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FULL PAPER

Iminodiacetate as a didentate ligand: base induced dealkylation

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Iminodiacetate has been incorporated into a complex as a didentate ligand. Control of pH is vital to the successful synthesis of the complex. At pH > 8 glycinato complexes have been observed to be significant products from the synthesis. Evidence is presented in support of the proposal that the glycine results from oxidative dealkylation of the coordinated iminodiacetate. An imine complex similar to a possible intermediate in this reaction has been prepared and shown to give rise to amino acid complexes on submission to similar reaction conditions. The amino acid complexes that are formed from the imine complex are derived from either the pendant or chelated parts of the ligand. Possible mechanisms are discussed.

Introduction

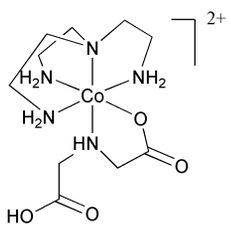
Complexes of iminodiacetate (ida) with cobalt(III) were first prepared in the early 1960s, with particular attention being paid to the stereochemistry of the compounds.[1,2] Coordination through the two carboxylate groups and the central amine donor results in the formation of two five-membered chelate rings, and the stability of structures of this kind is the reason that tridentate coordination is commonly observed for this ligand. The three donor atoms can be disposed either facially or meridionally around an octahedral metal ion, and mixtures of isomers are often formed. A preference for facial coordination of iminodiacetate has been noted.[2]

We have been interested in studying systems of this kind where the choice of binding mode of such a ligand is restricted. This involves choosing ligands for the remaining coordination sites around the metal ion in such a way that a flexible ligand such as iminodiacetate is forced to bind to the metal ion in a particular way. For example, tridentate coordination of a ligand such as 1,4,7-triazacyclononane (tacn) must occur in a facial manner, so that a flexible tridentate ligand occupying the other three coordination sites of an octahedral centre would also have to coordinate in a facial manner.

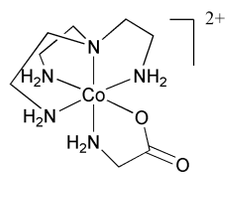
The study described in this paper arose from attempts to restrict the coordination of iminodiacetate to just two coordination sites on a metal ion. It would then be possible to compare the chemistry of the pendant and chelated portions of the ligand.

Such an aim requires the choice of a metal ion that is substitutionally inert, in order to minimise the chances of isomerisation occurring during the reactions that we might attempt. The cobalt(III) ion is an ideal choice, particularly as it allows characterisation of the resulting complexes by NMR techniques. The other requirement is a suitable ligand to block the four remaining coordination sites, thereby preventing coordination of the pendant carboxylate. It seemed reasonable to expect that a tetradentate ligand might be required in order to prevent all three donor groups of the iminodiacetate ligand coordinating to the metal ion. Polyamine ligands are particularly suitable for cobalt(III), and the amine ligand tris(2-aminoethylamine) (tren) was the choice for this role. Fewer stereoisomers are available to complexes of such tripodal ligands than to those of linear tetra-amine ligands.

This paper describes the synthesis of this complex, *p*-[Co(tren)(idaH)]$^{2+}$ (**1**), and the attempts to account for the formation of the related glycinato complex, *p*-[Co(tren)(gly)]$^{2+}$ (**2**), when the synthesis was performed at higher pH.



1
p-[Co(tren)(idaH)]$^{2+}$



2
p-[Co(tren)(gly)]$^{2+}$

Experimental

Materials and methods

Reagent grade reagents and solvents were obtained from commercial sources and used without further purification for all syntheses unless stated. Dowex 50WX4-400 cation exchange resin was used for chromatographic separations. Column dimensions are given as diameter × height. Concentration of solutions by removal of solvent was carried out at reduced pressure in a Büchi rotary evaporator equipped with a water aspirator and water bath (<40 °C).

