Supporting Information

Amidopyridine Outer-sphere Extractants for Zinc and Cobalt Chloridometallates

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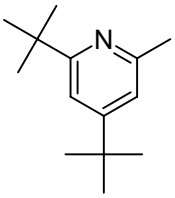
Full Experimental Details

All solvents and reagents were commercially available from Aldrich or Fisher. ^{1}H and ^{13}C NMR spectra were obatined on a Bruker ARX 250 spectrometer. The chemical shifts (δ) are reported in parts per million (ppm) relative to the residual solvent signal in CDCl3 (δ_H 7.26 and δ_C 77.0), DMSO-d_6 (δ_H 2.50 and δ_C 39.5). Electrospray (ES) mass spectra were recorded on a VG Autospec instrument. ICP-OES was carried out using the Perkin Elmer Optima 5300DV Spectrometer.

Ligand Synthesis

2,4-Di-*tert*-butyl-6-methylpyridine{Scalzi, 1971 #86} **L^4**

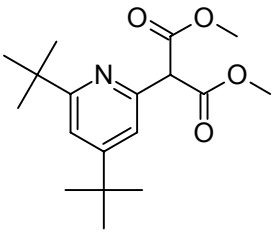
In a 500 ml, two-necked round bottomed flask, α-picoline (6.0 g, 64.6 mmol) dissolved in dry *n*-heptane (100 ml) was cooled, under N_2, to -75°C using an acetone-dry ice cooling bath. The solution was stirred under N_2 for 1 h, after which *tert*-butyllithium (1.5 M, 215 ml, in pentane) was carefully added using a pressure compensating addition funnel, resulting in the colourless solution turning bright yellow. The pentane was distilled off under N_2 and the remaining solution was refluxed for 1 h, over which time the colour changed from yellow to deep red. The reaction mixture was then cooled to 0°C in an ice bath and quenched by cautiously adding water (100 ml). The aqueous layer was extracted using hexane (3 x 100 ml) and the combined organic layers were dried over magnesium sulfate and then concentrated on a rotary evaporator, yielding **L^4** (9.4 g, 71%) as a red-brown oil. δ_H (250 MHz; $CDCl_3$) 1.18 (s, 9H, ^{t}Bu), 1.29 (s, 9H, ^{t}Bu), 2.43 (s, 3H, 6-Me), 6.82 (s, 1H, 3-H), 7.02 (s, 1H, 5-H); δ_C (63 MHz; $CDCl_3$) 25.5, 31.0, 31.1, 35.0, 38.5, 113.7, 116.1, 157.2, 160.2, 168.5.



L[4]

Dimethyl (4,6-di-*tert*-butylpyridin-2-yl)malonate 1

In a 500 ml, two-necked round bottomed flask, α-picoline (2.9 g, 31.2 mmol) dissolved in dry *n*-heptane (100 ml) was cooled, under N_2, to -75^{o}C using an acetone-dry ice cooling bath. The solution was stirred under N_2 for 1 h, after which *tert*-butyllithium (1.5 M, 104 ml, in pentane) was carefully added using a pressure compensating addition funnel, resulting in the colourless solution turning bright yellow. The pentane was distilled off under N_2 and the remaining solution was refluxed for 1 h, over which the colour changed from yellow to deep red. The reaction mixture was then cooled in an ice bath to 0^{o}C and dimethyl carbonate (14.5 g, 161 mmol) was added drop-wise, causing the mixture to effervesce and solidify. The residue was re-dissolved in ether and ammonium chloride (10 g) was cautiously added followed by water (100 ml). The aqueous layer was extracted with ethyl acetate (3 x 150 ml), and the combined organic layers were dried over magnesium sulfate, filtered and concentrated on a rotary evaporator. The crude product was purified by column chromatography on silica gel using 5% then 10% diethyl ether in hexane as eluent to give the malonate **1** (6.0 g, 60%) as a bright yellow crystalline solid. ν_{max}(KBr disc)/cm^{-1} 2962-2871 (C-H stretch), 1756 (C=O stretch); δ_H (250 MHz; DMSO-d_6) 1.25 (s, 18H, ^{t}Bu), 3.64 (s, 6H, OCH_3), 5.52 (s, 1H, CHCO), 7.19 (s 1H, 5-H), 7.28 (s 1H, 3-H); δ_C (63 MHz; $CDCl_3$) 28.4, 30.5, 31.3, 35.8, 38.1, 53.3, 61.0, 115.6, 118.0, 151.9, 161.1, 169.1; *m/z* (ES) 322 ($M+H^+$).

