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An amidine-functionalized cobalt(III) cage complex: synthesis, structure and properties

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The template synthesis, structure and properties of an unusual tricyclic amidine-functionalized triaza-trithia cobalt(III) cage complex are described.

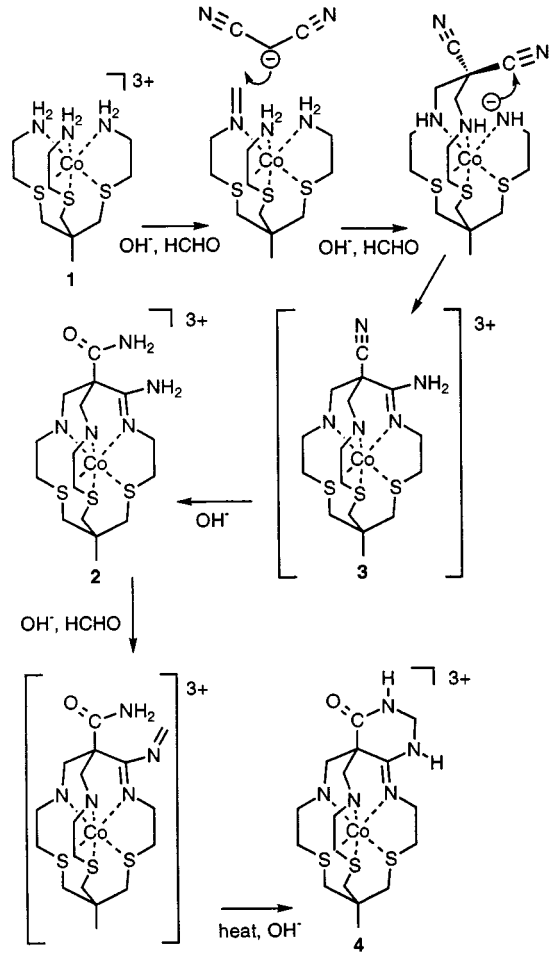
Functionalized cages have been prepared previously by condensing the templates $[Co(sen)]^{3+}$ [sen = 4,4′,4″-ethylidynetris(3-azabutan-1-amine)] and $[Co(ten)]^{3+}$ [ten = 4,4′,4″-ethylidynetris(3-thiabutan-1-amine)] with methanal and a carbon acid containing either an aldehyde, a ketone or an ester functional group. In the first two instances, condensation between the functional group and a coordinated amine resulted in the formation of a cage complex with an imine incorporated in the ligand framework whereas an amide-functionalized cage resulted when an ester was used.[1–3] Malononitrile (pK_a = 11)[4] is used here as a bifunctional carbon acid to form amidine-functionalized cobalt(III) cage complexes with three nitrogen and three sulfur donor atoms, the first example of a cage complex incorporating that functional group. The condensation of a coordinated amine with a pendant nitrile to form a coordinated amidine has not previously been applied to cage synthesis. These functionalized cage complexes are important because variations in functional groups and substituents, as well as in donor atoms, modulate substantially the physical properties of these complexes.[2,6,7]

Two red cage complexes were isolated by ion-exchange chromatography from the reaction of $[Co(ten)]Cl(ClO_4)_2$[2,8] and malononitrile in aqueous methanal at pH 10.† The first red species was assigned as an N_3S_3 amidine cage with an amide group as an apical substituent {$[Co(Me,H_2NCO\text{-}7\text{-amino}\ N_3S_3sar\text{-}6\text{-ene})]^{3+}$} (Scheme 1, **2**) using ^1H and ^{13}C NMR spectra recorded in DMSO-d_6 and microanalytical data; the same molecule was then prepared using 2-cyanoacetamide instead of malononitrile as the carbon acid.[9] The ^{13}C NMR spectrum of the second species showed that it contained two sp^2 functional groups (δ 162, 164), one of which might have been an amidine but the other could not be identified with certainty. Its surprising structure was revealed by an X-ray crystallographic analysis of the perchlorate salt and is shown in Fig. 1.‡ The ^1H and ^{13}C NMR spectra and the microanalysis of the whole fraction were consistent with this structure.§

