

Synthesis and properties of cobalt(III) complexes of tripodal ligands containing amide functional groups

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Two new, trigonally symmetrical, triamide tripodal ligands and their complexes with the cobalt(III) ion, [1,1,1-tris(4-amino-1-oxo-2-azabutyl)ethanato]cobalt(III) trihydrate **1** and [1,1,1-tris(4-amino-4-methyl-3-oxo-2-azapentyl)ethanato]cobalt(III)–water–ethanol (1/8/0.5) **2** have been prepared. The hexadentate structures of the neutral, trigonal, triamido complexes have been established by an X-ray study of **1** and ¹³C NMR spectrometry of both molecules. The chemical, spectroscopic and electrochemical properties of the complexes have been investigated as well as those of the monoamido tripodal complex [1,9-diamino-5-(4-amino-2-azabutyl)-5-ethoxycarbonyl-4-oxo-3,7-diazanonanato]cobalt(III) chloride.

Introduction

Varieties of tripodal ligands exist and most form stable complexes with various transition metal ions.¹ In fact, these complexes are capable of displaying high thermodynamic stability, kinetic inertness and unusual co-ordination modes. A typical example of a tripodal ligand is sen [1,1,1-tris(4-amino-2-azabutyl)ethane].²⁻⁴ The cobalt(III) complex of this ligand has been studied³⁻⁵ and it is a precursor to some interesting macrobicyclic cage complexes.^{6,7} Also, a range of different metal complexes with this ligand has been reported and the structure of the nickel(II) ion, [Ni^{II}(sen)]²⁺, has been described.⁸ Lions and co-workers^{1,2} pointed the way to the rich chemistry and stability of such molecules in the 1950s and 1960s. Since then numerous hexamine tripodal ligands and their complexes have been reported,⁹ including tripods with either 2-pyridylmethyl¹⁰ or 3-aminopropyl¹¹ arms. Furthermore, the quaternary cap carbon can be replaced by a tertiary amine atom.¹²⁻¹⁴ Also other analogues exist where donor atoms such as S¹⁵⁻¹⁸ and O¹⁴ have been substituted for some or all of the amines within the ligand. Varying the nature of the donor atoms produces ligands whose complexes have different cavity sizes and physical and chemical properties. Despite the wide variation among tripodal ligands there seem to be few examples containing amide groups.

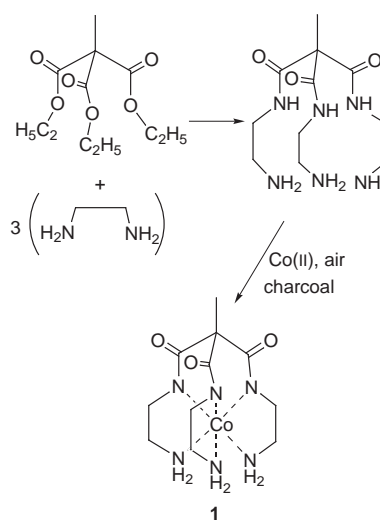
Amide groups usually bind through nitrogen as anions¹⁹ and their complexes have somewhat smaller metal–nitrogen bond lengths than their amine analogues. Such ligands are therefore useful in stabilising transition metal ions in higher oxidation states,^{20,21} and in polyamide-bearing ligands this stabilisation, especially of Ni^{III} and Cu^{III}, is ascribed mainly to the strong σ-donor properties of the deprotonated amide group.^{21,22} Also, incorporation of amido groups into macrocyclic ligands leads to chemical properties different to those observed for the analogous hexamines. For instance, the ligands are more selective in their interactions with different metal ions and different electronic properties are observed for the resultant metal complexes.²³ In this paper the syntheses of two different triamide tripodal ligands are described along with those of their cobalt(III) complexes. The chemical, redox and spectral characteristics of these two complexes were also examined and are compared to those of [Co^{III}(sen)]³⁺. In addition, the spectroscopic and electrochemical properties of a previously reported

monoamide tripodal complex, [1,9-diamino-5-(4-amino-2-azabutyl)-5-ethoxycarbonyl-4-oxo-3,7-diazanonanato]cobalt(III) chloride, [Co(CO₂Et-2-oxosen-H)Cl₂]²⁴ were examined and compared with those of its polyamide analogues. These tripods all have the potential to be capped at the open end to form a metal ion cage and this aspect was also investigated.

Results

Syntheses

The synthesis of the neutral complex [Co^{III}(2,2',2''-trioxosen-3H)]·3H₂O **1** (Scheme 1) was achieved through a six step pro-



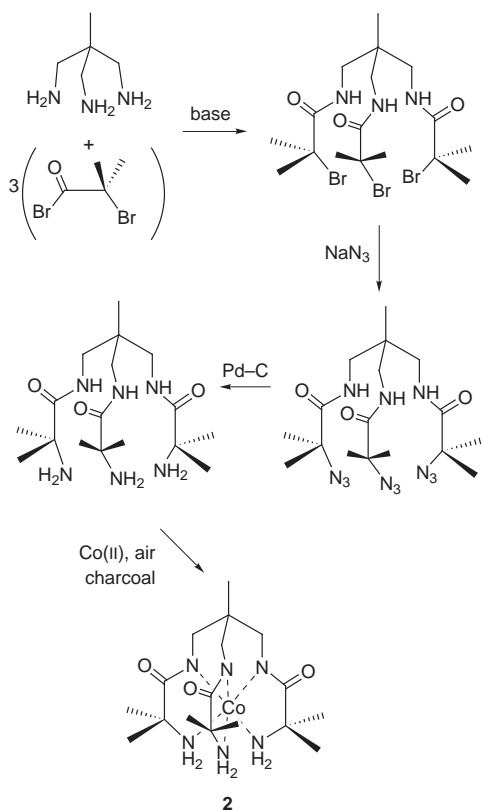
Scheme 1

cedure. Diethyl malonate was treated with ethyl chloroformate to replace one of the methylene hydrogen atoms with a third ester residue to produce a tripod with an apical hydrogen.²⁵ This was subsequently converted into the sodium salt by treating the tripod with sodium metal to eliminate dihydrogen. Methylation at the central carbon atom was ultimately achieved by treating the sodium salt with methyl iodide.²⁶ The methylated triester

