Synthesis, Characterization and Stereochemistry of Condensation Products between (1*R*)-3-Hydroxymethylenebornane-2-thione and Diamines and Their Metal Complexes

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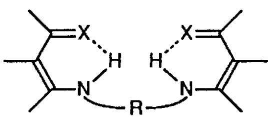
Tetradentate ligands derived from the condensation of (1*R*)-3-hydroxymethylenebornane-2-thione and symmetric diamines were synthesised together with their zinc(II) complexes. As deduced from cumulative spectral evidence, freshly prepared samples of the free ligands consist exclusively of the thioxoenamine tautomer, while binding to zinc(II) occurs through the enethiolate imine form. The circular dichroism (CD) spectrum of the ligand bearing an ethylene bridging chain shows very intense Cotton effects characteristic of exciton-coupled transitions. The pattern of CD bands associated with the thioxoenamine transitions suggests a *gauche* structure for the dominant conformer. The NMR spectra of zinc(II) complexes are indicative of the presence of several species resulting from geometric isomerism at the metal atom and conformational mobility of the flexible part of the ligands in the chelates. Lengthening of the carbon chain in the diamine moiety from two to four carbon atoms favours the adoption of tetrahedral structures at zinc(II) as is evidenced by the CD spectral behaviour of the complexes. The absolute configuration of the dominant structure is assigned on the basis of the CD spectrum.

The chemistry of β-thioxoketones has attracted some interest in view of the problems connected with their intramolecular tautomerism and the comparison with the much richer literature dealing with β-diketones.[1] Fewer studies are available on the imines corresponding to these compounds,[2–4] among which, again, the sulphur-containing derivatives are scarce. Molecules containing dimeric imine units, which can be involved in tautomeric equilibria of type **1** ⇌ **2**, are of special interest because of the stereochemical problems arising when the bridging diamine or β-dicarbonyl residues are chiral and because they may serve as ligands for metal chelates.[5–7] Complexes with chiral tetradentate ligands of this type are, in fact, sterically controlled and may be potentially useful in stereoselective reactions.

In this paper we report the synthesis, characterization and stereochemistry of the series of compounds **5** derived from condensation of (1*R*)-3-hydroxymethylenebornane-2-thione **3** and symmetric diamines **4** and their zinc(II) complexes **6**. Copper(II) complexes corresponding to **6** were reported recently by us.[4]



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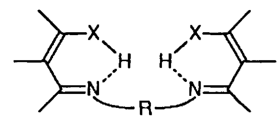

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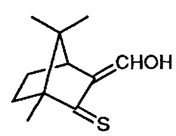

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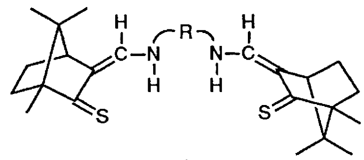
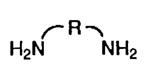


5



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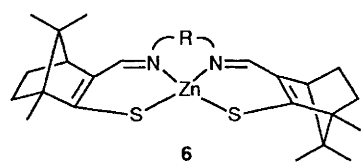
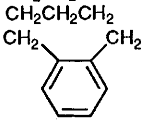


6

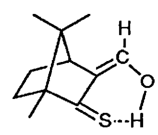
a R = CH_2CH_2
b R = $CH_2CH_2CH_2$
c R =



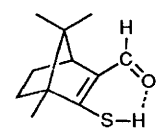
Results and Discussion

As it is known for other β-thioxoketones,[1] (1*R*)-3-hydroxymethylenebornane-2-thione can exist in several tautomeric forms, the most important of which are the intramolecularly hydrogen-bonded *Z*-enol and *Z*-enethiol forms **3a** and **3b**, respectively.