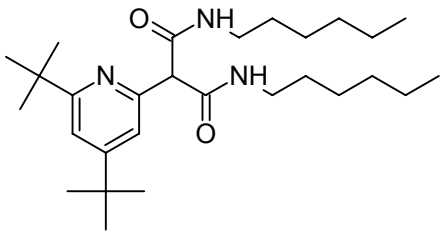


1

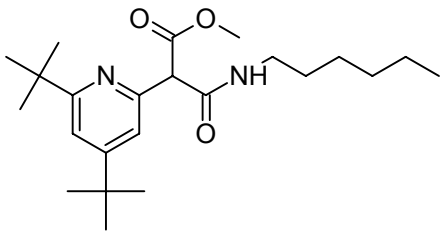
Methyl 2-(4,6-di-*tert*-butylpyridin-2-yl)-3-(hexylamino)-3-oxopropanoate 2 and 2-(4,6-di-*tert*-butylpyridin-2-yl)-*N*,*N'*-dihexylmalonamide L^2

Dimethyl (4,6-di-*tert*-butylpyridin-2-yl)malonate **1** (3 g, 9.3 mmol) and *n*-hexylamine (1.19 g, 11.8 mmol) were refluxed in a 500 ml round bottomed flask in toluene (250 ml) for 24 h. The reaction mixture was concentrated on a rotary evaporator and then purified by column chromatography on silica gel using 40% then 50% diethyl ether in hexane as elutent to give L^2 (1.91 g, 43%) as a pale brown oil as the low Rf component. (Found: C, 72.89; H, 10.68; N, 9.10. $C_{28}H_{49}N_3O_2$ requires C, 73.16; H, 10.74; N, 9.14); ν_{max}(KBr disc)/cm^{-1} 3324 (N-H stretch), 3029-2864 (C-H stretch), 1688 (C=O stretch); δ_H (250 MHz; $CDCl_3$) 0.95 (m, 6H, C*H*$_3$CH$_2$), 1.35 (m, 12H, CH$_3$C*H*$_2$C*H*$_2$C*H*$_2$), 1.40 (s, 9H, ^{t}Bu), 1.50 (s, 9H, ^{t}Bu), 1.66 (m, 4H, NCH$_2$C*H*$_2$), 3.24 (m, 4H, NCH$_2$), 4.65 (s, 1H, CHCO), 7.29 (s, 1H, 5-H), 7.40 (s, 1H, 3-H), 8.42 (t, 2H, NH); δ_C (63 MHz; $CDCl_3$) 14.6, 23.1, 27.3, 29.8, 30.0, 31.3, 32.0, 35.1, 38.1, 40.3, 62.4, 115.5, 119.4, 154.1, 162.6, 168.2, 169.4; *m/z* (ES) 430.6 (M+H$^+$)**.**

Methyl 2-(4,6-di-*tert*-butylpyridin-2-yl)-3-(hexylamino)-3-oxopropanoate **2** (2.01 g, 55%) was obtained as a pale brown oil. δ_H (250 MHz; $CDCl_3$) 1.00 (m, 6H, C*H*$_3$CH$_2$), 1.37 (m, 6H, CH$_3$C*H*$_2$C*H*$_2$C*H*$_2$), 1.42 (s, 9H, 2-^{t}Bu), 1.49 (s, 9H, ^{t}Bu), 1.65 (m, 2H, NCH$_2$C*H*$_2$), 3.42 (m, 2H, NCH$_2$), 3.86 (s, 3H, CH$_3$O), 4.80 (s, 1H, CHCO), 7.27 (s, 1H, 5-H), 7.41 (s, 1H, 3-H), 8.35 (t, 1H, NH); δ_C (63 MHz; $CDCl_3$) 14.1, 22.8, 26.9, 28.8, 30.1, 31.4, 32.3, 34.9, 37.0, 41.3, 53.5, 60.0, 114.5, 118.7, 153.7, 161.2, 169.1, 170.0; *m/z* (ES) 376.5 (M+H$^+$).



