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FULL PAPER

Use of a radical clock to study the photodecarboxylation of amino acidatocobalt(III) complexes †

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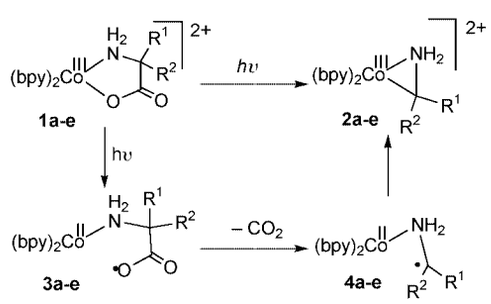
The products of steady state UV irradiation of amino acidatobis(2,2′-bipyridine)cobalt(III) complexes have been identified. The products of these photodecarboxylation reactions include a carbonyl compound derived from the amino acid side chain. The viability of an aminocyclopropylmethyl radical clock as a potential mechanistic probe for the reaction was assessed by *ab initio* methods. The required cyclopropylglycine containing substrate was synthesized and used to show that reaction of an α-carbon centred radical must be a fast step if it occurs in the reaction sequence leading to formation of the intermediate metallacyclic complexes.

Introduction

The investigation of photochemical reactions of ligands co-ordinated to transition metals is a relatively unheralded branch of inorganic chemistry,[1,2] but it is one which may provide synthetic avenues to interesting or otherwise inaccessible organic or co-ordination compounds. An example of this is the formation of a complex containing a three-membered Co–C–N metallacycle *via* irradiation of the bis(2,2′-bipyridine)glycinatocobalt(III) ion, $[Co(gly)(2,2'\text{-bpy})_2]^{2+}$ **1a**, with UV light.[3] This complex, $[Co(CH_2NH_2)(2,2'\text{-bpy})_2]^{2+}$ **2a**, is reasonably stable and has been characterised by X-ray crystallographic methods.[4]

A range of similar reactions has been reported, but the stability of the resulting cobalt–alkyl products varies considerably.[1a,c,3] For example, metallacycles with substituents on the α-carbon are thermally unstable, while more robust four membered metallacycles result from the photodecarboxylation of complexes of β-aminocarboxylates. Many of these latter metallacycles were part of polydentate frameworks.

A mechanism for these reactions has been proposed[1a] (Scheme 1), wherein absorption of UV light leads to homolysis



Scheme 1 **a**: gly, $R^1 = R^2 = H$; **b**: ala, $R^1 = CH_3$, $R^2 = H$; **c**: val, $R^1 = CH(CH_3)_2$, $R^2 = H$; **d**: cpg, R^1 = cyclopropyl, $R^2 = H$; **e**: aib, $R^1 = R^2 = CH_3$.

of the cobalt–oxygen bond, affording a cobalt(II)-bound aminoacyloxy radical intermediate **3**. This complex is proposed to undergo a decarboxylation reaction to give a species which contains a co-ordinated aminoalkyl radical, **4**. The alkyl radical is then thought to react with the cobalt(II) centre, yielding the metallacyclic product **2**.

A kinetic study of this reaction, using laser flash photolysis techniques, has been reported.[5] In that study the rates of formation of the metallacyclic products were monitored spectrophotometrically, and it was found that the observed absorbance changes could be analysed in terms of first order kinetics. Rate constants of around 4×10^3 s^{-1} were calculated for the formation of metallacyclic complexes from a range of α-amino acid complexes, including the glycinato example described above.

These data are consistent with any one of the three irreversible first order reactions in the proposed mechanism being rate determining, since the observations that were made were associated with formation of the metallacyclic product and not with the appearance or decay of any of the intermediates. However, in the discussion of their results, the authors assigned these rate constants to the final step of the reaction sequence, cobalt–carbon bond formation. There was little discussion of this assignment, which was presumably made on the assumption that photochemical bond homolysis and decarboxylation steps are likely to be fast processes.

There are two anomalies that arise as a result of this assignment of the rate determining step. First, intermolecular reactions between cobalt(II) complexes and methyl radicals have second order rate constants of greater than 10^7 M^{-1} s^{-1}.[6] We consider it remarkable that similar *intramolecular* reactions should have rate constants as small as 10^3 s^{-1}. Secondly, the measured rates would imply that the cobalt(II)–aminoalkyl radical intermediate **4** has a lifetime of the order of milliseconds. The aminoalkyl radical is a monodentate ligand at this point in the reaction sequence, and therefore relatively easily exchanged for other ligands. Indeed, given that cobalt(II) complexes can undergo ligand exchange reactions on the microsecond timescale in aqueous solution, one might expect that essentially all of the radical ligands would be lost before a reaction with the cobalt(II) ion at $\approx 10^3$ s^{-1} could occur.

We consider, on the basis of these inconsistencies, that there is some doubt concerning the assignment of the rate determining step in the proposed mechanism. Indeed, it may be that it is the mechanistic proposal itself which is incorrect.

Our approach to the further investigation of this system has been to attempt to measure the relative lifetime of the putative aminoalkyl radical intermediate, **4,** with the aid of a radical clock. In particular, we proposed to employ a cyclopropylmethyl radical clock, in which cyclopropane ring opening com-

† *Supplementary data available*: results of *ab initio* calculations. For direct electronic access see http://www.rsc.org/suppdata/dt/1999/3565/, otherwise available from BLDSC (No. SUP 57632, 5 pp.) or the RSC Library. See Instructions for Authors, 1999, Issue 1 (http://www.rsc.org/dalton).

petes with the radical reaction of interest. To this end we have synthesized a complex of cyclopropylglycinate, **1d**, and explored its photochemistry.

Knowledge of the rate of the radical clock rearrangement reaction is required before the results of a radical clock experiment can be used to infer anything about the reaction of interest. Unfortunately, no kinetic information was available for the rearrangement reaction of the aminocyclopropylmethyl radical, despite numerous approaches, both theoretical and experimental, to this problem for many related radicals. Certainly, there was no information available on the rates of rearrangement of such radicals when they are co-ordinated to metal ions. We therefore set out to obtain an estimate for the rate constant for the ring opening of the aminocyclopropylmethyl radical and its protonated analogue, according to the methods of Radom[7] and of Newcomb and co-workers.[8] These results, together with the trends relating the nature of the substituent and the rate constants for various related radicals, can be used to make a prediction for the rate of ring opening of the amino substituted radical.

