1,2-Bis[(2-dimethylamino-2-thioxo-1-phenylethylidene)hydrazino]-ethane: a new tetradentate ligand for Ni^{2+}

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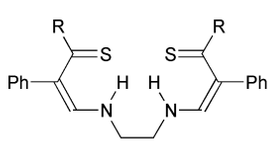
The preparation of a new type of N_2S_2 tetradentate ligand **3** with the bis(hydrazonothioamide) structure is reported in this paper. The key step in this synthesis is the condensation of the dihydrazine **7** with an α-ketoester. Ligand {1,2-bis[(2-dimethylamino-2-thioxo-1-phenylethylidene)hydrazino]ethane} **3** was obtained in 6 steps from secondary amine. This ligand is then used in the preparation of a nickel(II) complex **4** and the mesomeric forms of metallic complex NiN_2S_2 are discussed.

Introduction

Polyamine tetradentate ligands are very important synthetic intermediates and their metal complexes have attracted considerable attention as models for natural tetraazamacrocycles,[1] as contrast agents for magnetic resonance imaging[2] and for use in nuclear medicine.[3] These ligands have been extensively described in the literature. N_2S_2 tetradentate ligands are rarer and only a few have been reported.[4] Bis(aminopropenethiones) **1** first prepared by Holm[5] are the most common type of N_2S_2 ligand. This type of ligand has been shown to complex metal cations[6] such as Ni^{2+}, Cu^{2+}, Co^{2+}, Mn^{2+}, Zn^{2+} and Tc^{2+} and the resulting complexes have been shown to have medical applications.[7]

In the course of our studies on 4-amino-1-thia-4-azabutadienes, we have shown that α-hydrazonothioamides **2** are stable and can be easily synthesised in high yields.[8] This stability recently prompted us to prepare a new type of N_2S_2 tetradentate ligand **3** which is a bis(hydrazonothioamide).[9] We report here the synthesis of compound **3** and the behaviour of this tetradentate ligand towards Ni^{2+} to afford the metallic complex **4**.



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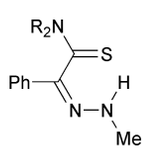

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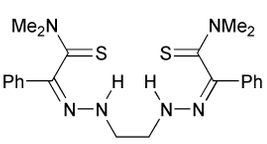

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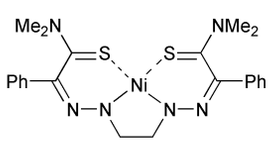

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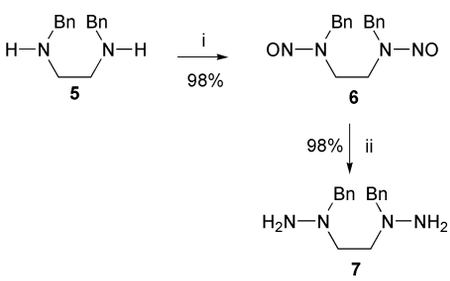
Results and discussion

The key step in the preparation of the bis(hydrazonothioamide) **3** was the condensation of an α-ketoester with the dihydrazine **7**. The latter compound was prepared from secondary amines[10] *via* the corresponding dinitrosoamines **6** in a well known two-step sequence to give high yields: the protected diamine **5** was transformed into the dinitrosoamine **6** in 98% yield by addition of sodium nitrite to the dihydrochloride of the diamine.[11] Reduction of the dinitrosoamine **6** with a titanium complex, generated *in situ* by the action of magnesium on titanium(IV) chloride, afforded the corresponding dihydrazine **7** in 98% yield (Scheme 1).[12,13]



5 **6** **7**

Scheme 1 *Reagents and conditions*: (i) $NaNO_2$–HCl, H_2O, 100 °C, 20 h; (ii) $TiCl_4$–Mg, CH_2Cl_2–Et_2O, rt, 5 h.

The protected dihydrazine **7** was then reacted with two equivalents of methyl benzoylformate to furnish the bis-(hydrazonoester) **8** in 81% yield. Thionation of this precursor of the N_2S_2 ligand using Lawesson's reagent proved to be unsuccessful. However, we have shown that α-hydrazonoamides are easily converted into their thionated analogues **2** using Lawesson's reagent,[8] and so the bis(hydrazonoester) **8** was transformed into the bis(hydrazonoamide) **9** by the action of dimethylaluminium dimethylamide, formed *in situ* by addition of dimethylamine to trimethylaluminium (Scheme 2).[14]

The compound **9** was prepared in 91% yield. Hydrogenolysis of the benzyl protecting groups was complicated by concomitant N–N bond cleavage (Scheme 3). Optimisation of the conditions involved variation of solvents, length of reaction time, ratios of catalyst to substrate and ratios of reagent to substrate. In each case, a mixture of monodeprotected compound **11** (recyclable), desired product **10** and the compound of decomposition **12** was obtained. Optimal conditions for yielding the deprotected N_2O_2 ligand **10** in 53% yield were found to be the use of 4.5 equivalents of formic acid in methanol with an equal amount of 10% palladium on charcoal.[15] Thionation of the compound **10** with Lawesson's reagent afforded the N_2S_2 tetradentate ligand **3** in 84% yield.

