–C(7)	1.38(1)	C(17)–N(4)	1.376(6)
C(7)–C(8)	1.37(1)	N(1)–Zn	2.279(4)
C(8)–C(9)	1.390(8)	N(2)–Zn	2.159(4)
C(9)–C(10)	1.482(8)	N(3)–Zn	2.149(4)
C(9)–N(2)	1.335(7)	N(4)–Zn	2.258(4)
C(10)–C(11)	1.402(9)	O(1)–Zn	2.066(3)
C(10)–N(3)	1.334(7)	O(2)–Zn	2.022(4)
C(11)–C(12)	1.37(1)		
Triflate anions			
C(19)–F(1)	1.333(7)	C(20)–F(4)	1.314(8)
C(19)–F(2)	1.314(6)	C(20)–F(5)	1.313(8)
C(19)–F(3)	1.312(7)	C(20)–F(6)	1.304(9)
C(19)–S(3)	1.818(5)	C(20)–S(4)	1.821(8)
O(3)–S(3)	1.437(4)	O(6)–S(4)	1.439(4)
O(4)–S(3)	1.444(4)	O(7)–S(4)	1.422(5)
O(5)–S(3)	1.422(4)	O(8)–S(4)	1.414(5)
Cation			
C(5)–C(1)–N(1)	121.8(5)	C(18)–C(17)–N(4)	119.5(5)
C(5)–C(1)–S(1)	123.4(5)	C(1)–N(1)–C(3)	111.8(5)
N(1)–C(1)–S(1)	114.7(5)	C(1)–N(1)–Zn	111.8(4)
C(3)–C(2)–S(1)	112.4(6)	C(3)–N(1)–Zn	135.9(4)
C(2)–C(3)–C(4)	128.3(7)	C(5)–N(2)–C(9)	120.4(5)
C(2)–C(3)–N(1)	111.8(7)	C(5)–N(2)–Zn	119.6(4)
C(4)–C(3)–N(1)	119.9(6)	C(9)–N(2)–Zn	119.9(4)
C(1)–C(5)–C(6)	126.0(6)	C(10)–N(3)–C(14)	120.7(5)
C(1)–C(5)–N(2)	112.5(5)	C(10)–N(3)–Zn	119.8(4)
C(6)–C(5)–N(2)	121.4(6)	C(14)–N(3)–Zn	119.5(3)
C(5)–C(6)–C(7)	117.7(6)	C(15)–N(4)–C(17)	111.2(4)
C(6)–C(7)–C(8)	120.8(6)	C(15)–N(4)–Zn	112.3(3)
C(7)–C(8)–C(9)	118.1(7)	C(17)–N(4)–Zn	136.5(3)
C(8)–C(9)–C(10)	125.2(6)	C(1)–S(1)–C(2)	89.3(3)
C(8)–C(9)–N(2)	121.5(6)	C(15)–S(2)–C(16)	89.7(3)
C(10)–C(9)–N(2)	113.3(5)	N(1)–Zn–N(2)	73.7(2)
C(9)–C(10)–C(11)	125.1(5)	N(1)–Zn–N(3)	146.3(2)
C(9)–C(10)–N(3)	114.2(5)	N(1)–Zn–N(4)	139.4(2)
C(11)–C(10)–N(3)	120.7(6)	N(1)–Zn–O(1)	84.7(1)
C(10)–C(11)–C(12)	117.9(6)	N(1)–Zn–O(2)	84.5(1)
C(11)–C(12)–C(13)	121.7(6)	N(2)–Zn–N(3)	72.8(2)
C(12)–C(13)–C(14)	117.2(6)	N(2)–Zn–N(4)	146.9(2)
C(13)–C(14)–C(15)	125.2(5)	N(2)–Zn–O(1)	99.5(1)
C(13)–C(14)–N(3)	121.8(5)	N(2)–Zn–O(2)	102.3(2)
C(15)–C(14)–N(3)	113.0(4)	N(3)–Zn–N(4)	74.2(2)
C(14)–C(15)–N(4)	121.0(4)	N(3)–Zn–O(1)	97.6(1)
C(14)–C(15)–S(2)	125.0(4)	N(3)–Zn–O(2)	105.7(2)
N(4)–C(15)–S(2)	114.0(4)	N(4)–Zn–O(1)	86.6(1)
C(17)–C(16)–S(2)	110.9(4)	N(4)–Zn–O(2)	84.8(1)
C(16)–C(17)–C(18)	126.3(5)	O(1)–Zn–O(2)	151.8(2)
C(16)–C(17)–N(4)	114.2(5)		
Triflate anions			
F(1)–C(19)–F(2)	107.4(5)	F(4)–C(20)–F(5)	106.3(6)
F(1)–C(19)–F(3)	107.4(5)	F(4)–C(20)–F(6)	109.3(8)
F(1)–C(19)–S(3)	111.0(4)	F(4)–C(20)–S(4)	112.0(6)
F(2)–C(19)–F(3)	107.3(5)	F(5)–C(20)–F(6)	106.9(7)
F(2)–C(19)–S(3)	111.7(4)	F(5)–C(20)–S(4)	111.0(6)
F(3)–C(19)–S(3)	111.6(4)	F(6)–C(20)–S(4)	111.1(5)
C(19)–S(3)–O(3)	103.6(3)	C(20)–S(4)–O(6)	103.0(3)
C(19)–S(3)–O(4)	102.5(3)	C(20)–S(4)–O(7)	102.9(3)
C(19)–S(3)–O(5)	104.1(3)	C(20)–S(4)–O(8)	102.9(4)
O(3)–S(3)–O(4)	113.5(3)	O(6)–S(4)–O(7)	115.2(3)
O(3)–S(3)–O(5)	115.2(3)	O(6)–S(4)–O(8)	114.0(3)
O(4)–S(3)–O(5)	115.6(3)	O(7)–S(4)–O(8)	116.3(4)

