Experimental Section

General Considerations. All reagents and starting materials were purchased from Aldrich and/or Lancaster and were used without further purification. ^{1}H NMR spectra were obtained on either a Bruker 400MHz or 500MHz NMR instrument and mass spectrometry was performed on a Micromass Quattro VG quadrupole and a Bruker MicroTOF LC mass spectrometer. **CAUTION**: Sodium cyanide is extremely toxic and all manipulations of this material should be done within a fume cupboard and any waste material should be disposed of accordingly. Also perchlorate salts are potentially explosive and should be treated with due care. Those complexes described below which were isolated as perchlorates were only prepared in small amounts (10 - 20 mg) and we had no problems with them.

Synthesis of 3,3'-diacetylamino-2,2'-bipyridine-*N,N*-dioxide (1). To a solution of 3,3'-diacetylamino-2,2'-bipyridine[7] (0.25 g, 0.92 mmol) in CH_2Cl_2 (50 ml) was added *m*CPBA (77%, 0.61 g, 2.76 mmol) and the reaction monitored by TLC (5% MeOH/CH_2Cl_2, Al_2O_3) over a period of 1 week. During this time the starting material disappeared and an intermediate spot appeared (presumably the mono-*N*-oxide). After this intermediate spot was consumed, which was facilitated by the addition of more *m*CPBA if necessary, the reaction was reduced in volume and the resulting solution purified by column chromatography (5% MeOH/CH_2Cl_2, Al_2O_3) giving the bis-*N,N*-oxide **1** (0.18 g, 65%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$, δ) 9.41 (s, 2H, NH), 8.15 (d, 2H, J = 6.4 Hz, py), 7.66 (d, 2H, J = 8.4 Hz), 7.46 (dd, 2H, J = 6.5, 8.4 Hz, py), 1.84 (s, 3H, -CH_3). High Res. ESI-MS found *m/z* 303.109326 $C_{14}H_{15}N_4O_4$ ($M + H^+$) requires m/z 303.108781.

Synthesis of 3,3'-diacetylamino-6,6'-dicyano-2,2'-bipyridine (2). To a 50ml round bottomed flask charged with the bis-*N,N*-dioxide (**1**) (0.25 g, 0.83 mmol) was added enough $(MeO)_2SO_2$ to completely cover the solid and the reaction heated at 80ºC under nitrogen overnight. The reaction was then cooled and ethyl acetate (10 ml) and diether ether (30 ml) added sequentially. After leaving to stand for 24 hrs the organic solvents were removed by decanting and the resulting brown oil washed with Et_2O (2 x 30 ml). The oil was then dissolved in water (25 ml) and neutralised with $NaHCO_3$. To this was added a solution of NaCN (0.12 g, 2.49 mmol) in water (10ml) and the reaction stirred for 30 mins. The resulting precipitate was isolated by filtration and

washed with water (2 x 15 ml) giving 3,3'-diacetylamino-6,6'-dicyano-2,2'-bipyridine **2** (0.19 g, 71%) as a cream solid. ^{1}H NMR (500 MHz, DMSO-d_6, δ) 8.57 (d, 2H, J = 8.6 Hz, py) 8.01 (brs, 2H, py), 1.98 (s, 6H, -CH_3). Due to the poor solubility of this compound the ^{1}H NMR is broadened and the signal corresponding to the amide proton is too broad to be observed. ESI-MS found *m/z* 343.091202 $C_{16}H_{12}N_6NaO_2$ ($M + Na^+$) requires m/z 343.091395.

Synthesis of 3,3'-diacetylamino-6,6'-dithioamide-2,2'-bipyridine (3). To a solution of the 6,6'-dicyano derivative (**2**) (0.10g, 0.31 mmol) and Et_3N (0.5 ml) in DMF (25 ml), H_2S gas was bubbled through the reaction for 20 mins. The reaction was then sealed and allowed to stand for 2 days. After this time the reaction was concentrated (ca. 10 ml) and the resulting solid isolated by filtration, giving the 6,6'-dithioamide derivative **3** (0.8 g, 66%) as a yellow solid. ^{1}H NMR (500 MHz, DMSO-d_6, δ) 10.48 (s, 2H, CONH), 10.15 (s, 2H, $CSNH_2$), 9.75 (s, 2H, $CSNH_2$), 8.65 (d, 2H, J = 8.7 Hz, py), 8.46 (d, 2H, J = 8.7 Hz, py), 2.03 (s, 6H, -CH_3). ESI-MS found *m/z* 389.084580 $C_{16}H_{17}N_6O_2S_2$ ($M + H^+$) requires m/z 389.084892.