Complexation of N_2S_2 tetradentate ligands with metallic cations has been described in previous works[6] and the method consisted of dissolving the ligand in the minimum amount of chloroform and adding a solution of the metal acetate in methanol dropwise. The metallic complex, insoluble in the

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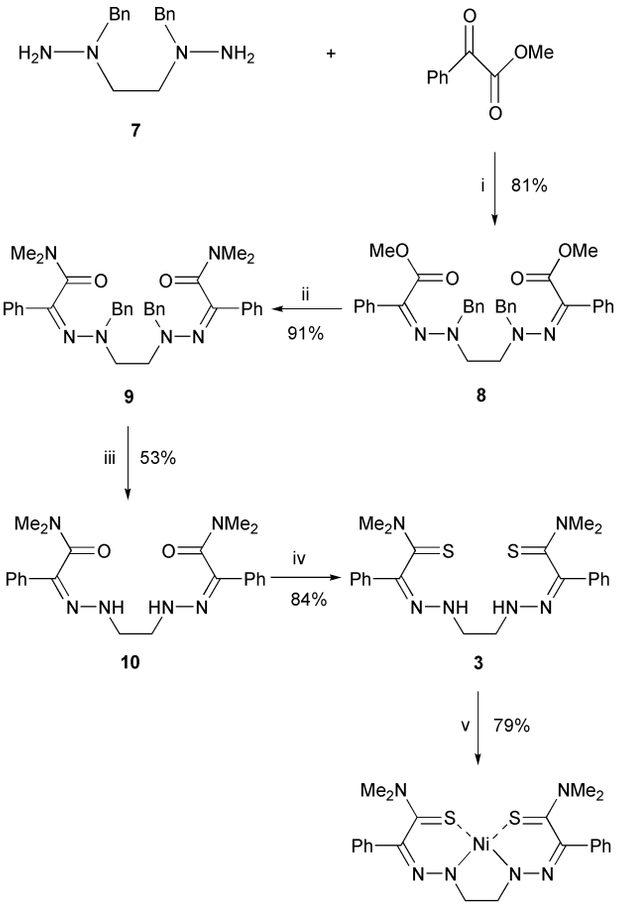
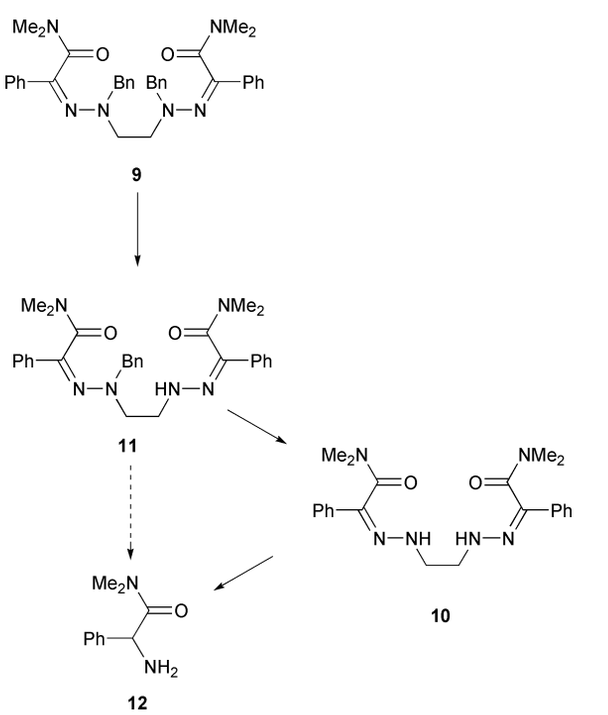


Scheme 2 *Reagents and conditions*: (i) CH_3CO_2H, MeOH, reflux, 24 h; (ii) Me_2NH, $AlMe_3$, C_6H_6, 0 °C to rt, 30 min; (iii) HCO_2H, 10% Pd on C, MeOH, rt, 2 h; (iv) Lawesson's reagent, C_6H_6, reflux, 20 h; (v) $Ni(OAc)_2$, MeOH–$CHCl_3$, rt, 20 h.