The results from the theoretical study and from the photochemical experiments are then brought together in a discussion of the mechanism of the photochemical reaction.

Experimental

Materials

Reagent grade reagents were used without further purification for all experimental work. D,L-Alanine, D,L-valine and 2-aminoisobutyric acid were obtained from Aldrich Chem. Co., glycine and 2,2′-bipyridine from BDH, deuterium oxide (D_2O), deuterium chloride (DCl) and dimethyl-d^6 sulfoxide (dmso-d^6) from Aldrich.

Measurements

The ^{1}H NMR spectra were taken at 300 MHz on a Varian Unity-300 spectrometer at 23 °C. For those recorded in dmso-d^6, the dmso-d^5 line (δ 2.50, multiplet) was used as a reference. Sodium 3-trimethylsilylpropanesulfonate (TMPS, δ 0, singlet) was used as in internal reference for those spectra recorded in D_2O. A Varian XL-300 spectrometer was employed for the ^{13}C NMR spectra at 75 MHz and all spectra were proton decoupled. The spectra were recorded at 23 °C and referenced to the dmso-d^6 peak (δ 39.5) or, in D_2O, to 1,4-dioxane (internal standard, δ 67.4). The signals are described as singlets (s), doublets (d), triplets (t), or multiplets (m), and broad (br) where appropriate. A GBC-920 spectrophotometer was used to record the UV-VIS spectra in water and the data are reported as λ_{max} (ε_{max}). Microanalyses were performed by the Campbell Microanalytical Laboratory, University of Otago. FAB Mass spectral data were obtained on a Kratos MS80RFA mass spectrometer equipped with an IonTech ZN11NF atom gun using xenon as the reagent gas and 3-nitrobenzyl alcohol as the matrix. Electron impact spectra were obtained at 70 eV.

CAUTION: perchlorate salts of metal complexes containing organic ligands are potentially explosive and should be handled with care and only in small quantities.

1. Preparation and isolation of 2-cyclopropylglycine (Hcpg)

(a) Tetraammine(2-cyclopropyl-2-iminoethanoato)cobalt(III) perchlorate was prepared by a modification of the method of Lawson *et al.*[9] Lithium 5-bromo-2-oxopentanoate (LiBOP) (2.95 g, 13 mmol) in ethanol (40 ml) was added in portions over two hours to a solution of pentaammineaquacobalt(III) perchlorate (7.40 g, 16 mmol) in water (60 ml) at 60 °C. The reaction mixture was kept at this temperature, with stirring for two hours while the pH was kept at 5.25–5.5 by the addition of Na_2CO_3. The solution was then acidified to pH 2 with $HClO_4$ and cooled overnight. The red plate-like crystals and mother-liquor were treated as in ref. 9, to yield pentaammine(2-cyclopropyl-2-oxo-ethanoato)cobalt(III) perchlorate and then tetraammine(2-cyclopropyl-2-iminoethanoato)cobalt(III) perchlorate (1.91 g, 4.4 mmol, 34% from LiBOP).

(b) 2-Cyclopropylglycine was produced and liberated from the cobalt centre of the tetraammine(2-cyclopropyl-2-iminoethanoato)cobalt(III) perchlorate (1.1 g, 2.5 mmol) by treatment with an excess of $NaBH_4$ (0.25 g) in a Na_2CO_3/$NaHCO_3$ buffer (pH 10, 90 ml). The solution was stirred for four minutes and then acidified with dilute HCl to pH 3. A black by-product deposited with concomitant generation of H_2 gas. The reaction mixture was filtered through Celite, and the pale pink filtrate loaded on to Dowex (H^+ form, 8 × 3 cm). The column was washed with 0.1 M HCl (300 ml), then eluted with 0.5 M NH_3 solution. Fractions of 30 ml were taken and the solvent removed on a rotary evaporator. The cyclopropylglycine, as identified by ^{1}H NMR, eluted after 90 ml. The hydrophobic amino acid was recrystallised twice by layering a supersaturated aqueous solution with Pr^{i}OH and cooling in a freezer. A white powder precipitated which was washed with Pr^{i}OH and diethyl ether, then air dried. Yield 82 mg, 59%. ^{1}H NMR (dilute DCl): δ 0.40–0.85 (complex peak, cyclopropyl CH_2, 4 H), 1.14 (m, cyclopropyl CH, 1 H) and 3.13 (d, α-H, 1 H, J = 10.7 Hz). ^{13}C NMR (D_2O): δ 5.38, 6.05 (cyclopropyl CH_2s), 14.06 (cyclopropyl CH), 61.40 (α-C) and 175.97 (COO). Calc. for $C_5H_9NO_2$: C, 52.16; H, 7.88; N, 12.17. Found: C, 51.94; H, 7.88; N, 11.96%. EI-MS: m/z 116 ($[C_5H_{10}NO_2]^+$).

2. Synthesis and spectroscopy of the amino acidatobis(bipyridyl)-cobalt(III) complexes

These complexes were prepared by the general method of Tatehata.[10] The amino acid (2.92 mmol) was added to a suspension of $[CoCl_2(2,2'\text{-bpy})_2]Cl\cdot 3H_2O$[11] (0.5 g, 2.92 mmol) in dry methanol (30 ml). Sodium acetate (0.2 g) was added and the mixture warmed at 45–50 °C with stirring. After one hour the orange solution was diluted with distilled water (300 ml) and loaded on to SP-Sephadex(C25) (Na^+ form, 3 × 20 cm). An orange band eluted with 0.2 M NaCl, preceded by a red-orange band and followed by a yellow band. The orange eluate was concentrated on a rotary evaporator and desalted on Sephadex G-10. This solution was concentrated once again, and an orange solid precipitated upon the addition of saturated $NaClO_4$ solution. Recrystallisation of the crude solid from hot dilute $HClO_4$ gave orange crystals suitable for the microanalyses and electronic spectra.