was then treated with an excess of ethanediamine to produce the triamide ligand (Scheme 1); using an excess of amine reagent helped to limit the reaction of two ester groups with one diamine. Purification was achieved through complexation with Co^{III} as shown in Scheme 1. The yield of the triamide was not high among other by-products, and converting the ligand into the cobalt(III) triamido complex using Co^{2+} and O_2 in the presence of charcoal was the easiest method of purification. Removal of the other products was achieved using an ion exchange resin and the desired product was crystallised from the effluent. Microanalysis indicated that the product was consistent with its elution characteristics from the resin, *i.e.* the hexadentate binds as a trianion.

Attempts to produce a cage complex from the triamido species $[\text{Co}^{\text{III}}(2,2',2''\text{-trioxosen} - 3\text{H})]$ with methanal and nitromethane under basic conditions were unsuccessful. Variations in solvents and reaction conditions produced none of the desired product. In all instances, either starting material or decomposition products or a combination of both arose from the respective reactions. Although the complex possessed three primary amines on one octahedral face which should, in principle, be susceptible to the capping process, no evidence for reaction of methanal with the tripodal amines was obtained using methods which have been productive in capping such facial amine groups in other instances.^{6,15} Even the use of methanal alone failed to generate the facial triimine.

The synthesis of $[\text{Co}^{\text{III}}\{5,5',5''\text{-tri}(\text{Me}_2)\text{-4,4',4''\text{-trioxosen} - 3\text{H}}\}]$ followed the procedures summarised in Scheme 2 and



Scheme 2

was adapted from a published polyamide macrocycle synthesis.²⁷ Initially, 1,1,1-tris(aminoethyl)ethane was treated with 2-bromo-2-methylpropionyl bromide and the next step involved substituting azide for bromide groups. Reduction of the triazide in ethanolic $\text{Pd/C}/\text{H}_2$ then afforded the triamidetriamine tripod (Scheme 2) in high yield. Production of the cobalt(III) complex 2 (Scheme 2) followed using Co^{2+} , the ligand, oxygen as the oxidant and charcoal as the catalyst. Isolation of this complex from the ion exchange column as a non-electrolyte and the

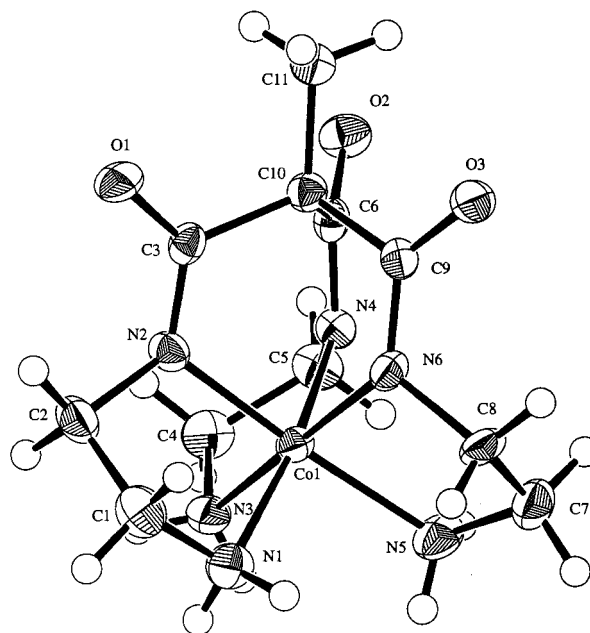


Fig. 1 Thermal ellipsoid diagram of $[\text{Co}^{\text{III}}(2,2',2''\text{-trioxosen} - 3\text{H})]\cdot 3\text{H}_2\text{O}$ showing atomic labelling. Ellipsoids show 50% probability levels, except for the hydrogen atoms which are drawn as circles of arbitrary radius.

microanalytical data indicated that the amide ligand was binding as a trianion.

X-Ray crystallography

The structure of $[\text{Co}^{\text{III}}(2,2',2''\text{-trioxosen}-3\text{H})]\cdot 3\text{H}_2\text{O}$ is shown in Fig. 1 and the bond distances and angles are given in Table 1. The crystallography confirms that the ligand binds as a hexadentate. Three facial co-ordination sites are occupied by deprotonated amide nitrogen atoms and the other three by the primary amine groups. Each of the five membered chelate rings has adopted an *ob* conformation about the C_3 axis through the metal.²⁸ The triamide cap conformation also fixes the orientation of the trigonal primary amine face giving the complex an overall conformation of C_3ob_3 . This structure is different to that observed for the tripodal hexadentate complex $[\text{Co}^{\text{III}}(\text{sen})]^{3+}$ which has a *lel_3* conformation.⁵