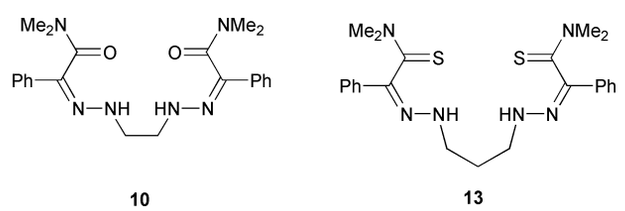


Scheme 3

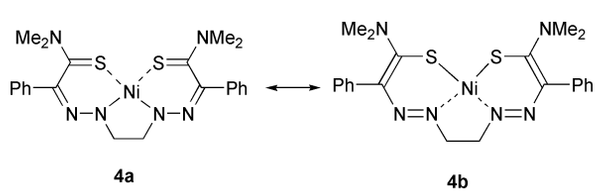
binary system of solvents, was simply collected by filtration. This procedure was remarkably successful in complexing the ligand **3** with Ni^{2+} to afford the metallic complex NiN_2S_2 **4** in 79% yield after crystallisation.

Unlike ligands of the type bis(aminopropenethione) **1**, **3** was highly specific for Ni^{2+} since all attempts to complex other metallic cations proved to be totally unsuccessful. Thus, reaction of **3** with Mn^{2+}, Cu^{2+}, Co^{2+} or Zn^{2+} did not yield the corresponding metallic complexes under the conditions described above. This failure is surprising, particularly with copper. Indeed, comparison between Cu^{2+} and Ni^{2+}complexes is justified by the similar size of these two elements (0.63 Å for Ni^{2+} *versus* 0.71 Å for Cu^{2+} in a square planar environment)[16] and by their nearly identical complexation constants.[17] On the basis of the behaviour of these two elements in coordination chemistry, we can expect square planar complexes with nickel[16] while for copper complexes tetrahedral environments have usually been observed (planar environments are possible with orthogonal anionic ligands).[18] In our case, we have not observed the formation of the complex of CuN_2S_2. It is suggested that the nature of the ligand might have a crucial influence on the geometry of the complex and perhaps a larger distortion from the plane cannot be tolerated.

It should be noted that a change in the electron environment (ligand **10**) and the variation in chain length (ligand **13**)[19] have an important influence on the formation of these complexes. In our hands, the metallic complexes failed to form with these ligands.



Scanning electron microscopy was consistent with the proposed structure and gave a ratio S : Ni = 2. Nevertheless, **4** can in fact be written in two mesomeric forms **4a** and **4b** (Scheme 4) and nuclear magnetic resonance was used to afford



Scheme 4

more information about the electron distribution in the complex. Proton and carbon NMR showed that the non-equivalence of the two methyl groups in the ligand **3**, consistent with the presence of a thioamide function, disappeared in **4**; moreover, the chemical shift for CH_2N changed from 50.5 ppm in **3** to 63.5 ppm in **4**, the latter value is in agreement with the shift expected for Nsp^2–CH_2. Finally, the large difference of chemical shift in C=S (193.3 ppm in **3** to 161.3 ppm in **4**) could be attributed to a decrease in the bond order. All these arguments seem to show that the complex **4** is more likely to exist as form **4b**. To fully characterise the mesomeric form we would like to perform a crystal structure analysis but complex **4** exists as an amorphous powder.

In conclusion, we have prepared a new type of ligand N_2S_2 in 7 steps with an overall yield of 25%. This ligand has a high selectivity for Ni^{2+} compared with other metallic cations and the metallic complex **4** has been shown to be in the form **4b** rather than **4a**.

Experimental

All reagents were purchased from Acros Organics and Aldrich. 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. Thin layer chromatography 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 ^{13}C and ^{1}H 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. The IR spectra were obtained using a Bruker Vector22 spectrometer.

