

Decarboxylation of an α -amino acid coordinated to cobalt(III): kinetic stabilisation and molecular structure of a Co-C-N three-membered ring incorporated into a cobalt(III) macrocyclic ligand complex†‡

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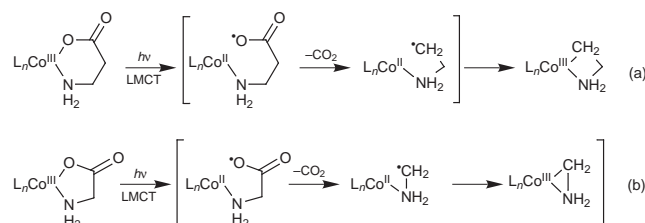
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Photochemically-induced decarboxylation of a cobalt(III) cyclam complex bearing two coordinated *N*-carboxymethyl pendant arms results in kinetic stabilisation of the resulting aminoalkyl three-membered Co-C-N ring, which has been characterised by an X-ray crystal structure determination.

Cobalt(III) complexes containing chelated amino acids have been subjected to intense investigation, with most attention being paid to α -amino acid complexes. They have been used as activating and protecting groups in peptide synthesis, and they undergo a variety of useful reactions, many of which cannot be achieved with non-complexed α -amino acids.¹ These include alkylation at the α -carbon, imine formation, and condensation, oxidation and decarboxylation reactions.

The mechanism proposed for the photochemical decarboxylation of cobalt amino acid complexes involves, in sequence, excitation into the LMCT band, homolytic cleavage of the cobalt–oxygen bond, loss of carbon dioxide and recombination to produce a new cobalt(III)–carbon bond as part of a chelating aminoalkyl group (Scheme 1).^{2,3} When the substrate contains a β -amino acid the resulting aminoalkyl group comprises a four-membered Co-C-C-N ring [Scheme 1(a)], and several such examples have been structurally characterised.⁴ However, the corresponding three-membered rings that would result from decarboxylation of a chelated α -amino acid ligand [Scheme 1(b)] have proved to be more elusive.² In just one case, the use of the π -acids bipyridine or phenanthroline as the ancillary ligands on cobalt led to isolable products containing three-membered Co-C-N rings.⁵ The compound resulting from the decarboxylation of the glycinate ligand in $[\text{Co}(\text{gly})(\text{bipy})_2]^{2+}$ was characterised by crystallography. Although the hydrogen atoms in the cobalt aminoalkyl moiety were not located and the structural and spectroscopic data were not fully reconciled, this structure did serve to demonstrate the formation of a three-membered ring by a decarboxylation reaction.

We have investigated kinetic stabilisation of the Co-C-N three-membered ring. As part of our interest in reactions of ligands coordinated to cobalt(III) we have prepared complexes of macrocyclic and acyclic hexadentate ligands bearing pendant coordinated α -amino acid groups.^{6,7} They are ideal substrates for investigation of decarboxylation reactions, as the resulting aminoalkyl group would be appended to a macrocyclic ligand. One such candidate is $[\text{Co}(1,4\text{-bcc})]\text{ClO}_4$ (1,4-bcc = 1,4-bis-(carboxymethyl)cyclam) which contains a cyclam-based tetraazamacrocycle bearing two *N*-carboxymethyl substituents.⁷ An

