

Synthesis of new chiral and nonchiral N₂O₂ and N₂S₂ tetradentate ligands and their metal complexes

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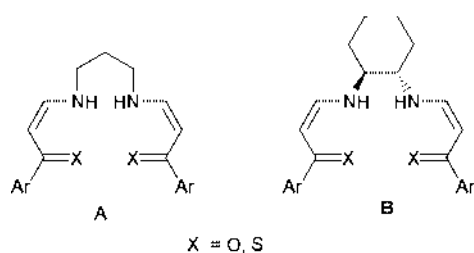
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N,N'-Bis(3-aryl-3-oxoprop-1-enyl)diamines and *N,N'*-bis(3-aryl-3-thioxoprop-1-enyl)diamines are synthesised by condensation of chiral or nonchiral diamines on the corresponding functionalised ketoenolate **2** or dithiolylium salt **4**. Complexation of the obtained N₂O₂ and N₂S₂ ligands with transition metals is investigated.

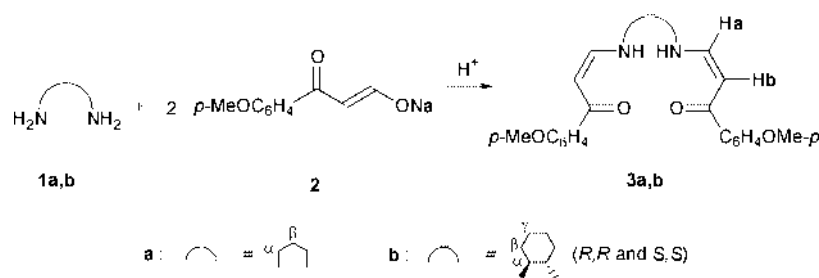
Introduction

Over the past few years, N₂S₂ and N₂O₂ ligands have been extensively investigated with regard to their numerous applications in organic synthesis as well as in medicine. Indeed, such ligands are of interest not only in the field of optical sensors¹ and liquid crystals,² but also as transition-metal-chelating agents for applications in nuclear medicine^{3–8} and asymmetric catalysis.^{9,10}

Several different N₂S₂ and N₂O₂ ligands have already been synthesised and used as chelating agents.^{11–15} In connection with our ongoing project aiming at the design of new ligands by combination of reactions well known in our laboratory and high throughput evaluation, we became interested in the synthesis of new tetradentate ligands of types **A** and **B**.



In both cases, oxo- and thioxo-analogues have been studied.^{16–19} Model **A** was first considered, to allow us to tune the synthetic pathway, and model **B** to elaborate chiral ligands using the same strategy. Complexation of this type of ligand with classical transition metals (Ni, Cu, Mn and Zn) was also investigated in this work before attempting experiments using other metals such as Ru, Rh, or Ir for applications in asymmetric catalysis. Ligands derived from ethylenediamine were also synthesised. However, due to solubility problems, complexation with transition metals was not tested.



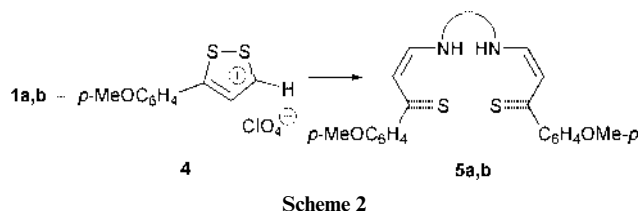
Scheme 1

Results and discussion

The synthetic strategy used to synthesise *N,N'*-bis[2-(*p*-methoxybenzoyl)vinyl]diamines (**A** and **B** with X = O) was based on Benary's method.²⁰ This method consisted of the addition of a diamine **1** to the β -ketoenolate **2** under acidic conditions with EtOH as solvent (Scheme 1).

For cyclohexyl derivatives, diastereoisomerically pure cyclohexanediammonium tartrate²¹ was used as a cheap source of chiral cyclohexanediamine. Following this procedure, compounds **3a** and **3b** (*R,R* and *S,S* forms) were readily isolated after chromatography and crystallisation with yields in the 55–70% range. The *Z* configuration of the double bonds was confirmed by ¹H NMR analysis, with a coupling constant of 7.5 Hz between H_a and H_b for **3a** and **3b**.