N,*N*′-Dibenzyl-*N*,*N*′-dinitroso-1,2-diaminoethane 6

To a solution of *N*,*N*′-dibenzyl-1,2-diaminoethane **5** (10^{-2} mol) in water (80 mL) was added 12 M hydrochloric acid (5×10^{-2} mol). The reaction mixture was heated to reflux and sodium nitrite (2.4×10^{-2} mol) in water (10 mL) was added dropwise over 10 min. The solution was refluxed for 20 h, cooled to room temperature and extracted with dichloromethane (100 mL × 2). The organic phase was washed with brine, dried ($MgSO_4$), filtered and evaporated. Compound **6** was crystallized from ethyl acetate (98%); mp 75 °C (Found: C, 64.12; H, 6.11; N, 19.06. $C_{16}H_{18}N_4O_2$ requires C, 64.41; H, 6.08; N, 18.78%); NMR spectra of compound **6** showed 3 rotamers **A**, **B** and **C**. ^{1}H NMR (DMSO-d_6) δ 3.39 (**A**, s, 4H, 2NCH_2CH$_2$), 3.74 and 3.98 (**B**, 2t, 4H, 2NCH_2CH$_2$, *J* 6.1 Hz), 4.33 (**C**, s, 4H, 2NCH_2CH$_2$), 4.69 and 5.23 (**B**, 2s, 4H, 2CH_2Ph), 4.75 (**C**, s, 4H, 2CH_2Ph), 5.16 (**A**, s, 4H, 2CH_2Ph), 7.04–7.42 (**A** + **B** + **C**, m, 10H, C*H*ar); ^{13}C NMR (DMSO-d_6) δ 39.45 (**A**, 2C, 2N*C*H$_2$CH$_2$), 41.14 and 46.76 (**B**, 2C, 2N*C*H$_2$CH$_2$), 48.61 (**C**, 2C, 2N*C*H$_2$CH$_2$), 46.09 (**C**, 2C, 2*C*H$_2$Ph), 46.48 and 56.35 (**B**, 2C, 2*C*H$_2$Ph), 56.48 (**A**, 2C, 2*C*H$_2$Ph), 128.01, 128.09, 128.27, 128.29, 128.37, 128.66, 128.74, 128.85, 128.93, 128.99, 129.10 (**A** + **B** + **C**, 10*C*Har), 133.39 (**C**, 2*C*ar), 133.63 and 133.90 (**B**, 2*C*ar), 133.93 (**A**, 2*C*ar); MS, *m*/*z* (%) 268 (9, (M − NO)$^+$), 238 (9, (M − 2NO)$^+$), 118 (22), 92 (10), 91 (100); IR/cm^{-1} (KBr) 1496 (m), 1453 (w), 1416 (m), 1369 (w), 1353 (vw), 1300 (w), 1279 (w), 1173 (m), 1152 (m), 1104 (w), 1074 (w), 1029 (m), 941 (m), 866 (m), 791 (m), 743 (m), 703 (vw), 681 (m).

N,*N*′-Diamino-*N*,*N*′-dibenzyl-1,2-diaminoethane 7

Titanium(IV) chloride (0.16 mol) was slowly added under N_2 to a mixture of dichloromethane–diethyl ether (4 : 1) (250 mL). Magnesium turnings (0.16 mol) were added and the reaction mixture was stirred at room temperature for 3 h. Dinitrosoamine **6** (2×10^{-2} mol) was added to the black suspension and the reaction was stirred for a further 45 min, 0.3 M (41 mL) hydrochloric acid was added and the reaction was stirred for another hour. The reaction mixture was made alkaline by addition of dilute sodium hydroxide. The mixture was filtered through a pad of Celite and the filtrate was extracted with dichloromethane (300 mL). The organic phase was washed with brine, dried ($MgSO_4$), filtered and evaporated. Compound **7** was crystallised from ethanol (98%); mp 62 °C (Found: C, 71.47; H, 8.33; N, 20.56. $C_{16}H_{22}N_4$ requires C, 71.11; H, 8.15; N, 20.74%); ^{1}H NMR ($CDCl_3$) δ 2.83 (s, 8H, 2NCH_2CH$_2$ + 2NH_2), 3.72 (s, 4H, 2*C*H$_2$Ph), 7.25–7.36 (m, 10H, C*H*ar); ^{13}C NMR ($CDCl_3$) δ 58.03 (2C, 2N*C*H$_2$CH$_2$), 66.79 (2C, 2*C*H$_2$Ph), 127.53, 128.60, 129.47 (10*C*Har), 137.77 (2*C*ar); IR/cm^{-1} (KBr) 3128 (m), 2814 (m), 1604 (m), 1496 (m), 1456 (w), 1368 (m), 1330 (m), 1296 (m), 1243 (m), 1163 (m), 1051 (w), 1028 (m), 1007 (w), 989 (w), 912 (m), 841 (m), 825 (m), 800 (m), 735 (vw), 700 (vw).