The three $\text{Co}-\text{N}_{(\text{amine})}$ distances [1.989(4), 2.003(4) and 1.995(4) Å] are significantly longer than the average $\text{Co}-\text{N}_{(\text{amine})}$ bond length observed for $[\text{Co}^{\text{III}}(\text{sen})]^{3+}$, 1.971(3) Å,⁵ and of *ob*₃ sar type cages such as $[\text{Co}^{\text{III}}\{(\text{NMe}_3)_2\text{-sar}\}]^{5+}$ which has an average $\text{Co}-\text{N}_{(\text{amine})}$ distance of 1.961(6) Å.²⁹ This was not unexpected, however, as bonding the amido-*N* group to the cobalt(III) ion leads to a lengthening of the bond *trans* to it, since the anionic amido-*N* group is a stronger σ donor than an amine. The $\text{Co}-\text{N}_{(\text{amido})}$ bonds [1.895(4), 1.902(4) and 1.895(4) Å] are all significantly shorter than the three $\text{Co}-\text{N}_{(\text{amine})}$ bonds and comparable to those observed in cobalt(III) amido cage complexes.²⁴ The $\text{Co}-\text{N}_{(\text{amido})}$ bond lengths of the triamide compound are shorter than the comparable distance [1.911(8) Å]³⁰ observed for the $[\text{Co}^{\text{III}}(\text{CH}_3\text{CONH})(\text{NH}_3)_5]^{2+}$ cation, but longer than that quoted for the bis(glycylglycinato)cobalt(III) ion (1.87 Å).³¹ In addition the $\text{N}-\text{C}_{(\text{amido})}$ and the $\text{C}-\text{O}_{(\text{amido})}$ bond lengths (Table 1) are similar (within 3σ) to the expected co-ordinated $\text{N}-\text{C}_{(\text{peptide})}$ (1.30 Å)¹⁹ and $\text{C}-\text{O}_{(\text{peptide})}$ (1.27 Å)¹⁹ bond distances (where all of the amide groups are deprotonated).

The $\text{N}-\text{Co}-\text{N}$ bond angles (Table 1) of $[\text{Co}^{\text{III}}(2,2',2''\text{-trioxosen} - 3\text{H})]\cdot 3\text{H}_2\text{O}$ deviate slightly from the angles required for octahedral symmetry of the CoN_6 core ($\approx 2-7^\circ$). In addition, the average twist angle between the two sets of N_3 planes, perpendicular to the C_3 axis, is 51° ; also the two N_3

Table 1 Bond distances (Å) and angles (°) for [Co^{III}(2,2',2''-trioxosen - 3H)]·3H₂O

Co–N(1)	1.989(4)	Co–N(2)	1.895(4)
Co–N(2)	2.003(4)	Co–N(4)	1.902(4)
Co–N(5)	1.995(4)	Co–N(6)	1.895(4)
O(1)–C(3)	1.260(6)	O(2)–C(6)	1.267(6)
O(3)–C(9)	1.254(6)	N(1)–C(1)	1.491(7)
N(2)–C(2)	1.480(7)	N(2)–C(3)	1.312(6)
N(3)–C(4)	1.457(7)	N(4)–C(5)	1.469(6)
N(4)–C(6)	1.291(6)	N(5)–C(7)	1.466(7)
N(6)–C(8)	1.480(6)	N(6)–C(9)	1.296(6)
C(1)–C(2)	1.522(8)	C(3)–C(10)	1.561(7)
C(4)–C(5)	1.487(8)	C(6)–C(10)	1.575(7)
C(7)–C(8)	1.514(9)	C(9)–C(10)	1.564(7)
C(10)–C(11)	1.505(7)		
N(1)–Co–N(2)	86.0(2)	N(1)–Co–N(3)	89.4(2)
N(1)–Co–N(4)	171.5(2)	N(1)–Co–N(5)	91.7(2)
N(1)–Co–N(6)	96.6(2)	N(2)–Co–N(3)	94.5(2)
N(2)–Co–N(4)	89.8(2)	N(2)–Co–N(5)	171.2(2)
N(2)–Co–N(6)	88.6(2)	N(3)–Co–N(4)	83.6(2)
N(3)–Co–N(5)	93.9(2)	N(3)–Co–N(6)	173.2(2)
N(4)–Co–N(5)	93.5(2)	N(4)–Co–N(6)	90.6(2)
N(5)–Co–N(6)	83.3(2)	Co–N(1)–C(1)	108.4(3)
Co–N(2)–C(2)	112.7(3)	Co–N(2)–C(3)	119.7(3)
C(2)–N(2)–C(3)	118.9(4)	Co–N(3)–C(4)	110.0(3)
Co–N(4)–C(5)	113.0(3)	Co–N(4)–C(6)	121.6(3)
C(5)–N(4)–C(6)	119.6(4)	Co–N(5)–C(7)	111.9(3)
Co–N(6)–C(8)	112.5(3)	Co–N(6)–C(9)	122.2(3)
C(8)–N(6)–C(9)	120.5(4)	N(1)–C(1)–C(2)	108.1(4)
N(2)–C(2)–C(1)	106.3(4)	O(1)–C(3)–N(2)	126.1(5)
O(1)–C(3)–C(10)	118.2(5)	N(2)–C(3)–C(10)	115.6(4)
N(3)–C(4)–C(5)	108.8(4)	N(4)–C(5)–C(4)	106.2(4)
O(2)–C(6)–N(4)	127.0(5)	O(2)–C(6)–C(10)	118.2(4)
N(4)–C(6)–C(10)	114.8(4)	N(5)–C(7)–C(8)	109.4(4)
N(6)–C(8)–C(7)	105.2(4)	O(3)–C(9)–N(6)	127.9(5)
O(3)–C(9)–C(10)	118.4(4)	N(6)–C(9)–C(10)	113.7(4)
C(3)–C(10)–C(6)	109.4(4)	C(3)–C(10)–C(9)	105.6(4)
C(3)–C(10)–C(11)	111.6(4)	C(6)–C(10)–C(9)	107.5(4)
C(6)–C(10)–C(11)	111.0(4)	C(9)–C(10)–C(11)	111.6(4)

planes are not exactly parallel (tipped $\approx 3^\circ$), which indicates the metal possesses a pseudo-octahedral character resulting largely from the rotation of the two N₃ planes. Lastly, the torsion angles of the three five-membered rings of the triamide are $-46.4(5)^\circ$ for N(1)–C(1)–C(2)–N(2), $-45.9(6)^\circ$ for N(3)–C(4)–C(5)–N(4) and $-41.2(6)^\circ$ for N(5)–C(7)–C(8)–N(6) respectively. The small CoN₆ angle deformations, the slightly non-parallel N₃ planes and the variations in the torsion angles are probably due to crystallographic influences rather than electronic effects within the molecule. The low-spin d⁶ cobalt(III) electronic configuration and the tripodal ligand would be expected to confer a C₃ symmetric configuration on the complex overall. Suitable crystals of the other complex were not obtained.