Measurements

^{1}H and ^{13}C NMR spectra were recorded either on a Varian XL-300 spectrometer, or on a Varian Unity 300 MHz spectrometer, at 23 °C. D_2O was used as the solvent, and sodium trimethylsilylpropanesulfonate (TMPS, δ 0, singlet) was added as an internal reference. A Hewlett Packard 8452A spectrophotometer was used to record the UV–visible spectra in H_2O and the data are reported as λ_{max} (ε_{max}, L mol^{-1}cm^{-1}). Elemental analyses were performed by the University of Otago Microanalytical Service. Electrospray mass spectra were obtained on a Micromass LCT mass spectrometer equipped with an electrospray probe (capillary voltage 3200 V, probe temperature 150 °C, source temperature 80 °C, and cone voltage 10 V).

Syntheses

***p*-[Co(tren)(idaH)]Cl$_2$·0.5H$_2$O.** [Co(tren)Cl$_2$]Cl·H$_2$O (2.5 g, 7.6 mmol) and iminodiacetic acid (1.01 g, 7.6 mmol) were suspended in water (150 ml). The pH was adjusted to 8 with NaOH solution three times over approximately 15 min. The reaction mixture was heated on a steam bath for 4 h, cooled to room temperature and acidifed with HCl. The orange–red solution

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was diluted to 500 ml, and adsorbed onto a column (5 × 10 cm) of H^+ form Dowex 50WX4 resin. The column was washed with water (500 ml) and then eluted with 1 M HCl. A minor pink band was eluted first and discarded, followed by the major orange band that was collected. The orange band was taken to dryness at reduced pressure, and the residue triturated in a small volume of 3 M HCl. The fine orange precipitate that formed was filtered, and washed with a small amount of 3 M HCl, and then with methanol and diethyl ether. Yield 2.5 g (80 %). ^{13}C NMR: δ 185.2, 173.0, 64.78, 64.55, 62.23, 59.07, 57.05, 48.26, 47.59, 47.19. Calc. for $[CoC_{10}H_{24}N_5O_4]Cl_2 \cdot 0.5H_2O$: C 28.79, H 6.04, N 16.79. Found: C 28.70, H 5.93, N 17.07 %. UV/vis: 346 nm (130), 478 nm (122).

***p*-[Co(tren)(cmi)]Cl$_2$·HCl·H$_2$O.** *p*-[Co(tren)(NH=C{CH$_3$}-CO$_2$)]Cl$_2$[3] (3.0 g, 8.3 mmol) and excess chloroacetic acid (5 g, 53 mmol) were dissolved in water (20 ml). 4 M NaOH solution was added dropwise until the colour of the solution deepened, indicating deprotonation of the imine complex. Several more drops were added and the solution was stirred at room temperature for 4 h. The reaction mixture was acidified with conc. HCl, diluted to 500 ml with water and then adsorbed onto a column (5 × 40 cm) of H^+ form Dowex 50WX4 resin. The column was washed with acidified water and then eluted with 0.5 M HCl. A series of bands developed on the column. The yellow–orange band of the desired product was preceded by a yellow band, and followed sequentially by a red band, a yellow band, and an orange band. The second, yellow–orange, band was collected and taken to dryness to give a powdery residue. Yield 1.15 g (30%). ^{13}C NMR: δ 188.3, 174.5, 171.9, 64.76 (2), 62.39, 58.63, 48.04 (2), 46.97, 20.77. Calc. for $[CoC_{11}H_{24}N_5O_4]Cl_2 \cdot HCl \cdot H_2O$: C 27.84, H 5.73, N 14.75. Found: C 28.07, H 5.71, N 14.66 %. UV/vis: 470 nm (125).