Table 2 Fractional atomic coordinates for $[ZnL^6(H_2O)_2][CF_3SO_3]_2$ with e.s.d.s in parentheses

Atom	*X/a*	*Y/b*	*Z/c*
Cation			
C(1)	0.3852(4)	−0.1239(1)	0.2155(2)
C(2)	0.6111(5)	−0.1334(2)	0.1352(3)
C(3)	0.5754(4)	−0.0749(2)	0.1553(2)
C(4)	0.6590(5)	−0.0196(2)	0.1354(3)
C(5)	0.2477(4)	−0.1316(1)	0.2651(2)
C(6)	0.1878(5)	−0.1863(1)	0.2938(3)
C(7)	0.0576(5)	−0.1844(2)	0.3422(3)
C(8)	−0.0090(4)	−0.1302(2)	0.3617(3)
C(9)	0.0575(4)	−0.0775(1)	0.3309(2)
C(10)	0.0028(4)	−0.0154(1)	0.3477(2)
C(11)	−0.1232(4)	−0.0010(2)	0.3978(3)
C(12)	−0.1596(4)	0.0590(2)	0.4065(3)
C(13)	−0.0751(4)	0.1039(2)	0.3689(3)
C(14)	0.0491(3)	0.0861(1)	0.3207(2)
C(15)	0.1521(3)	0.1270(1)	0.2761(2)
C(16)	0.2887(4)	0.2076(1)	0.2067(2)
C(17)	0.3469(3)	0.1523(1)	0.1942(2)
C(18)	0.4845(4)	0.1379(2)	0.1428(3)
N(1)	0.4418(3)	−0.0711(1)	0.2012(2)
N(2)	0.1826(3)	−0.0789(1)	0.2838(2)
N(3)	0.0853(3)	0.0279(1)	0.3109(2)
N(4)	0.2687(3)	0.1062(1)	0.2342(1)
S(1)	0.4840(2)	−0.1828(1)	0.1720(1)
S(2)	0.1325(1)	0.2036(1)	0.2697(1)
Zn	0.2847(1)	0.0045(1)	0.2415(1)
Coordinated water molecules			
O(1)	0.4302(2)	0.0171(1)	0.3519(1)
O(2)	0.2329(3)	0.0074(1)	0.1050(1)
Triflate anions			
C(19)	0.9832(4)	0.6889(1)	0.5387(2)
F(1)	0.9325(3)	0.6645(1)	0.6160(1)
F(2)	1.0781(3)	0.7313(1)	0.5630(2)
F(3)	0.8717(3)	0.7156(1)	0.4959(2)
S(3)	1.0674(1)	0.6319(1)	0.4664(1)
O(3)	1.1780(2)	0.6050(1)	0.5262(2)
O(4)	0.9447(3)	0.5921(1)	0.4450(2)
O(5)	1.1229(3)	0.6652(1)	0.3906(2)
C(20)	0.0429(5)	0.8172(2)	0.0199(3)
F(4)	−0.0730(4)	0.7916(2)	−0.0199(2)
F(5)	0.0013(3)	0.8347(2)	0.1019(2)
F(6)	0.1463(4)	0.7769(1)	0.0329(3)
S(4)	0.1098(1)	0.8810(1)	−0.0469(1)
O(6)	0.2344(3)	0.9020(1)	0.0077(2)
O(7)	0.1455(3)	0.8540(1)	−0.1327(2)
O(8)	−0.0121(4)	0.9210(2)	−0.0483(3)