The X-ray analysis established that the cobalt(III) ion was fully encapsulated in a pseudo-octahedral environment and that an amidine functional group was incorporated into the cage framework. The conformation of the strand containing the amidine functional group was *ob* while that of the other strands was characteristically *lel*.[10] The carbon–nitrogen bond lengths in the amidine group {C(2)–N(1) 1.915, C(2)–N(5) 1.318 Å} are comparable with those reported for other secondary amidines chelated to cobalt(III) and so is the cobalt(III)–amidine nitrogen bond length (1.915 Å).[5] An unusual feature of this cage is the structure of the cap. The amidine and amide functional groups have been cross-linked with a methylene group to form a near-planar diazine heterocycle fused to the cap as a subsidiary feature which is surprisingly stable to hydrolysis.

A mechanism for the formation of the cage complex is described in Scheme 1. The initial product (not detected) has to be an amidine cage with a nitrile substituent at the apex (Scheme 1, **3**). Clearly the nitrile group undergoes rapid intermolecular hydrolysis to give the amidine cage complex with an apical amide substituent (Scheme 1, **2**). This degree of activation of a remote functional group towards intermolecular attack is unusual. In amide cage complexes of cobalt(III), in which the cage ligand is deprotonated and bonded at the amide nitrogen, nitrile substituents are inert.[3] Similarly in monodentate cobalt(III) complexes of ligands containing a remote nitrile group and coordinated through nitrile, amide or amidine groups, no intermolecular hydrolysis of the remote functional group has been observed under basic conditions.[11] Here, the facile hydrolysis of the apical nitrile group reflects the attachment of this section of the neutral cage ligand to cobalt(III) through *three* chelate rings, thus maximizing its activation by the metal ion.

In the final stage of the synthesis methanal has added to the *exo*-nitrogen of the amidine in aqueous base and the resulting



Scheme 1

imine is attacked by the neighbouring deprotonated amide so that the groups were cross-linked to complete the heterocyclic ring. Aldehydes readily and reversibly add to amidines,[12] and this was doubtless facilitated in the present case by the increased acidity of the amidine coordinated to cobalt(III).[5] Such cross-linking between nitrogenous functional groups is a well known reaction when proteins and peptides are treated with aqueous methanal and a variety of functional groups may be connected in this way.[13] The heterocyclic cage was also synthesized directly from the amide-substituted amidine cage (**2**) and aqueous methanal but only at 60 °C or higher. At ambient temperature only a dimeric species was detected, formed by intramolecular cross-linking between two amidine functional groups. In the original synthesis the heat necessary for intramolecular cross-linking was produced by polymerization of malononitrile in aqueous base, a rapid, exothermic reaction which occurred in parallel with cage formation.

In the electronic spectrum of the heterocyclic amidine cage complex, bands arising from the d–d transitions were found at 496 and 363 (shoulder) nm (ε = 720 and 815 dm^3 mol^{-1} cm^{-1}, respectively). These were intermediate in energy and intensity between those of triamine and amide-functionalized N_3S_3 cage complexes.[2,7b] The UV region of the spectrum contained two intense bands at 288 and 210 nm (ε = 140 00 and 20 000 dm^3 mol^{-1} cm^{-1}, respectively). These are attributed to S→Co charge transfer bands. These low-spin Co$^{III/II}$ molecules should display rapid electron transfer characteristics and the chemistry in general points to useful paths for tying other functional groups and sensors to the cage complex.

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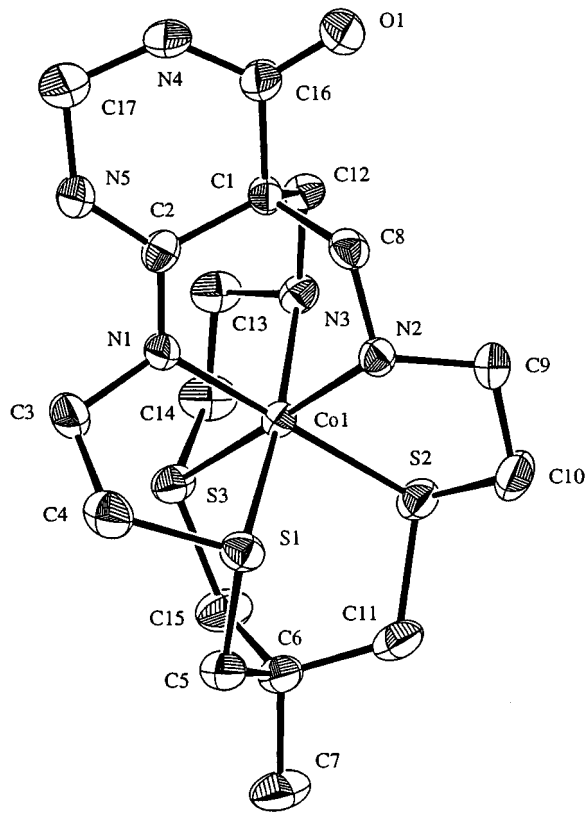