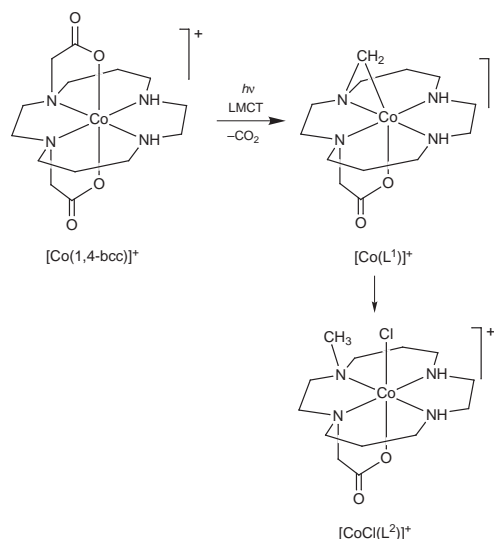


Scheme 1

aqueous solution containing $[\text{Co}(1,4\text{-bcc})]\text{ClO}_4$ was irradiated for 120 minutes at 0°C , resulting in a colour change from pink to pale orange. The product was purified by ion exchange chromatography, isolated as the salt $[\text{Co}(\text{L}^1)]\text{BPh}_4$, and characterised by elemental analysis, cyclic voltammetry, UV-visible, ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy and an X-ray crystal structure determination.[§] The complex contains a substituted cyclam macrocycle bearing one intact *N*-carboxymethyl arm, but loss of CO_2 from the other *N*-carboxymethyl group results in a three-membered ring containing a cobalt σ -alkyl group (Scheme 2).

The molecular structure of the $[\text{Co}(\text{L}^1)]^+$ cation is shown in Fig. 1. The four nitrogens of the cyclam ring remain coordinated in the equatorial plane and the axial sites are occupied by an oxygen of the one remaining *N*-carboxymethyl group and the newly formed σ -bonded CH_2 group. The presence of the strained three-membered Co-C-N ring results in very irregular geometry around the cobalt atom, as exemplified by the $\text{O}(1)\text{-Co-C}(13)$ and $\text{N}(1)\text{-Co-C}(13)$ angles. The $\text{C}(13)\text{-N}(1)$ bond length is shorter than the other C-N bond lengths in this complex but is still within the range observed for a C-N single bond (1.47 Å).⁸ Both hydrogen atoms on $\text{C}(13)$ were located crystallographically. The $\text{C}(1)\text{-N}(1)\text{-C}(10)$ and $\text{H}(13\text{A})\text{-C}(13)\text{-H}(13\text{B})$ angles of $110.4(2)^\circ$ and $108(3)^\circ$, respectively, indicate sp^3 hybridization at $\text{N}(1)$ and $\text{C}(13)$.

Relative to the precursor $[\text{Co}(1,4\text{-bcc})]^+$, the lengthening of the $\text{Co-O}(1)$ bond,⁴ the shift of the $d\text{-d}$ bands in the UV-visible spectrum⁹ and the more negative reduction potential observed by cyclic voltammetry⁷ are all consistent with the presence of the strong-field σ -bonded alkyl ligand in $[\text{Co}(\text{L}^1)]^+$. The cation has C_1 symmetry and the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum exhibits a unique signal for each of the 13 carbon atoms.



Scheme 2

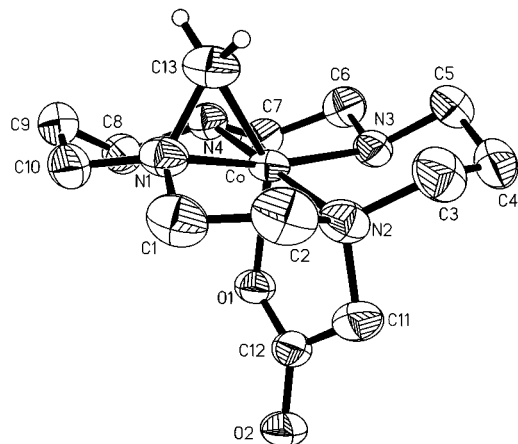


Fig. 1 Molecular structure of $[\text{Co}(\text{L}^1)]\text{BPh}_4$. Selected bond lengths (\AA) and angles ($^\circ$): Co–O(1) 1.993(2), Co–N(1) 1.920(2), Co–N(2) 1.993(2), Co–N(3) 1.987(2), Co–N(4) 1.961(2), Co–C(13) 1.980(3), C(13)–N(1) 1.447(4), C(13)–H(13A) 0.93(4), C(13)–H(13B) 0.96(4), O(1)–Co–C(13) 143.90(12), N(1)–Co–C(13) 43.52(12), Co–N(1)–C(13) 70.44(17), Co–C(13)–N(1) 66.06(15), O(1)–Co–N(1) 100.54(9).