Freshly prepared samples of **3** consist of **3a** as the only component. Its proton NMR spectrum ($CDCl_3$) exhibits a doublet signal at δ 13.20 (J = 12.6 Hz) for the chelate enol proton, coupled with a doublet at δ 7.32 belonging to the vinylic proton, which becomes a broad singlet on exchange with D_2O; in the ^{13}C NMR spectrum the singlet at δ 241.3 (C=S), the



3a



3b

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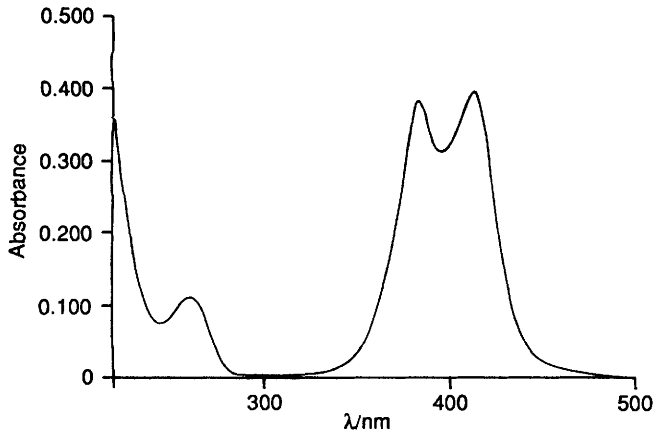


Fig. 1 Electronic spectrum of compound **5a** in methanol solution (1.54×10^{-3} mol dm^{-3}, cell path 0.01 cm)

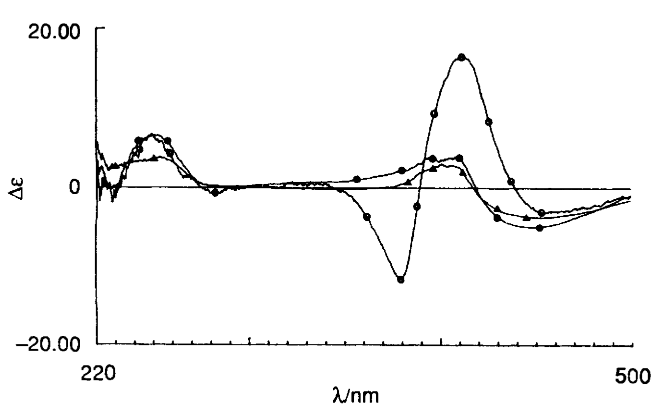


Fig. 2 Circular dichroism spectra of compound **5a** (○), **5b** (●) and **5c** (▲) in methanol solution

doublet at δ 156.0 (C=CH) and the singlet at δ 131.6 (*C*=CH) fully confirm the structure assignment. On standing in methanol solution a very slow conversion of **3a** into **3b** takes place and after about 10 d at room temperature the spectroscopic data reveal the existence of **3b** as the major tautomer. This is characterized by a proton NMR singlet signal at δ 10.07 for the aldehyde proton, while in the ^{13}C NMR spectrum the resonance at δ 241.3 of the thiocarbonyl group is replaced by a singlet at δ 186.0.

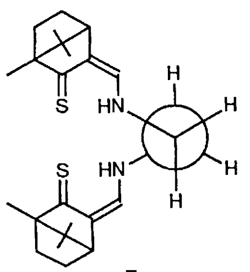
The tautomers **3a** and **3b** are also clearly differentiated by IR, UV and circular dichroism (CD) spectroscopy. Freshly prepared samples exhibit an IR stretching mode at 1610 cm^{-1} and an intense UV absorption at 348 nm (ε = 9000 dm^3 mol^{-1} cm^{-1}) for the conjugated chromophore of the *Z*-enol form, while for aged samples an IR band at 1670 cm^{-1} and an UV absorption at 263 nm for the chelate, unsaturated, aldehyde group of **3b** grow in. The possibility of obtaining a practically complete conversion of **3a** into **3b** confirms the view[8] that the absorption associated with the $\pi \longrightarrow \pi^*$ transition of the *Z*-enol chromophore is approximately twice as intense as that of the corresponding transition of the *Z*-enethiol chromophore. The CD spectrum of **3a** clearly evidences a negative band at 480 nm ($\Delta\varepsilon$ = −1.20 dm^3 mol^{-1} cm^{-1}) that is extremely weak in absorption ($\varepsilon \approx$ 10 dm^3 mol^{-1} cm^{-1}). This is associated with the magnetic dipole allowed transition $n \longrightarrow \pi^*$ of the thione group,[9] since a similar band is exhibited by (1*R*)-thiocamphor {(1*R*)-1,7,7-trimethylbicyclo[2.2.1]heptane-2-thione}.[4] The $\pi \longrightarrow \pi^*$ transition of **3a** displays comparable CD intensity ($\Delta\varepsilon$ = −1.50 dm^3 mol^{-1} cm^{-1}), while positive CD bands occur at higher energy. The tautomeric conversion into **3b** is accompanied by the appearance of a considerably more intense CD activity at 260 nm ($\Delta\varepsilon$ = −6.50 dm^3 mol^{-1} cm^{-1}), associated with the $\pi \longrightarrow \pi^*$ transition of the *Z*-enethiol chromophore, and 320 nm ($\Delta\varepsilon$ = −2.85 dm^3 mol^{-1} cm^{-1}), attributable to the $n \longrightarrow \pi^*$ transition of the aldehydic group.