(a) $[Co(gly)(2,2'\text{-bpy})_2][ClO_4]_2\cdot H_2O$. ^{1}H NMR (dmso-$d^6$): δ 3.15–3.32 and 3.75–3.85 (m, α-H, 2 H), 6.16 (br m, NH, 1 H), 6.64 (br m, NH, 1 H), 7.18 (d, 1 H), 7.62 (m, 3H), 8.22 (m, 2 H), 8.41 (m, 2 H), 8.57 (d, 1 H), 8.73 (m, 2 H), 8.89 (t, 2 H), 9.03 (d, 2 H) and 9.20 (d, 1 H). ^{13}C NMR (dmso-d^6): δ 44.46 (α-C), 124.84, 125.70, 126.14, 128.81, 129.07, 139.93, 130.08, 142.17, 142.89, 143.22, 149.54, 150.99, 152.32, 153.48, 155.94, 156.38, 156.70, 156.95 and 180.67 (COO). Calc. for $[C_{22}H_{26}Cl_2CoN_5O_{10}\cdot H_2O$: C, 39.90; H, 3.35; N, 10.57. Found: C, 39.67; H, 3.00; N, 10.34%. UV-VIS: 486 nm (93 M^{-1} cm^{-1}). MS (FAB): m/z 544 ($\{[Co(gly)(2,2'\text{-bpy})_2]ClO_4\}^+$).

(b) $[Co(ala)(2,2'\text{-bpy})_2][ClO_4]_2\cdot H_2O$. Two diastereoisomers were found in the crude product. A COSY spectrum aided the assignment of peaks in the ^{1}H NMR spectrum for the minor isomer as the signal of the α-H was fully obscured by the residual H_2O peak. This assignment was confirmed by obtaining a spectrum in D_2O which revealed the resonances for both α-H. ^{1}H NMR (dmso-d^6): major isomer, δ 1.18 (d, CH_3, 3 H, J = 6.8 Hz), 3.85 (q, α-H, 1 H), 5.82 (br t, NH, 1 H), 7.11–7.18 (d, bpy H overlapping with NH, 2 H), 7.59–7.73 (br m), 8.15–8.21 (m), 8.38–8.45 (m), 8.68–8.73 (m), 8.90 (m), 8.98–9.05 (m)

and 9.18 (d, 1 H); minor isomer, δ 1.39 (d, CH_3, 3 H, $J = 7.3$ Hz), 3.36 (α-H, obscured by H_2O peak), 6.17 (br m, NH, 1 H) and 6.63 (br m, NH, 1 H); most of the bipyridine resonances overlapped those of the major isomer, however the following peaks could be seen clearly, δ 8.49 (d, 1 H, $J = 5.4$) and 9.28 (d, 1 H, $J = 5.4$ Hz). ^{13}C NMR (dmso-d^6): major isomer, δ 19.34 (CH_3), 52.06 (α-C), 124.95 (2C), 125.72, 126.36, 128.89, 129.14, 130.01, 130.19, 142.31 (2C), 142.98, 143.41, 148.85, 150.99, 152.73, 153.58, 156.37, 156.52, 157.19, 157.26 and 182.12 (COO); minor isomer, δ 18.74 (CH_3), 51.82 (α-C) and 182.48 (COO); again most of the bipyridine signals were obscured by the major isomer, however nine peaks were identifiable, δ 125.12, 125.72, 129.25, 129.71, 143.09, 149.69, 151.42, 156.58 and 157.10. Calc. For $[C_{23}H_{22}Cl_2CoN_5O_{10}\cdot H_2O$: C, 40.85; H, 3.58; N, 10.36. Found: C, 40.80; H, 3.30; N, 10.04%. UV-VIS: 482 nm (92 M^{-1} cm^{-1}). MS (FAB): *m*/*z* 558 ({[Co(ala)(2,2′-bpy)$_2$]ClO_4}$^+$).

(c) [Co(val)(2,2′-bpy)$_2$][ClO$_4$]$_2$. A mixture of diastereoisomers was present in the crude product. A diastereoisomerically pure product was obtained by recrystallising the crude product from dilute $HClO_4$ several times. ^{1}H NMR (dmso-d^6): major isomer, δ 0.60 (d, $CH(CH_3)_2$, 3 H, $J = 7.0$), 0.96 (d, $CH(CH_3)_2$, 3 H, $J = 7.0$ Hz), 2.08 (br m, $CH(CH_3)_2$, 1 H), 3.77 (br m, α-H, 1 H), 5.04 (br t, NH, 1 H), 7.03 (br m, NH coincident with bpy H, 2 H), 7.60–7.71 (m, 3 H), 8.15 (br s, 2 H), 8.40–8.46 (br m, 3 H), 8.68–8.72 (m, 2 H), 8.87–9.00 (m, 3 H), 9.07 (d, 1 H) and 9.27 (d, 1 H). ^{13}C NMR (dmso-d^6): major isomer, δ 15.80, 18.06 (both $CH(CH_3)_2$), 30.54 ($CH(CH_3)_2$), 61.34 (α-C), 124.67, 124.81, 125.52, 125.96, 128.48, 128.96, 129.42, 129.79, 142.08 (2C), 142.72, 143.23, 149.14, 150.73, 152.94, 153.55, 156.44, 156.67, 156.94, 157.70 and 180.54 (COO). Calc. for $[C_{25}H_{26}Cl_2CoN_5O_{10}$: C, 43.75; H, 3.82; N, 10.20. Found: C, 43.44; H, 3.90; N, 9.86%. UV-VIS: 483 nm (99 M^{-1} cm^{-1}). MS (FAB): *m*/*z* 586 ({[Co(val)(2,2′-bpy)$_2$]ClO_4}$^+$).