Table 3 Structural comparisons of $[M(N_4)L_2]^{2+}$ species



M	Ni	Co	Zn
N_4 ligand	L^8	L^8	L^6
L	MeCN	OH_2	OH_2
M–N(2),N(3) (av.)/Å	2.004(3)	2.080	2.154(4)
M–N(1),N(4) (av.)/Å	2.106(4)	2.127	2.269(4)
N(2)–M–N(3)/°	77.6(2)	75.2(4)	72.8(2)
N(1)–M–N(4)/°	126.0(2)	132.7(4)	139.4(2)
L–M–L/°	168.0(2)	165.9(4)	151.8(2)
N(1) · · · N(4)	3.754(6)	3.897(7)	4.255(4)
Ref.	2	11	This work

lengths. A detailed investigation of the complexation behaviour of ligands L^6 and L^7 with other transition metals is currently in progress.

Experimental

2,2′-Bipyridine was purchased from Aldrich, and was converted to the *N,N*′-dioxide.[13] **CAUTION**: this reaction is potentially explosive. Infrared spectra of materials as sublimed films on KBr discs were recorded on a Mattson Alpha Centauri Fourier transform (FT) IR instrument interfaced with an AT&T UNIX PC. Proton and ^{13}C NMR spectra were measured using a JEOL GX270 FT spectrometer at 270 MHz for ^1H and 67.80 MHz for ^{13}C resonances; δ values in ppm relative to internal $SiMe_4$, *J* values in Hz.

6,6′-Dicyano-2,2′-bipyridine, L^1.—*Method A*. Finely powdered 6,6′-dibromo-2,2′-bipyridine[7] (3.01 g, 9.61 mmol) and copper(I) cyanide (2.24 g, 0.025 mmol) in dry pyridine (30 cm^3) contained in a flask (50 cm^3) fitted with a condenser and $CaCl_2$-drying tube was refluxed (oil-bath) at 180–185 °C for 12–14 h. After cooling to room temperature, the dark brown mixture was poured into an excess of concentrated aqueous potassium cyanide solution (50 cm^3). **CAUTION**: the use of potassium cyanide may involve the evolution of hydrogen cyanide in these reactions.

The mixture was diluted with water to complete precipitation if necessary. The application of heat, or prolonged contact with the aqueous KCN solution must be avoided because the suspended solid product is readily hydrolysed to form 2,2′-bipyridine-6,6′-dicarboxamide. Filtration of the tan coloured precipitate under vacuum, followed by washing with water, pumping dry, and sublimation (160 °C, 0.05 Torr) yields L^1 (1.92 g, 9.32 mmol) as an off-white crystalline solid, m.p. 259–260 °C (lit.[6] 255 °C) (Found: C, 69.4; H, 2.7; N, 27.0. $C_{12}H_6N_4$ requires C, 69.9; H, 3.0; N, 27.2%); $\delta_H(CDCl_3)$ 8.73 (1 H, dd, H^3, *J* 8.1, 1.0), 8.02 (1 H, dd, H^4, *J* 8.2, 7.7) and 7.79 (1 H, dd, H^5, *J* 7.7, 1.1); $\delta_C(CDCl_3)$ 155.64 (C^2), 138.40 (C^4), 133.54 (C^6), 124.68 and 129.08 ($C^{3,5}$) and 117.03 (CN); *m*/*z* (%) 206 (M^+, 100), 180 (16) 153 (9), 103 (13) and 76 (13); IR (sublimed thin film) 3096, 3080, 2237 (CN), 2011, 1854, 1710, 1578, 1557, 1434, 1425, 1377, 1208, 1158, 1102, 1081, 990, 982, 803, 788, 735, 638, 593 and 564 cm^{-1}.