The ligands **5** were obtained in good yields by treating (1*R*)-3(*Z*)-hydroxymethylenebornane-2-thione **3a** with the appropriate diamine **4** in methanol at 4 °C. As indicated by their spectroscopic characteristics, freshly prepared samples of these compounds consist exclusively of the thioxoenamine tautomer. The common features in the proton NMR spectra of **5**, run in $CDCl_3$ solutions, are a multiplet at low field (δ 11.50–11.80) for the chelate NH proton and a doublet for the enamine CH proton (δ 6.80–7.00) collapsing to a singlet on treatment with D_2O. The large coupling constant (J = 12.5 Hz) between these protons indicates their *trans* arrangement in structure **5**. In the ^{13}C NMR spectra in $CDCl_3$ a singlet signal near δ 227 is typical for the conjugated C=S group,[10] and a doublet near δ 147 is associated with the nitrogen-bonded methyne group.

While the proton NMR spectra of compound **5a** in $CDCl_3$ do not show any appreciable changes on standing at room temperature, the spectra of the same compound in CD_3OD are indicative of a progressive inversion of the stereochemistry of the double bond present in **5a** from a *Z* to an *E* configuration, in agreement with data already reported for the condensation products of (1*R*)-3-formylcamphor with amines.[2] The proton NMR spectrum of **5a** in CD_3OD shows, besides a doublet near δ 6.50, a broad singlet at δ 6.40–6.50 which becomes largely predominant after 4 d at room temperature. Also the ^{13}C NMR spectrum is indicative for the inversion of stereochemistry: the singlet at δ 238.8 for the C=S group and the doublet at δ 154.1 for the nitrogen-bonded methyne group exclude the presence of the tautomeric enethiol form.

The absorption and CD spectra of compounds **5a**–**5c** exhibit surprising differences at first sight. Each shows an intense absorption band in the region of 400 nm but the band is clearly split into two components for compound **5a** containing the ethylenediamine bridge (Fig. 1). The presence of the two components can be deduced in the spectra of **5b** and **5c** from the asymmetric shape of the absorption band, but the separation of the two components decreases from 30 (for **5a**) to 10–15 nm. These bands originate from $\pi \longrightarrow \pi^*$ transitions of the conjugated chromophores in the two halves of the molecules and the separation into two components observed for **5a** (about 2000 cm^{-1}) is typical for exciton-coupled dimeric molecules.[5a] Very intense Cotton effects, with positive and negative components, are usually associated with exciton-coupled transitions and this is actually the case for **5a**, while the circular dichroism spectra of **5b** and **5c** are much weaker (Fig. 2). In the latter compounds the separation between the thioxoenamine groups imposed by the R bridge is large and the electronic coupling during excitation is ineffective.[11] The dominant optical activity in the CD spectra of **5b** and **5c** occurs near 450 nm, where no appreciable absorption band can be detected, and is associated with the $n \longrightarrow \pi^*$ transition of the thioxo group, while only weak CD activity is observed in the region corresponding to strong absorption (around 400 nm). In the CD spectrum of **5a** the intense positive and negative exciton components almost coincide with the absorption maxima, indicating that reciprocal cancellation is scarce.