(d) [Co(cpg)(2,2′-bpy)$_2$][ClO$_4$]$_2$·H$_2$O. Both diastereoisomers were found in the crude product. Again, a COSY spectrum helped in the interpretation of the ^{1}H NMR spectra. ^{1}H NMR (dmso-d^6): major diastereoisomer, δ 0.40–0.70 (br m, cyclopropyl CH_2s, 4 H), 0.75–0.85 (br m, cyclopropyl CH, 1 H), 3.01–3.09 (m, α-H, 1 H), 6.00–6.06 (br m, NH, 1 H), 7.08 (d,1H), 7.13–7.19 (br m, NH, 1 H), 7.59–7.67 (m, 3 H), 8.11–8.21 (m, 2 H), 8.36–8.43 (m, 2 H), 8.49 (d, 1 H), 8.63–8.74 (m, 2 H), 8.86–8.91 (m, 2 H), 8.96–9.04 (m, 2 H), 9.12 (d, 1 H); ^{1}H NMR (dmso-d^6): minor diastereoisomer, δ 0.40–0.70 (br m, cyclopropyl CH_2), 1.18 (br m, cyclopropyl CH, 1 H), 2.62 (m, α-H, 1 H), 6.38 (br m, NH, 1 H) and 6.62 (br m, NH, 1 H); most of the bipyridine resonances were coincident with those of the major isomer except δ 9.35 (d, 1 H, $J = 5.3$ Hz). ^{13}C NMR (dmso-d^6): major isomer, δ 2.91, 4.93 (both cyclopropyl CH_2s), 14.95 (cyclopropyl CH), 60.45 (α-C), 124.63, 124.72, 125.48, 126.06, 128.55, 128.92, 129.89, 129.92, 142.03 (2C), 142.65, 143.09, 148.72, 150.66, 152.57, 153.40, 156.33 (2C), 156.90, 156.26 and 180.12 (COO); minor isomer, a few peaks were distinguishable from those of the major diastereoisomer, δ 5.70 (cyclopropyl CH_2), 14.12 (cyclopropyl CH) and 180.65 (COO). Calc. for $[C_{25}H_{24}Cl_2CoN_5O_{10}\cdot H_2O$: C, 42.75; H, 3.73; N, 9.97. Found: C, 42.71; H, 3.75; N, 10.01%. UV-VIS: 479 nm (105 M^{-1} cm^{-1}). MS (FAB): *m*/*z* 584 ({[Co(cpg)(2,2′-bpy)$_2$]ClO_4}$^+$).

(e) [Co(aib)(2,2′-bpy)$_2$][ClO$_4$]$_2$·H$_2$O. ^{1}H NMR (dmso-d^6): δ 1.01, 1.35 (both s, CH_3, total 6 H), 6.10 (d, 1 H, NH), 6.61 (d, 1 H, NH), 7.03 (d, 1 H), 7.63 (t, 1 H), 7.70 (t, 1 H), 7.86 (d, 1 H), 8.16 (t, 1 H), 8.24 (t, 1 H), 8.39–8.45 (m, 3 H), 8.72 (m, 2 H), 8.89 (m, 2 H), 9.00 (d, 1 H), 9.08 (d, 1 H) and 9.52 (d, 1 H). ^{13}C NMR (dmso-d^6): δ 27.50, 28.38 (both CH_3), 58.75 (α-C), 124.73, 124.94, 125.59, 126.31, 128.52 (2C), 128.91, 129.54, 142.07, 142.13, 143.01, 143.33, 149.26, 150.82, 152.42, 153.59, 156.66, 156.81, 157.31, 157.78 and 184.49 (COO). Calc. for $[C_{24}H_{24}Cl_2CoN_5O_{10}\cdot H_2O$: C, 41.76; H, 3.80; N, 10.14. Found: C, 41.58; H, 4.07; N, 9.86%. UV-VIS: 482 nm (99 M^{-1} cm^{-1}). MS (FAB): *m*/*z* 572 ({[Co(aib)(2,2′-bpy)$_2$]ClO_4}$^+$).

3. Steady state photolysis

These experiments were performed using a 200 W high pressure mercury arc lamp equipped with a 254 nm Pyrex filter (Corning 7-54). The D_2O solutions, in NMR tubes or UV cells, were cooled in a quartz ice–water bath during irradiation. The ^{1}H NMR spectra were run following 60–70 min of photolysis.

(a) [Co(ala)(2,2′-bpy)$_2$][ClO$_4$]$_2$·H$_2$O. ^{1}H NMR spectrum following photolysis (DCl): free alanine, δ 1.59 (d, 3 H, CH_3, $J = 7.3$ Hz) and 4.12 (m, 1 H, α-H); acetaldehyde, δ 2.23 (br s, 3 H, CH_3) and 9.66 (br s, 1 H); hydrated acetaldehyde, δ 1.31 (d, 3 H, CH_3) and 5.23 (d, 1 H); free bipyridine, δ 7.98 (m, 2 H), 8.52 (m, 4 H) and 8.91 (m, 4 H); $[Co(2,2'\text{-bpy})_3]^{3+}$, δ 7.51 (d, 6 H, $J = 5.8$), 7.83 (t, 6 H, $J = 7.3$), 8.58 (t, 6 H, $J = 7.8$) and 8.88 (d, 6 H, $J = 7.8$ Hz).

(b) [Co(val)(2,2′-bpy)$_2$][ClO$_4$]$_2$. ^{1}H NMR spectrum following photolysis (DCl): free valine, δ 0.97–1.04 (m, 6 H, both $CH(CH_3)_2$), 2.26 (m, 1 H, $CH(CH_3)_2$) and 4.04 (d, 1 H, α-H, $J = 2.5$ Hz); 2-methylpropanal, δ 0.89 (d, $CH(CH_3)_2$), 1.71 (m, $CH(CH_3)_2$) and 9.57 (d, 1 H, $J = 1.4$ Hz); hydrated 2-methylpropanal, δ 1.08 (d, $CH(CH_3)_2$), 2.61 (m, 1 H, $CH(CH_3)_2$) and 4.71 (d, 1 H, $J = 5.4$ Hz); free bipyridine, δ 7.98 (m, 2 H), 8.52 (m, 4 H) and 8.91 (m, 4 H); $[Co(2,2'\text{-bpy})_3]^{3+}$, δ 7.51 (d, 6 H), 7.83 (t, 6 H), 8.58 (t, 6 H) and 8.88 (d, 6 H).