L^2

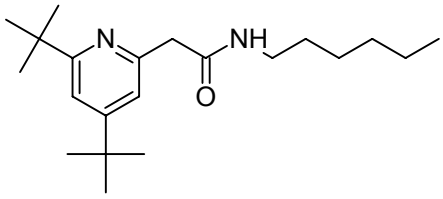


2

2-(4,6-Di-*tert*-butylpyridin-2-yl)-*N*-hexylacetamide L^1

In a 250 ml round bottomed flask, **2** (1.0 g, 2.6 mmol) was dissolved in methanol (100 ml) and refluxed with NaOH solution (2.1 ml, 6 M) for 3 h after which HCl (4.3 ml, 6 M) was added and stirred for 1 h. The methanol was removed on a rotary evaporator and the product was extracted with ethyl acetate (3 x 100ml), dried over magnesium

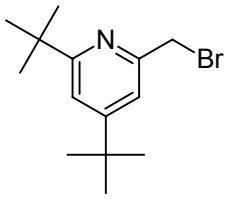
sulfate and concentrated on a rotary evaporator to give **L**[1] (0.82 g, 95%) as a pale brown oil (Found: C, 75.41; H, 10.82; N, 8.49. $C_{21}H_{36}N_2O$ requires C, 75.85; H, 10.91; N, 8.42); ν_{max}(KBr disc)/cm^{-1} 3296 (N-H stretch), 2957-2864 (C-H stretch), 1652 (C=O stretch); δ_H (250 MHz; $CDCl_3$) 0.78 (m, 3H, C*H*$_3$CH$_2$), 1.15 (m, 6H, CH$_3$C*H*$_2$C*H*$_2$C*H*$_2$), 1.33 (s, 9H, ^{t}Bu), 1.59 (s, 9H, ^{t}Bu), 1.76 (m, 2H, NCH$_2$C*H*$_2$), 3.15 (q, 2H, NCH$_2$), 4.40 (s, 2H, CH$_2$CO), 7.45 (s, 1H, 5-H), 7.69 (s, 1H, 3-H), 8.82 (t, 1H, NH); δ_C (63 MHz, $CDCl_3$) 14.6, 23.1, 27.3, 30.1, 31.3, 32.1, 33.5, 35.2, 38.2, 40.1, 45.5, 114.6, 118.8, 154.8, 162.0, 168.9, 170.2; *m/z* (ES) 333 (M+H$^+$).



L[1]

2-(Bromomethyl)-4,6-di-*tert*-butylpyridine 3

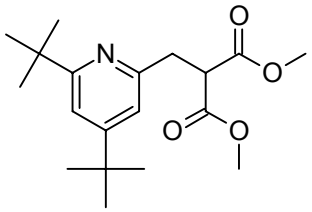
To a solution of **L**[4] (6.1 g, 30.0 mmol) in chloroform (150 ml) was added 1,1'-azobis(cyclohexanecarbonitrile) (0.37 g, 1.5 mmol) followed by *N*-bromosuccinimide (6.78 g, 39.0 mmol) and the mixture was irradiated with a 500 W visible light source in a round bottomed flask (250 ml). The heat from the lamp was sufficient to bring the reaction to reflux. After 7 h the lamp was turned off and the sample was concentrated on a rotary evaporator and then dissolved in hexane. The solid was filtered off, the filtrate was concentrated on a rotary evaporator and then purified by column chromatography on silica gel using 1 % diethyl ether in hexane as eluent to give 2-(bromomethyl)-4,6-di-*tert*-butylpyridine **3** (4.5 g, 53%) as a colourless oil. δ_H (250 MHz; $CDCl_3$) 1.22 (s, 9H, ^{t}Bu), 1.28 (s, 9H, $_t$Bu), 4.45 (s, 2H, CH$_2$), 7.13 (s, 2H, CH); δ_C (63 MHz; $CDCl_3$) 30.4, 32.2, 35.6, 36.4, 37.9, 115.8, 117.7, 155.9, 162.2, 168.6.