It is interesting that the Schiff-base condensate of ethylenediamine with two molecules of thioacetylacetone, which corresponds to **5a**, and also the analogous compound derived from cyclohexane-1,2-diamine, do not show any exciton splitting of the $\pi \longrightarrow \pi^*$ transitions.[7b] It is only with the thioacetylacetone condensate of the bulky 1,2-diphenylethane-1,2-diamine that the characteristic CD feature can be observed.[7b] Thus the hydroxymethylenethiocamphor residues serve the same role of minimizing the spatial separation between the two thioxoenamine chromophores and force their interaction as do the phenyl groups on the ethane bridge in the thioacetylacetone series. However, unlike in the latter case, this result may not simply be due to a steric effect. Exciton coupling



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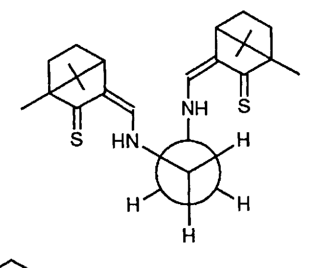

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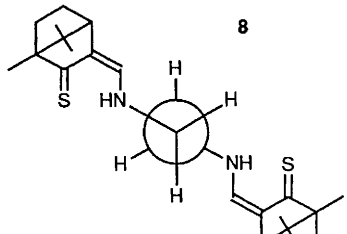

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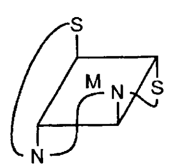
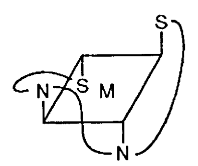


Δ
10



Λ
11

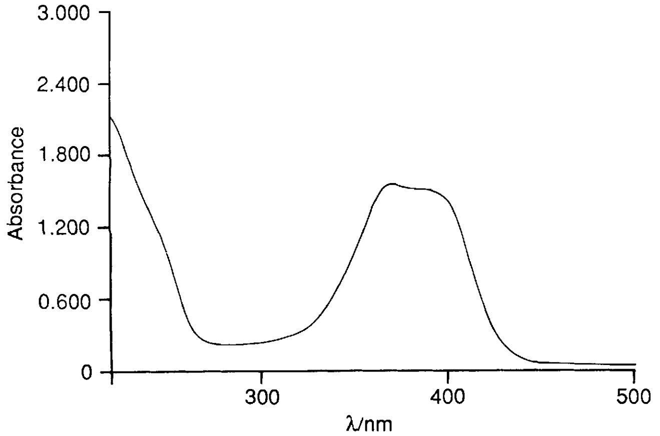


Fig. 3 Electronic spectrum of the zinc(II) complex **6a** in methanol solution (1.71 × 10^{-3} mol dm^{-3}, cell path 0.1 cm)

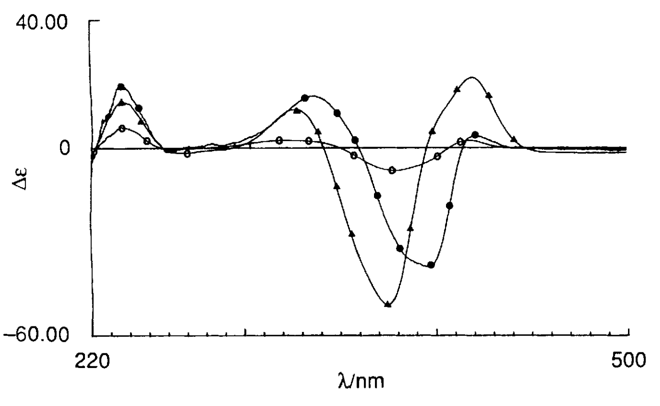


Fig. 4 Circular dichroism spectra of the zinc(II) complexes **6a** (○), **6b** (●) and **6c** (▲) in methanol solution

by the thioxoenamine transitions can only occur in the *gauche* rotamers **7** and **8** of **5a**, while the *trans* disposition **9** implies too large a distance between the chromophores for an efficient coupling mechanism. It is quite possible that besides favourable dipole–dipole interactions and, possibly, intramolecular hydrogen bonding, also hydrophobic interactions,[12] between adjacent thiocamphor residues contribute to the stabilization of the *gauche* rotamer(s). Assuming that the established correlations between CD spectra and structures in the ketoenamine series[5d,e] are valid for the thioxoenamine derivatives, from the sign of the low-energy component of the CD exciton couplet we can tentatively conclude that the dominant conformer of **5a** is **8**, which corresponds to the most stable isomer of the derivatives of *trans*-(*S*,*S*)-cyclohexane-1,2-diamine with acetylacetone or hydroxymethylenecamphor.[5d]

