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Functionalised dithiocarbamate complexes: Complexes based on indoline, indole and substituted piperazine backbones – X-ray crystal structure of [Ni($S_2CNC_3H_6C_6H_4$)$_2$]

Charalampos Anastasiadis [a], Graeme Hogarth [a,*], James D.E.T. Wilton-Ely [b]

[a] Department of Chemistry, University College London, 20 Gordon Street, London WC1H OAJ, UK
[b] Department of Chemistry, Imperial College London, South Kensington Campus, London SW7 2AZ, UK

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ABSTRACT

A range of new nickel, copper and zinc bis(dithiocarbamate) complexes has been prepared from secondary amines with functionalised backbones. These include complexes derived from iso-indoline, tetrahydro-isoindoline, 1,2,3,4-tetrahydroisoquinoline and a number of functionalised piperazines. The crystal structure of [Ni($S_2CNC_3H_6C_6H_4$)$_2$] derived from 1,2,3,4-tetrahydroisoquinoline is reported.

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1. Introduction

Dithiocarbamates are versatile ligands which have been shown to bind to all the transition elements supporting a wide range of oxidation states [1]. However, while dithiocarbamate complexes have been known for over a century, with many thousands having been prepared, the vast majority of these contain only simple alkyl substituents such as methyl and ethyl. A developing interest in the area of dithiocarbamate chemistry is the functionalization of the backbone such that new applications and interactions can be developed. This area is still in its early stages but already interesting potential applications have been noted including the functionalization of gold nanoparticles [2–7], the stepwise build-up of multimetallic arrays [5–10], the synthesis of dithiocarbamate-containing supramolecular systems which can be used for anion binding [11–17], the development of technetium radiopharmaceuticals [18–22] and efficient chelators for the treatment of acute cadmium intoxication [23–25].

In this contribution we extend some of our recent work in the area of functionalized dithiocarbamate complexes [26,27] and report the synthesis of some simple homoleptic dithiocarbamate complexes based on iso-indoline, iso-indole and functionalized 1-piperazine backbones. The aim of the work was initially to see if it was possible to prepare such complexes easy and efficiently, and then we hoped to investigate structural characteristics such as hydrogen-bonding, secondary amine coordination and $\pi-\pi$ stacking using X-ray crystallography. We herein report that while such complexes are easy and efficiently prepared, the generation of high quality single crystals required for X-ray crystallography is much more of a challenge.

2. Results and discussion

Eight amines were utilised in this study (Chart 1). Tetrahydro-iso-quinoline (**A**) and the substituted piperazines (**E**–**G**) were purchased and used as supplied. Tetrahydro-isoindoline (**B**) [28] and isoindoline (**C**) [29] were prepared from the respective phthalimides upon reduction with $LiAlH_4$ and $BH_3{\cdot}thf$ respectively, while iso-indole was also prepared from o-xylene dibromide *via* the sulphonamide [30] (Scheme 1). Better yields were obtained by this latter route although the extra step makes it more time-consuming. 1-p-Tolylpiperazine (**D**) [31] was easily prepared as an ammonium salt upon heating bis(2-chloroethyl)amine [32] and p-toluidene in diglyme for 24 h, and diamine (**H**) [33] was similarly prepared from p-phenylenediamine (Scheme 2).

Dithiocarbamate salts of amines **A**–**G** were easily prepared upon slow addition of carbon disulfide to a methanol solution of equimolar amounts of KOH and the respective amine. No attempt was made to isolate or characterise these salts. Rather, addition of

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* Corresponding author.
E-mail address: g.hogarth@ucl.ac.uk (G. Hogarth).