3

Dimethyl [(4,6-di-*tert*-butylpyridin-2-yl)methyl]malonate 4

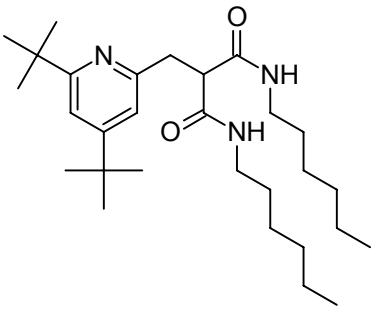
To a suspension of 60% sodium hydride in paraffin oil (1.3 g, 32.2 mmol) in THF (100 ml), dimethyl malonate (4.59 g, 40.2 mmol) was added causing evolution of $H_{2(g)}$. Once the reaction had subsided, 2-(bromomethyl)-4,6-di-*tert*-butylpyridine (7.6 g, 26.8 mmol) in THF (30 ml) was added and the mixture was refluxed for 30 min. The reaction mixture was allowed to cool to room temperature and was then concentrated on a rotary evaporator. The residue was suspended in hexane (200 ml) which was then extracted with water (50 ml). The aqueous phase was re-extracted with DCM (100 ml) and the combined organic layers were dried over magnesium sulfate and concentrated on a rotary evaporator. The residue was purified by column chromatography using 10% diethyl ether in hexane as eluent to give dimethyl [(4,6-di-*tert*-butylpyridin-2-yl)methyl]malonate **4** (6.9 g, 77% yield) as a pale yellow oil. δ_H (250 MHz; $CDCl_3$) 1.43 (s, 9H, ^{t}Bu), 1.46 (s, 9H, ^{t}Bu), 3.60 (d, 2H, CH_2), 3.91 (s, 6H, CH_3O), 4.42 (t, 1H, CHCO), 7.11 (s, 1H, 5-H), 7.26 (s, 1H, 3-H); δ_C (63 MHz; $CDCl_3$) 30.6, 32.0, 35.1, 32.5, 33.8, 51.4, 53.6, 114.1, 117.5, 156.0, 160.8, 167.6, 172.8.



4

2-[(4,6-Di-*tert*-butylpyridin-2-yl)methyl]-*N*,*N*'-dihexylmalonamide L^3

Dimethyl [(4,6-di-*tert*-butylpyridin-2-yl)methyl]malonate (2.6 g, 7.8 mmol) was heated to 80^{o}C in *n*-hexylamine (5.5 g, 54.0 mmol) for 48 h. The solution was purified by column chromatography on silica gel using 20% ethyl acetate in hexane as eluent to give $\mathbf{L}^3$ (2.9 g, 80%) as a brown solid. δ_H (250 MHz; $CDCl_3$) 0.75 (t, 6H, C*H*$_3$CH$_2$), 1.16 (m, 12H, $CH_3CH_2CH_2CH_2$), 1.15 (s, 9H, ^{t}Bu), 1.26 (s, 9H, ^{t}Bu), 1.35 (m, 4H, $CH_3CH_2CH_2$) 3.10 (q, 4H, NCH_2), 3.27 (d, 2H, C*H*$_2$CH), 3.75 (t, 1H, CH$_2$C*H*), 6.89 (s, 1H, 5-H), 7.09 (s, 1H, 3-H) 7.39 (t, 2H, NH); δ_C (63 MHz; $CDCl_3$) 30.6, 32.0, 35.1, 32.5, 33.8, 51.4, 53.6, 114.1, 117.5, 156.0, 160.8, 167.6, 172.8.



