Metal-mediated Conversion of a 5-Aminothiatriazole into a 5-Mercaptotetrazolyl Ligand by Reaction with a Solid Metal Hydroxide: Synthesis and Crystal Structure of [NaphthylN·N=N·N–C(–S)]$_2$Ba·3HMPA

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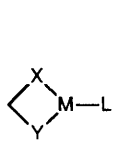
Solid $Ba(OH)_2$ suspended in toluene containing HMPA [$O=P(NMe_2)_3$] reacts with the 5-aminothiatriazole, naphthylNH·C=N·N=N·S, to give the monomeric 5-mercaptotetrazolylbarium complex, [naphthylN·N=N·N–C(–S)]$_2$Ba·3HMPA, **1**; the isolation and structural characterisation of **1** sheds new light on the known alkali-promoted rearrangement of 5-amino-substituted thiatriazoles into 5-thio-substituted tetrazoles.

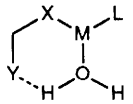
Recently we described the syntheses and structures of several alkali (Li, Na) and alkaline earth (Ca, Sr, Ba) metal complexes of types $(Y–R–X)_nM·xL$ and $(Y–R–X)_nM·xL·yH_2O$ (**A** and **B**, respectively; shown for $n = 1$, $x = 1$, $y = 1$).[1] In these, the anion $(Y–R–X)^-$ contains two electronegative centres (X and Y, combinations of N, O, S), *e.g.* as in 2-mercaptobenzoxazolyl $[C_6H_4O·C(–S)–N]^-$ (OxS^-; X = N, Y = S), and L is a neutral Lewis base, *e.g.* HMPA [$O=P(NMe_2)_3$]. The aqua complexes are made either (*i*) indirectly, by adding H_2O to a toluene solution of the anhydrous complex (itself made by metallating the organic acid Y–R–XH using the metal or its hydride),[1a,b] or (*ii*) directly, assembling the required H_2O by reacting the solid metal hydroxide with a solution of Y–R–XH.[1c] Key structural features are that X and Y chelate M^{n+} in the anhydrous complexes (**A**), but that in the aqua complexes (**B**), H_2O coordination to M^{n+} displaces one of these centres (say, Y) which in turn stabilises the H_2O by hydrogen bonding to it. These features implied that metal salts ($^{\delta+}M'Z_n{}^{\delta-}$) might, like $^{\delta+}H_2O^{\delta-}$, be captured by such displaceable side-arm chelate complexes to give species such as **C**. This idea was confirmed recently by reactions of $(OxS)_2Ca·2HMPA$ solutions with solid $PtCl_2$ or $HgCl_2$; these give the mixed-metal cocomplexes $[(HMPA)_3Ca·(\mu_2\text{-}Cl)_3·Ca(HMPA)_3]^+·[Pt(OxS)_4·CaCl]^-$,[2a] and $[(OxS)CaCl·2HMPA]_2·(OxS)_2Ca·(HgCl_2)_2$,[2b] respectively.

With the eventual aim of exploring the selectivity of chelate complexes towards capture of specific metal salts, it was decided to metallate organic acids of type R–NH–Y in which Y is a *group* (rather than a single atom, as in OxSH *etc.*) containing several potential donor atoms. One such amine examined was 5-(1-naphthylamino)-1,2,3,4-thiatriazole, naphthylNH·C=N–N=N–S, **I**. Thus, it was envisaged that S or one of the heterocyclic N atoms would join the *exo*-amido N atom in chelating to the inserted metal M, leaving N centres, with or without the sole S centre, available to coordinate to any subsequently added metal salt, $M'Z_n$. In fact, however, metallation [using solid $Ba(OH)_2$] causes a rearrangement of the organic ligand to deprotonated forms of a mercaptotetrazole, naphthylN·N=N·N=C(SH) **IIA** or naphthylN·N=N·NH·C(=S) **IIB**.

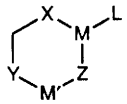
Solid $Ba(OH)_2$ dissolves in a hot solution of the 5-aminothiatriazole **I** in toluene containing HMPA. Cooling of the