Binding of the ligands **5** to zinc(II) occurs in their enethiolate imine form: in the proton NMR spectra the doublet for the enamine CH proton is completely absent and replaced by a broad singlet at δ 7.40–7.80 due to the imine proton, and in the ^{13}C NMR spectra the signals above δ 200 are replaced by imine carbon signals at δ ≈ 180. The NMR spectra of the zinc(II) complexes **6a** and **6b** show multiple signals for the various groups due to the presence of several species deriving from the geometric arrangement assumed by the metal atom and the conformational mobility of the ligands in the chelates. On the other hand, ^{1}H and ^{13}C NMR spectra of compound **6c** clearly indicate the presence of only two diastereomeric species in a ratio of 1:2.3, as evaluated by integration of the methynic hydrogen of the camphor skeleton which resonates at δ 2.33 and 2.26 in the two diastereoisomers. The presence of the two diastereoisomers is also confirmed by two well resolved AB systems of the benzylic protons at δ 5.10 and 4.28 with a geminal coupling constant of 14.2 Hz and at δ 5.12 and 4.29 with a geminal coupling constant of 14.1 Hz.

The zinc(II) ion of compounds **6a**–**6c** becomes dissymmetric if the ligands adopt a tetrahedral or pseudo-tetrahedral arrangement of the donor groups, affording the Δ and Λ absolute configurations, with respect to the C_2 axis,[13] shown by structures **10** and **11**, according to the handedness of the pair of lines connecting the N and S donor atoms of each chromophore. Other chiral structures at the metal atom can be obtained if the complex becomes five-co-ordinate, *e.g.* by binding a solvent molecule in axial position; in a perfectly planar complex the metal centre obviously cannot be a stereocentre. In general, we have to expect that lengthening the carbon chain R in the diamine moiety from two to four carbon atoms will strongly favour the adoption of tetrahedral structures,[4] while the two-carbon-atom bridge R of **6a** will allow only slight tetrahedral distortion of the metal chromophore.[6c] These effects are made evident by the CD spectral behaviour of the complexes.

The near-UV spectrum of the zinc(II) complexes is dominated by absorption bands with multicomponent structure associated with the intense $\pi \longrightarrow \pi^*$ transitions of the enethiolate–imine chromophores (Fig. 3). These are slightly blue shifted with respect to the corresponding transitions in the free ligands, where the chromophores have thioxoenamine nature, in agreement with the trend established for the tautomeric equilibria involving ketoenamine and enolimine forms.[1,14] The CD spectra of compounds **6a**–**6c** are similar in shape but remarkably different in intensity, since the optical activity increases by about one order of magnitude on passing from **6a** to **6c** (Fig. 4). A similar trend was noted in the CD spectra of the corresponding copper(II) complexes, although the spectra contained also bands due to charge-transfer transitions in the near-UV region.[4] Of the three CD bands above 300 nm only those near 380 nm (negative, dominant) and 420 nm (positive) correspond to the intense near-UV absorption. The CD band near 320 nm (positive) corresponds to very weak, undefined electronic absorption and is therefore assigned to a n(sulphur) $\longrightarrow \pi^*$ transition, which is shifted to higher energy on co-ordination to zinc(II). The two-component CD curve at low energy can be considered to result from exciton splitting of the ligand $\pi \longrightarrow \pi^*$ transitions, since at least for **6b** and **6c** the

Cotton effects are large.[15] The asymmetry in CD intensity distribution between the two components of the exciton couplet has been observed for other chiral zinc(II) complexes,[16] and can be due to mixing with other transitions at higher energy or the presence of minor diastereoisomers in solution. For **6a**–**6c** the shape of the CD curves in Fig. 4 shows that the major negative CD component near 380 nm is not symmetric; a shoulder or peak near 395 nm, which is negative for **6a** and **6b** and positive for **6c**, occurs on its low-energy side. In the former two cases this accounts for the partial cancellation of the positive component of the exciton couplet at lower energy. The additional CD absorptions near 395 nm are associated with the minor diastereoisomeric forms of the complexes shown by the NMR spectra. These are probably five-co-ordinate structures with a bound solvent molecule and 'umbrella-shaped' ligand conformation.[17]