Synthesis of 3,3'-diacetylamino-6,6'-bis(4-methylthiazol-2-yl)-2,2'-bipyridine (4). To a solution of 3,3'-diacetylamino-6,6'-dithioamide-2,2'-bipyridine (**3**) (0.1 g, 0.25 mmol) in DMF (10 ml) was added chloroacetone (0.1ml) and the reaction heated at 80ºC. After 4 hrs the resulting precipitate was isolated by filtration, washed with EtOH (2 x 10 ml) and Et_2O (2 x 10 ml), giving **4** (0.09 g, 77%) as a pale yellow solid. ^{1}H NMR (500 MHz, DMSO-d_6, δ) 10.44 (s, 2H, NH), 8.76 (d, 2H, J = 8.7 Hz, py), 8.18 (d, 2H, J = 8.7 Hz, py), 7.41 (s, 2H, tz), 2.47 (s, 3H, -CH_3), 2.08 (s, 3H, $COCH_3$). ESI-MS found *m/z* 465.117072 $C_{22}H_{21}N_6O_2S_2$ ($M + H^+$) requires m/z 465.116192.

Synthesis of 3,3'-diamino-6,6'-bis(4-methylthiazol-2-yl)-2,2'-bipyridine (L^1). To a 50 ml round bottomed flask charged with the 3,3'-diacetylamino derivative (**4**) (0.1 g, 0.21 mmol) was added HCl (conc, 25 ml) and the reaction refluxed for 3hrs. After this time the solution was poured onto water (50 ml) and the resulting orange precipitate isolated by filtration. This solid was then suspended in NH_3 (conc) overnight during which time the colour changed from orange to yellow. Filtration and washing with H_2O (2 x 10 ml), EtOH (2 x 10 ml) and Et_2O (2 x 10 ml) gave ligand $\mathbf{L^1}$ (0.05g, 63%) as a bright yellow solid. ^{1}H NMR (500 MHz, DMSO-d_6, δ) 7.90 (d, 2H, J = 8.55 Hz,

py), 7.77 (brs, 4H, -NH_2), 7.35 (d, 2H, J = 8.55 Hz), 7.26 (s, 2H, tz), 2.43 (s, 6H, -CH_3). ESI-MS found *m/z* 381.096178 $C_{18}H_{17}N_6S_2$ ($M + H^+$) requires m/z 381.095062.

$[Cd_2(L^1)_2](ClO_4)_4$. To a suspension of $\mathbf{L^1}$ (10 mg, 0.026 mmol) in MeCN (2 ml) was added a solution of $[Cd(ClO_4)_2]\cdot 6H_2O$ (11 mg, 0.026 mmol) in MeCN (1 ml) and the resulting suspension sonicated until complete dissolution occured. Filtration followed by slow vapour diffusion of ethyl acetate into the solution gave $[Cd_2(\mathbf{L^1})_2](ClO_4)_4$ (12 mg, 67%) as a yellow crystalline solid. ^{1}H NMR (500 MHz, MeCN –d_3, δ) 7.94 (d, 2H, J = 8.5 Hz, py (m)), 7.63 (d, 2H, J = 8.5 Hz, py (m)), 7.44 (d, 2H, J = 8.9 Hz, py (h)), 7.43 (s, 2H, tz (m)), 7.34 (s, 2H, tz), 7.14 (d, 2H, J = 8.9 Hz, py (h)), 5.58 (s, 4H, -NH_2 (m)), 5.47 (s, 4H, -NH_2 (h)), 2.67 (s, 6H, -CH_3 (m)), 2.43 (s, 6H, -CH_3 (h)). The letters h and m refer to helicate ($[Cd_2(\mathbf{L^1})_2]^{4+}$) and ($[Cd(\mathbf{L^1})]^{2+}$) mononuclear species respectively. ESI-MS m/z 593 $\{[Cd(\mathbf{L^1})](ClO_4)\}^+$ and 1285 $\{[Cd_2(\mathbf{L^1})_2](ClO_4)_3\}^+$. Elemental analysis calculated for $C_{36}H_{32}N_{12}Cd_2Cl_4O_{16}S_4\cdot 2MeCN$, C, 32.8; H, 2.6; N, 13.4 %. Found: C, 32.2; H, 2.9; N, 13.1 %.