In many cases, thioxo ligands were obtained by thionation of the oxo-analogues.^{22,23} To avoid this delicate step, it was better to synthesise these compounds using the slightly modified method described by Quiniou and Quintard and co-workers²⁵ by reaction between a dithiolylium perchlorate²⁶ with a diamine **1a,b** (Scheme 2) rather than by using thionating agents.



As for **3b**, optically pure cyclohexanediammonium tartrate was used as a chiral source of cyclohexanediamine. In this case, the tartrate was first neutralised by addition of potassium hydroxide before addition of the dithiolylium salt **4**. Compounds **5a** and **5b** were then obtained in satisfactory yields after

Table 1 Complexation of N₂O₂ and N₂S₂ ligands with transition metals

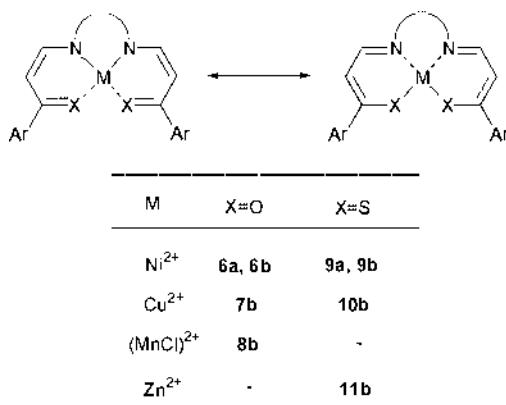
Entry	Ligand	Metal	Yield (%)	Compound
1	3a	Ni ²⁺	61	6a
2	5a	Ni ²⁺	92	9a
3	(<i>S,S</i>)- 3b	Ni ²⁺	95	(<i>S,S</i>)- 6b
4	(<i>R,R</i>)- 3b	Ni ²⁺	89	(<i>R,R</i>)- 6b
5	(<i>R,R</i>)- 3b	Cu ²⁺	88	(<i>R,R</i>)- 7b
6	(<i>R,R</i>)- 3b	Mn ³⁺	74	(<i>R,R</i>)- 8b
7	(<i>S,S</i>)- 5b	Ni ²⁺	78	(<i>S,S</i>)- 9b
8	(<i>R,R</i>)- 5b	Ni ²⁺	86	(<i>R,R</i>)- 9b
9	(<i>R,R</i>)- 5b	Cu ²⁺	84	(<i>R,R</i>)- 10b
10	(<i>R,R</i>)- 5b	Zn ²⁺	88	(<i>R,R</i>)- 11b

purification by chromatography followed by crystallisation from EtOH. Optical purities of **3b** and **5b** (*RR* and *SS*) were confirmed by measuring their optical rotations.

Since these efficient methods for the synthesis of such ligands may be adapted to other amines, we were interested in the affinity of the obtained ligands **3** and **5** with various metals. The diamagnetic character of Ni(II) chelates encouraged us to start with Ni²⁺ as metal to facilitate structural studies by ¹H and ¹³C NMR. The corresponding chelates were obtained by reaction of nickel acetate with a given ligand. After stirring at room temperature for 24 hours, all complexes were isolated by filtration in good to excellent yields. The Ni(II) chelate compounds prepared in this investigation are summarised in Table 1.

As mentioned above, complexations with **3a** and **5a** were first performed (entries 1 and 2). Afterwards, chiral ligands **3b** and **5b** were used in both enantiomeric forms (entries 3, 4, 7, 8). After checking that the chelation did not depend on the enantiomeric form of the ligand, other metals (Cu, Zn and Mn) were investigated following the same experimental procedure with **3b** and **5b** with only the (*R,R*) form (entries 5, 6, 9, 10). The obtained Schiff bases were all characterised by ¹H and ¹³C NMR, IR, elemental analysis and mass spectroscopy except for those presenting broad peaks in the NMR spectrum due to their paramagnetic configuration (Cu, Mn). In the case of **8b**, the Mn : Cl ratio measured by energy-dispersive X-ray spectroscopy (EDXS) was in good agreement with the expected value, confirming that one chlorine atom was engaged in the complex.