L^3

Complex Synthesis

$(L^2H)_2MCl_4$ (M=Co or Zn)

An aqueous HCl (9 M) solution (10 ml) containing MCl_2 ($CoCl_2$: 0.2 g, 1.54 mmol; $ZnCl_2$: 0.2 g, 1.47mmol) was stirred with a toluene solution (10 ml) containing L^2 (0.7 g, 1.54 mmol) in a 100 ml Schotte flask. After 3 h the phases were separated and the toluene phase was evaporated under vacuum leaving an oily residue, which was dissolved in a 50:50 diethyl ether-hexane mix (10 ml) from which blue crystals formed during slow evaporation at 4 ^{0}C over the course of 4 days.

$(HL^2)_2CoCl_4$: (Found: C, 59.75; H, 8.86; N, 7.31. $C_{56}H_{100}Cl_4CoN_6O_4$ requires: C, 59.94; H, 8.98; N, 7.49.)

$(HL^2)_2ZnCl_4$: (Found C, 59.75; H. 8.93; N, 7.44. $C_{56}H_{100}Cl_4ZnN_6O_4$ requires: C, 59.59; H, 8.93; N, 7.45 δ_H (250 MHz; $CDCl_3$) 0.75 (m, 6H, CH_3CH$_2$), 1.20 (m, 12H, CH$_3$CH_2CH_2CH_2), 1.32 (s, 9H, ^{t}Bu), 1.49 (s, 9H, ^{t}Bu), 1.52 (m, 4H, NCH$_2$CH_2), 3.10 (m, 2H, NCH$_2$), 3.26 (m, 2H, NCH$_2$), 5.82 (s, 1H, CHCO), 7.46 (s, 1H, 5-H), 8.26 (t, 2H, NH 7.40), 8.51 (s, 1H, 3-H),

General Experimental Procedure for Extractions

Analytical grade toluene from a commercial source was used to prepare ligand solutions without further purification. Water used to prepare metal chloride solutions was purified using a commercial filtration. MCl_2 (M=Co or Zn) powders were purchased from Aldrich. Calibration curves for ICP-OES were prepared by dilution of commercially available standards. Solutions of ligand were prepared at varying concentrations between 0.0005 - 0.05 M by weighing aliquots of 0.05 M ligand stock solution in toluene into 5 ml volumetric flasks and diluting to the mark with toluene. Metal chloride solutions were prepared by weighing MCl_2 powder ($CoCl_2$: 0.33 g, 2.5

mmol; $ZnCl_2$: 0.34 g, 2.5 mmol into a 250 ml volumetric flask and diluting to the mark with an acidic chloride solution (one part 6 M LiCl to five parts 6 M HCl). Extractions were prepared by charging 100 cm3 Schott flasks fitted with a magnetic stir bar with 5ml of the ligand solution and 5 ml of metal chloride solution. The extractions were stirred at 25ºC for 4 h, after which the phases were separated. Aqueous samples for ICP-OES analysis were prepared by weighing 2 ml of the aqueous phase into 5 ml volumetric flasks diluted to the mark with the acidic chloride diluent.

Crystal structure of $[CoCl_4]\cdot 2L$

A crystalline sample was obtained which was suitable for X-ray diffraction. The crystals produced were blue blocks and one measuring 0.33 x 0.26 x 0.21 mm was selected and diffraction data were collected on a 3 circle Bruker Smart Apex CCD diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) equipped with an Oxford Cryosystems low temperature device operating at 150 K. The crystal was indexed using the Bruker Smart software[1] and found to be *I*-centred tetragonal with $a = b = 19.5947(3)$, $c = 33.4454(11)$ Å. From initial indexing a data collection strategy was refined which aimed to collect fully complete data to a resolution of 53° in 2θ in as short a time as possible. In total 31199 reflections were collected and from these the space group was determined to be $I4_1/a$. Absorption correction was performed using a multi-scan method by applying the SADABS[2] program to the data. The data were merged according to the crystal system in SHELX[3] which gave 5662 unique reflections with a merging R-factor of 0.0972. The initial solution was determined by direct methods with the SHELXS[3] program. All heavy atoms were refined anisotropically and hydrogen atoms were placed geometrically and allowed to ride on their host atom. Some static disorder was encountered in one of the alkyl chains which was refined as two components with the main component assigned a 0.6 site occupancy factor occupancy and the secondary component, 0.4. Full matrix least squares refinement was carried out against F^2 producing a final conventional R-Factor of 0.0493 based on 3794 reflections.