Base induced dealkylation studies

Reaction of [Co(tren)(idaH)]Cl$_2$. In a typical experiment, [Co(tren)(idaH)]Cl$_2$ (0.75 g, 1.8 mmol) and [Co(en)$_3$]Cl$_3$·2H$_2$O (2.1 g, 5.5 mmol) were suspended in water (75 ml). The pH of the resulting solution was adjusted to 9.5 with triethylamine. The solution was heated on the steambath for a total of 4 h, with the pH being readjusted to 9.5 every hour or so. The reaction mixture was allowed to cool to room temperature and acidified before being diluted to 500 ml and adsorbed onto a column (5 × 10 cm) of H^+ form Dowex 50WX4 resin. The column was washed with water and then eluted with 1 M HCl. A pink band containing cobalt(II) was rapidly eluted from the column and discarded. The orange band that followed was collected, taken to dryness under reduced pressure, and the residue analysed by ^{13}C NMR spectroscopy. In general, the reaction mixture was open to the atmosphere, but identical results were obtained when reactions were performed under a N_2 atmosphere. The [Co(en)$_3$]Cl$_3$·2H$_2$O was replaced with [Co(en)$_2$(OH)(OH$_2$)](ClO$_4$)$_2$, [Co(NH$_3$)$_6$]Cl$_3$, [Co(tren)Cl$_2$]Cl·H$_2$O in separate experiments.

Reaction of *p*-[Co(tren)(cmi)]Cl$_2$·HCl·H$_2$O. *p*-[Co(tren)(cmi)]-Cl$_2$·HCl·H$_2$O (0.45 g, 0.9 mmol) and [Co(tren)(OH)(OH$_2$)]-(ClO$_4$)$_2$ (0.7 g, 1.6 mmol) were suspended in water (50 ml). The pH of the resulting solution was adjusted to ~11.5 with triethylamine. The solution was heated on the steambath for 3 h. At the end of this time the pH was 8.5. The reaction was quenched by the addition of concentrated HCl (2 ml), diluted to 500 ml with water, and adsorbed onto a column (5 × 8 cm) of H^+ form Dowex 50WX4 resin. The column was washed with water and then eluted with 0.5 M HCl. A small amount of some orange material was rapidly eluted from the column and was discarded. A red–purple band that appeared to have a more orange tail was eluted, and the tail was collected separately. The orange tail band was taken to dryness, and analysed by ^{13}C NMR spectroscopy and mass spectrometry.

Standard complexes for analysis of mass spectra and ^{13}C NMR spectra

***p*-[Co(tren)(gly)]Cl$_2$.** *p*-[Co(tren)(gly)](ClO$_4$)$_2$ was prepared according to the literature method.[4] The chloride salt was prepared by adsorbing the complex onto a column of H^+ form Dowex 50WX4 resin, eluting with HCl, and then taking the eluate to dryness. ^{13}C NMR: δ 187.2, 64.34 (2), 61.74, 49.25, 48.20 (2), 47.48.

***p*- and *t*-[Co(tren)(ala)]Cl$_2$.** [Co(tren)(OH)(OH$_2$)](ClO$_4$)$_2$[4,5] (2 g, 4.6 mmol) and L-alanine (0.75 g, Mr 89.09, 5.6 mmol) were suspended in water (20 ml). The reaction mixture was heated on a steam bath for 1.5 h and then allowed to cool to room temperature before being diluted to 500 ml and adsorbed onto a column (5 × 10 cm) of H^+ form Dowex 50WX4 resin. The column was washed with water, and then eluted with 1.5 M HCl. An orange band was eluted ahead of a purple band.

The orange band was taken to dryness. Yield ~1.5 g (90 %). The product was a 4 : 1 mixture of the two isomers. ^{13}C NMR major isomer: δ 188.0, 64.18 (2), 61.54, 56.60, 48.24, 48.18, 47.49, 20.88. ^{13}C NMR minor isomer: δ 188.4, 66.02, 65.59, 64.49, 56.94, 54.98, 46.87, 46.16, 20.41.

Results and discussion

The early attempts to prepare *p*-[Co(tren)(idaH)]$^{2+}$ were not very successful. The yield of the desired complex was poor, and what material there was was contaminated with another complex. This contaminant was identified as the glycinato complex, *p*-[Co(tren)(gly)]$^{2+}$, initially by comparison of its ^{13}C NMR spectrum with that of an authentic sample, and subsequently by spiking experiments.

^{13}C NMR spectroscopy proved to be significantly more useful than ^{1}H NMR spectroscopy for the work described in this paper. The ^{1}H NMR spectra of the compounds are generally made up of complex multiplets in a restricted region of the spectrum, which made identification of compounds present in a mixture rather difficult by that technique. Decoupling, together with the greater chemical shift range seen in ^{13}C NMR spectra, made the task of identification much easier.