Nevertheless, for both oxo and thioxo complexes, the two mesomeric forms, enamino ketone/enolimine and enamino thioketone/enethiolimine, respectively, can be considered (Scheme 3). ¹³C NMR analysis has shown differences in

**Scheme 3**

chemical shifts for CH_α (or CH_{2α}) and C–X between free ligands and chelated ones. These differences are more pronounced for thioxo-analogues. Indeed, for **9b** and **11b**, the chemical shift for C=S changed from δ 206.6 for **5b** to δ 163.2 and δ 169.9, respectively. These variations could be attributed to

a decrease in the bond order confirming the preferred imine form for the metal chelate complex. To fully characterise the mesomeric forms, we would like to perform crystal-structure analysis but all of our complexes exist as amorphous powders.

In summary, we have developed an easy access to chiral and nonchiral N₂O₂ and N₂S₂ tetradentate ligands. In order to study their potential activity in asymmetric catalysis, complexations with different metals have been performed. Depending on the nature of the metal, these ligands could be used also in nuclear medicine.

Experimental

All reagents were purchased from Acros Organics and Aldrich and all solvents were freshly distilled before use. The C.N.R.S. Analysis Laboratory (Vernaison) performed the elemental analyses. Column chromatography was conducted on silica gel 60 (40–63 μm), available from E. Merck. TLC was performed on 0.5 mm × 20 cm × 20 cm E. Merck silica gel plates (60 F-254). Melting points measured using a Reichert microscope were uncorrected. The ¹³C and ¹H NMR spectra were recorded at room temperature using a Bruker AC200 at 50 and 200 MHz, respectively. Chemical shifts (δ) are given in ppm downfield from tetramethylsilane as internal standard. Mass spectra were determined with a Hewlett-Packard 5989 spectrometer. TLC FAB-MS were obtained on a JEOL SX 102 (*m*-nitrobenzyl alcohol matrix). Energy-dispersive X-ray spectroscopy (EDXS) measurements were carried out using a JEOL JM-35C SEM with a Tracor TN5500 micro Z attachment. Optical rotations were determined using a Perkin-Elmer 341 polarimeter and concentrations are expressed in grams/100 mL. [α]_D-Values are given in units of 10⁻¹ deg cm² g⁻¹. IR spectra were obtained using a Bruker Vector22 spectrometer. All chemicals were reagent grade and used without further purification.

N,N'-Bis[2-(*p*-methoxybenzoyl)vinyl]propane-1,3-diamine **3a**

Conc. HCl (0.5 mL) was added dropwise to a mixture of propane-1,3-diamine (0.185 g, 2.5 mmol) and sodium 2-(*p*-methoxybenzoyl)ethenolate (1 g, 5 mmol) in EtOH (10 mL) at room temperature. After 30 min the mixture was stirred and refluxed for 30 min. After cooling, the solution was poured into brine and extracted with EtOAc. The combined organic layers were concentrated *in vacuo* to give a residual syrup, which was chromatographed on silica gel column using a mixture of EtOAc and CH₂Cl₂ (1 : 1) as eluent. Crystallisation from Et₂O furnished compound **3a** as a light yellow solid (70%); mp 140 °C (Found: C, 70.33; H, 6.62; N, 7.16. C₂₃H₂₆N₂O₄ requires C, 70.03; H, 6.64; N, 7.10%); ¹H NMR (CD₃COCD₃) δ 1.90 (qt, *J* 6.5 Hz, 2H, CH₂β), 3.42 (dd, *J* 6.4, 6.6 Hz, 4H, 2 × CH₂α), 3.83 (s, 6H, 2 × OCH₃), 5.71 (d, *J* 7.5 Hz, 2H, 2 × CH^b), 6.94 and 7.86 (d, *J* 8.9 Hz, 8 × ArH), 7.09 (dd, *J* 7.5, 12.7 Hz, 2H, 2 × CH^a), 10.29 (br s, 2H, 2 × NH); ¹³C (CDCl₃) δ 31.85 (CH₂β), 45.56 (2 × CH₂α), 55.17 (2 × OCH₃), 90.10 (2 × CH^b), 113.34 and 128.81 (8 × CH^{ar}), 132.19 (2 × C^{ar}CO), 153.54 (2 × CH^a), 161.87 (2 × C^{ar}OCH₃), 180.16 (2 × CO); MS (EI): *m/z* (%) 394 (M⁺, 14), 259 (22), 244 (15), 217 (16), 204 (20), 190 (66), 135 (100), 82 (14), 77 (15); IR/cm⁻¹ (KBr) 2840, 1641, 1537, 1442, 1368, 1307, 1240, 1176, 1023.