(c) [Co(cpg)(2,2′-bpy)$_2$][ClO$_4$]$_2$·H$_2$O. ^{1}H NMR spectrum following photolysis (DCl): free cpg, δ 0.40–0.85, 1.14 and 3.13 (peaks assigned in section 1(b)); cyclopropanecarbaldehyde, δ 1.38 (br m, cyclopropyl CH_2, 4 H), 1.95 (br m, 1 H, cyclopropyl CH) and 8.79 (d, 1 H, $J = 7.4$ Hz); free bipyridine, δ 7.98 (m, 2 H), 8.52 (m, 4 H) and 8.91 (m, 4 H); $[Co(2,2'\text{-bpy})_3]^{3+}$, δ 7.51 (d, 6 H), 7.83 (t, 6 H), 8.58 (t, 6 H) and 8.88 (d, 6 H). The D_2O photolysate was extracted with $CDCl_3$. ^{1}H NMR ($CDCl_3$): δ 1.08 (complex peak, 4 H), 1.84 (br m, 1 H) and 8.91 (d, 1 H, $J = 5.8$ Hz). ^{13}C NMR ($CDCl_3$): δ 7.29, 22.66 and 201.33.

(d) [Co(aib)(2,2′-bpy)$_2$][ClO$_4$]$_2$·H$_2$O. ^{1}H NMR spectrum following photolysis (DCl): free aib, δ 1.61 (s, 6 H); acetone, δ 2.23 (s); free bipyridine, δ 7.98 (m, 2 H), 8.52 (m, 4 H) and 8.91 (m, 4 H); $[Co(2,2'\text{-bpy})_3]^{3+}$, δ 7.51 (d, 6 H), 7.83 (t, 6 H), 8.58 (t, 6 H) and 8.88 (d, 6 H).

4. Theoretical procedures

Ab initio calculations were performed with GAUSSIAN94.[12] Reactant and transition state structures were optimised at the B3LYP level of theory using the 6-31G* basis set. Vibrational frequencies were also calculated with these methods, and scaled with appropriate factors (1.0013 for the vibrational partition function and 0.9806 for the zero point energy).[13] The partition functions and, subsequently, the rate constants were evaluated at three different temperatures, and numerical differentiation of $\ln(k)$ with respect to T^{-1} yielded the Arrhenius parameters, A and E_{act}. All vibrational modes were treated as harmonic oscillators for the evaluation of the vibrational partition functions. Errors associated with this approximation will be small as the vibrational partition functions for the transition state and the reactant, $Q^{\ddagger}_{vib}$ and Q_{vib}, are treated in the same manner.[14]

Results

Ab initio calculations

Although the calculations in this study were initiated before

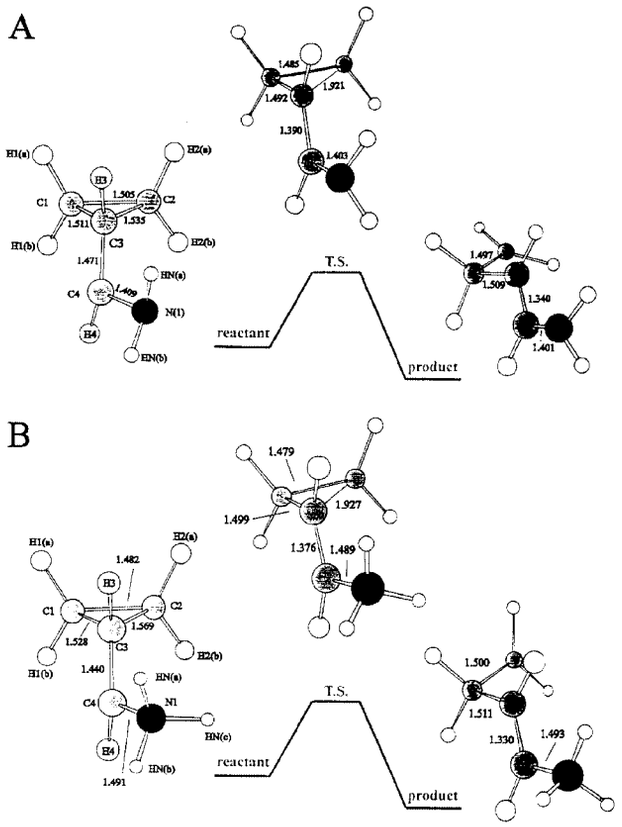


Fig. 1 The calculated geometries for the reactants, transition states and calculated products of the unprotonated (A) and protonated (B) radicals; bond lengths in Å.

publication of the paper by Smith *et al*,[7] the recommendations in that report subsequently shaped our approach to the theoretical determination of a rate constant for ring opening of the aminocyclopropylmethyl radical. The calculated geometries for the reactants, products, and transition states of the protonated and unprotonated radicals, along with selected bond lengths, are displayed in Fig. 1. The energies, zero-point corrections, spin distributions, and atomic co-ordinates for all the radicals and the transition states are given in SUP 57632.

The unprotonated radical is predicted to have C_1 symmetry and the geometry around the spin-bearing carbon is marginally non-planar (sum of bond angles = 351.9°, RMS deviation from plane = 0.094 Å), like the aminomethyl radical.[15] The shortness of the C4–N1 bond (1.409 Å) and the calculated spin density on the nitrogen centre are indicative of significant delocalisation of the unpaired electron. This is a well documented phenomenon for α-aminoalkyl radicals.[16]

The atoms which are part of, or attached to, the incipient double bond are predicted to be close to planar in the calculated geometry of the transition state for the ring opening of the aminocyclopropylmethyl radical (RMS deviation from plane for C1,C3, H3, C4, H4, N1 = 0.042 Å, *cf.* 0.028 Å for the product). The constant length of the C4–N1 bond throughout the reaction is consistent with continued delocalisation of the nitrogen lone pair.

The geometry of the protonated aminocyclopropylmethyl radical is broadly similar to that of its unprotonated analogue. The relative conformation of the amine group remains unchanged, with a hydrogen atom being present in the position the nitrogen lone pair occupies in the unprotonated molecule. Protonation of the lone pair appears to mitigate its ability to overlap with the radical centre, hence the longer C4–N1 bond (1.491 Å), and the absence of spin density on N1. The radical centre, C4, is marginally non-planar (bond angle sum = 354.6°, RMS deviation from plane = 0.076 Å). The location of spin density on C2 implies that the radical has a significant interaction with the cyclopropyl ring.