The iminodiacetic acid starting material was checked and found to be free of any significant glycine impurity (none could be detected by NMR spectroscopy). Therefore, the glycine that was found in the complex product must have been produced from the iminodiacetic acid during the reaction. There was no sign of any glycine being produced in the absence of the cobalt starting material, and significant amounts of cobalt(II) species were produced only in reactions in which glycine was also seen.

Taken together, these observations lead to the conclusions that the glycine found in the product resulted from redox reactions of some kind and that complexation of the ligand may be involved. Indeed, the target complex, *p*-[Co(tren)(idaH)]$^{2+}$, was clearly a possible intermediate on the reaction path leading from [Co(tren)Cl$_2$]$^+$ to the glycinato complex.

The desire to explore this possibility by resubmission experiments required either that the problems with the synthesis of *p*-[Co(tren)(idaH)]$^{2+}$ be resolved, or that it and the glycinato complex impurity be separated. Further experimentation revealed that the impurity was present in greater amounts when the synthesis was attempted at higher pH, and that it could be essentially eliminated if the reaction is performed below pH 8. Significant amounts of *p*-[Co(tren)(idaH)]$^{2+}$ could therefore be prepared, in good yield, and it was apparent from these results that pH is a critical parameter in the dealkylation chemistry.

Submitting the isolated complex to the higher pH reaction conditions resulted in the formation of the glycinato complex, as well as substantial amounts of cobalt(II). The quantity of the

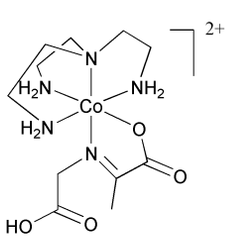
glycinato complex that was produced was comparable to that found in the initial attempts to synthesise *p*-[Co(tren)(idaH)]$^{2+}$. These results are consistent with the proposal that the *p*-[Co(tren)(idaH)]$^{2+}$ complex is an intermediate in the dealkylation reaction.

The yields of glycinato complexes could be significantly increased by the addition of other cobalt(III) complexes to the reaction mixture. On the other hand, the yields were not affected when the reaction was conducted under a nitrogen atmosphere. When [Co(en)$_3$]$^{3+}$ or [Co(en)$_2$(OH)(OH$_2$)]$^{2+}$ were used as the sacrificial complexes with *p*-[Co(tren)(idaH)]$^{2+}$, both [Co(en)$_2$(gly)]$^{2+}$ and *p*-[Co(tren)(gly)]$^{2+}$ were identified in the product mixture. The most likely explanation of this 'cross-over' result, where glycine appears in complexes containing en ligands, is that free glycine is formed during the reaction and then recomplexed. It is, however, possible that dinuclear species, in which the pendant carboxylate group of the iminodiacetate complex (or a subsequent complex in the reaction path) is coordinated to another cobalt centre, could be involved.

The [Co(en)$_2$(gly)]$^{2+}$ to *p*-[Co(tren)(gly)]$^{2+}$ ratios that were observed for experiments containing [Co(en)$_3$]$^{3+}$ or [Co(en)$_2$(OH)(OH$_2$)]$^{2+}$ were identical. This was surprising, at first sight, since the latter complex might be expected to be a better scavenger for free glycine than [Co(en)$_3$]$^{3+}$, as it possesses relatively labile monodentate ligands and is a known precursor for the observed glycinato complex.[6] The presence of significant amounts of cobalt(II) presumably catalyses the required ligand exchange reactions to a sufficient degree to nullify this advantage. This observation may also be circumstantial evidence against the involvement of dinuclear species, since the labile ligands of the [Co(en)$_2$(OH)(OH$_2$)]$^{2+}$ complex would make it better able to form a bridged complex.