1,2-Bis[(2-methoxy-2-oxo-1-phenylethylidene)-*N*-benzylhydrazino]ethane 8

To a solution of methyl benzoylformate (2.1×10^{-2} mol) and acetic acid (2.1×10^{-2} mol) in methanol (20 mL) was added the dihydrazine **7** at room temperature, under N_2. The solution was refluxed for 24 h and cooled to room temperature. Solvents were evaporated and the residue was dissolved in ethyl acetate (20 mL) and extracted. The organic phase was washed with saturated aqueous sodium hydrogen carbonate, brine, dried ($MgSO_4$), filtered and evaporated. The residue was purified by chromatography on silica using dichloromethane as eluent. Compound **8** was crystallised from diethyl ether (81%); mp 95 °C (Found: C, 72.45; H, 5.94; N, 9.91. $C_{34}H_{34}N_4O_4$ requires C, 72.58; H, 6.09; N, 9.96%); NMR spectra of compound **8** showed 2 symmetric rotamers **A** and **C** and 1 dissymmetric rotamer **B**. ^{1}H NMR ($CDCl_3$) δ 2.97 and 3.20 (**B**, 2t, 4H, 2NCH_2CH$_2$), 3.08 (**A**, s, 4H, 2NCH_2CH$_2$), 3.40 (**C**, s, 4H, 2NCH_2CH$_2$), 3.68 (**A**, s, 6H, 2OCH_3), 3.70 (**B**, s, 6H, 2OCH_3), 3.74 (**C**, s, 6H, 2OCH_3), 3.92 and 4.38 (**B**, 2s, 4H, 2*C*H$_2$Ph), 4.06 (**A**, s, 4H, 2*C*H$_2$Ph), 4.24 (**C**, s, 4H, 2*C*H$_2$Ph), 6.91–7.60 (**A** + **B** + **C**, m, 20H, C*H*ar); ^{13}C NMR ($CDCl_3$) δ 51.63 (**C**, 2C, 2O*C*H$_3$), 51.75 and 51.99 (**B**, 2C, 2O*C*H$_3$), 52.07 (**A**, 2C, 2O*C*H$_3$), 53.03 and 53.50 (**B**, 2C, 2N*C*H$_2$CH$_2$), 54.11 (**A**, 2C, 2N*C*H$_2$CH$_2$), 54.56 (**C**, 2C, 2N*C*H$_2$CH$_2$), 59.00 (**A**, 2C, 2*C*H$_2$Ph), 60.46 and 62.49 (**B**, 2C, 2*C*H$_2$Ph), 62.27 (**C**, 2C, 2*C*H$_2$Ph), 126.61, 126.77, 127.05, 127.08, 127.20, 127.23, 127.32, 127.39, 127.50, 127.58, 127.69, 127.96, 128.09, 128.24, 128.36, 128.38, 128.46, 128.52, 128.87, 129.00, 129.42, 129.50, 130.01, 130.51 (**A** + **B** + **C**, 20*C*Har), 129.83, 131.20, 132.40, 132.95, 134.76, 135.07, 136.16, 136.64, 136.68, 137.02, 153.90, 156.67 (**A** + **B** + **C**, 4*C*ar + 2*C*=N), 165.93 and 166.22 (**B**, 2*C*=O), 166.08 (**A**, 2*C*=O), 166.19 (**C**, 2*C*=O); MS, *m*/*z* (%) 562 (<1, M$^+$), 400 (3), 340 (6), 281 (22), 237 (10), 235 (8), 133 (13), 92 (8), 91 (100); IR/cm^{-1} (KBr) 1700 (vw), 1560 (w), 1496 (m), 1431 (w), 1319 (m), 1283 (vw), 1216 (w), 1140 (w), 1109 (w), 1075 (m), 1049 (w), 1023 (m), 959 (m), 942 (m), 730 (m), 718 (w), 696 (w).