Table 1 Arrhenius parameters for the rearrangement of the unprotonated and protonated aminocyclopropylmethyl (acp) radicals

	log *A*	E_{act}/kJ mol^{-1}	k/s^{-1} (298 K)
acp ring opening	13.1	39.6	1×10^6
acp ring closing	12.4	49.6	5×10^3
Hacp$^+$ ring opening	13.0	21.9	2×10^9
Hacp$^+$ ring closing	12.2	29.0	1×10^7

The Arrhenius parameters predicted for the rearrangement reactions of the amine substituted radical (acp) and its protonated form (Hacp$^+$) are shown in Table 1. The inclusion of an unprotonated amine substituent at the radical centre is predicted to decrease the rate of the ring opening reaction from that seen for the unsubstituted case. The ring-closing reverse reaction is predicted to have a rate constant two hundred times smaller than that for the ring-opening reaction. The rate constants for the ring-opening and -closing reactions of the protonated forms are both significantly larger than for the unprotonated species.

Synthesis and characterisation

R,S-Cyclopropylglycine was prepared from lithium 5-bromo-2-oxopentanoate *via* a template synthesis on cobalt(III), extending the work of Lawson *et al*.[9] In that work a cobalt(III) complex of cyclopropylglycinate was prepared *via* the reduction of a chelated 2-cyclopropyl-2-iminoethanoate ligand. We employed more vigorous conditions to reduce the cobalt centre to the +2 oxidation state at the same time, thereby liberating the amino acid from the metal centre. The cyclopropylglycine was then purified by ion-exchange chromatography in order to avoid contamination from NH_4^+ and cobalt(II) species, and recrystallised to give a microanalytically pure product.

It was important to optimise the synthetic route to the $[Co(aa)(2,2'\text{-bpy})_2]^{2+}$ (aa = α-amino acidate) complexes, given the small amount of cyclopropylglycine (Hcpg) which we were able to isolate, and its comparatively laborious preparation. We employed the valinato (val) complex as a model and found the method of Tatehata[10] superior to several alternatives which appear in the literature.[17] Tatehata prepared a series of $[Co(S\text{-aa})(phen)_2]^{2+}$ complexes (phen = 1,10-phenanthroline), from $[CoCl_2(phen)_2]^+$ in basic methanol, and separated the reaction products by ion-exchange chromatography. The yields following this procedure, substituting 2,2′-bpy for phen, were greater than those obtained when using $[Co(CO_3)(2,2'\text{-bpy})_2]^+$ as a precursor, or *via* the PbO_2 oxidation of an aqueous solution containing Co^{II}, an amino acid, and bipyridine. The formation of side-products, notably $[Co(aa)_2(2,2'\text{-bpy})]^+$ and $[Co(2,2'\text{-bpy})_3]^{3+}$, persisted however.

Complexes $[Co(aa)(2,2'\text{-bpy})_2]^{2+}$ of chiral amino acids may exist as two diastereoisomers. A preference for one diastereoisomer was noted in the preparation of the alaninato (3:1), valinato (9:1) and cyclopropylglycinato (5:2) complexes. In the case of the $[Co(val)(2,2'\text{-bpy})_2]^{2+}$ complex it was possible to purify one of the diastereoisomers by fractional crystallisation, however both isomers persisted to some degree for the $[Co(ala)(2,2'\text{-bpy})_2]^{2+}$ and $[Co(cpg)(2,2'\text{-bpy})_2]^{2+}$ complexes. Alternative separation methods were not explored as, for the purposes of our photolysis experiments, the presence of two diastereoisomers was considered to be of little consequence. The acquisition of COSY spectra proved useful for the assignment of the ^{1}H NMR spectra, especially in the cases where both diastereoisomers were present.

A similar degree of stereoselectivity in the formation of $[Co(S\text{-aa})(phen)_2]^{2+}$ complexes was observed by Tatehata[10] who

postulated that the energy differences between the diastereoisomers was a result of repulsive interactions between the α-H of the diimine ligand and the α-substituent of the amino acid. He concluded that the major diastereoisomer had the Λ-*S* configuration after analysis of both CD and ^{1}H NMR spectra.

Anisotropic magnetic fields in the vicinity of the 2,2′-bpy ligands leads to the observation of significant differences in the ^{1}H NMR chemical shifts for the two diastereoisomers of the alaninato, valinato, and cyclopropylglycinato complexes. These differences were consistent with the Δ-*R*/Λ-*S* configuration also being preferred for the complexes we have studied.

Steady state photochemistry

Steady state photolysis experiments were performed on D_2O solutions of a series of $[Co(aa)(2,2'\text{-bpy})_2]^{2+}$ complexes and ^{1}H NMR spectroscopy was used to identify the photolysis products. Acetaldehyde, 2-methylpropanal, and acetone were identified as photolysis products from the alaninato, valinato, and 2-aminoisobutyrato complexes respectively. The hydrated forms of the two aldehydes were also present, as would be expected in aqueous solution. Free amino acid was always present in solution following photolysis, and we were also able to identify $[Co(2,2'\text{-bpy})_3]^{3+}$ and free 2,2′-bipyridine. The relative concentrations of the products were determined by reference to an added internal standard (TMPS), and the identities of the products were confirmed by spiking the solution with authentic samples.

Addition of DCl to the neutral photolysates resulted in large increases in the integrals of the free bipyridine and free amino acid signals in the ^{1}H NMR spectra. It has been noted previously[3] that a significant amount of Co^{II} is produced during irradiation of $[Co(aa)(2,2'\text{-bpy})_2]^{2+}$ complexes. The interaction of this paramagnetic cation with the free bipyridine and free amino acid is likely to reduce the intensity of their ^{1}H NMR peaks. However, this association, and the accompanying reduction of the NMR integrals, will be lessened in the presence of acid, accounting for the above observation.