Only two other structurally characterised examples of a $\text{Co}-\text{CH}_2-\text{NR}_2$ ring have been reported, both incorporated into a polydentate ligand, although they were prepared by quite different routes to that reported here.^{10,11} In one of these examples, the ring was formed by C–H activation of an N–CH₃ group incorporated in a tetraaza macrocycle.¹¹ We observe the complementary reaction to this, wherein $[\text{Co}(\text{L}^1)]\text{BPh}_4$ undergoes Co–CH₂ bond cleavage upon heating in aqueous dilute HCl. The product, $[\text{CoCl}(\text{L}^2)]^+$, was characterised by an X-ray crystal structure determination§ and contains a chloro ligand *trans* to the N-carboxymethyl pendant arm and an N–CH₃ group derived from the CH₂ group (Scheme 2).

$[\text{Co}(\text{L}^1)]^+$ arises from the decarboxylation of a coordinated α -amino acid. Its successful isolation is attributed to the fact that the nitrogen atoms of the α -amino acid moieties in the $[\text{Co}(\text{1,4-bcc})]^+$ precursor are attached to a macrocyclic ligand, resulting in kinetic stabilisation of the aminoalkyl three-membered ring. This complements the earlier report concerning the photochemical decarboxylation of $[\text{Co}(\text{gly})(\text{bipy})_2]^{2+}$ in which stabilisation of the Co–C–N three-membered ring in the product has been attributed to the presence of the π -acid bipyridine ligands.² Our result is general and we have isolated further examples of Co–C–N three-membered rings resulting from photochemical decarboxylation of cobalt(III) complexes containing coordinated α -amino acid groups incorporated into other macrocyclic ligands.

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Notes and references

† This paper is dedicated to our colleague and friend Professor Warren Roper on the occasion of his 60th birthday.

‡ See <http://www.rsc.org/suppdata/cc/1998/2593/>, for experimental data for the complexes reported in this communication.

§ *Crystal data*: $[\text{Co}(\text{L}^1)]\text{BPh}_4 \cdot p\text{-xylene}$: Crystals were grown from acetonitrile–*p*-xylene. $\text{C}_{49}\text{H}_{59}\text{BCoN}_4\text{O}_2$, $M = 805.74$, monoclinic, space

group $P2_1/n$, $a = 14.8555(5)$, $b = 17.4488(6)$, $c = 17.2455(6)$ \AA , $\beta = 110.2770(10)^\circ$, $U = 4193.2(2)$ \AA^3 , $F(000) = 1716$, $D_c = 1.276$ g cm^{-3} , $Z = 4$, $\mu(\text{Mo-K}\alpha)$, $\lambda = 0.71073$ \AA = 0.454 mm^{-1} . Intensity data were collected to a θ limit of 26° on a Siemens 'SMART' diffractometer¹² at 203(2) K and corrected for absorption.¹³ The structure was solved from Patterson and heavy-atom electron density maps¹⁴ and refined by full-matrix least-squares analysis on F^2 employing SHELXL93.¹⁵ All non-hydrogen atoms were allowed to assume anisotropic motion. The two hydrogen atoms on C(13) were located and individually refined. Other hydrogens were placed in calculated positions and refined using a riding model. Refinement converged to 0.0504 ($R_w = 0.1356$) for 6384 reflections for which $I > 2\sigma(I)$.

