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The nickel, copper and zinc complexes of potentially heptadentate nitrogen–sulfur donor ligands

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ABSTRACT

The multidentate compound, tris-(*o*-^{t}butylthiobenzyl)-aminoethylamine (L^4), which contains four nitrogen and three sulfur donors has been synthesised by combining 2-amino-methyl-1,3-diamino-propane (tren) with *o*-^{t}butylthiobenzaldehyde. L^4 has been reacted with the nitrate salts of nickel, copper and zinc to give a series of $L^4M(NO_3)$ complexes which were crystallographically characterised. In all cases the metal binds to the N_4 motif proffered by the tren moiety. The nickel complex achieves a hexacoordinate geometry by ligating with a didentate (–O,O′) nitrate. Copper and zinc both produced five coordinate species by ligating with a unidentate nitrate. None of the species reported include the thio-ethers in the coordination sphere of the metal. Replacing nitrate with nitrite in the copper system allows the synthesis of a five coordinate unidentate, oxygen bound, nitrite complex. A number of unsuccessful attempts have been made, using Cd, Pb and Au, to assemble the three thioethers groups into a secondary coordination motif for metals. These reactions produce a series of L^4M–halide complexes which have again been crystallographically characterised.

1. Introduction

Reduced Schiff base ligands constructed from salicylaldehyde and tris(aminomethyl)-alkanes (L^1, L^2) or 2-aminomethyl-1,3-diamino-propane (L^3 Fig. 1) generate a wide range of metal complexes. With trivalent metals simple monometallic complexes form [1,2]. Divalent nickel with its preference for octahedral geometry allows the synthesis of elegant trimetallic species due to the charge imbalance between the metal and tri-anionic ligand [3–5]. Copper, however, with its preference for four coordinate planar geometry, forms intriguing open trimetallic and tetrametallic complexes and complex mixed octa-metallic species [2,6]. This intriguing range of complexes brought about by the imbalance in the preferred coordination number of the metal centre and the denticity of the ligand suggested that we should explore this motif further. An obvious and simple way of diversifying this system is to change the donor atoms from oxygen to sulfur (Fig. 1, L^2) [7].

Potentially hepta-dentate N_4S_3 donor species of this type are rare (Fig. 1). These have mainly employed sulfur containing heterocycles as the pendant donor group [8]. However, placing the peripheral donor atoms within an organic ring restricts the behaviour of the donor sites. This suggests that any attempt to increase the structural diversity of the family of N_4S_3 donor Schiff base ligands will be more successful if the donor atoms are removed from the constraining influence of a pendant heterocycle as is the case in the system reported by Kersting and Siedle (L^2, Fig. 1) [7]. A similar modification is reported here by replacing salicylaldehyde by *o*-^{t}butylthiobenzaldehyde (Fig. 1, L^4) in the primary Schiff base condensation reaction (Scheme 1). The subsequent reduction of the imine generates L^4.

Multidentate phenolate ligands such as tris(2-hydroxybenzylidene)aminoethylamine have been known for over 70 years [9]. In contrast the corresponding ligands with pendant thioether donors remain poorly reported. Research using these multidentate phenolate ligands has recently recommenced due to an interest in the magnetic properties of multimetallic complexes which commonly form [3,4]. In the belief that thioether species (Fig. 1) might have as rich and diverse chemistry as their parent phenolate ligands we have sought to identify simple routes into their synthesis. Previous studies have shown that the divalent metals cations such as nickel, copper and zinc generate a wide range of structural motifs with L^1 and L^3 (Fig. 1) [1–6]. As such, the combination of these metals with L^4 is explored in an attempt to unlock the behaviour of these N_4S_3 thioether species.

Abbreviations: tren, 2-aminomethyl-1,3-diamino-propane; (L^{4s}), tris-((*o*-^{t}butylthiobenzylidene)-aminoethylamine; (L^4), tris-(*o*-^{t}butylthiobenzyl)-aminoethyl amine.

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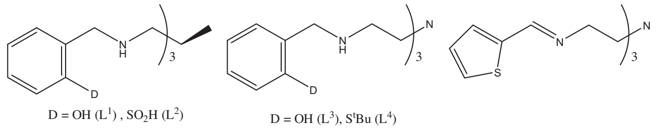


Fig. 1. The N_3O_3 (L^1), N_3S_3 (L^2) and N_4O_3 (L^3), multi-dentate ligands [1–6]. L^4 is the subject of this report.