The production of significant amounts of cobalt(II) in the reaction mixtures in which the dealkylation is observed would be consistent with the dealkylation reaction occurring *via* an oxidative pathway. This kind of reaction involves oxidation of an amine to an imine. Hydrolysis of the imine would then give the glycine that is required to form the observed glycinato complexes. Such reactions have been observed before in cobalt(III) complexes.[7] Redox reactions leading to the production of an imine intermediate would account for the low yields of the glycinato product, since two cobalt(III) ions would need to be reduced in order to produce each imine. In the absence of any added source of cobalt(III) ions, the maximum yield that could then be expected would be ~33%.

A straight-forward initial test for the possible intermediacy of such an imine complex would involve an independent synthesis of the complex, followed by its submission to the reaction conditions. A closely related compound, *p*-[Co(tren)(cmi)]$^{2+}$ (**3**), derived from the known imine complex, *p*-[Co(tren)(Aim)]$^{2+}$ (**4**), was prepared, *via* alkylation with chloroacetate, and isolated following ion exchange chromatography of a reasonably complex mixture.



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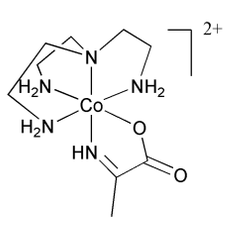
p-[Co(tren)(cmi)]$^{2+}$



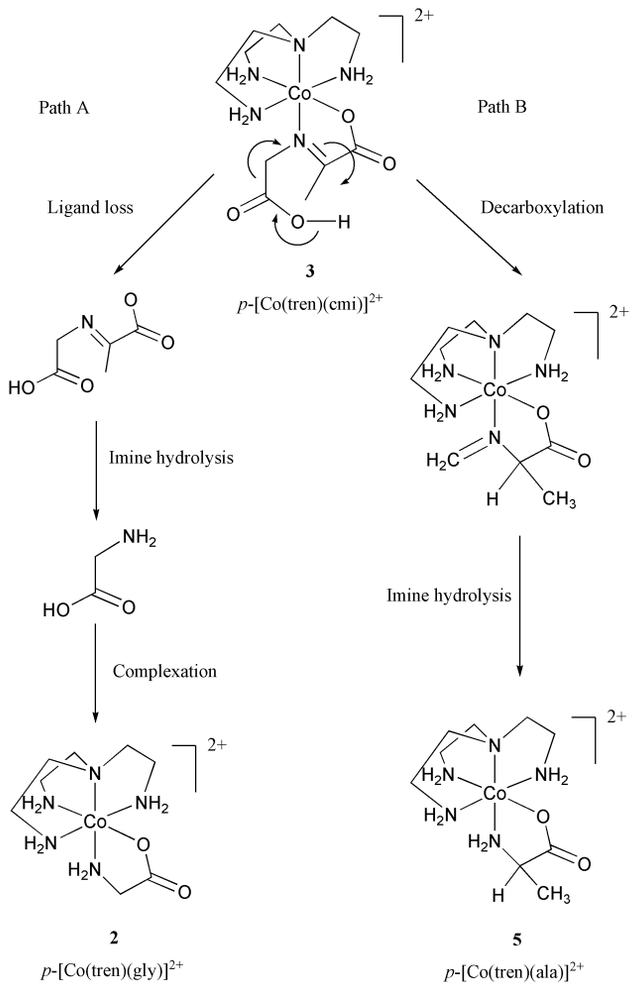
4

p-[Co(tren)(Aim)]$^{2+}$

While this compound is not exactly that which may be an intermediate in the reaction of the iminodiacetate complex, the methyl group in the chelated portion of the ligand acts as a label for the chelating arm. This allows the two possible

Table 1 Peaks observed in electrospray mass spectra (*m*/*z*)

[Co(tren)(gly)]Cl$_2$	[Co(tren)(ala)]Cl$_2$	Assignment
314.0	328.0	M − Cl
278.1	292.1	M − Cl − HCl
221.6	228.6	2+ ion
201.0	208.1	2+ ion
180.5	187.6	2+ ion



Scheme 1

reaction paths shown in Scheme 1 to be distinguished. Path A, ligand loss followed by hydrolysis of the imine and subsequent chelation of the resulting amino acid, would result in the formation of a glycinato complex. On the other hand, path B, decarboxylation, followed by imine hydrolysis would give rise to alaninato complexes such as **5**.