$[Cu_2(L^1)_2](PF_6)_2$. To a suspension of $\mathbf{L^1}$ (10 mg, 0.026 mmol) in MeCN (2 ml) was added a solution of $[Cu(NCMe)_4]PF_6$ (10 mg, 0.027 mmol) in MeCN (1 ml) and the resulting suspension sonicated until complete dissolution occurred. Filtration followed by slow vapour diffusion of diethyl ether into the solution gave $[Cu_2(\mathbf{L^1})_2](PF_6)_2$ (10 mg, 65 %) as a red crystalline solid. ^{1}H NMR (500 MHz, MeCN –d_3, δ) 7.39 (d, 2H, J = 8.7 Hz, py), 7.16 (s, 2H, tz), 6.72 (d, 2H, J = 8.7 Hz, py), 4.74 (s, 4H, -NH_2), 2.19 (s, 6H, -CH_3). ESI-MS *m/z* 444 $\{[Cu_2(\mathbf{L^1})_2]\}^{2+}$ and 1033 $\{[Cu_2(\mathbf{L^1})_2]PF_6\}^+$. Elemental analysis calculated for $C_{36}H_{32}N_{12}Cu_2F_{12}P_2S_4$, C, 36.7; H, 2.7; N, 14.3 %. Found: C, 36.9; H, 2.9; N, 14.0 %.

$[Cd(L^{1a})](ClO_4)_2$. To a solution of $[Cd_2(\mathbf{L^1})_2](ClO_4)_4$ (10 mg, 0.007 mmol) in MeCN (1 ml) was added camphorsulfonic acid (≈1mg) and two drops of acetone. Slow diffusion of ethyl acetate into the solution gave dark yellow crystals of $[Cd(\mathbf{L^{1a}})](ClO_4)_2$ (8 mg, 75 %). ^{1}H NMR (500 MHz, MeCN-d_3, δ) 7.82 (d, 2H, J = 8.6 Hz, py), 7.48 (d, 2H, J = 8.6 Hz, py), 7.39 (s, 2H, tz), 6.35 (s, 2H, NH), 2.75 (s, 6H, -CH_3), 1.60 (s, 6H, -CH_3). ESI-MS m/z 633 $\{[Cd(\mathbf{L^{1a}})](ClO_4)\}^+$. Elemental analysis calculated for $C_{21}H_{20}N_6CdCl_2O_8S_2$, C, 34.5; H, 2.7; N, 11.5 %. Found: C, 34.0; H, 2.9; N, 11.1 %.

Crystallography

X-ray Crystallography. Crystals were visually inspected for defects and singularity under a binocular microscope fitted with a polarising attachment. Suitable crystals were then coated with epoxy resin, mounted on a glass fibre and quickly transferred to a Bruker-AXS PROTEUM or APEX (CCD area-detector) diffractometer under a stream of cold N_2 gas. Preliminary scans were employed to assess crystal quality, lattice symmetry, ideal exposure time *etc*. prior to collecting a sphere or hemisphere (for low- and high-symmetry crystal systems respectively) of diffraction intensity data using SMART operating software.[1] Intensities were then integrated from several series of exposures (each exposure covering 0.3° in ω), merged and corrected for Lorentz and polarisation effects using SAINT software.[2] Solutions were generated by conventional heavy atom Patterson or direct methods and refined by full-matrix non-linear least squares on all F^2 data, using SHELXS-97 and SHELXL software respectively (as implemented in the SHELXTL suite of programs).[3] Empirical absorption corrections were applied based on multiple and symmetry-equivalent measurements using SADABS[4] and, where stated, the scattering contributions from diffuse solvent moieties were removed using the SQUEEZE function in PLATON.[5] All structures were refined until convergence (max shift/esd < 0.01) and in each case, the final Fourier difference map showed no chemically sensible features. Crystallographic refinement parameters for all complexes are summarised in Table 2.

1 *SMART Diffractometer Control Software*, Bruker Analytical X-ray Instruments Inc., Madison, WI, **1998**.

2 *SAINT Integration Software*, Siemens Analytical X-ray Instruments Inc., Madison, WI, **1998**.