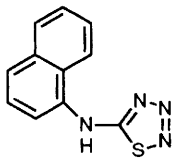
A



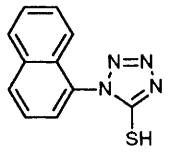
B



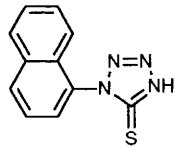
C



I



IIA



IIB

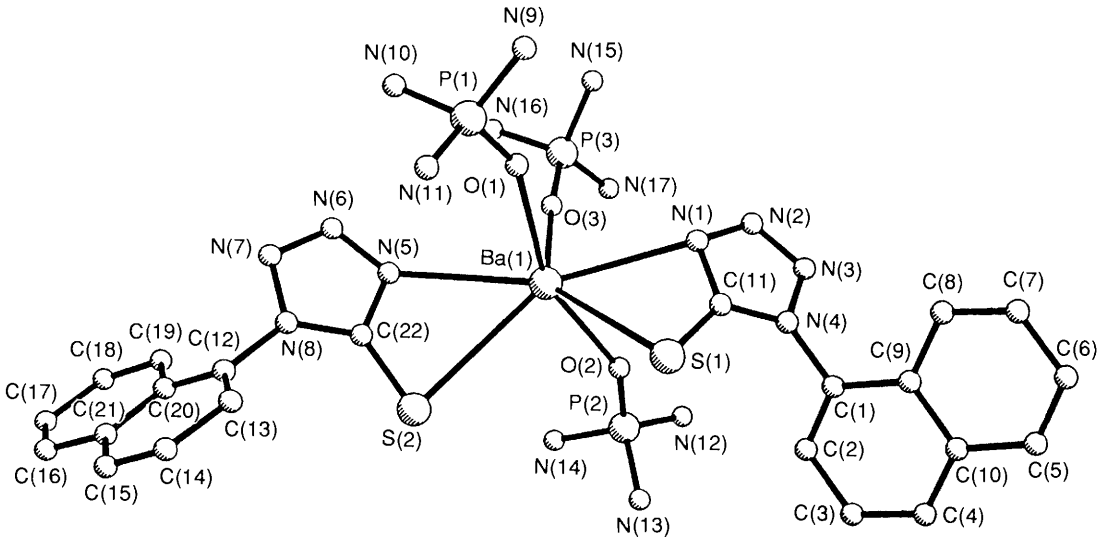
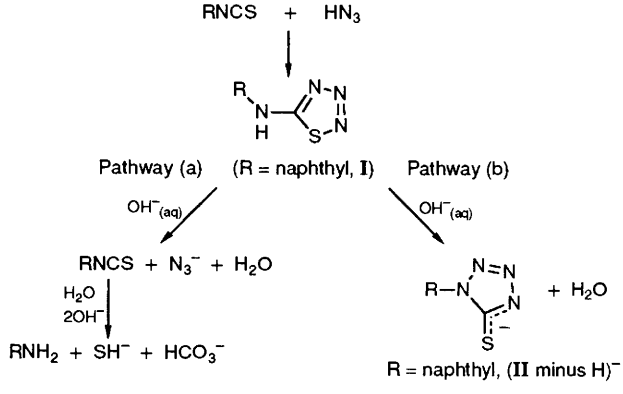


Fig. 1 The molecular structure of **1** showing the atom numbering scheme. Hydrogen atoms on the naphthyl and methyl groups on the HMPA ligands have been omitted for clarity.

resulting orange solution affords crystals of [naphthylN·N=N·N=C(–S)]$_2$Ba·3HMPA, **1**, in high yield.† An X-ray diffraction study‡ on **1** reveals (Fig. 1) that **I** has rearranged on deprotonation such that the Ba^{2+} centre in the monomeric complex is coordinated by two mercaptotetrazolyl anions, (**II** – H)$^-$. Thus, in each anion, the original *exo*-amino nitrogen (N-4 in **I**) becomes part of a tetrazole ring, and S is displaced from the original thiatriazole ring; the Ba^{2+} cation is then chelated by this *exo*-S centre [mean Ba–S distance, 3.31(2) Å] and by an N atom [N-1 in **II**, *i.e.* one of the N atoms of the original ring; mean Ba–N distance, 2.86(1) Å]. Sevenfold coordination of the Ba^{2+} is then completed by three HMPA ligands [mean Ba–O distance, 2.59(1) Å]. Presumably it is the presence of these strongly coordinating ligands which prevents incorporation of H_2O molecules (two of which, per Ba^{2+}, are assembled during the synthesis of **1**); their bulk may also explain the marked twisting of the anionic ligands relative to each other.

† **1**: Solid $Ba(OH)_2$ [0.428 g, 2.5 mmol] was added under nitrogen to a solution of 5-(1-naphthylamino)-1,2,3,4-thiatriazole (1.140 g, 5.0 mmol) in toluene (10 ml) containing HMPA (1.343 g, 7.5 mmol). Heating at 90 °C for 18 h caused dissolution of the $Ba(OH)_2$ to give an orange solution and a small amount of a yellow solid. Filtration, then refrigeration of the clear orange filtrate gave crystals of **1**; these contain one toluene solvate molecule per structural formula unit. First batch yield, 1.50 49% (more prolonged refrigeration of the filtrate gave a further 0.30 g of crystals, taking the total isolable yield of **1** to 59%); m.p. 103–106 °C; satisfactory analyses were obtained for **1**·toluene. ^{1}H NMR (250 MHz, CD_3CN, 25 °C) δ 8.10–7.10 (m, 19H, 2 naphthyl + C_6H_5·Me), 2.57 (d, 54H of 3HMPA), 2.33 (s, 3H, C_6H_5·*Me*).