N,N'-Bis[2-(*p*-methoxybenzoyl)vinyl]cyclohexane-1,2-diamine **3b**; general procedure

Diastereoisomerically pure *trans*-cyclohexane-1,2-diammonium tartrate (*RR*, + or *SS*, -) (0.660 g, 2.5 mmol) was added to a solution of sodium 2-(*p*-methoxybenzoyl)ethenolate **2** (1 g, 5 mmol) in EtOH (10 mL). The mixture was stirred for 30 min at rt followed by 30 min at reflux. After cooling, the solution was poured into brine and extracted with EtOAc. The combined organic layers were concentrated *in vacuo* to give a residual syrup, which was chromatographed on a silica gel

column using a mixture of EtOAc and CH₂Cl₂ (1 : 1) as eluent. Crystallisation from Et₂O furnished compound **3b** as a yellow solid; mp 140 °C; ¹H NMR (CDCl₃) δ 1.40 (m, 4H, 2 × CH₂^γ), 1.87 and 2.17 (2 br s, 4H, 2 × CH₂^β), 2.87 (br s, 2H, 2 × CH_α), 3.86 (s, 6H, 2 × OCH₃), 5.60 (d, *J* 7.5 Hz, 2H, 2 × CH^b), 6.84 (dd, *J* 7.5, 12.4 Hz, 2H, 2 × CH^a), 6.92 and 7.84 (d, *J* 8.9 Hz, 8 × ArH), 10.22 (br s, 2H, 2 × NH); ¹³C (CDCl₃) δ 24.49 (2 × CH₂^γ), 32.51 (2 × CH₂^β), 55.19 (2 × OCH₃), 64.33 (2 × CH_α), 89.97 (2 × CH^b), 113.33 and 128.86 (8 × CH^{ar}), 132.23 (2 × C^{ar}CO), 153.13 (2 × CH^a), 161.87 (2 × C^{ar}OCH₃), 189.13 (2 × CO); MS (EI) *m/z* (%) 434 (M⁺, 17), 299 (24), 257 (100), 176 (14), 135 (79), 122 (51), 96 (13), 77 (13); IR/cm⁻¹ (KBr) 2934, 1635, 1633, 1482, 1251, 1236, 1161, 1025.

(*R,R*)-*N,N'*-Bis[2-(*p*-methoxybenzoyl)vinyl]cyclohexane-1,2-diamine (*R,R*)-3b**.** Yield 55%, [α]_D²⁰ -1750 (*c* 1.996, CHCl₃) (Found: C, 72.08; H, 6.91; N, 6.45. C₂₆H₃₀N₂O₄ requires C, 71.87; H, 6.96; N, 6.45%).

(*S,S*)-*N,N'*-Bis[2-(*p*-methoxybenzoyl)vinyl]cyclohexane-1,2-diamine (*S,S*)-3b**.** Yield 58%, [α]_D²⁰ +1792 (*c* 1.096, CHCl₃) (Found: C, 71.99; H, 6.91; N, 6.48. C₂₆H₃₀N₂O₄ requires C, 71.87; H, 6.96; N, 6.45%).