NMR Spectroscopy

The fully N-deuteriated, proton-decoupled ¹³C NMR spectra of both triamide complexes show that each possesses average C₃ symmetry at least for that NMR timescale. The carbon atoms within each arm of the tripods are inequivalent to each other but equivalent to the corresponding carbon atoms on the other arms. Consequently, five signals appear in the spectrum of [Co^{III}(2,2',2''-trioxosen-3H)] while seven signals occur for the [Co^{III}{5,5',5''-tri(Me₂)-4,4',4''-trioxosen - 3H}]. The ¹H NMR spectra are not so simple: for [Co^{III}(2,2',2''-trioxosen - 3H)] a singlet arises from the methyl group in the apical position of the complex (δ 1.17) while a complex ABCD spin system arises from the ethylene link protons over δ 2.20–3.60. For [Co^{III}{5,5',5''-tri(Me₂)-4,4',4''-trioxosen - 3H}] a singlet occurs at δ 1.02 for the apical methyl protons while a distorted AB doublet pair arises for the remaining *gem*-methylene hydrogens. The protons within each methyl group located on the five membered chelate rings appear equivalent to each other, but the *gem*

Table 2 Electrochemical data for Co^{III}–Co^{II} couples of triamido monoamido and saturated tripodal complexes (vs. SCE). HMDE electrode; 1 mM solutions of complex in 0.05 M KH₃(C₂O₄)₂·2H₂O, 0.1 M NaClO₄ and 0.05 M Na₃PO₄ at 20 °C with a scan rate of 20 mV s⁻¹

Complex	pH	E _{1/2} /V	E _{pc} /mV
[Co ^{III} (2,2',2''-trioxosen - 3H)]	1.68 ^a	—	-565
	$\approx 7^b$	—	-954
	12.04 ^c	—	-1100
[Co ^{III} {5,5',5''-tri(Me ₂)-4,4',4''-trioxosen - 3H}]	1.68 ^a	—	-782
	$\approx 7^b$	—	-1330
	12.04 ^c	— ^d	—
[Co ^{III} (CO ₂ Et-2-oxosen - H)] ²⁺	1.68 ^a	—	-462
	$\approx 7^b$	—	-500
	12.04 ^c	-0.76	-795 ^e
[Co ^{III} (sen)] ³⁺	7.0	-0.5	—

^a 0.05 M KH₃(C₂O₄)₂·2H₂O, ^b 0.1 M NaClO₄, ^c 0.05 M Na₃PO₄, ^d Not observable by HMDE. ^e E_{pa} -720 mV, i_{pc}/i_{pa} 0.98, ΔE_p 75 mV.

methyl groups of each arm of the tripod are chemically different. One signal occurs for each type of methyl group and AB coupling might be expected. However, the coupling between the two methyl groups is small so the peak intensities are distorted and deviate from the classical AB pattern. The two expected AB doublet pairs merge and appear as a broad multiplet at δ 1.40. The two methylene protons within the cap of this complex are also inequivalent and coupled to each other, giving rise to two AB doublets centred on δ 2.47 and 3.13. The NMR spectra of [Co^{III}(CO₂Et-2-oxosen - H)]²⁺ were reported previously²⁴ and because that complex has only one amide group in the ligand it lacks the threefold symmetry of the other tripods.

Infrared spectroscopy

A single, strong absorption band attributed to the C=O stretching vibration of the deprotonated co-ordinated amide group is displayed at 1609 cm⁻¹ for [Co^{III}(2,2',2''-trioxosen - 3H)] and at 1568 cm⁻¹ for [Co^{III}{5,5',5''-tri(Me₂)-4,4',4''-trioxosen - 3H}]. This is consistent with the C₃ symmetry of both molecules. The complex [Co^{III}(CO₂Et-2-oxosen - H)]²⁺ has an amide C=O stretching vibration at 1600 cm⁻¹.²⁴

Electronic absorption spectroscopy

The d–d absorption bands occur at 358 and 490 nm for [Co^{III}(2,2',2''-trioxosen - 3H)] and 350 and 482 nm for [Co^{III}{5,5',5''-tri(Me₂)-4,4',4''-trioxosen - 3H}]. The spectra do not differ greatly from that of the [Co^{III}(CO₂Et-2-oxosen - H)]²⁺ ion whose d–d bands occur at 342 and 492 nm ($\epsilon = 163$ and 159 M⁻¹ cm⁻¹ respectively). Comparison between the two systems is valid because the apical substituent has little influence on the position of the d–d bands for molecules of this kind.³² In each instance, characteristic absorption bands arise from the Laporte forbidden transitions of origin ¹T_{1g} ← ¹A_{1g} and ¹T_{2g} ← ¹A_{1g} (O_h parentage) for low spin Co^{III} and a red shift occurs in the lower energy d–d transition of both complexes compared to that of [Co^{III}(sen)]³⁺. In addition the band intensities of the triamides are significantly greater than those of [Co^{III}(sen)]³⁺, characteristic of some charge transfer component. The spectra were unchanged when recorded in acid solution.