Measurement of ^{1}H NMR signal integrals in the acidified samples against an internal standard allowed us to account for all of the starting material following irradiation of the $[Co(aib)(2,2'\text{-bpy})_2]^{2+}$ complex. We found that, for a 50 mM solution, the ratio of free aib : acetone in the photolysate was approximately 3 : 1. The ratio increases with increasing concentration of starting material. Free bipyridine and $[Co(2,2'\text{-bpy})_3]^{3+}$ were usually present in approximately equal amounts, although the concentration $[Co(2,2'\text{-bpy})_3]^{3+}$ increased gradually over time.

Unfortunately, full material balances could not be achieved for the other complexes. We ascribe this to a combination of (i) the volatility of the aldehydes, (ii) persistent interactions of the free amino acids with the paramagnetic cobalt(II) cation, (iii) poor signal to noise ratio in the NMR spectra at high concentrations of DCl and (iv) possible aldol polymerisation of the aldehydes.

The results from ^{1}H NMR analysis of irradiated solutions of $[Co(cpg)(2,2'\text{-bpy})_2]^{2+}$ were entirely analogous to those obtained for the other amino acid complexes. The products identified were free amino acid, $[Co(2,2'\text{-bpy})_3]^{3+}$, free 2,2′-bipyridine, and cyclopropanecarbaldehyde. A COSY spectrum was obtained in order to confirm the identification of the latter. Also, the aldehyde was extracted into $CDCl_3$ so that the ^{1}H and ^{13}C NMR spectra could be compared to those previously published for this compound.[18] The coupling pattern shown by the COSY spectrum was fully consistent with that expected with the methine proton, displaying a correlation with the cyclopropyl ring protons and the aldehyde proton. The spectra run in chloroform were nearly identical to those published for authentic samples.

Discussion

Ab initio calculations

The geometries, energies, and vibrational frequencies of a reacting species and of the transition state along the reaction pathway are the fundamental properties required to evaluate a rate constant with transition state theory. In the present study these values were assessed at the B3LYP/6-31G* level of theory which has been shown to produce accurate values for a number of related systems.[7]

Although the B3LYP technique has gained reputation for underestimating reaction barriers,[19] the reverse appears to be true for cyclopropylmethyl radicals. For example, in the case of the cyclopropylmethyl radical, the B3LYP/6-31G* level of theory actually *overestimates* the reaction barrier by 3.8 kJ mol^{-1}. Moreover, for the key reaction in the present study, the rearrangement of the protonated aminocyclopropylmethyl radical, a 5 kJ mol^{-1} increase in the reaction barrier would induce a mere sixfold reduction in the rate constant (298 K).

The differences between the rates calculated for the reactions of the protonated and unprotonated radicals are presumably related to the degree to which the unpaired electron is delocalised towards or away from the nitrogen substituent, and therefore the degree to which it can interact with the cyclopropyl ring. The equilibria for both the unprotonated and protonated cases are predicted to lie towards the ring opened forms. We consider that the protonated case is likely better to model the cobalt bound system since the absence of a lone pair on the nitrogen atom drastically reduces the degree to which the spin density can be delocalised onto the nitrogen atom.

All calculations were based on the presumption that the reacting species are in the gas phase. This means that favourable transition-state polarisation effects may be overlooked by the theoretical procedure, as no account is made for solvation effects. Experimentally, ring opening of an ester-substituted cyclopropylmethyl radical was found to accelerate with increasing solvent polarity,[20] and it rearranges faster than its unsubstituted parent. This contrasts with theoretical predictions at the B3LYP/6-31G* level which estimate a 30-fold drop in the rate constant upon ester substitution.[8c] A possible contribution from an iminium resonance form in the ring opening of the unprotonated radical may lead to the calculated rate constants being less reliable than for other cases.

Our best prediction for the rate constant for ring opening of the protonated aminocyclopropylmethyl radical is in the range of 10^8–10^9 s^{-1}. It is this reaction that we expect to be the closer model for our cobalt containing system.

Provided the structural, steric, and electronic differences will not have major implications for the rate constant for ring opening, the best estimate for the rate of rearrangement of the co-ordinated aminocyclopropylmethyl radical has an upper bound at 10^9 s^{-1} at room temperature and a reasonable lower bound could be set at 10^7 s^{-1}. Furthermore, the rate constant for the reverse reaction should be around two orders of magnitude smaller than that of the forward reaction.

Given that formation of the metallacycle from the radical and cobalt(II) is proposed to occur with a rate constant (k_c) of 10^3 s^{-1}, it should be several orders of magnitude too slow to compete with the rearrangement reaction. Thus, the currently accepted mechanism would predict that exclusively ring-opened products will be observed following the photolysis of $[Co(cpg)(bpy)_2]^{2+}$.

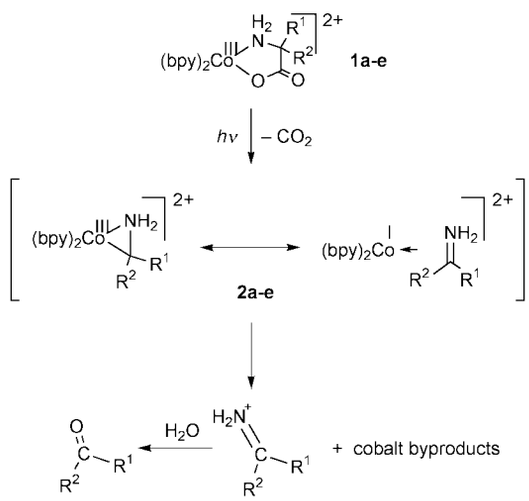
Steady state photolysis products

The use of ^{1}H NMR spectroscopy has allowed us to show that carbonyl compounds, derived from the C–N fragment of the amino acid, are produced in the photolysis of $[Co(aa)(2,2'\text{-bpy})_2]^{2+}$ complexes. It has been noted by Povlovskii and Poznyak[3] that substituents on either the α-carbon or the

nitrogen atom will destabilise the cobalt(III)–alkyl photoproduct, although this is the first report detailing the nature of the decomposition products. Similar behaviour has been reported for the complexes $[Co(edta)]^-$ [21] (edta = ethylenedinitrilotetraacetate), $[Co(gly)_3]$ and $[Co(ala)_3]$,[22] for which aldehydes were detected as photooxidation products of the aminocarboxylato ligands.