Method B. A solution of 2,2′-bipyridine *N,N*′-dioxide (1.007 g, 5.35 mmol) in dimethyl sulfate (4 cm^3) contained in a loosely stoppered flask was heated with stirring at 100 °C for 4 h. After cooling to room temperature, the viscous solution was added dropwise over 0.5 h to a rapidly stirred, cooled (−30 to −40 °C) saturated aqueous potassium cyanide solution (15 cm^3). A fawn coloured solid developed during the course of this reaction. The mixture was stirred for a further 0.6 h at this temperature and then allowed to warm to −20 °C at which point the pH of the mixture was adjusted to pH 8 by the addition of concentrated aqueous ammonia solution (33% w/w). The mixture was filtered, washed with distilled water and then with ice-cold acetone, and pumped dry. The resulting solid was then sublimed (170 °C, 0.05 Torr) and recrystallised (acetonitrile) to yield L^1 (0.546 g, 50%), m.p. 263.5–264.0 °C.

Method C. A mixture of benzoyl chloride (13.32 g, 95 mmol) in thf (9 cm^3) was added in small portions to a rapidly stirred solution of 2,2′-bipyridine *N,N*′-dioxide (2.015 g, 10.7 mmol) and potassium cyanide (5 g, 77 mmol) (note **CAUTION** above) in distilled water (30 cm^3) during 1 h. During addition, the reaction mixture was maintained at room temperature by periodic cooling of the flask in a water-bath. The solid product which formed was collected by filtration under vacuum, washed thoroughly with methanol and the solid remaining pumped dry and sublimed (170 °C, 0.5 Torr) to yield analytically pure L^1 (1.17 g, 53%), m.p. 263.5–264 °C. NMR and mass spectra of the product from this reaction are identical to those obtained using Method A. The following compounds were prepared in a similar manner from the corresponding *N,N*′-dioxide. The *N,N*′-dioxide was prepared by the same general method[13] as was used for 2,2′-bipyridine *N,N*′-dioxide (note **CAUTION** already given). Using a solution of benzoyl chloride (9.69 g, 69 mmol) in thf (8 cm^3) and 4,4′-dimethyl-2,2′-bipyridine *N,N*′-dioxide (0.46 g, 2.13 mmol) with KCN (1.8 g, 2.8 mmol) in water (20 cm^3) gives 6,6′-dicyano-4,4′-dimethyl-2,2′-bipyridine as colourless needles, m.p. 255–255.5 °C (from MeCN). Yield 0.200 g, 36%. Note: yield is highly dependent on proportions of solvents and reagents (Found: C, 71.5; H, 4.2; N, 23.9. $C_{14}H_{10}N_4$ requires C, 71.8; H, 4.3; N, 23.9%); $\delta_H(CDCl_3)$ 8.51 (1 H, d, H^3, *J* 1.5), 7.58 (1 H, d, H^5, *J* 1.5) and 2.54 (3 H, CH_3); $\delta_C(CDCl_3)$ 155.5 (C^2), 150.3 (C^4), 133.2 (C^6), 129.8 (C^5), 125.5 (C^3), 117.3 (CN) and 21.2 (CH_3); *m*/*z* (%) 235 (16), 234 (M^+, 100) and 233 (25). 4,4′-Di(*tert*-butyl)-6,6′-dicyano-2,2′-bipyridine, colourless needles, m.p. > 300 °C. Yield 34% (from toluene) (Found: C, 75.4; H, 7.2; N, 17.4. $C_{20}H_{22}N_4$ requires C, 75.4; H, 7.0; N, 17.6%); $\delta_H(CDCl_3)$ 8.68 (1 H, d, H^3, *J* 1.6), 7.75 (1 H, d, H^5, *J* 1.9) and 1.42 (9 H, CH_3); $\delta_C(CDCl_3)$ 163.3 (C^4), 155.8 (C^2), 133.3 (C^6), 126.5 and 121.9 ($C^{3,5}$), 117.7 (CN) and 30.4 (CH_3); *m*/*z* (%) 318 (M^+, 100), 303 (42), 235 (16), 234 (10) and 233 (21). 6,6′-Dicyano-5,5′-dimethyl-2,2′-bipyridine, colourless needles, m.p. 248.5–249.5 °C. Yield 75% (Found: C, 72.0; H, 4.0; N, 24.0. $C_{14}H_{10}N_4$ requires C, 71.8; H, 4.3; N, 23.9%; $\delta_H(CDCl_3)$ 8.55 (1 H, d, H^3, *J* 8.2), 7.82 (1 H, d, H^4, *J* 8.2) and 2.63 (3 H, CH_3); $\delta_C(CDCl_3)$ 153.3 (C^2), 139.3 (C^4), 139.1 (C^5), 133.3 (C^6), 124.1 (C^3), 116.3 (CN) and 18.6 (CH_3); *m*/*z* (%) 235 (16), 234 (M^+, 100) and 233 (26).