Electrochemistry

The cyclic voltammetry reduction potentials, measured in aqueous solution with a hanging mercury drop electrode, of the triamides and [Co^{III}(CO₂Et-2-oxosen - H)]²⁺ and [Co^{III}(sen)]²⁺ appear in Table 2. For [Co^{III}(2,2',2''-trioxosen - 3H)] the reduction wave occurs at E_{pc} = -0.95 V (vs. SCE) at pH ≈ 7 while for [Co^{III}{5,5',5''-tri(Me₂)-4,4',4''-trioxosen - 3H}] the potential appears at E_{pc} = -1.33 V under the same conditions. Both

complexes displayed irreversible behaviour in all media at scan rates of 20 mV s⁻¹ and higher. These results indicate however that the electrode potentials of both triamido complexes are much more negative and much less reversible than that of [Co^{III}(sen)]³⁺ ($E_{1/2} = -0.5$ V vs. SCE).³³ The potential of the Co^{III}-Co^{II} reduction wave varied with the pH of the medium employed for each complex. In more basic solution the redox couples shifted to more negative values. The largely irreversible behaviour in acidic, neutral and basic solutions indicates that protons are involved. Partial ligand dissociation is likely in the cobalt(II) state of the triamides which would account for the irreversibility. Given the substantial irreversibility involved, it is difficult to relate the reduction wave potential to the chemical changes. From the oxidation scan it also appeared that Co^{IV} was inaccessible in water with these triamide complexes. No oxidation waves were observed for either complex when scanned to 1.4 V with a carbon electrode. This was unexpected since higher oxidation states of nickel,²¹ copper²² and possibly cobalt²⁰ appear to have been obtained with macrocyclic polyamido-*N* complexes. The [Co^{III}(CO₂Et-2-oxosen - H)]²⁺ molecule has a reduction potential 0.2–0.3 V (according to pH) more negative than that for [Co^{III}(sen)]³⁺. The reduction potential for a triamido complex therefore could be 0.6–0.9 V more negative, and the results in this study sustain this estimate.

Discussion

The synthesis of two new tripodal triamide ligands and their cobalt(III) complexes has permitted the study of the chemical and physical properties of octahedral cobalt(III) complexes containing multiple amido-*N* groups and the structure of one of these complexes has been confirmed by X-ray analysis. The amide groups in these tripods produce a smaller cavity for the metal ion than do hexamine tripodal ligands and deprotonation of the three amides on co-ordination to cobalt(III) leads to the formation of neutral complexes. The complexes [Co^{III}(2,2',2''-trioxosen - 3H)], [Co^{III}{5,5',5''-tri(Me₂)-4,4',4''-trioxosen - 3H}] and [Co^{III}(CO₂Et-2-oxosen - H)]²⁺ were resistant to nucleophilic attack by OH⁻ at the amide group, as is common in amido-*N*-bonded complexes.¹⁹ In addition protonation at the amide oxygen or nitrogen was not observed in these complexes, a property also shown by amide-functionalised cobalt(III) cage complexes.²⁴

The lack of reactivity of the amide functional groups may be attributed to the changes in their electronic structure brought about by co-ordination to cobalt(III). The nature of these changes has been probed by spectroscopy and electrochemistry of [Co^{III}(2,2',2''-trioxosen - 3H)], [Co^{III}{5,5',5''-tri(Me₂)-4,4',4''-trioxosen - 3H}] and [Co^{III}(CO₂Et-2-oxosen - H)]²⁺. In the infrared spectra the C=O stretching vibrations fall well below those expected for unbound secondary amides (1680–1630 cm⁻¹) and this is the predicted consequence of co-ordination and deprotonation.³⁴ In the electronic spectra the absorption bands have greater intensities than those found in the [Co^{III}(sen)]³⁺ spectrum and also more metal-ligand charge transfer properties; in addition the bands occur at lower frequencies.

The triamide complexes have three amine and three amido functional groups, making the environment about the metal ion distorted along the C₃ axis. Consequently, the O_h symmetry restrictions are somewhat diminished and the intensity of the observed transitions has increased. There may also be a charge transfer component arising from the trianionic ligand. The red shift arises from the π interaction of the lone pair of electrons on the amido nitrogen with the metal-based t_{2g} non-bonded electrons; this causes an increase in the energy of the t_{2g} orbitals and they are consequently closer to the e_g* set.³⁵ The deprotonated ligand can be expected to be a better ligand in a σ sense than an amine but this is not detected in the value of Δ which is

the difference between the e_g* and t_{2g} energy levels. In relevant hexamine cage systems the absorption bands for the ob₃ conformation are 30 nm lower in wavelength and the intensities are less than those in the corresponding lel₃ conformation.³⁶ This wavelength shift however is not observed in this case because the opposing effects of the amido-*N* donors dominate the issue.

The Co^{III}-Co^{II} reduction waves of the triamido complexes in water appear to be the most negative of the reported cobalt(III) amido complexes doubtless because the three amido groups within the tripodal ligand reduce the formal charge on the complex to zero. This lack of charge leads to stabilisation of the higher oxidation state and the charge at the metal centre is also reduced by charge donation from the anionic ligand. Both effects influence the redox potential, making it easier to stabilise the metal ion in a higher oxidation state. These effects taken threefold were anticipated to make the cobalt(IV) state accessible, however this oxidation state was not detected in any of these studies. This was surprising since Cu^{III}, Ni^{III} and Ni^{IV}³⁷ are readily accessible in water in complexes in which the ligand is an open-chain triamido species.

The tripodal triamido complexes differ from those of open-chain and macrocyclic amido systems in two ways. First, the latter type ligands tend to favour square-planar co-ordination of metal ions. This is mostly due to the planarity of the amido groups and in those cases the atoms of the amido groups are commonly coplanar with the metal ion of the complex. Secondly in square-planar systems the d-d absorption bands are usually blue-shifted when compared to those of equivalent polyamine complexes. In contrast, the two tripodal triamido ligands bind the cobalt(III) ion in a near-octahedral manner that results in the planar amido groups being not co-planar with the central cobalt(III) ion. Also, with the octahedrally co-ordinated triamido complexes the electronic transitions are red-shifted when compared to those of [Co(sen)]³⁺. Hence the observed differences in co-ordination between the two forms of amide ligand may be a factor in the differing electronic properties of the two systems.