1,2-Bis[(2-dimethylamino-2-oxo-1-phenylethylidene)-*N*-benzylhydrazino]ethane 9

To a solution of trimethylaluminium (21 mmol) in benzene (25 mL) was added dimethylamine (20 mmol) at 0 °C under N_2. The reaction was stirred at 0 °C for 20 min and allowed to warm to room temperature over 45 min. Compound **8** (5 mmol) was added and the reaction mixture was refluxed for 20 h, cooled to room temperature and hydrolysed by dropwise addition of dilute hydrochloric acid (21 mmol). The reaction mixture was extracted with ethyl acetate and the organic phase was washed with saturated aqueous sodium hydrogen carbonate, brine, dried ($MgSO_4$), filtered and evaporated. The residue was purified by chromatography on silica using a mixture of dichloromethane–ethyl acetate (9 : 1) as eluent. Compound **9** was crystallized from ethyl acetate (91%); mp 127 °C (Found: C, 73.51; H, 6.79; N, 14.23. $C_{36}H_{40}N_6O_2$ requires C, 73.44; H, 6.85; N, 14.27%); ^{1}H NMR (C_6D_6) (recorded at 60 °C) δ 2.28 and 2.65 (2s, 12H, 2N(CH_3)$_2$), 3.50 (br s, 4H, 2NCH_2CH$_2$), 4.23 and 4.57 (2br s, 4H, 2CH_2Ph), 7.04–7.20, 7.32–7.37 and 7.80–7.85 (3m, 20H, C*H*ar); ^{13}C NMR (C_6D_6) (recorded at 60 °C) δ 33.60 and 36.82 (4C, 2N(*C*H$_3$)$_2$), 55.73 (2N*C*H$_2$CH$_2$), 61.53 (2*C*H$_2$Ph), 126.14, 126.98, 128.17, 128.44, 128.77, 129.18 (20*C*Har), 134.87, 138.42 (4*C*ar), 151.25 (2*C*=N), 167.53 (2*C*=O); MS, *m*/*z* (%) 413 (12), 294 (11), 237 (32), 104 (11), 91 (100), 72 (80), 58 (53); IR/cm^{-1} (KBr) 1636 (vw), 1494 (m), 1445 (m), 1404 (m), 1253 (m), 1151 (m), 960 (m), 741 (m), 719 (m), 698 (w).

1,2-Bis[(2-dimethylamino-2-oxo-1-phenylethylidene)hydrazino]ethane 10

To a suspension of **9** (1 mmol) in methanol (10 mL) was added formic acid (4.5 mmol) at room temperature. An equal amount (589 mg) of 10% palladium on charcoal was added and the reaction mixture was stirred for 2 h at room temperature. The mixture was filtered through a pad of Celite and the cake was washed with ethyl acetate. The solvents were evaporated and the residue was purified by chromatography on silica using a

mixture of ethyl acetate–acetone (19 : 1) as eluent. Compound **10** was crystallised from ethyl acetate (53%); mp 180 °C (Found: C, 64.71; H, 6.86; N, 20.59; O, 7.84. $C_{22}H_{28}N_6O_2$ requires C, 64.64; H, 6.91; N, 20.67; O, 7.94%); ^{1}H NMR ($CDCl_3$) δ 2.78 and 3.00 (2s, 12H, 2N(CH_3)$_2$), 3.48 (m, 4H, 2NCH_2CH_2), 5.95 (br s, 2H, 2N*H*), 7.14–7.32 and 7.43–7.48 (2m, 10H, C*H*ar); ^{13}C NMR ($CDCl_3$) δ 33.77 and 36.98 (4C, 2N(CH_3)$_2$), 50.30 (2NCH_2CH_2), 124.85, 128.24, 128.58 (10C *C*Har), 134.18 (2*C*ar), 141.65 (2*C*=N), 166.03 (2*C*=O); MS, *m*/*z* (%) 408 (6, M^+), 205 (29), 204 (27), 178 (13), 177 (100), 131 (30), 105 (12), 104 (52), 77 (14), 72 (52), 58 (21), 44 (10); IR/cm^{-1} (KBr) 3260 (w), 2928 (m), 1626 (vw), 1561 (m), 1483 (w), 1444 (m), 1395 (w), 1260 (m), 1181 (m), 1117 (w), 1052 (m), 728 (m), 701 (m).