2,2′-Bipyridine-6,6′-bis(thiocarboxamide), L^5.—Finely powdered L^1 (0.345 g, 1.67 mmol) dissolved in a mixture of thf (120 cm^3) and methanol (45 cm^3) was purged with ammonia gas for 0.6 h. The flask was tightly closed and the mixture was magnetically stirred for 48 h, then purged with hydrogen sulfide gas for 1 h and the flask resealed. The yellow reaction mixture was stirred for a further 48 h. Removal of solvent under reduced pressure gave a pungent yellow solid which was recrystallised from nitromethane to yield L^5 as yellow needles (0.297 g, 65%), m.p. 247–257 °C (slow decomposition) (Found: C, 52.6; H, 3.6; N, 20.3. $C_{12}H_{10}N_4S_2$ requires C, 52.5; H, 3.7; N, 20.4%); $\delta_H[(CD_3)_2SO]$ 10.32, 10.26 (2 H, NH_2), 9.09 (1 H, d, H^3, *J* 7.7), 8.65 (1 H, d, H^5, *J* 7.8) and 8.15 (dd, H^4, *J* 7.8, 7.8); $\delta_C[(CD_3)_2SO]$ 194.2 (CS), 152.5 (C^2), 151.0 (C^6), 138.3 (C^4), 125.2 and 123.9 (C^3 and C^5); *m*/*z* (%) 274 (M^+, 41), 240 (75), 207 (61), 206 (49), 181 (100), 180 (64) and 153 (24).

6,6′-Bis(4-methylthiazol-2-yl)-2,2′-bipyridine, L^6.—A suspension of L^5 (0.268 g, 0.98 mmol) in a mixture of thf (8 cm^3) and 1-chloropropan-2-one (8 cm^3) was heated at 90 °C for 3 h. After cooling, the reaction mixture was poured onto water (50 cm^3), stirred for 0.5 h, filtered, washed with water, pumped dry and then sublimed (200 °C, 0.05 Torr) to give L^6 as a cream coloured solid (0.258 g, 75%), m.p. 264–266 °C (from benzene) (Found: C, 62.1; H, 3.9; N, 15.9. $C_{18}H_{14}N_4S_2$ requires C, 61.7; H, 4.0; N, 16.0%); $\delta_H(CDCl_3)$ 8.58 (1 H, dd, H^3, *J* 8.0, 1.1), 8.20 (1 H, dd, H^5, *J* 7.7, 1.1), 7.95 (1 H, dd, H^4, *J* 8.0, 7.7), 7.03 (1 H, s, thiazole H^5) and 2.55 (1 H, s, CH_3); $\delta_C(CDCl_3)$ 168.7 (C^2 thiazole), 155.0 (C^2 bipyridine), 154.3 (C^4 thiazole), 150.8 (C^6 bipyridine), 138.1 (C^4 bipyridine), 121.7 and 119.6 ($C^{3,5}$ bipyridine), 116.2 (C^5 thiazole) and 17.4 (CH_3); *m*/*z* (%) 351 (48), 350 (M^+, 100), 279 (34), 278 (13), 175 (12), 72 (68) and 71 (63).

6,6′-Bis[4-(2-pyridyl)thiazol-2-yl]-2,2′-bipyridine, L^7.—2-Bromoacetylpyridine[14] (2.24 g, 11.2 mmol) was added dropwise to a stirred suspension of L^5 (0.185 g, 0.674 mmol) in thf (9 cm^3) heated at reflux (95 °C). After the addition was complete, heating was continued for a further 2 h. Initially, a yellow precipitate developed which slowly thickened and became pale fawn in colour. After cooling, the mixture was poured onto methanol (60 cm^3), stirred for 0.75 h, filtered, washed with methanol and pumped dry. The solid was dissolved in hot pyridine (85 cm^3) containing decolourising charcoal (0.1 g), and the mixture boiled with stirring (0.4 h). Neutral alumina (grade 1, 0.2 g) was added with rapid stirring and boiling continued (0.1 h). **CAUTION**: The presence of alumina causes violent bumping if stirring is insufficiently vigorous. The mixture was filtered hot and the filtrate was concentrated (to about 50 cm^3). After standing for 24 h the crystals which had formed were isolated by filtration, washed with ice-cold pyridine (2 cm^3) and then pumped dry (0.05 Torr, 24 h) to give L^7 (0.21 g, 65%) as a cream coloured microcrystalline solid m.p. >300 °C (Found: C, 65.5; H, 3.2; N, 17.8. $C_{26}H_{16}N_6S_2$ requires C, 65.5; H, 3.4; N, 17.6%); *m*/*z* (%) (FAB) 476 (M^+, 47), 342 (23), 135 (100), 108 (10), 91 (15) and 78 (34). The insolubility of L^7 in most organic solvents prevented its characterisation by NMR spectroscopy.