The CD sign pattern of the exciton splitting in tetradentate bis(imine) complexes can be used for conformational and configurational assignments.[6,15] The positive CD component at lower energy indicates that the configuration of the pseudo-tetrahedral complexes is Λ. In the case of compounds **6a**–**6c** this is clearly imposed by the chirality of the hydroxymethylenethiocamphor residues, probably for the more favourable intramolecular interactions involved in the skew arrangement of these residues shown in structure **11**. The degree of tetrahedral distortion of the zinc(II) centres is associated with the angle, θ, between the transition dipole moments of the two enethiolateimine chromophores of the ligand, since the direction of these transition moments can be assumed to be approximately parallel to the lines connecting the nitrogen and sulphur donor atoms.[7b] As the distance between the interacting transition moments presumably is invariant in the series **6a**–**6c**, the increase in rotatory strength of the CD components along this series is directly correlated with the increase in θ angle.[15] A nearly regular tetrahedral arrangement (θ = 90°) involves relatively large separation between the nitrogen atoms of the diamine residue, and even though the zinc(II) atom will favour the adoption of such a geometry it can only be achieved in the compound **6c** containing the four-carbon chain R. A similar trend was deduced for the corresponding copper(II) complexes from examination of their ESR spectral behaviour,[4] but there a regular tetrahedral structure was not adopted in the more favourable case because of the well known reluctancy of copper(II) to assume this type of geometric arrangement.[18]

Experimental

Elemental analyses were by the microanalytical laboratory of our Department. Infrared spectra were recorded with a Nicolet MX-1E FT instrument, electronic spectra on a HP 8452 diode-array spectrophotometer, CD spectra with a JASCO J-500C dichrograph, ^1H and ^{13}C NMR spectra at 200 MHz on a Bruker AC-200 spectrometer. (1*R*)-3-Hydroxymethylenebornane-2-thione was prepared as reported in ref. 4.

Preparation of the Ligands **5**.—To a cold solution (about 0 °C) of (1*R*)-3(*Z*)-hydroxymethylenebornane-2-thione **3** (1 mmol) in methanol (3 cm^3) was added the appropriate diamine **4** (0.05 mmol). The mixture was left overnight at 4 °C, with stirring. Compounds **5a** and **5c** precipitated and were filtered off. After washing with cold methanol (2 cm^3) and drying under vacuum, the pure compounds were obtained in nearly quantitative yields. For compound **5b**, the reaction mixture was evaporated under vacuum and the residue purified by silica gel chromatography. By eluting with light petroleum (b.p. 40–60°C)–ethyl acetate (20:80) the pure compound was obtained in 90% yield.

Compound **5a** (Found: C, 69.10; H, 8.50; N, 6.65. Calc. for $C_{24}H_{36}N_2S_2$: C, 69.25; H, 8.65; N, 6.75%). IR (Nujol mull, cm^{-1}): 3350 (br), 1629s, 1573s, 1326m, 1194m and 1076m. UV (MeOH), λ/nm (ε/dm^3 mol^{-1} cm^{-1}): 259 (7100), 384 (24 600) and 414 (25 200). CD (MeOH), λ/nm (Δε/dm^3 mol^{-1} cm^{-1}): 250 (+5.30), 284 (−0.70), 380 (−13.80), 413 (+14.80) and 450 (−4.40). NMR ($CDCl_3$): ^1H, δ 11.56 (m, 2 H), 6.89 (d, *J* = 12.6, 2 H), 3.44 (m, 4 H), 2.33 (d, *J* = 3.4 Hz, 2 H), 2.10–1.15 (m, 8 H), 1.07 (s, 6 H), 0.87 (s, 6 H) and 0.69 (s, 6 H); ^{13}C, δ 227.6 (s), 147.4 (d), 127.3 (s), 66.9 (s), 53.5 (s), 52.4 (d), 49.9 (t), 32.4 (t), 27.8 (t), 19.8 (q), 19.6 (q) and 12.2 (q). Mass spectrum: *m*/*z* 416 (M^+, 40), 383 (8), 221 (85), 208 (46), 196 (100), 178 (15), 105 (8) and 91 (10%).