1,2-Bis[(2-dimethylamino-2-thioxo-1-phenylethylidene)-hydrazino]ethane 3

To a solution of **10** (0.75 mmol) in benzene (3 mL) was added Lawesson's reagent (0.97 mmol) at room temperature. The reaction mixture was refluxed for 20 h and cooled to room temperature. The solvents were evaporated and the residue was purified by chromatography on silica using dichloromethane as eluent. Compound **3** was crystallised from diethyl ether (84%); mp 183 °C (Found: C, 59.92; H, 6.37; N, 19.21; S, 14.61. $C_{22}H_{28}N_6S_2$ requires C, 60.00; H, 6.36; N, 19.09; S, 14.55%); ^{1}H NMR ($CDCl_3$) δ 3.09 and 3.49 (2s, 12H, 2N(CH_3)$_2$), 3.53 (m, 4H, 2NCH_2CH_2), 5.70 (br s, 2H, 2N*H*), 7.28–7.31 and 7.56–7.59 (2m, 10H, C*H*ar); ^{13}C NMR ($CDCl_3$) δ 40.85 and 42.38 (4C, 2N(CH_3)$_2$), 50.51 (2NCH_2CH_2), 124.94, 128.19, 128.39 (10*C*Har), 133.95 (2*C*ar), 144.53 (2*C*=N), 193.35 (2*C*=S); MS, *m*/*z* (%) 440 (2, M^+), 249 (19), 248 (100), 221 (14), 220 (34), 219 (72), 193 (44), 192 (19), 191 (34), 176 (10), 149 (11), 145 (43), 131 (12), 121 (17), 104 (36), 103 (12), 90 (16), 89 (34), 88 (52), 77 (13), 44 (17), 42 (11); IR/cm^{-1} (KBr) 3240 (m), 1582 (m), 1554 (w), 1522 (vw), 1494 (m), 1475 (w), 1445 (m), 1406 (m), 1393 (w), 1324 (m), 1304 (m), 1263 (w), 1145 (vw), 1098 (w), 1028 (m), 941 (m), 759 (w), 690 (w).

1,2-Bis[(2-dimethylamino-2-thioxo-1-phenylethylidene)-hydrazino]ethane nickel(II) 4

To a solution of **3** (0.2 mmol) in chloroform (2 mL) was added $Ni(OAc)_2 \cdot 4H_2O$ (0.22 mmol) in methanol (5 mL) at room temperature. The reaction mixture was stirred for 2 h at room temperature and the brown precipitate was filtered and washed with methanol. Compound **4** was crystallised from a mixture of methanol–chloroform (79%); mp > 300 °C (Found: C, 53.18; H, 5.32; N, 17.08; S, 13.15. $C_{22}H_{26}N_6NiS_2$ requires C, 53.13; H, 5.27; N, 16.90; S, 12.89%); ^{1}H NMR ($CDCl_3$) δ 2.91 (s, 12H, 2N(CH_3)$_2$), 3.73 (s, 4H, 2NCH_2CH_2), 7.13 and 7.31 (2m, 10H, C*H*ar); ^{13}C NMR ($CDCl_3$) δ 45.45 (4C, 2N(CH_3)$_2$), 63.50 (2NCH_2CH_2), 125.36, 127.79, 128.39 (10C, *C*Har), 129.03 (2*C*ar), 142.02 (2*C*=N), 161.34 (2*C*=S); MS, *m*/*z* (%) 500 (11, $(M + 2)^{+\bullet}/^{60}$Ni), 499 (15, $(M + 1)^{+\bullet}/^{60}$Ni), 498 (54, $M^{+\bullet}/^{60}$Ni + $(M+2)^{+\bullet}/^{58}$Ni), 497 (28, $(M + 1)^{+\bullet}/^{58}$Ni), 496 (100, $M^{+\bullet}/^{58}$Ni), 470 (11), 468 (21), 367 (38), 366 (15), 365 (77), 338 (46), 279 (17), 278 (11), 277 (34), 252 (11), 251 (31), 250 (22), 249 (70), 248 (23), 236 (34), 235 (14), 234 (74), 225 (16), 223 (37), 221 (12), 219 (22), 192 (22), 179 (12), 161 (18), 149 (30), 148 (33), 147 (62), 146 (70), 145 (12), 144 (17), 131 (13), 121 (26), 104 (26), 103 (25), 101 (17), 89 (32), 88 (27), 77 (15), 58 (21), 44 (22); IR/cm^{-1} (KBr) 1136 (vw), 1066 (vw), 994 (w), 956 (m), 853 (m), 794 (m), 725 (m).