Fig. 1 ORTEP plot of the tricyclic amidine-functionalized N_3S_3 cage complex cation (the hydrogens attached to carbon and nitrogen atoms have been omitted for clarity).

Notes and references

† [Co(ten)]Cl(ClO$_4$)$_2$ (1.0 g) and malononitrile (5 mL) were dissolved in aqueous methanal (38%, 30 mL) in a 750 mL beaker in a fumehood and gradually treated with Na_2CO_3 (0.5 g). There was considerable effervescence and the solution became quite hot. After 30 min the reaction was quenched with acetic acid to pH 5 and water (200 mL) was added. The mixture was extracted with chloroform to remove excess polymeric material, then the aqueous phase was filtered and absorbed on Dowex 50W-X2 cation exchange resin. The column was washed with water then eluted with 2 M HCl which removed some Co^{II} species, ten·3HCl and some non-encapsulated by-products. Elution with 3 M HCl removed a large tripositive red band which was evaporated to dryness, dissolved in water (300 mL) and chromatographed on SP-Sepahadex cation exchange resin. The column was eluted with 0.1 M K_2SO_4 solution which separated trace amounts of the addition products then two red bands which were collected and desalted separately by chromatography on Dowex and elution with 3 M HCl followed by rotary evaporation. The first complex was recrystallized as the chloride–tetrachlorozincate salt {7-amino-8-carboxamide-1-methyl-3,13,16-trithia-6,10,19-triazabicyclo[6.6.6]icosa-6-enecobalt(III) chloride-tetrachlorozincate hydrate}, 0.22 g, 17% yield {^{1}H NMR (δ, DMSO-d^6): 1.30 (3H), CH_3; 2.50–4.05, complex methylene envelope; 7.35, 7.51, amine NH; 7.66, 7.83, amide NH_2; 8.12, 8,64, amidine NH_2}. The second complex (Scheme 1, **4**) was crystallized from aqueous sodium perchlorate solution with ethanol (0.20 g, 14% yield). **CAUTION**: perchlorate salts are potentially explosive and should only be handled in small quantities.

‡ *Crystal data*: $CoC_{17}H_{33}N_5O_{14}S_3Cl_3$; M = 792.95, monoclinic, space group $P2_1/c$ (no. 14), a = 12.931(2), b = 10.404(2), c = 21.463(4) Å, β = 99.65(1)°, U = 2846.6(8) Å^3, T = 23 ± 1 °C, Z = 4, μ(Mo-Kα) = 11.81 cm^{-1}, 7086 reflections measured (Philips PW1100/20 diffractometer), 6908 unique (R_{int} = 0.018) and 4290 > 3σ. The final R was 0.042. One of the anions is disordered. CCDC 182/1392. See http://www.rsc.org/suppdata/cc/1999/1975/ for crystallographic files in .cif format.

§ ^{1}H NMR spectrum (δ, DMSO-d_6): 1.28 (3H, CH_3), 2.9–3.85 (complex methylene envelope), 4.66 (m, NCH_2N), 7.44 (1H), 7.58 (1H) (amine NH), 9.22 (1H), 9.53 (1H), (amide and amidine NH). ^{13}C NMR spectrum (δ, DMSO-d_6): 28.8 (CH_3), 35.9, 37.3, 38.2, 38.4, 42.1 (2C) (CH_2S), 41.8 ($C_{q(S)}$); 50.1, 51.5, 51.6, 51.7, 52.5, 52.9, 53.2 (CH_2N, $C_{q(N)}$); 162.3, 164.1 (HNC=N, O=CNH).

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