$[\text{CoCl}(\text{L}^2)]\text{ClO}_4$ (see <http://www.rsc.org/suppdata/cc/1998/2593/>, for molecular structure (Figure S1)): Crystals were grown from aqueous solution. $\text{C}_{13}\text{H}_{27}\text{Cl}_2\text{CoN}_4\text{O}_6$, $M = 465.22$, triclinic, space group $P\bar{1}$, $a = 8.456(2)$, $b = 9.689(3)$, $c = 12.161(6)$ \AA , $\alpha = 90.95(3)$, $\beta = 109.51(3)$, $\gamma = 96.09^\circ$, $U = 932.4(6)$ \AA^3 , $F(000) = 480$, $D_c = 1.650$ g cm^{-3} , $Z = 2$, $\mu(\text{Mo-K}\alpha)$, $\lambda = 0.71069$ = 1.245 mm^{-1} . Intensity data were collected to a θ limit of 25° on an Enraf-Nonius CAD-4 diffractometer¹⁶ at 292(2) K and corrected for absorption.¹⁷ Structure solution as above. The riding model was used for all hydrogens. Refinement converged to 0.0571 ($R_w = 0.1546$) for 2561 reflections for which $I > 2\sigma(I)$. CCDC 182/1072. See <http://www.rsc.org/suppdata/cc/1998/2593/>, for crystallographic files in .cif format.

- J. M. Harrowfield, A. M. Sargeson and P. O. Whimp, *Inorg. Chem.*, 1991, **30**, 1792.
- A. L. Poznyak and V. I. Pavlovski, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 773.
- E. Natarajan and P. Natarajan, *Inorg. Chem.*, 1992, **31**, 1215.
- H. Kawaguchi, M. Yoshida, T. Yonemura, T. Ama, K. Okamoto and T. Yasui, *Bull. Chem. Soc. Jpn.*, 1995, **68**, 874; A. L. Poznyak, V. I. Pawlowski, L. M. Schkolnikowa, N. M. Dzatlowa and A. B. Ilijuchin, *J. Organomet. Chem.*, 1986, **314**, C59; A. V. Gasparyan, L. M. Shkol'nikova, V. K. Bel'skii, A. L. Poznyak, V. E. Stel'mashok and N. M. Dyatlova, *Koord. Khim.*, 1987, **13**, 1710; L. M. Shkol'nikova, A. V. Gasparyan, V. K. Bel'skii, V. E. Stel'mashok, A. L. Poznyak and N. M. Dyatlova, *Koord. Khim.*, 1987, **13**, 823.
- A. L. Poznyak, V. I. Pavlovski, E. B. Chuklanova, T. N. Polynova and M. A. Porai-Koshits, *Monatsh. Chem.*, 1982, **113**, 561; E. B. Chuklanova, T. N. Polynova, M. A. Porai-Koshits, A. L. Poznyak and V. I. Pavlovskii, *Koord. Khim.*, 1988, **14**, 103.
- P. J. Brothers, G. R. Clark, H. R. Palmer and D. C. Ware, *Inorg. Chem.*, 1997, **37**, 5470.
- D. C. Ware, D. M. Tonei, L.-J. Baker, P. J. Brothers and G. R. Clark, *Chem. Commun.*, 1996, 1303.
- J. A. Huheey, E. A. Keiter and R. L. Keiter, *Inorganic Chemistry*, Harper Collins, New York, 2nd edn., 1993, p. A-30.
- M. P. Granchi and B. E. Douglas, *Inorg. Nucl. Chem. Lett.*, 1978, **14**, 23.
- S. M. Polson, L. Hansen and L. G. Marzilli, *J. Am. Chem. Soc.*, 1996, **118**, 4804.
- C.-K. Poon, W.-K. Wan and S. S. T. Liao, *J. Chem. Soc., Dalton Trans.*, 1977, 1247.
- SMART & SAINT, Siemens Analytical Instruments Inc., Madison, Wisconsin, USA, 1994.
- R. H. Blessing, *Acta Crystallogr., Sect. A*, 1995, **51**, 33.
- G. M. Sheldrick, SHELXS-97, Program for the Solution of Crystal Structures, Universität Göttingen, Germany, 1990; SHELXTL, Siemens Analytical Instruments Inc., Madison, Wisconsin, USA, 1994.
- G. M. Sheldrick, SHELXL-93, Program for the Refinement of Crystal Structures, Universität Göttingen, Germany, 1997.
- Enraf-Nonius, CAD-4 Software, Delft, The Netherlands, 1989.
- A. C. T. North, D. C. Phillips and F. S. Matthews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.

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