2. Experimental

All experiments were carried out using standard apparatus and commercially available chemicals. NMR analysis was carried out on a Bruker AMX 400 operating at 400 MHz for ^1H for proton and 100 MHz for ^{13}C. Solid reflectance spectra (400–900 nm) were recorded on a Photonics CCD array UV–Vis spectrophotometer. Mass spectra were recorded in house on a Thermo Finnigan LCQ-Duo by electrospray ion trap (4.5 kW, 200 °C). Infra red spectra were recorded as potassium bromide discs using a Nicolet Avatar 360 FT–IR spectrometer. Elemental microanalysis was carried out in house on a Perkin Elmer 2400 CHN Analyser.

2.1. Synthesis of tris-((o-^{t}butylthiobenzylidene)-aminoethylamine (L^{4s})

2-Aminomethyl-1,3-diamino-propane (tren, 0. 75 g, 5.1 mmol) was mixed with *o*-^{t}butylthiobenzaldehyde (2.98 g, 15.3 mmol) in methanol (50 ml). The solution was refluxed for 1 h. The solution was allowed to cool and the methanol removed under vacuum to produce a yellow oil. The oil was resuspended in chloroform (50 ml), filtered and dried over anhydrous Na_2SO_4. The solution was filtered and the chloroform removed under vacuum to obtain a yellow oil which was used as received. Yield 75%, ^1H NMR (400 MHz, $CDCl_3$; δ): 9.1 (s, 1H, –HC=N); 8.0 (d, 1H, arom); 7.5 (d, 1H, arom); 7.5 (m, 2H, arom); 3.8 (t, 2H, $-CH_2-$); 3.0 (t, 2H, $-CH_2-$); 1.26 (s, 9H t-Bu), $^{13}C-\{^1H\}$ NMR (100 MHz, $CDCl_3$; δ): 162, 141, 139, 133, 130, 129, 127, 60, 55, 31. FTIR (KBr) ν/cm^{-1}: 1634 (C=N); 1460 (C=C); 758 (arom), MS (ESI, *m*/*e*): 675 (100%).

2.2. Synthesis of tris-(o-^{t}butylthiobenzyl)-aminoethylamine (L^4)

2-Aminomethyl-1,3-diamino-propane (tren, 2.25 g, 15.4 mmol) was mixed with *o*-^{t}butylthiobenzaldehyde (7.0 g, 43.2 mmol) in methanol (50 ml). The solution was refluxed for 1 h. The yellow solution was allowed to cool and then transferred to a 3-neck round bottom flask. $NaBH_4$ (3 g, 79 mmol) was added to the solution over a 1 h period under the blanket of nitrogen. The solution was allowed to stir overnight visibly becoming paler over this time period. The methanol was removed under reduced pressure to produce a pale yellow oil. An aqueous solution of ammonium acetate (3 g in 50 ml) was added to the oil and the mixture extract with chloroform (3 × 100 ml). The chloroform solution was dried over anhydrous Na_2SO_4, filtered and the solvent removed to give a pale yellow oil. Yield 81%. ^1H NMR (400 MHz, $CDCl_3$; δ): 7.5 (t, 1H, arom); 7.4 (d, 1H, arom); 7.3 (d, 1H, arom); 7.2 (d, 1H, arom); 4.0 (s, 2H, $-CH_2-$); 2.6 (t, 2H, $-CH_2-$); 2.5 (t, 2H, $-CH_2-$); 1.7 (s, 9H, $-CH_3$). $^{13}C-\{^1H\}$ NMR (100 MHz, $CDCl_3$; δ): 145, 139, 132, 130, 129, 126, 115, 54, 52, 47,46, 40. FTIR (KBr) ν/cm^{-1}: 2960 (NH), 1455 (C=C), 1360, 1165, 760 (arom). MS (ESI, *m*/*e*): 681 (100%),

2.3. The synthesis of nickel, copper and zinc nitrate complexes of tris-(o-^{t}butylthiobenzyl)-aminoethylamine

Equimolar amounts of metal nitrate (0.3 mmol) were mixed with L^4 (0.21 g, 0.3 mmol) in methanol (20 ml) containing 2-drops of triethylamine. The mixture was stirred for 15 min at 60 °C. The solvent was removed and the products recrystallised from dimethylformamide and diethyl-ether by vapour diffusion. Typical yields 50%.