In conclusion, two new tripodal triamide ligands have been synthesized, and they formed octahedral cobalt(III) complexes. We were unable to prepare triamido cage complexes from them and clearly the presence of the three amido groups within the ligands affects their ability to react with methanal, presumably the amine groups are less acidic in the neutral complexes. Previous work has shown that a complex of a tripod with a single amide group could be capped.²⁴ However, the triamido complexes themselves display some interesting properties that will merit further investigation, especially in relation to promoting higher oxidation states and non-square-planar configurations in complexes of Fe, Cu and Ni.

Experimental

The ¹H and ¹³C NMR spectra were acquired on a Varian 300 MHz spectrometer and referenced externally against 1,4-dioxane (δ 3.70 {¹H} and 67.4 {¹³C} vs. TMS), infra-red spectra with a Perkin-Elmer 1800 FTIR spectrometer as KBr disks. Standard electrochemical measurements were performed on a BAS 100 Electrochemical Analyser using 1 × 10⁻³ M solutions under a nitrogen atmosphere. In all cases, a three electrode system was used with full *iR* compensation. The auxiliary electrode consisted of a platinum wire and the reference electrode was Hg-Hg₂Cl₂-KCl (saturated) (SCE), 241 mV vs. SHE. The working electrode consisted of either an edge plane pyrolytic graphite (EPG) carbon or mercury electrode. The mercury electrode (Metrohm 663 VA stand, interfaced with an RSC Model-411 interface unit) was generally used as a hanging mercury drop electrode (HMDE). Electronic absorption spectra were obtained with a Hewlett-Packard 8450A UV/Visible spectrophotometer in 1 cm quartz cells.

Syntheses

CAUTION: Reactions involving methanal in basic solution were carried out in a well ventilated fumehood and quenched with acetic acid to avoid formation of carcinogenic halogenoethers. Whilst no problems were encountered in the course of this work, azide compounds are potentially explosive and should be handled with appropriate care and on a small scale.

The complex $[\text{Co}^{\text{III}}(\text{CO}_2\text{Et}-2\text{-oxosen} - \text{H})\text{Cl}_2 \cdot 3\text{H}_2\text{O}]$ was prepared according to a published method:²⁴ $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1} \text{cm}^{-1}$) (H_2O) 342 (163) and 492 (159).

Methanetricarboxylic acid triethyl ester. This compound was prepared by reaction of diethyl malonate and ethyl chloroformate.²⁵ $\delta_{\text{H}}(\text{CDCl}_3)$ 1.30 (t, 9 H, CH_3 ester), 4.27 (q, 6 H, CH_2 ester) and 4.41 (s, 1 H, CH); $\delta_{\text{C}}(\text{CDCl}_3)$ 13.4 (CH_3CH_2), 58.5 ($\text{C}_q\text{C}=\text{O}$), 61.8 (CH_3CH_2) and 163.5 ($\text{C}=\text{O}$).

Sodium methanetricarboxylic acid triethyl ester. This compound was prepared by reaction of methanetricarboxylic acid triethyl ester with sodium.²⁶ $\delta_{\text{H}}(\text{D}_2\text{O})$ 1.19 (t, 9 H, CH_3 ester) and 4.04 (q, 6 H, CH_2 ester); $\delta_{\text{C}}(\text{D}_2\text{O})$ 14.7 (CH_3CH_2), 58.3 ($\text{C}_q\text{C}=\text{O}$), 60.7 (CH_3CH_2) and 172.7 ($\text{C}=\text{O}$).

1,1,1-Ethanetricarboxylic acid triethyl ester. This compound was prepared by reaction of sodium methanetricarboxylic acid triethyl ester with methyl iodide.²⁶ $\delta_{\text{H}}(\text{CDCl}_3)$ 1.29 (t, 9 H, CH_3 ester), 1.71 (s, 3 H, C_qCH_3) and 4.26 (q, 6 H, CH_2 ester); $\delta_{\text{C}}(\text{CDCl}_3)$ 13.3 (CH_3CH_2), 18.2 (CH_3C_q), 61.5 (CH_3C_q), 61.6 (CH_3CH_2) and 167.2 ($\text{C}=\text{O}$).

1,1,1-Tris(4-amino-1-oxo-2-azabutyl)ethane. Ethanetricarboxylic acid triethyl ester (60 g; 0.24 mol) in ethanol (250 cm^3) was added dropwise to a refluxing solution of ethane-1,2-diamine (600 cm^3 ; 9.0 mol) under nitrogen. The solution was then refluxed for 72 h and cooled; excess of ethane-1,2-diamine was removed by rotary evaporation yielding an impure dark brown oil (74.4 g). The isolation of pure material (1 g) involved absorbing crude product (3 g) on silica gel and elution with CHCl_3 - CH_3OH -28% aqueous ammonia (8:3:1). $\delta_{\text{H}}(\text{D}_2\text{O})$ 1.27 (s, 3 H, C_qCH_3), 2.69 (t, 6 H, CH_2 en) and 3.21 (t, 6 H, CH_2 en); $\delta_{\text{C}}(\text{D}_2\text{O})$ 14.7 (CH_3C_q), 40.5 (H_2NCH_2), 42.1 ($\text{CH}_2\text{-NHC}=\text{O}$) 48.6 (CH_3C_q) and 174.3 ($\text{C}=\text{O}$).