N,N'-Bis[2-(*p*-methoxythiobenzoyl)vinyl]propane-1,3-diamine **5a**

Propane-1,3-diamine (0.244 g, 3.3 mmol) as a solution in EtOH (15 mL) was added dropwise at rt to a stirred suspension of the dithioliylum perchlorate **4** (1 g, 3.3 mmol) in a water–ethanol mixture (1 : 1; 25 mL). After 20 h of stirring, the mixture was evaporated and the residue was purified by silica gel flash column chromatography using CH₂Cl₂ as eluent. Crystallisation from EtOH gave **5a** as a red solid (67%); mp 180 °C (Found: C, 64.54; H, 6.13; N, 6.76; S, 14.91. C₂₃H₂₆N₂O₂S₂ requires C, 64.76; H, 6.14; N, 6.57; S, 15.03%); ¹H NMR (CDCl₃) δ 2.06 (qt, *J* 6.6 Hz, 2H, CH₂^β), 3.59 (dd, *J* 6.4, 6.2 Hz, 4H, 2 × CH₂^α), 3.83 (s, 6H, 2 × OCH₃), 6.51 (d, *J* 7.5 Hz, 2H, 2 CH^b), 6.86 and 7.79 (d, *J* 8.8 Hz, 8 × ArH), 7.38 (dd, *J* 7.5, 13.0 Hz, 2H, 2 × CH^a), 12.83 (br s, 2H, 2 × NH); ¹³C (CDCl₃) δ 30.89 (CH₂^β), 40.16 (2 × CH₂^α), 55.41 (2 × OCH₃), 107.99 (2 × CH^b), 113.27 and 128.64 (8 × CH^{ar}), 143.6 (2 × C^{ar}CS), 155.44 (2 × CH^a), 161.47 (2 × C^{ar}OCH₃), 206.98 (2 × CS); MS (EI) *m/z* (%) 250 (25), 227 (9), 220 (44), 166 (59), 151 (100), 133 (55), 108 (19), 84 (29), 77 (15), 30 (29); IR/cm⁻¹ (KBr) 2834, 1624, 1597, 1491, 1298, 1239, 1110, 1030.

N,N'-Bis[2-(*p*-methoxythiobenzoyl)vinyl]cyclohexane-1,2-diamine **5b**; general procedure

A mixture of diastereoisomerically pure *trans*-cyclohexane-1,2-diammonium tartrate (*RR*, + or *SS*, -) (0.871 g, 3.6 mmol), potassium hydroxide (0.384 g, 3.3 mmol) and water (10 mL) was stirred for 1 h at rt. To this solution was added a solution of the dithioliylum perchlorate **4** (0.925 g, 3 mmol) in EtOH (30 mL) and the resulting mixture was stirred for 24 h at room temperature. The solution was extracted with CH₂Cl₂ and evaporated under reduced pressure. The residue was purified by silica gel chromatography (CH₂Cl₂) and crystallised from EtOH to give compound **5b** as a red solid; mp 176 °C; ¹H NMR (CDCl₃) δ 1.53 (m, 4H, 2 × CH₂^γ), 1.92 and 2.27 (2 br s, 4H, 2 × CH₂^β), 3.13 (m, 2H, 2 × CH_α), 3.82 (s, 6H, 2 × OCH₃), 6.37 (d, *J* 7.5 Hz, 2H, 2 × CH^b), 6.81 and 7.74 (d, *J* 9.0 Hz, 8 × ArH), 7.25 (dd, *J* 7.5, 13.0 Hz, 2H, 2 × CH^a), 10.39 (br s, 2H, 2 × NH); ¹³C (CDCl₃) δ 24.18 (2 × CH₂^γ), 32.02 (2 × CH₂^β), 55.39 (2 × OCH₃), 64.96 (2 × CH_α), 107.83 (2 × CH^b), 113.19 and 128.71 (8 × CH^{ar}), 140.23 (2 × C^{ar}CS), 154.50 (2 × CH^a), 161.44 (2 × C^{ar}OCH₃), 206.58 (2 × CS); FAB-MS, *m/z* (%) 933 (2M⁺ + H), 467 (M + H, 100), 433, 309, 274, 240, 192, 151, 81; IR/cm⁻¹ (KBr) 2937, 1612, 1597, 1509, 1331, 1247, 1239, 1172, 1123.

(*R,R*)-*N,N'*-Bis[2-(*p*-methoxythiobenzoyl)vinyl]cyclohexane-1,2-diamine (*R,R*)-5b**.** Yield 90%, [α]_D²⁰ -3677 (*c* 0.456, CHCl₃) (Found: C, 66.85; H, 6.49; N, 5.98; S, 13.51. C₂₆H₃₀N₂O₂S₂ requires C, 66.92; H, 6.48; N, 6.00; S, 13.74%).