Compound **5b** (Found: C, 70.00; H, 8.75; N, 6.40. Calc. for $C_{25}H_{38}N_2S_2$: C, 69.75; H, 8.85; N, 6.50%). IR (Nujol mull, cm^{-1}): 3300w, 1630s, 1330s, 1197s and 1079s. UV (MeOH), λ/nm (ε/dm^3 mol^{-1} cm^{-1}): 262 (7500), 396 (sh) (26 500) and 407 (30 300). CD (MeOH), λ/nm (Δε/dm^3 mol^{-1} cm^{-1}): 251 (+5.80), 394 (+2.90), 408 (+3.10) and 450 (−5.60). NMR ($CDCl_3$): ^1H, δ 11.60 (m, 2 H), 6.96 (d, *J* = 12.7, 2 H), 3.42 (m, 4 H), 2.40 (d, *J* = 3.3 Hz, 2 H), 2.10–1.14 (m, 10 H), 1.12 (s, 6 H), 0.92 (s, 6 H) and 0.74 (s, 6 H); ^{13}C, δ 225.7 (s), 147.8 (d), 127.2 (s), 66.8 (s), 53.7 (s), 52.6 (d), 45.6 (t), 32.4 (t), 31.2 (t), 27.9 (t), 19.8 (q), 19.7 (q) and 12.3 (q). Mass spectrum: *m*/*z* 430 (M^+, 32), 397 (12), 222 (87), 209 (100), 194 (42), 181 (28), 105 (18) and 91 (27%).

Compound **5c** (Found: C, 73.10; H, 8.05; N, 5.75. Calc. for $C_{30}H_{40}N_2S_2$: C, 73.15; H, 8.15; N, 5.70%). IR (Nujol mull, cm^{-1}): 3300w, 1630s, 1590w, 1330s, 750m and 723w. UV (MeOH), λ/nm (ε/dm^3 mol^{-1} cm^{-1}): 260 (7400), 392 (sh) (23 500) and 405 (24 800). CD(MeOH), λ/nm (Δε/dm^3 mol^{-1} cm^{-1}): 253 (+3.80), 403 (+3.00) and 452 (−4.80). NMR ($CDCl_3$): ^1H, δ 11.80 (m, 2 H), 7.34 (m, 4 H), 6.94 (d, *J* = 12.5, 2 H), 4.50 (m, 4 H), 2.38 (d, *J* = 3.3 Hz, 2 H), 2.10–1.15 (m, 8 H), 1.11 (s, 6 H), 0.91 (s, 6 H) and 0.74 (s, 6 H); ^{13}C, δ 227.2 (s), 147.0 (d), 146.7 (d), 134.8 (s), 128.8 (d), 128.6 (d), 127.6 (s), 67.0 (s), 53.6 (s), 52.6 (d), 50.1 (t), 32.4 (t), 27.9 (t), 19.8 (q), 19.6 (q) and 12.2 (q). Mass spectrum: *m*/*z* 492 (M^+, 20), 459 (10), 297 (100), 282 (30), 196 (15), 105 (30) and 91 (30).

Preparation of Zinc(II) *Complexes* **6**.—To a cold solution of the ligand **5** (1 mmol) in methanol (3 cm^3) were added 2 equivalents of methanolic 1 mol dm^{-3} sodium hydroxide followed by a solution of zinc(II) perchlorate hexahydrate (1 mmol) in methanol (3 cm^3). Yellow precipitates started to form; precipitation was completed by the addition of a few drops of cold water. The product was rapidly filtered off, washed with small amounts of methanol, and dried under vacuum.