Diaqua[6,6′-*bis*(4-*methylthiazol*-2-*yl*)-2,2′-*bipyridine*]*zinc*(II) *Bis*(*trifluoromethanesulfonate*).—A mixture of L^6 (0.05 g, 0.14 mmol) and zinc(II) trifluoromethanesulfonate (0.03 g, 0.13 mmol) was added to acetonitrile (6 cm^3). The mixture was heated until all the solids had dissolved. Filtration and concentration produced a solution from which colourless prismatic crystals of $[ZnL^6(H_2O)_2][CF_3SO_3]_2$ were isolated after 24 h (Found: C, 31.7; H, 2.3; N, 7.5. $C_{20}H_{18}F_6N_4O_8S_4Zn$ requires C, 32.0; H, 2.4; N, 7.5%); IR (Nujol) 3360(br), 1590, 1565, 1522, 1300, 1160, 1025, 865, 802, 760, 740, 642 and 630 cm^{-1}; $\delta_H(CD_3OD)$ 8.76 (1 H, dd, H^3, *J* 7.7, 0.8), 8.55 (1 H, d, H^4, *J* 7.8), 8.45 (1 H, dd, H^5, *J*, 8.0, 0.8), 7.85 (1 H, m, H^5 thiazole, *J* 1.1) and 2.85 (3 H, m, CH_3, *J* 1.1); $\delta_C(CD_3OD)$ 165.3, 154.5, 148.8, 147.1, 143.2, 125.0, 124.2, 122.2, 119.5 and 17.6.

X-Ray Structure Determination of $[ZnL^6(H_2O)_2][CF_3SO_3]_2$.—*Crystal data*. $C_{20}H_{18}F_6N_4O_8S_4Zn$, *M* 749.9, monoclinic, space group $P2_1/a$, $a = 9.048(4)$, $b = 22.126(9)$, $c = 14.476(4)$ Å, $\beta = 91.30(3)°$, $U = 2897.3$ Å^3, $Z = 4$, $D_c = 1.72$ g cm^{-3}, Mo-Kα radiation, $\lambda = 0.710\ 69$ Å, $\mu = 12.30$ cm^{-1}, $F(000) = 1512$, $T = 296$ K. A suitable crystal (0.45 × 0.30 × 0.25 mm) was grown by evaporation of an acetonitrile solution. X-Ray diffraction intensities were collected on an Enraf-Nonius CAD-4 diffractometer with ω–2θ scans out to a maximum in $(\sin\theta/\lambda)$ of 0.64 Å^{-1}. 6920 Measured reflections, 6471 unique and 4926 counted as observed $[I > 3\sigma(I)]$. The structure was solved by Patterson methods using SHELXS 86[15] and refined on *F* by full-matrix least-squares analyses with SHELX 76[16] including anisotropic thermal parameters for non-hydrogen atoms. Hydrogen-atom positions were calculated and assigned a fixed isotropic thermal parameter of 0.1 Å^2 with the exception of hydrogen atoms of the water molecules which were located in Fourier difference maps. An extinction parameter (final value 1.3×10^{-3}) was included in the refinement and with a weighting scheme, $w = \{2.9958[\sigma^2(F) + 0.000\ 15F^2]\}^{-1}$ the model converged with $R = 0.038$ and $R' = 0.042$. Maximum $\Delta/\sigma = 0.19$ in final cycle for positional parameters and 0.4 for thermal parameters. Maximum and minimum residual electron density in final Fourier difference synthesis 0.56 and −0.59 e Å^{-3}. Atomic scattering factors for non-hydrogen atoms from Cromer and Mann,[17] for hydrogen from Stewart *et al.*[18] Fig. 1 was drawn using ORTEP II[19] and Fig. 2 using PLUTO.[20]

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

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