Crystal Structure of $[ZnCl_4]\cdot 2L$

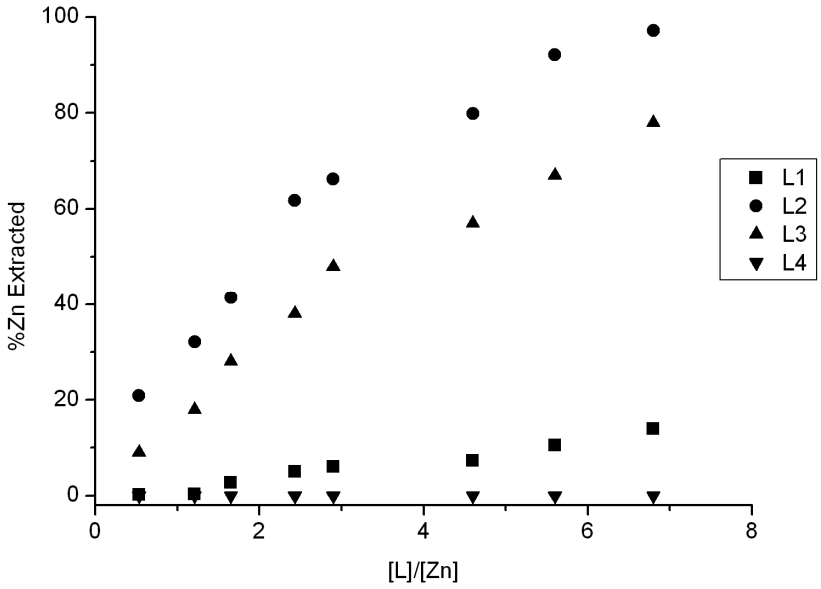
A crystalline sample was obtained which was suitable for X-ray diffraction. The crystals produced were colourless wedges and one measuring 0.58 x 0.39 x 0.13 mm

was selected and diffraction data were collected on a 3 circle Bruker Smart Apex CCD diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) and equipped with an Oxford Cryosystems low temperature device operating at 150 K. The crystal was indexed using the Bruker Smart software[1] and found to be *I*-centred tetragonal with $a = b = 19.6101(4)$, $c = 33.3823(15)$ Å. From initial indexing a data collection strategy was refined which aimed to collect fully complete data to a resolution of 53° in 2θ in as short a time as possible. In total 62514 reflections were collected and from these the space group was determined to be $I4_1/a$. Absorption correction was performed using a multi-scan method by applying the SADABS[2] program to the data. The data were merged according to the crystal system in SHELX[3] which gave 5642 unique reflections with a merging R-factor of 0.0687. The initial solution was determined by direct methods with the SHELXS[3] program. All heavy atoms were refined anisotropically and most hydrogen atoms were placed geometrically and allowed to ride on their host atom. Hydrogen atoms on oxygen and nitrogen atoms were found in a Fourier difference map and their positions refined with a restraint on their distance from their host. Full matrix least squares refinement was carried out against F^2 producing a final conventional R-Factor of 0.0874 based on 5226 reflections. The Sheldrick weighting scheme refined to co-efficients of 0.075200 and 92.070396. The large second parameter is an indication that the experiment sigmas require significant modification due weak diffuse data which is a consequence of disorder in the model.

1 Bruker-Nonius, Bruker-AXS, Madison, Wisconsin, USA, Editon edn., 2002.

2 G. M. Sheldrick, Bruker-AXS, Madison, Wisconsin, USA, Editon edn., 2004.

3 G. M. Sheldrick, University of Gottingen, Germany and Bruker-AXS, Gottingen,


100
80
60
40
20
0
%Zn Extracted
0
2
4
6
8
[L]/[Zn]
L1
L2
L3
L4