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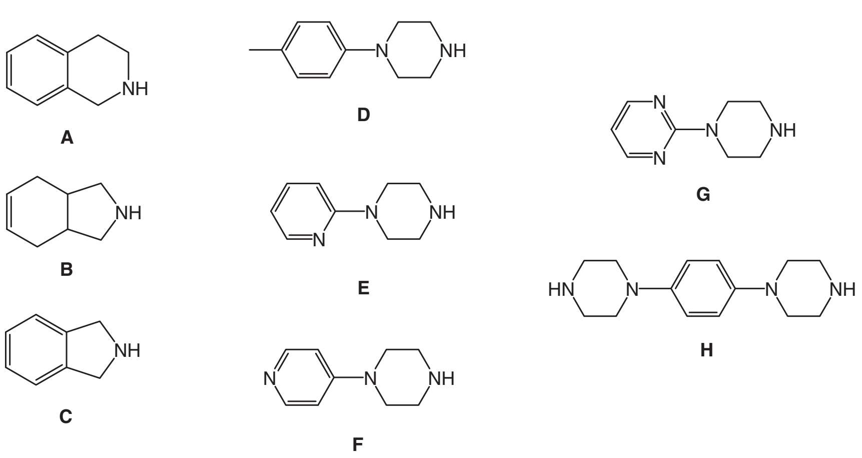
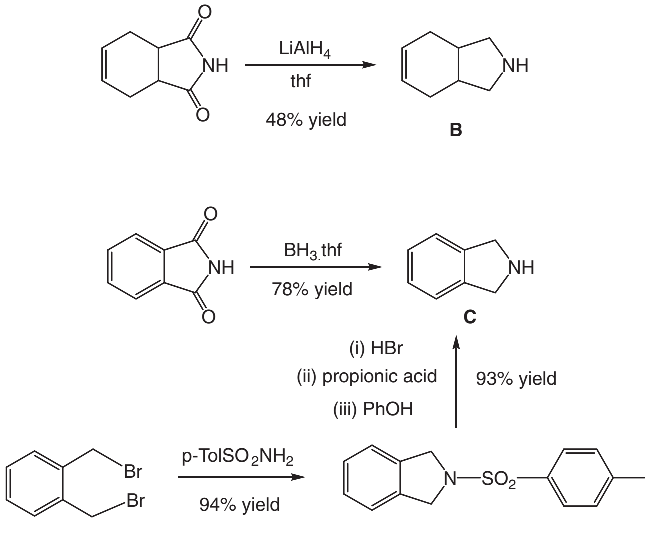


Chart 1.

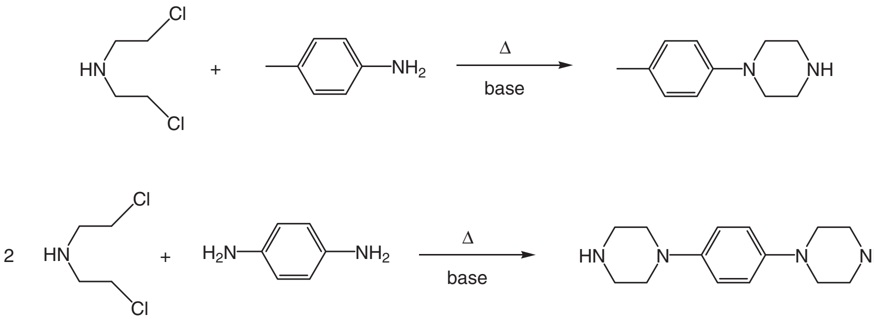


Scheme 1. Synthesis of tetrahydro-iso-indoline and iso-indoline.

the metal(II) acetates (M = Ni, Cu, Zn) resulted in the clean formation of the bis(dithiocarbamate) complexes which were isolated by filtration (Chart 2). Yields were typically between 50–90% and in general isolation and purification were straightforward. All complexes were characterised by IR spectroscopy and the majority gave satisfactory elemental analyses. We had hoped to look at the solid-state structures of many of these complexes in some detail in order to probe packing and intermolecular interactions but the recrystallisation of almost all proved problematic. For many, solubility in common organic solvents was poor. This was especially the case for complexes derived from isoindoline (**3**) and 4-pyridylpiperazine (**7**). This can be an issue with dithiocarbamate salts derived from dimethylamine, but generally as the backbone are extended solubility increases markedly [1]. The poor solubility of the majority of these complexes most likely relates to the very intermolecular interactions we had hoped to probe. A second issue was that many of the samples gave only very thin plates upon recrystallisation and these proved to be unsuitable for X-ray crystallography. We were able to obtain suitably sized single crystals of **1a**, the nickel complex derived from tetrahydro-isoquinoline and the results of this study are summarised in Fig. 1.

The complex is similar to other structurally characterised nickel bis(dithiocarbamate)complexes [1]. The metal atom lies on an inversion centre and is bound by two dithiocarbamate ligands in a square-planar array, the bite-angle of 79.02(5)° being typical. Thirteen atoms lie approximately in a plane and then the molecule folds about the C(2)–C(10) vector. The molecules pack in a herring-bone-type manner (Fig. 2) and there are a series of short intermolecular interactions. Most notable is the π-stacking of the arene components the distance between ring centroids being 3.659 Å with the shortest carbon–carbon contact of 3.350 Å between C(4) and C(6A). Other short intermolecular contacts include; S(1)–H(7A) 2.968 Å, C(7)–H(3A) 2.798 Å, C(1)–H(6A) 2.850 Å and H(2B)–H(2B′) 2.388 Å. While a number of tetrahydro-isoquinoline derived dithiocarbamate complexes have previously been reported [34–37] this is the first to be crystallographically characterised.

The nickel and zinc complexes, when sufficiently soluble in $CDCl_3$ or other commonly available deuterated solvents, were characterised by ^1H NMR spectroscopy. The spectrum of **1a** confirmed that the solid-state structure was maintained in solution. Together with a multiplet in the aromatic region there were three signals of equal intensity in the aliphatic region. A singlet at δ 4.86



Scheme 2. Synthesis of functionalised piperazines.

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