[1,1,1-Tris(4-amino-1-oxo-2-azabutyl)ethanato]cobalt(III)-trihydrate, $[\text{Co}^{\text{III}}(2,2',2''\text{-trioxosen} - 3\text{H}) \cdot 3\text{H}_2\text{O}]$ 1. Crude 1,1,1-Tris(4-amino-1-oxo-2-azabutyl)ethane (6 g) was dissolved in water (100 cm^3) and $\text{Co}^{\text{II}}\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ (6 g) dissolved in water (100 cm^3) and charcoal (10 g) were added; the solution was then aerated for 12 h. After filtration, the orange solution was diluted to 4 L and sorbed onto a column (20 \times 5 cm) of SP Sephadex C-25 cation exchange resin. An orange band not retained by the resin was reduced to 20 cm^3 by rotary evaporation and then allowed to evaporate in air until dark red-orange crystals (1 g) were formed (Found: C, 32.7; H, 6.8; Co, 14.4; N, 20.7. $\text{C}_{11}\text{H}_{21}\text{CoN}_6\text{O}_3 \cdot 3\text{H}_2\text{O}$ requires C, 33.2; H, 6.8; Co, 14.8; N, 21.1%). $\delta_{\text{H}}(\text{D}_2\text{O})$ 1.17 (s, 3 H, $\text{C}_q\text{-CH}_3$), 2.20, 2.60, 2.71 and 3.60 (ABCD spin system, 12 H, CH_2 en); $\delta_{\text{C}}(\text{D}_2\text{O})$ 16.2 (CH_3C_q), 44.8 (H_2NCH_2), 47.8 ($\text{CH}_2\text{NC}=\text{O}$), 67.1 (CH_3C_q) and 178.5 ($\text{C}=\text{O}$); $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$ ($\text{C}=\text{O}$ amide stretch) 1609; $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1} \text{cm}^{-1}$) (H_2O) 358 (323) and 490 (398).

1,1,1-Tris(4-bromo-4-methyl-3-oxo-2-azapentyl)ethane. 1,1,1-tris(aminomethyl)ethane (tame) (3 g; 0.026 mol) and Et_3N (12.5 cm^3 ; 0.09 mol) were added to CH_2Cl_2 (200 cm^3). The mixture was dried over Na_2SO_4 (1 h) and then filtered into a three-neck round-bottomed flask (1 dm^3) equipped with a reflux condenser and a pressure-equalising addition funnel. Under a nitrogen atmosphere, 2-bromo-2-methylpropionyl bromide (9.5 cm^3 ; 0.077 mol) was carefully added to the solution from the addi-

tion funnel to avoid boiling the solvent since the reaction was VERY exothermic. The solution became cloudy upon production of $[\text{Et}_3\text{NH}]\text{Br}$. After stirring the solution for 1 h, the reaction mixture was washed twice with dilute aqueous HCl and twice with dilute aqueous Na_2CO_3 . The resultant CH_2Cl_2 solution was dried over Na_2SO_4 to give a clear, pale yellow solution. The CH_2Cl_2 was removed under reduced pressure to leave a yellow oil (13.6 g, 97%). $\delta_{\text{H}}(\text{CDCl}_3)$ 0.90 (s, 3 H, C_qCH_3), 1.95 [s, 18 H, $\text{C}(\text{CH}_3)_2$], 2.99 (s, 3 H, CH_2 cap), 3.02 (s, 3 H, CH_2 cap) and 7.72 (s, 3 H amide NH); $\delta_{\text{C}}(\text{CDCl}_3)$ 19.2 (CH_3C_q), 31.9 [$\text{C}(\text{CH}_3)_2$], 41.8 (CH_3C_q), 42.0 ($\text{CH}_3\text{C}_q\text{CH}_2$), 60.4 [$\text{C}(\text{CH}_3)_2$] and 172.8 ($\text{C}=\text{O}$).

1,1,1-Tris(4-amino-4-methyl-3-oxo-2-azapentyl)ethane. 1,1,1-Tris(4-bromo-4-methyl-3-oxo-2-azapentyl)ethane (13.6 g, 0.025 mol) was dissolved in ethanol (250 cm^3), an aqueous solution of NaN_3 (5.85 g, 0.09 mol) (fumehood, **CAUTION**) was added and the mixture was heated under reflux (12 h). Solvent was removed under reduced pressure until precipitation was initiated. The aqueous solution was extracted twice with CH_2Cl_2 and the extract dried over anhydrous Na_2SO_4 . It is important to execute this procedure to remove the NaN_3 , since the product is exposed to Pd/C in the next step and care should be taken to avoid the formation of a heavy metal azide. The CH_2Cl_2 was again removed under reduced pressure until precipitation was initiated. Ethanol ($\approx 500 \text{ cm}^3$) was added and the solution was again concentrated under reduced pressure. **CAUTION:** a small sample ($\approx 5 \text{ mg}$) of 1,1,1-tris(4-azido-4-methyl-3-oxo-2-azapentyl)ethane was isolated as a solid for spectroscopic analysis. $\delta_{\text{H}}(\text{CDCl}_3)$ 0.74 (s, 3 H, CH_3C_q), 1.49 [s, 18 H, $\text{CH}_3\text{C}(\text{CH}_3)_2$], 2.86 (s, 3 H, CH_2 cap), 2.88 (s, 3 H, CH_2 cap) and 7.67 (s, 3 H amide NH); $\delta_{\text{C}}(\text{CDCl}_3)$ 18.6 (CH_3C_q), 24.5 [$\text{C}(\text{CH}_3)_2$], 41.3 (CH_3C_q), 42.3 ($\text{CH}_3\text{C}_q\text{CH}_2$), 64.2 [$\text{C}(\text{CH}_3)_2$] and 173.8 ($\text{C}=\text{O}$). The bulk triazide product was reduced in portions with H_2 in an autoclave (50 psi) with 10% Pd/C. Since the reaction evolves one N_2 molecule for every H_2 molecule absorbed, frequent evacuation of the bomb and refilling with H_2 is advantageous (*i.e.* H_2 from the high pressure reservoir is not efficiently consumed). The mixture was filtered to remove the catalyst and the filtrate evaporated to dryness yielding a grey-white solid consistent with the desired product (7.4 g, 79%). $\delta_{\text{H}}(\text{D}_2\text{O})$ 0.72 (s, 3 H, CH_3C_q), 1.36 [s, 18 H, $\text{C}(\text{CH}_3)_2$] and 3.01 (s, 6 H, CH_2 cap); $\delta_{\text{C}}(\text{D}_2\text{O})$ 19.8 (CH_3C_q), 28.2 [$\text{C}(\text{CH}_3)_2$], 41.9 (CH_3C_q), 42.9 ($\text{CH}_3\text{C}_q\text{CH}_2$), 55.8 [$\text{C}(\text{CH}_3)_2$] and 181.7 ($\text{C}=\text{O}$).