2.3.1. [(L^4)NiO_2NO] NO_3

Anal. Calc. for $C_{39}H_{60}N_6NiO_6S_3 \cdot H_2O$: C, 53.12; H, 7.09; N, 9.52. Found: C, 53.62; H, 5.15; N, 9.60% FTIR (KBr) ν/cm^{-1} 2960, 1570, 1380, 1000, 760. MS (ESI, *m*/*e*): 737 (60%), 800 (100% L^4NiNO_3), λmax/nm (solid) 550, 900.

2.3.2. [(L^4)$CuONO_2$] NO_3

Anal. Calc. for $C_{39}H_{60}CuN_6O_6S_3$:DMF·$2H_2O$: C, 51.59; H, 7.32; N, 10.02. Found: C, 51.51; H, 6.83; N, 10.16%. FTIR (KBr) ν/cm^{-1} 2955, 1670, 1380, 1130, 615. MS (ESI, *m*/*e*): 742 (100% L^4Cu), λmax/nm (solid) 650 (shoulder), 850.

2.3.3. [(L^4)$ZnONO_2$] NO_3

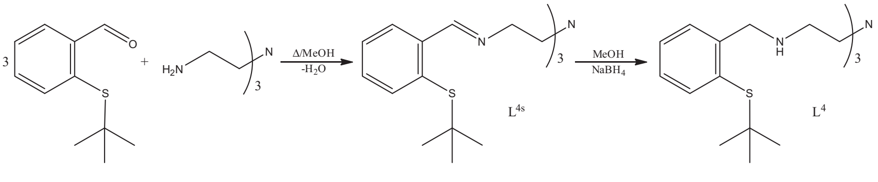
Anal. Calc. for $C_{39}H_{60}N_4S_3Zn.(NO_3)_2 \cdot C_3H_7NO$: C, 53.46; H, 7.16; N, 10.40. Found: C, 53.10; H, 7.20; N, 10.35%. FTIR (KBr) ν/cm^{-1}: 2966, 1483, 1368, 1170, 1023, 765. MS (ESI, *m*/*e*): 806 (100% $L^{4-}ZnNO_3^{+}$). λmax/nm (solid) 380.

2.4. The synthesis of [L^4CuBr] Br

Copper bromide (0.062 g, 0.278 mmol) was mixed with L^4 (0.20 g, 0.30 mmol) in methanol (50 ml) and stirred for 1 h. The product was filtered through anhydrous Na_2SO_4 and the solvent removed under reduced pressure. The product was recrystallised from methanol and diethyl-ether by vapour diffusion. *Anal.* Calc. for $C_{39}H_{60}N_4S_3CuBr_2$: C, 51.78; H, 6.69; N, 6.20. Found: C, 50.93; H, 6.39; N, 5.73%. FTIR (KBr) ν/cm^{-1} 3154, 2965, 1639, 1472, 1363, 1285, 1168, 1089, 998, 763, 518. MS (ESI, *m*/*e*): 824 (100% $L^{4-}CuBr^{+1}$), λmax/nm (solid) 380, 703, 800.

2.5. The synthesis of [L^4CuNCS] SCN

Copper nitrate (0.29 g, 1.24 mmol) was mixed with sodium thiocyanate (0.22 g, 2.67 mmol) in ethanol (50 ml) and stirred for 45 min. The precipitate from this solution was collected, washed with ethanol and dried. 0.05 g of the product was mixed with L_4 (0.21 g, 0.31 mmol) in methanol (50 ml) and the solution stirred for 1 h. The product was filtered through anhydrous Na_2SO_4 and the solvent removed under reduced pressure. The product was recrystallised from methanol and diethyl-ether by vapour diffusion. *Anal.* Calc. for $C_{41}H_{60}N_5S_5Cu.2H_2O$: C, 54.92; H, 7.20; N, 9.38. Found: C, 54.56; H, 7.04; N, 8.67%. FTIR (KBr) ν/cm^{-1} 3162,



Scheme 1.