Poznyak and co-workers have characterised, by electronic spectroscopy, the primary photoproducts of the $[Co(val)(2,2'\text{-bpy})_2]^{2+}$,[3] $[Co(val)(en)_2]^{2+}$ [2a] and $[Co(ala)(trien)]^{2+}$ [2a] complexes, following UV irradiation at low temperature (trien = triethylenetetramine). The UV-Vis spectrum of the thermally unstable photoproduct of $[Co(val)(2,2'\text{-bpy})_2]^{2+}$ closely resembled that of the crystallographically characterised $[Co(CH_2NH_2)(2,2'\text{-bpy})_2]^{2+}$ complex ion and, on this basis, the authors concluded that photolysis of the valinato complex also yielded a Co–C–N metallacycle.

Given that irradiation of the complexes of α-substituted amino acids does indeed lead to the formation of metallacyclic complexes, the carbonyl compounds which we observe are likely the result of the thermal decomposition of these metallacycles. A possible pathway is shown in Scheme 2, where



Scheme 2

the Co–C–N metallacycles **2a–2e**, which can also be considered as π-bound cobalt(I)–methyliminium complexes,[4] lose the C–N fragment as an iminium ion, leaving the cobalt centre in the +1 oxidation state. Iminium ions are prone to hydrolysis and, in D_2O, will readily convert into the corresponding carbonyl compound.

The cobalt(I) species could then undergo redox reactions, either with starting material or with water, eventually to give the observed cobalt(II) compounds. Redox reactions with starting material would also account for the presence of free amino acid following photolysis, as the resulting cobalt(II) complexes would be substitutionally labile and could catalyse ligand exchange reactions of further molecules of starting material. The concentration dependence of the aib : acetone ratio is consistent with these proposals, since the rates of the second order redox reactions that could lead to production of the free amino acid would have a greater dependence on the concentration of the complex ions than those of reactions leading to the carbonyl compounds, which would be expected to be first order in complex concentration. Amino acid products would therefore be favoured at higher concentrations.

The use of a cyclopropylglycinato complex as a radical clock

The cyclopropylmethyl radical is a well calibrated radical clock which ring-opens to the 1-butenyl radical at 1.0×10^8 s^{-1} (298 K),[23] and the foregoing discussion led to the conclusion that the aminocyclopropyl radical co-ordinated to cobalt(II) could reasonably be predicted to have a rate constant for ring opening in the range 10^7–10^9 s^{-1}, with an equilibrium constant of approximately 200, favouring the ring opened form.

The cyclopropylmethyl radical clock, and many substituted analogues, have found wide application in the investigation of reaction mechanisms involving radical intermediates.[24] It is generally accepted that the appearance of ring-opened products is direct evidence that a discrete free radical is formed on the α-carbon, with the ratio of ring-opened to ring-intact products providing an indication of the relative rates of the intramolecular rearrangement and the reaction of interest. However, if only products containing a cyclopropane ring are isolated, then several possibilities exist. The first is that there is no radical intermediate involved in the reaction. The second is that there is a radical intermediate, but that its lifetime is so short that the ring-opening reaction cannot compete with the reaction that is being probed. The final possibility is that reaction of the ring-opened radical is so slow that, in spite of the equilibrium constant favouring the ring-opened radical, all the products result from reaction of the ring-closed form. It would be remarkable if reaction of a reactive species like the ring-opened radical could not compete with a reaction which is proposed to proceed with a rate constant of 10^3 s^{-1}. This is particularly so when the equilibrium gives the ring-opened radical a significant concentration advantage (by a factor of 200) over the ring-closed radical. We therefore feel able to discount this third possibility.

According to the published mechanism for formation of the metallacyclic complexes, photoinduced homolysis of the Co–O bond will lead to decarboxylation and the generation of a cobalt(II)-bound aminocyclopropylmethyl radical. This radical can act as a radical clock, whereby ring opening will compete with recombination with the metal centre. The relative rates of these two competing processes, k_c versus k_r, will determine the ratio of ring-opened to ring-intact products.

The cyclopropane ring was found to survive the photolysis of $[Co(cpg)(2,2'\text{-bpy})_2]^{2+}$ and, as expected on the basis of our investigation of analogous complexes, it was found as cyclopropanecarbaldehyde. No ring-opened products were detected by ^1H NMR spectroscopy.

The appearance of an intact cyclopropane ring in the photolysis products demonstrates that, if the co-ordinated radical is formed, reaction to give a cobalt(III)-alkyl complex dominates the potential ring-opening reaction. Therefore, provided any further reaction of the ring-opened radical species is not very slow, the rate of this Co–C bond formation step (k_c) must be significantly faster than 10^7 s^{-1}. This means that the co-ordinated aminocyclopropylmethyl radical, if formed at all, has a lifetime much shorter than 10^{-7} s. This lifetime is four orders of magnitude shorter than that inferred by the assignment of the rate determining step in the original kinetic study.

Conclusion

We have shown that the lifetime of any cobalt(III)-bound aminoalkyl radical that may be formed in the UV photolysis of complexes of the type $[Co(aa)(2,2'\text{-bpy})_2]^{2+}$ is less than 10^{-7} s. On the basis of our results and those of the flash photolysis study,[5] either the currently accepted mechanism for the photodecarboxylation of cobalt(III)-amino acid complexes is incorrect or, at least, the rate determining step has been incorrectly assigned. If the latter is true then one of the other steps, Co–O bond homolysis or decarboxylation,[25] must be significantly slower than has been observed previously. We are continuing our investigations of these reactions with the aim of obtaining information which may give us further insights into the mechanism of metallacycle formation. In particular, we will have to consider the possibilities that the reaction does not proceed by a radical pathway, or that a radical intermediate is involved, but reacts rapidly (*e.g.* by β scission of the radical to generate a

cobalt(I) species and iminium ion) to give other intermediates which can then give rise to metallacycles and their eventual decomposition products.

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