(*S,S*)-*N,N'*-Bis[2-(*p*-methoxythiobenzoyl)vinyl]cyclohexane-1,2-diamine (*S,S*)-5b**.** Yield 93%, [α]_D²⁰ +3698 (*c* 0.524, CHCl₃) (Found: C, 66.89; H, 6.51; N, 5.96; S, 13.63. C₂₆H₃₀N₂O₂S₂ requires C, 66.92; H, 6.48; N, 6.00; S, 13.74%).

Metallation: general procedure

A 50 mL round-bottom flask equipped with a magnetic stirrer was charged with a solution of ligand (0.4 mmol) in chloroform (3 mL). To this solution was added dropwise a solution of a metallic acetate (0.6 mmol) in MeOH (10 mL) and the resulting mixture was stirred for 24 h at room temperature. The resulting solid was filtered off and washed with MeOH.

***N,N'*-Bis[2-(*p*-methoxybenzoyl)vinyl]propane-1,3-diamine-nickel(II) **6a**.** Yield 61%, green solid, mp 131 °C (Found: C, 61.37; H, 5.31; N, 6.22. C₂₃H₂₄N₂NiO₄ requires C, 61.23; H, 5.36; N, 6.21%); ¹H NMR (CDCl₃) δ 1.75 (qt, *J* 5.8 Hz, 2H, CH₂^β), 3.08 (t, *J* 5.8 Hz, 4H, 2 × CH₂^α), 3.82 (s, 6H, 2 × OCH₃), 5.55 (d, *J* 5.9 Hz, 2H, 2 × CH^b), 6.57 (d, *J* 5.9, 2H, 2 × CH^a), 6.84 and 7.73 (d, *J* 8.5 Hz, 8 × ArH); ¹³C (CDCl₃) δ 28.27 (CH₂^β), 55.28 (2 × OCH₃), 55.82 (2 × CH₂^α), 91.73 (2 × CH^b), 113.32 and 128.10 (8 × CH^{ar}), 128.97 (2 × C^{ar}CO), 159.41 (2 × CH^a), 161.03 (2 × C^{ar}OCH₃), 171.11 (2 × CO); FAB-MS, *m/z* (%) 901 (2M⁺ + H), 451 (100, M + 1), 395, 343, 247, 135; IR/cm⁻¹ (KBr) 1592, 1571, 1529, 1496, 1438, 1397, 1271, 1260, 1178, 1025, 841.

(*R,R*)-*N,N'*-Bis[2-(*p*-methoxybenzoyl)vinyl]cyclohexane-1,2-diaminenickel(II) (*R,R*)-6b**.** Yield 89%, brown solid, mp >300 °C (Found: C, 63.79; H, 5.75; N, 5.89. C₂₆H₂₈N₂NiO₄ requires C, 63.57; H, 5.75; N, 5.70%); ¹H NMR (CDCl₃) δ 1.22 (m, 4H, 2 × CH₂^γ), 1.79 and 2.26 (2 br s, 4H, 2 × CH₂^β), 2.89 (br s, 2H, CH_α), 3.82 (s, 6H, 2 × OCH₃), 5.65 (d, *J* 5.9 Hz, 2H, 2 × CH^b), 6.77 (d, *J* 5.9, 2H, 2 × CH^a), 6.85 and 7.76 (d, *J* 8.9 Hz, 8 × ArH); ¹³C (CDCl₃) δ 24.77 (2 × CH₂^γ), 28.70 (2 × CH₂^β), 55.29 (2 × OCH₃), 70.22 (2 × CH_α), 91.69 (2 × CH^b), 113.34 and 128.20 (8 × CH^{ar}), 130.20 (2 × C^{ar}CO), 151.46 (2 × CH^a), 161.33 (2 × C^{ar}OCH₃), 172.41 (2 × CO); FAB-MS *m/z* (%) 981 (2M⁺ + H), 490 (100, M⁺), 460, 383, 307, 235, 176, 136, 77; IR/cm⁻¹ (KBr) 2932, 1604, 1529, 1496, 1491, 1484, 1255, 1178, 1041.