Compound **6a** (Found: C, 60.15; H, 7.00; N, 5.80. Calc. for $C_{24}H_{34}N_2S_2Zn$: C, 60.10; H, 7.10; N, 5.85%). IR (Nujol mull, cm^{-1}): 1636w, 1560s, 1491s, 1458s, 1286m, 1253m and 721m. UV (MeOH), λ/nm (ε/dm^3 mol^{-1} cm^{-1}): 246 (6700), 370 (9100) and 392 (8750). CD (MeOH), λ/nm (Δε/dm^3 mol^{-1} cm^{-1}): 235 (+7.00), 321 (+2.80), 379 (−6.80) and 418 (+2.70). NMR ($CDCl_3$): ^1H, δ 7.56–7.44 (m, 2 H), 3.90–3.30 (m, 4 H), 2.34–1.14 (m, 10 H), 1.09 (s), 0.90 (s), 0.83 (s), 0.77 (s), 0.74 (s) and 0.70 (s); ^{13}C, δ 182.9 (s), 163.6 (d), 163.1 (d), 129.9 (s), 128.9 (s), 63.3 (s), 63.0 (s), 60.4 (t), 55.1 (d), 54.9 (d), 54.4 (s), 31.9 (t), 31.3 (t), 27.5 (t), 27.1 (t), 20.1 (q), 19.7 (q), 19.5 (q), 11.9 (q) and 11.8 (q).

Compound **6b** (Found: C, 60.75; H, 7.25; N, 5.60. Calc. for $C_{25}H_{36}N_2S_2Zn$: C, 60.80; H, 7.30; N, 5.65%). IR (Nujol mull, cm^{-1}): 1630w, 1584s, 1493s, 1460s, 1253w, 1081w and 721m. UV (MeOH), λ/nm (ε/dm^3 mol^{-1} cm^{-1}): 244(sh) (10 850), 378 (12 700) and 402(sh) (10 950). CD (MeOH), λ/nm (Δε/dm^3 mol^{-1} cm^{-1}): 235 (+14.60), 337 (+16.10), 384 (sh) (−34.20), 396 (−37.80) and 412 (+3.70). NMR ($CDCl_3$): ^1H, δ 7.65 and 7.45 (two br s, 2 H), 3.72 and 3.12 (two m, 4 H), 2.31 (d, *J* = 2.9 Hz), 1.97–1.11 (m and s, 18 H), 0.86 (s), 0.83 (s), 0.81 (s) and 0.75 (s); ^{13}C, δ 179.5 (s), 161.2 (d), 129.1 (s), 62.8 (s), 55.6 (t), 54.9 (d), 54.1(s), 31.5 (t), 31.4 (t), 28.8 (t), 27.3 (t), 19.8 (q), 19.7 (q), 19.5 (q) and 11.9 (q).

Compound **6c** (Found: C, 65.00; H, 6.80; N, 5.15. Calc. for $C_{30}H_{38}N_2S_2Zn$: C, 64.80; H, 6.85; N, 5.05%). IR (Nujol mull, cm^{-1}): 1628w, 1586s, 1489s, 1464s, 1286s, 1249m, 1207m, 1073m, 1036m, 1008m, 748m and 723m. UV (MeOH), λ/nm (ε/dm^3 mol^{-1} cm^{-1}): 248 (sh) (12 600), 386 (15 750) and 414 (sh) (8650).

CD (MeOH), λ/nm ($\Delta\varepsilon$/dm^3 mol^{-1} cm^{-1}): 236 (+13.00), 328 (+10.60), 375 (−51.40), 403 (sh) (+9.10) and 420 (+20.40). NMR ($CDCl_3$): ^{1}H, δ 7.72 (br s, 2 H), 7.20 (m, 4 H), 5.12 and 5.10 (2 d, J = 14.1 and 14.2 respectively, 2 H), 4.29 and 4.28 (2 d, J = 14.1 and 14.2 respectively, 2 H), 2.33 and 2.26 (2 d, J = 3.1 Hz, 2 H), 2.10–1.40 (m, 8 H), 1.12 (s), 1.10 (s), 0.80 (s), 0.76 (s) and 0.67 (s); ^{13}C, δ 179.8 (s), 164.3 (d), 164.0 (d), 138.7 (s), 138.3 (s), 130.5 (s), 130.0 (d), 127.2 (d), 62.9 (s), 62.1 (t), 61.9 (t), 55.0 (s), 54.7 (d), 54.3 (d), 31.5 (t), 27.4 (t), 26.9 (t), 19.7 (q), 19.5 (q), 12.2 (q) and 11.7 (q).

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