Submission of the imine probe complex to the reaction conditions results in formation of *both* glycinato and alaninato complexes. The amino acid complexes were isolated as a mixture following ion exchange chromatography, and the presence of both complexes was confirmed by ^{13}C NMR spectroscopy and electrospray mass spectrometry data. Assignment of observed peaks in the electrospray mass spectrum of the mixture to a parent compound was achieved by a combination of comparison with spectra obtained from the authentic compounds and by spiking the mixture with samples of the authentic compounds (Table 1). Identification of the ions that were detected has not been achieved in many cases, but it is clear from the mass differences observed between the ions derived from the glycinato and alaninato complexes that some of them are doubly charged.

Observation of both the glycinato and alaninato complexes following submission of the imine complex to the reaction

conditions clearly implies that more than one reaction pathway is available. The most likely origin of the glycine required for the formation of the glycinato complex is straight-forward hydrolysis of the imine in the probe complex. Given that imino acid chelates of the kind shown are stable towards imine hydrolysis (they are generally formed by condensation reactions[8]), it is likely that the imine ligand must be removed from the metal or, at least, that the chelate ring is opened, prior to hydrolysis.

Path B in Scheme 1 shows decarboxylation leading to formation of the alaninato complex. An alternative might involve a tautomerisation to a structure in which the imine is not in the chelate ring, followed by hydrolysis to produce alanine and glyoxylic acid. In the former case decarboxylation would provide a considerable driving force for the reaction, and that possibility is preferred on this basis.

In summary then, it has been established that the glycinate complexes are produced from iminodiacetate when cobalt(III) is present, and that cobalt(II) species are by-products from the reaction. The complex with iminodiacetate bound as a didentate ligand has been shown to give the same products under the reaction conditions, which is a necessary condition for it to be considered a potential intermediate. Further, a complex containing an imine in the chelate ring has been shown to give the same type of product under the reaction conditions. This complex also showed that the amino acid could be derived from either the chelate ring or the pendant portion of the imine ligand, even though the imine was located initially in the chelate ring.

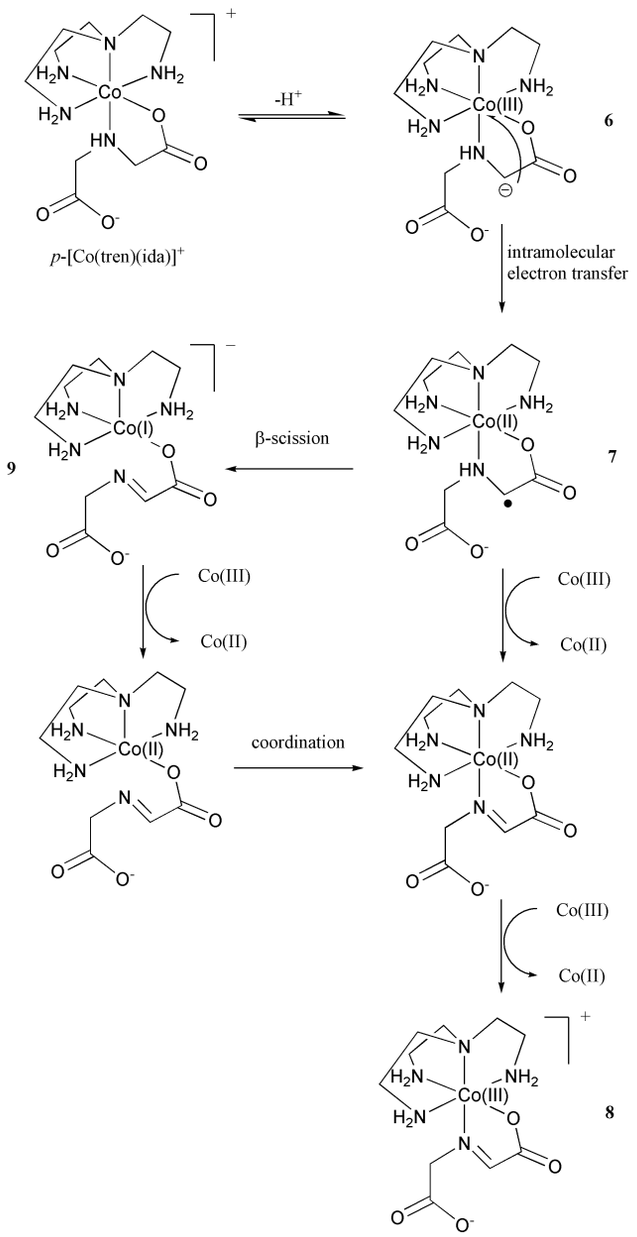
These results are consistent with an overall scheme in which the iminodiacetate is bound to the cobalt(III) ion as a didentate ligand and then oxidised to an imine species, with concomitant reduction of two equivalents of cobalt(III). The resulting imine species then gives rise to amino acid complexes through the paths shown in Scheme 1 and discussed above.