(*S,S*)-*N,N'*-Bis[2-(*p*-methoxybenzoyl)vinyl]cyclohexane-1,2-diaminenickel(II) *S,S*-6b**.** Yield 95%, brown solid, mp >300 °C (Found: C, 63.69; H, 5.56; N, 5.74. C₂₆H₂₈N₂NiO₄ requires C, 63.57; H, 5.75; N, 5.70%).

(*R,R*)-*N,N'*-Bis[2-(*p*-methoxybenzoyl)vinyl]cyclohexane-1,2-diaminecopper(II) *R,R*-7b**.** Yield 88%, grey solid, mp 245–250 °C (Found: C, 63.04; H, 5.63; N, 5.71. C₂₆H₂₈CuN₂O₄ requires C, 62.95; H, 5.69; N, 5.65%); FAB-MS *m/z* (%) 495 (100, M⁺), 318, 288, 188, 170, 147, 108, 92, 63; IR/cm⁻¹ (KBr) 2938, 1604, 1575, 1520, 1494, 1460, 1251, 1183.

***N,N'*-Bis[2-(*p*-methoxythiobenzoyl)vinyl]propane-1,3-diaminenickel(II) **9a**.** Yield 92%, brown solid, mp 195 °C (Found: C, 57.21; H, 4.98; N, 5.81; S, 13.08. C₂₃H₂₄N₂NiO₂S₂ requires C, 57.16; H, 5.01; N, 5.80; S, 13.27%); ¹H NMR (CDCl₃) δ 1.93 (qt, *J* 6.8 Hz, 2H, CH₂^β), 3.74 (t, *J* 6.8 Hz, 4H, 2 × CH₂^α), 3.80 (s, 6H, 2 × OCH₃), 6.33 (d, *J* 5.6 Hz, 2H, 2 × CH^b), 6.84 and 7.67 (d, *J* 8.9 Hz, 8 × ArH), 7.30 (d, *J* 5.6, 2H, 2 × CH^a); ¹³C (CDCl₃) δ 28.36 (CH₂^β), 55.35 (2 × OCH₃), 55.82 (2 × CH₂^α), 112.70 (2 × CH^b), 113.46 and 128.62 (8 × CH^{ar}), 133.81 (2 × C^{ar}CS), 159.87 (2 × CH^a), 160.54 (2 × C^{ar}OCH₃),

162.44 (2 × CS); FAB-MS m/z (%) 483 (M^{+}), 109, 95, 69, 55 (100); IR/cm⁻¹ (KBr) 1592, 1572, 1508, 1458, 1358, 1244, 1174, 1126, 1028, 840.

(*R,R*)-*N,N'*-Bis[2-(*p*-methoxythiobenzoyl)vinyl]cyclohexane-1,2-diaminenickel(II) (*R,R*)-9b. Yield 86%, brown solid, mp 256 °C (Found: C, 59.91; H, 5.46; N, 5.60; S, 11.94. C₂₆H₂₈N₂NiO₂S₂ requires C, 59.67; H, 5.39; N, 5.35; S, 12.25%); ¹H NMR (CDCl₃) δ 1.34 (m, 4H, 2 × CH₂γ), 1.90 and 2.36 (2 br s, 4H, 2 × CH₂β), 3.33 (m, 2H, CHα), 3.81 (s, 6H, 2 × OCH₃), 6.41 (d, *J* 6.2 Hz, 2H, 2 × CH^b), 6.84 and 7.68 (d, *J* 9.0 Hz, 8 × ArH), 7.56 (d, *J* 6.2, 2H, 2 × CH^a); ¹³C (CDCl₃) δ 24.82 (2 × CH₂γ), 30.13 (2 × CH₂β), 55.36 (2 × OCH₃), 71.30 (2 × CHα), 112.52 (2 × CH^b), 113.47 and 128.45 (8 × CH^{ar}), 134.47 (2 × C^{ar}CS), 153.20 (2 × CH^a), 160.48 (2 × C^{ar}OCH₃), 163.17 (2 × CS); FAB-MS m/z (%) 522 (M^{+}), 505, 460, 307, 289, 176, 154 (100), 136, 107, 89, 57; IR/cm⁻¹ (KBr) 2928, 1599, 1496, 1439, 1393, 1249, 1174, 1034.