3 *SHELXTL Program System, Vers. 5.1*, Bruker Analytical X-ray Instruments Inc., Madison, WI, **1998**.

4 G. M. Sheldrick, *SADABS: A Program for Absorption Correction with the Siemens SMART System*, University of Göttingen (Germany), **1996**.

5 A. L. Spek, *Acta Cryst.* **1990**, *A46*, C-34; PLATON – A Multipurpose Crystallographic ool; Utrecht, The Netherlands, A. L. Spek, 2003.

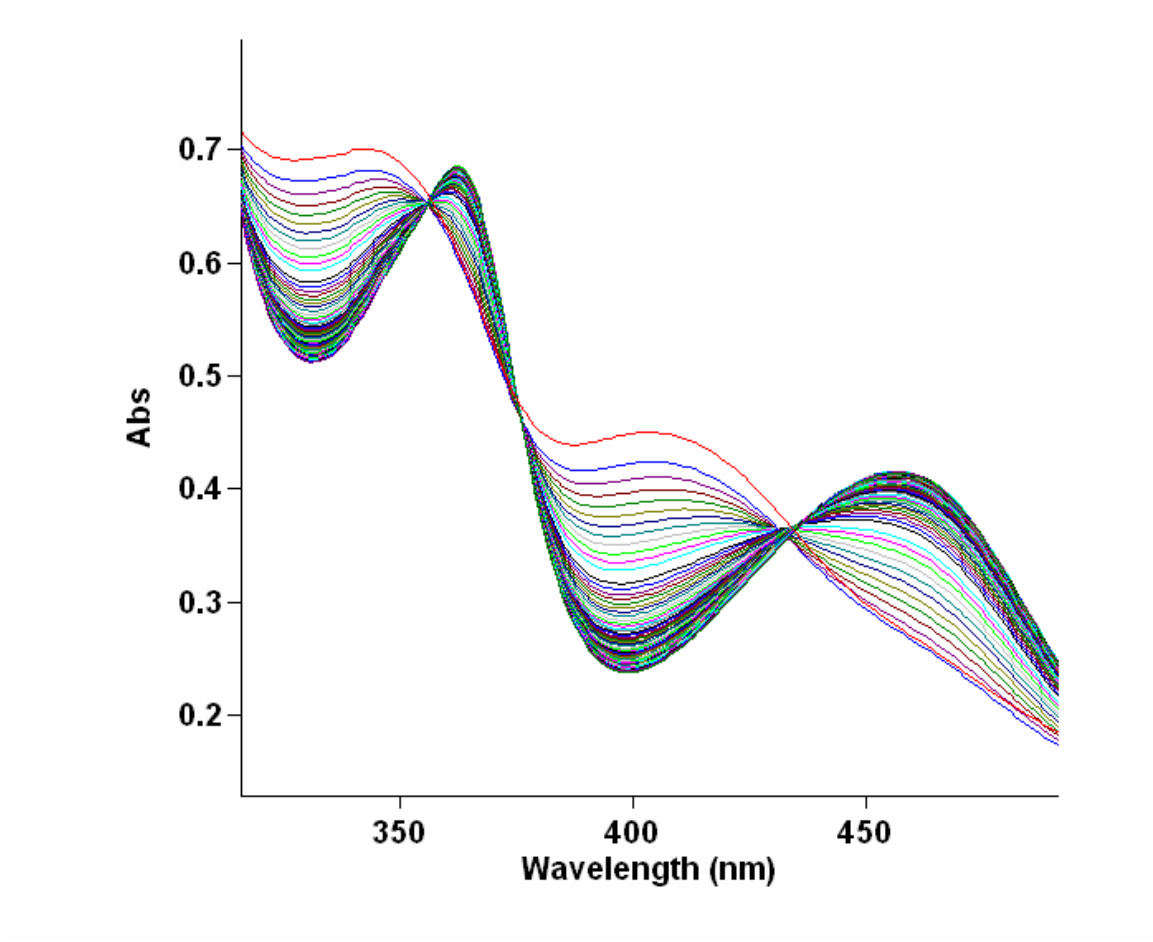

Figure 1. UV-Vis spectrum of $[Cd(\mathbf{L}^{1})]^{2+}$ in CH_3CN (1×10^{-5}M) upon acid catalysed reaction with acetone.