While oxidation of amine containing ligands to imines has been observed before for cobalt complexes,[7] there has been little discussion of mechanism. However, in one case,[7l] a mechanistic proposal has been put forward that is particularly relevant because it also involved an amino acid based system (*N*,*O*-bound *S*-methylmethionine) and conditions that are reasonably similar to those employed in this work.

That proposal postulated base induced deprotonation of the α-carbon atom in the chelate ring, followed by electron transfer from the carbanion to the cobalt(III) ion, generating cobalt(II) and a radical centre. Intermolecular electron transfer from the radical centre to another cobalt(III) ion, along with proton loss, was proposed to generate the imine. A series of hydrolysis and rearrangement reactions was then proposed to lead to the isolated product.

The evidence that was presented to support the proposal of a radical intermediate is not particularly strong, consisting principally of an assessment of reactivity patterns in a series of related complexes in relation to the expected properties of such radical intermediates. That having been said, it does seem likely that formation of a two-electron-oxidised compound through reaction with two equivalents of single electron oxidant (cobalt(III) complexes) would involve a radical intermediate at some point. Obtaining evidence for radical intermediates in such systems is not easy, as they are short-lived species that are present in low concentration, and the conditions under which these experiments are conducted (water, pH > 8, 80 °C, significant cobalt(II) concentrations) are far from ideal for techniques such as ESR spectroscopy and radical trapping.

The first steps of the published reaction mechanism are of most interest with respect to the proposal for the present system, shown in Scheme 2. The deprotonation of the α-carbon atom in the chelate ring to give the carbanion, **6**, is consistent



Scheme 2

both with the fact that the iminodiacetate chemistry is base induced and the known chemistry of chelated amino acids.[9] Electron transfer to cobalt(III) would generate the cobalt(II)-radical intermediate, **7**, and subsequent intermolecular electron transfer reactions with cobalt(III) species would result in the formation of the imine complex, **8**.

The lability of cobalt(II) complexes means that once this oxidation state has been reached, as in **7**, the ligands may exchange with solvent and some of the subsequent reactions could be occurring off the metal. Indeed, the free imine may be formed from uncoordinated radical, hydrolysed, and the resulting glycinate ion trapped by the metal as the final step. If this is occurring, then the results for the reaction of the imine probe complex, where the amino acid is shown to be derived from either the pendant or chelated portions of the ligand, though interesting in their own right, may not be relevant to the iminodiacetate system.

It is also possible that, given the strongly reducing nature of some α-amino radicals,[10] **7** could react *via* a β-scission reaction to give a cobalt(I)-imine species, **9**, which could then undergo the electron transfer reactions and coordination of the imine to give **8**.

Conclusion

It has been established that the base-induced dealkylation of iminodiacetate occurs *via* an oxidative pathway, with cobalt(III) species being the oxidant. The mechanism of the oxidation process is unclear at this time, but it appears likely that a cobalt-iminodiacetate complex is an intermediate, as such a complex has been shown to give the same products when submitted to the reaction conditions. Imine containing intermediates are also implicated. The chemistry of a closely related imine complex has been studied under the reaction conditions and this revealed that degradation of such a complex can occur by more than one pathway, giving amino acids derived from either the chelated or pendant parts of the ligand.

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