[1,1,1-Tris(4-amino-4-methyl-3-oxo-2-azapentyl)ethanato]cobalt(III)-water-ethanol (1/8/0.5), $[\text{Co}^{\text{III}}\{5,5',5''\text{-tri}(\text{Me}_2)\text{-4,4',4''\text{-trioxosen} - 3\text{H}}\} \cdot 8\text{H}_2\text{O} \cdot 0.5\text{C}_2\text{H}_5\text{OH}]$ 2. 1,1,1-Tris(4-amino-4-methyl-3-oxo-2-azapentyl)ethane (1 g, 2.68×10^{-3} mol) was dissolved in water (200 cm^3), a solution of $\text{Co}^{\text{II}}\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ (0.65 g, 2.68×10^{-3} mol) in water (200 cm^3) and charcoal (10 g) were added and the mixture aerated for 12 h. The cobalt(III) complex was isolated in the same way as that for $[\text{Co}(2,2',2''\text{-trioxosen} - 3\text{H}) \cdot 3\text{H}_2\text{O}]$ except that the eluate was evaporated to dryness and the product recrystallised from aqueous ethanol to yield a dark red solid (1.1 g, 68%). (Found: C, 35.7; H, 8.1; N, 13.9. $\text{C}_{17}\text{H}_{33}\text{CoN}_6\text{O}_3 \cdot 8\text{H}_2\text{O} \cdot 0.5\text{C}_2\text{H}_5\text{OH}$ requires C, 35.8; H, 8.8; N, 13.9%). $\delta_{\text{H}}(\text{D}_2\text{O})$ 1.02 (s, 3 H, C_qCH_3), 1.40 [m, 18 H, $\text{CH}_3\text{H}_2\text{NC}(\text{CH}_3)_2$], 2.47 and 3.13 (AB doublet of doublets, 6 H, CH_2 cap); $\delta_{\text{C}}(\text{D}_2\text{O})$ 21.7 (CH_3C_q), 27.1 [$\text{H}_2\text{NC}(\text{CH}_3)_2$], 30.2 [$\text{H}_2\text{NC}(\text{CH}_3)_2$], 44.6 (CH_3C_q), 51.9 ($\text{CH}_3\text{C}_q\text{-CH}_2$), 61.5 [$\text{H}_2\text{NC}(\text{CH}_3)_2$] and 184.0 ($\text{C}=\text{O}$); $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$ ($\text{C}=\text{O}$ amide stretch) 1568; $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1} \text{cm}^{-1}$) (H_2O) 350 (214) and 482 (292).

Attempted cage syntheses using $[\text{Co}^{\text{III}}(2,2',2''\text{-trioxosen} - 3\text{H}) \cdot 3\text{H}_2\text{O}]$. The complex $[\text{Co}^{\text{III}}(2,2',2''\text{-trioxosen} - 3\text{H}) \cdot 3\text{H}_2\text{O}]$ (a) (0.5 g, 1.45×10^{-3} mol), (b) (1.0 g, 2.9×10^{-3} mol) or (c) (0.5 g, 1.45×10^{-3} mol), was dissolved in (a) aceto-

nitrile (30 cm³)–water (25 cm³), (b) methanol (50 cm³) or (c) water (100 cm³) and to each of these solutions was added (a) 36% aqueous methanal (5 cm³; 0.06 mol), (b) paraformaldehyde (0.8 g, 0.027 mol) or (c) 36% aqueous methanal (2.35 g, 0.08 mol), nitromethane (a) (5 cm³, 0.09 mol), (b) (0.2 g, 3.3 × 10⁻³ mol) or (c) (1.25 g, 0.02 mol) and triethylamine {(a) (3 cm³, 0.022 mol) or (b) (0.2 cm³, 1.45 × 10⁻³ mol)} or NaOH {(c), 1 M added until reaction solution pH ≈ 12}. The mixtures were (a) stirred for 4 d during which time methanal (0.5 cm³) and nitromethane (0.5 cm³) were added at regular intervals, (b) refluxed for 4 d or (c) stirred for 5 d, then treated with acetic acid, diluted to 1 dm³ with water and chromatographed on a 50W × 2 Dowex column. The single red-orange band that eluted straight from the column with water in each instance was collected and taken to dryness. Investigation of the residues by ¹³C NMR spectroscopy indicated the bands were starting material.

Crystal structure analysis of [Co^{III}(2,2',2''-trioxosen – 3H)]·3H₂O

Crystal data. C₁₁H₂₇CoN₆O₆, *M* = 398.30, hexagonal, space group *P*6₅ (no. 170), *a* = 8.040(3), *c* = 43.730(4) Å, *U* = 2447.8(5) Å³, *T* = 23 ± 1 °C, *Z* = 6, μ(Cu-Kα) = 86.50 cm⁻¹, 3956 reflections measured (Rigaku AFC6R diffractometer), 1259 unique (*R*_{int} = 0.050) and 1090 > 3σ which were used in all calculations. The final *R* was 0.027, *R*' = 0.029. Refinement in space group *P*6₁ with inverted co-ordinates gave a much higher *R* factor, indicating that the absolute configuration of the molecule is as shown in the Figure.

CCDC reference number 186/1337.

See <http://www.rsc.org/suppdata/dt/1999/1131/> for crystallographic files in .cif format.

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