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References

1 E. Kimura, *Tetrahedron*, 1992, **48**, 6175.
2 (*a*) G. C. R. Ellis-Davies, *Tetrahedron Lett.*, 1998, **39**, 953; (*b*) P. L. Anelli, I. Bertini, M. Fragai, L. Lattuada, C. Luchinat and G. Parigi, *Eur. J. Inorg. Chem.*, 2000, **4**, 625; (*c*) W. C. Baker, M. Choi, D. C. Hill, J. Thompson and P. Petillo, *J. Org. Chem.*, 1999, **64**, 2683.
3 (*a*) A. Heppeler, S. Froidevaux, H. R. Mäcke, E. Jermann, M. Béhé, P. Powell and M. Hennig, *Chem. Eur. J.*, 1999, **5**, 1974; (*b*) W. A. Volkert and T. Hoffman, *Chem. Rev.*, 1999, **99**, 2269.
4 E. Benoist, G. Charbonnel-Jobic, C. Courseille, J. F. Gestin, J. L. Parrain, J. F. Chatal and J. P. Quintard, *New J. Chem.*, 1998, **20**, 615.
5 S. C. Tang, S. Koch, G. N. Weinstein, R. Lane and R. H. Holm, *Inorg. Chem.*, 1973, **12**, 2589.
6 (*a*) B. Adélaère, PhD Thesis, University of Nantes, 1989; (*b*) G. Charbonnel-Jobic, PhD Thesis, University of Nantes, 1994; (*c*) G. Charbonnel-Jobic, J. P. Guémas, B. Adélaère, J. L. Parrain and J. P. Quintard, *Bull. Soc. Chim. Fr.*, 1995, **132**, 624.
7 S. Jurisson and J. Lydon, *Chem. Rev.*, 1999, **99**, 2205.
8 M. J. Gil, A. Reliquet, F. Reliquet and J. C. Meslin, *Phosphorus, Sulfur Silicon Relat. Elem.*, 1994, **97**, 89.
9 J. D. Charrier, A. Reliquet and J. C. Meslin, *Tetrahedron Lett.*, 1998, **39**, 8645.
10 W. Sucrow, *Methodicum Chimicum*, ed. F. Korte, Georg Thieme Verlag, Stuttgart, Academic Press: New York, San Francisco, London, 1975, 6, p. 91.
11 H. Zimmer, L. F. Audrieth and R. A. Rowe, *J. Am. Chem. Soc.*, 1955, **77**, 790.
12 I. D. Entwistle, R. A. W. Johnstone and A. H. Wilby, *Tetrahedron*, 1982, **38**, 419.
13 **CAUTION!** Nitrosoamines and hydrazines are carcinogenic agents. Handle with care.
14 (*a*) M. F. Lipton, A. Basha and S. M. Weinreb, *Org. Synth.*, 1979, **59**, 49; (*b*) A. Basha, M. F. Lipton and S. M. Weinreb, *Tetrahedron Lett.*, 1977, **48**, 4171; (*c*) J. I. Levin, E. Turos and S. M. Weinreb, *Synth. Commun.*, 1982, **12**, 989.
15 B. D. Gray and P. W. Jeffs, *J. Chem. Soc., Chem. Commun.*, 1987, **18**, 1329.
16 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Wiley and Sons, New York, 5th edn., 1988, p. 1385.
17 G. Anderegg, in *Comprehensive Coordination Chemistry*, ed. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon Press, Oxford, 1987, vol. 2, p. 777.
18 M. Zehnder, C. Bolm, S. Schaffner, D. Kaufmann and J. Müller, *Liebigs Ann.*, 1995, 125.
19 1,2-Bis[(2-dimethylamino-2-thioxo-1-phenylethylidene)hydrazino]-propane **13**: mp 117 °C; ^{1}H NMR ($CDCl_3$) δ 1.93 (q, *J* 6.4, 2H), 3.06 and 3.49 (2s, 12H), 3.40 (t, *J* 6.4, 4H), 5. 83 (br s, 2H), 7.24–7.34 and 7.54–7.58 (2m, 10H); ^{13}C NMR ($CDCl_3$) δ 30.13, 40.76 and 42.15 (2C), 47.84 (2C), 124.70, 127.93, 128.30 (10C), 133.97 (2C), 143.40 (2C), 193.52 (2C); MS, *m*/*z* (%) 455 (7, $(M + 1)^+$), 263 (29), 262 (100), 261 (19), 249 (45), 246 (12), 245 (55), 234 (11), 220 (34), 219 (21), 218 (88), 207 (19), 206 (58), 205 (15), 194 (13), 193 (85), 192 (12), 191 (45), 178 (21), 177 (91), 176 (33), 149 (12), 148 (12), 145 (28), 144 (13), 135 (10), 134 (13), 131 (17), 130 (38), 122 (16), 121 (45), 104 (46), 103 (17), 91 (25), 90 (25), 89 (41), 88 (80), 77 (17), 74 (13), 71 (13), 58 (13), 56 (13), 44 (50), 42 (24); IR/cm^{-1} (KBr) 3242 (m), 2931 (w), 2856 (m), 1520 (vw), 1494 (m), 1445 (m), 1393 (w), 1319 (m), 1300 (m), 1261 (w), 1142 (vw), 1100 (s), 1074 (m), 1028 (m), 766 (m), 692 (w).