(*S,S*)-*N,N'*-Bis[2-(*p*-methoxythiobenzoyl)vinyl]cyclohexane-1,2-diaminenickel(II) (*S,S*)-9b. Yield 78%, brown solid, mp 256 °C (Found: C, 59.85; H, 5.42; N, 5.50; S, 12.14. C₂₆H₂₈N₂NiO₂S₂ requires C, 59.67; H, 5.39; N, 5.35; S, 12.25%).

(*R,R*)-*N,N'*-Bis[2-(*p*-methoxythiobenzoyl)vinyl]cyclohexane-1,2-diaminecopper(II) (*R,R*)-10b. Yield 84%, green solid, mp 215–218 °C (Found: C, 59.43; H, 5.36; N, 5.42; S, 11.93. C₂₆H₂₈CuN₂O₂S₂ requires C, 59.12; H, 5.34; N, 5.30; S, 12.14%); FAB-MS m/z (%) 527 (M^{+}), 279, 237, 192, 151 (100); IR/cm⁻¹ (KBr) 2928, 2362, 1597, 1513, 1500, 1286, 1174, 1035.

(*R,R*)-*N,N'*-Bis[2-(*p*-methoxythiobenzoyl)vinyl]cyclohexane-1,2-diaminezinc(II) (*R,R*)-11b. Yield 88%, orange solid, mp >300 °C (Found: C, 59.10; H, 5.45; N, 5.45; S, 11.91. C₂₆H₂₈N₂O₂S₂ requires C, 59.12; H, 5.34; N, 5.29; S, 12.10%); ¹H NMR (CDCl₃) δ 1.08–1.86 (m, 8H, 2 × CH₂γ and 2 × CH₂β), 3.79 (s, 6H, 2 × OCH₃), 3.81 (br s, 2H, 2 × CHα), 6.25 (d, *J* 6.1 Hz, 2H, 2 × CH^b), 6.72 and 7.50 (d, *J* 8.4 Hz, 8 × ArH), 7.74 (d, *J* 6.1, 2H, 2 × CH^a); ¹³C (CDCl₃) δ 24.67 (2 × CH₂γ), 31.61 (2 × CH₂β), 55.33 (2 × OCH₃), 74.17 (2 × CHα), 113.10 and 128.84 (8 × CH^{ar}), 113.23 (2 × CH^b), 160.50 (2 × C^{ar}CS), 160.50 (2 × CH^a), 165.82 (2 × C^{ar}OCH₃), 169.87 (2 × CS); FAB-MS m/z (%) 529 (M^{+}), 353, 307, 289, 226, 192, 176, 155 (100), 107, 91, 69, 55; IR/cm⁻¹ (KBr) 2927, 1601, 1518, 1500, 1462, 1410, 1326, 1250, 1174, 1033.

(*R,R*)-*N,N'*-Bis[2-(*p*-methoxybenzoyl)vinyl]cyclohexane-1,2-diaminemanganese(III) chloride (*R,R*)-8b. A 50 mL round-bottom flask equipped with a magnetic stirrer was charged with ligand (*R,R*)-3b (0.273 g, 0.3 mmol), manganese acetate tetrahydrate (0.147 g, 0.6 mmol) and MeOH (8 mL). The resulting solution was stirred for 12 h at reflux and was then evaporated to dryness. The residue was chromatographed on a silica gel column using a mixture of EtOH and CH₂Cl₂ (5 : 95)

as eluent. The appropriate fraction, dissolved in CH₂Cl₂, was stirred over NaCl for 10 min, filtered, and evaporated to give (*R,R*)-8b. Crystallisation from Et₂O furnished this compound as a brown solid (74%); mp 280 °C (Found: C, 59.47; H, 5.40; N, 5.19. C₂₆H₂₈ClMnN₂O₄ requires C, 59.71; H, 5.36; N, 5.36%); FAB-MS m/z (%) 523, 487, 257, 188, 150, 135 (100), 122, 107, 92, 77; IR/cm⁻¹ (KBr) 2935, 1592, 1571, 1496, 1384, 1280, 1176, 1023. The Mn : Cl ratio measured by EDXS was in good agreement with the expected values.

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