‡ *Crystal data* for **1**·toluene: [$C_{10}H_7$N·N=N·N=C(–S)]$_2$Ba·3[O = P(NMe$_2$)$_3$]·C_7H_8:$C_{40}H_{68}BaN_{17}O_3P_3S_2$·$C_7H_8$, M = 1221.61, triclinic, space group $P\bar{1}$ (No. 2), a = 11.563(6), b = 14.412(8), c = 19.069(11) Å, α = 76.78(4), β = 82.37(4), γ = 75.60(3)°, U = 2987(2) Å^3, T = 150 K, Z = 2, D_c = 1.358 g cm^{-3}, F(000) = 1268, λ(Mo-Kα) = 0.71073 Å, μ(Mo-Kα) = 8.69 cm^{-1}, 8205 reflections collected on a Stoe four-circle diffractometer in range $7 \leq 2\theta \leq 45°$. Structure solved by a combination of direct methods and Fourier difference techniques, and refined by full-matrix least-squares analysis (all non-hydrogen atoms anisotropic; methyl and aromatic H-atoms placed in idealised positions; disordered toluene solvent refined with partial occupancies and a common isotropic thermal parameter) to R = 0.091 for 4757 unique reflections [$F > 4\sigma(F)$]. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



Scheme 1

Aspects of the rearrangement of **I** to **II** have been reported before.[3–5] In the most comprehensive study,[4] it was shown that 5-amino-1,2,3,4-thiatriazoles, made by reactions of isothiocyanates with hydrazoic acid, react with aqueous NaOH solution along two competitive deprotonation pathways (see Scheme 1): (a) degradation to isothiocyanate and azide, followed by base hydrolysis of the former to an amine, and (b) isomerisation to a mercaptotetrazolyl anion.

However, these reactions were carried out using an *excess of aqueous* alkali. Under these conditions, pathway (a) and its subsequent step dominate, such that yields of 5-mercaptotetrazoles [obtained by acidification after step (b)] were only 20–35%. In contrast, in making **1** only *one* equivalent of OH$^-$ was provided per equivalent of the aminothiatriazole, and furthermore a *solid* hydroxide was employed. The lack of an excess of OH$^-$ discriminates against pathway (a) and its subsequent hydrolysis step (Scheme 1) and favours pathway (b), so giving high yields of **1**. This point is underlined by the fact that reaction of **I** and HMPA in toluene with Sr metal (*i.e.* avoiding OH$^-$ altogether) affords crystals of (**II**–H)$_2^-$·Sr^{2+}·3HMPA—presumably isostructural with **1**—in 80% yield.

There is a further difference between these two preparative methodologies (use of an excess of aqueous metal hydroxide *vs.* use of stoichiometric amounts of a Lewis base donor and a solid metallating agent), and it concerns the actual role of the *metal ion* and its accompanying ligands in determining the course of reactions such as these. Selection of a large cation

(Ba^{2+}) and provision of stoichiometric amounts of a large and strongly coordinating ligand (three equivalents of HMPA) favours strongly the formation of the mercaptotetrazole form of the anion, $(\mathbf{II}-H)^-$, over the aminothiatriazole form, $(\mathbf{I}-H)^-$. Thus, the effect of ligand rearrangement has been to distance the naphthyl group from the chelation system [$(N1\cdots C\cdots S)^-$ in $(\mathbf{II}-H)^-$]. This allows Ba^{2+} to attach three HMPA ligands and to be contacted to the anion, hence affording **1**. Without such ligand reorganisation, NCS^- chelation [by $(N4\cdots C\cdots S)^-$ in $(\mathbf{I}-H)^-$] to a $Ba(HMPA)_3^{2+}$ fragment would be sterically impossible; either fewer HMPA ligands could have attached to Ba^{2+} and/or a looser ion-separated species would have been formed, *i.e.* there are knock-on electronic effects also. The use of Na^+ and (excess) H_2O ligands is probably less discriminating in these respects. A small $Na(H_2O)_x^+$ fragment (*e.g.* with $x = 2$) might be able to contact the NCS^- unit in either $(\mathbf{I}-H)^-$ or $(\mathbf{II}-H)^-$. More likely, given the high concentration of H_2O ligands, a $Na(H_2O)_6^+$ fragment would form, and be ion-separated from the anion; *which* anion then depends only on the relative electronic stabilities of the two forms, and any metal/ligand-based discrimination is lost.

The above findings illustrate an important consideration in alkali-promoted reactions (especially rearrangements) of organic compounds: that the overall relative stabilities of systems containing isomeric organic anions are not just a function of electronic stabilisation within the anions. Such stabilities depend also on the size of the counter-cation, the size and number of neutral ligands complexing this cation, and the thermodynamic strength of such complexation. These factors are in turn decided by the preparative method used. A key implication of this current work is that many deprotonations of organics may be better (or differently) achieved by use of stoichiometric amounts of solid metal hydroxides suspended in toluene containing limited amounts of a Lewis base, rather than by use of an excess of metal hydroxide aqueous solutions.

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