DALTON
FULL PAPER

The photodecarboxylation of [*N*,*N*-bis(2-pyridylmethyl)amino acidato]phenanthrolinecobalt(III) complexes: – formation and decomposition of metallacyclic species†

Richard M. Hartshorn* and Shane G. Telfer

Department of Chemistry, University of Canterbury, Private Bag 4800, Christchurch, New Zealand. E-mail: r.hartshorn@chem.canterbury.ac.nz

Received 17th April 2000, Accepted 28th June 2000
Published on the Web 27th July 2000

Photolysis of [*N*,*N*-bis(2-pyridylmethyl)amino acidato]phenanthrolinecobalt(III) complexes (amino acidato = glycinato (dpg) or alaninato (dpa) or 2-cyclopropylglycinato (dpc)) with UV light led to elimination of carbon dioxide from the amino acidato chelate and the formation of cobalt(III) complexes which contain a Co–C–N metallacycle. These photolysis products were characterised by NMR and UV-vis spectroscopy and, in the case of dpg, by X-ray crystallography. The eventual decomposition reactions of the photolysis products were monitored by NMR spectroscopy in both D_2O and dilute DCl. The decomposition products included bis(2-pyridylmethyl)amine (bpa) and an aldehyde derived from the carbon atom of the metallacycle and its alkyl substituents. A μ-peroxo dinuclear cobalt(III) complex, $[(bpa)(phen)(Co(O_2)Co(phen)(bpa)]^{4+}$, was formed from the decomposition products and its structure determined by X-ray crystallography. Experiments with a cyclopropyl derivative demonstrate that any intermediates with a radical centre on what was the α-carbon of the amino acid must be very short-lived.

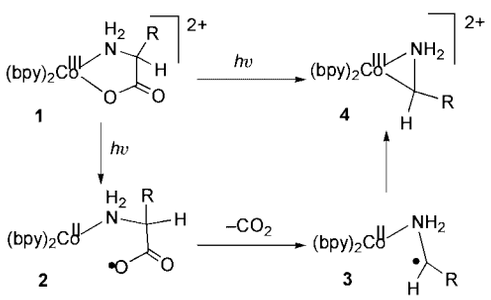
Introduction

The investigation of photochemical reactions of ligands co-ordinated to transition metals is a branch of inorganic chemistry which has not attracted a great deal of attention.[1,2] Reactions of this kind have the potential to provide synthetic avenues to interesting or otherwise inaccessible organic or co-ordination compounds. The reagent (light) is cheap, readily available and is compatible with most solvents and temperatures.

An example of this kind of chemistry can be found in the formation of a complex containing a three-membered Co–C–N metallacycle *via* irradiation of the bis(2,2′-bipyridine)-glycinatocobalt(III) ion, $[Co(gly)(2,2'\text{-bpy})_2]^{2+}$ **1**, with UV light.[3] The metallacyclic product, $[Co(CH_2NH_2)(2,2'\text{-bpy})_2]^{2+}$ **2**, is reasonably stable and has been characterised by X-ray crystallography.[4]

A range of similar reactions has been reported, but the stability of the resulting cobalt–alkyl products varies considerably.[1a,c,3] In particular, photolysis of complexes where the amino acid is substituted at the α position gives metallacycles which have been characterised only by UV-vis spectroscopy in frozen solutions. The decomposition products that are observed from these photochemical reactions include carbonyl compounds in which the substituents are derived from the α-substituents of the original amino acid ligand.[5] It has been noted, however, that the stability of the metallacyclic products is enhanced when the metallacycle is part of a polydentate ligand and when the remaining co-ordination sites on the metal ion are occupied by π-acidic ligands.[1a]

A mechanism for the formation of the metallacyclic compounds has been proposed[1a] (Scheme 1), wherein absorption of UV light leads to homolysis of the cobalt–oxygen bond, affording a cobalt(II)-bound aminoacyloxy radical intermediate **2**. This complex is proposed to undergo a decarboxylation reaction to give a species which contains a co-ordinated aminoalkyl radical, **3**. The alkyl radical is then thought to react with the cobalt(II) centre, yielding the metallacyclic product **4**.



Scheme 1

We have examined the photochemistry of a cyclopropylglycinato complex **1** (R = cyclopropyl) as part of a mechanistic study of this reaction.[5] We found that the cyclopropane ring was retained in the final product, cyclopropanecarbaldehyde. This aldehyde was presumed to result from decomposition of the metallacyclic compound **4**. This presumption, together with the results of a flash photolysis study of this system,[6] means that the final step shown in Scheme 1 cannot be rate determining.

It remained a possibility that the cyclopropanecarbaldehyde was not formed *via* compound **4** (R = cyclopropyl), but rather resulted from some other reaction pathway. The purpose of the study described in this article was to attempt to stabilise metallacyclic species derived from α-substituted amino acidate ligands by incorporating the amino acid (and hence the metallacycle) into a polydentate ligand framework. The subsequent reactions could then be monitored to establish whether the observed carbonyl compounds do indeed result from the decomposition of the metallacycles.

† Electronic supplementary information (ESI) available: details of decomposition experiments and crystallographic experimental. See http://www.rsc.org/suppdata/dt/b0/b003095n/

DOI: 10.1039/b003095n

Experimental

Materials

Reagent grade reagents and solvents were obtained from commercial sources and used without further purification for all syntheses unless stated. 2-Cyclopropylglycine was prepared by a modification of a literature method.[5,7] All ion-exchange resins and NMR solvents were purchased from Aldrich Chem. Co.

Measurements

^{1}H NMR spectra were recorded on a Varian Unity 300 MHz spectrometer at 23 °C. For those recorded in dimethyl-d_6 sulfoxide (DMSO-d_6) the DMSO-d_5 line (δ 2.50) was used as a reference. Sodium 3-trimethylsilylpropanesulfonate (TMPS, δ 0, singlet) was added as an internal reference for those recorded in D_2O. The signals are described as singlets (s), doublets (d), triplets (t), quartets (q) or multiplets (AB, ABX or m), and broad (br) where appropriate. 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_5 peak (δ 39.5) or, in D_2O, to added 1,4-dioxane (δ 67.4). A GBC-920 spectrophotometer was used to record the UV-visible spectra in water and the data are reported as λ_{max} (ε_{max}, L mol^{-1} cm^{-1}). The abbreviation sh refers to a shoulder. Elemental analyses were performed by the University of Otago Microanalytical Service. 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.

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

Preparation of *N*,*N*-bis(2-pyridylmethyl)amino acid (Hdpx) ligands

General method. The synthesis of this series of ligands was based on a literature method,[8] however the work-up procedure differed from the original account. Following the extraction of the aqueous reaction mixture with CH_2Cl_2 the aqueous portion was acidified and loaded on to a column of Dowex AG50W-X2 ion exchange resin. Elution with 1.5 M HCl gave a yellow band identified as the monoalkylated amino acid. Elution with 2.5 M HCl gave the desired product as a pale yellow eluate which yielded a pale yellow oil when taken to dryness on a rotary evaporator. Precipitation of the ligand as the hydrochloride salt was induced by the addition of acetone–Pr^{i}OH (1 : 1), and the off-white solid was filtered off, washed with Pr^{i}OH and diethyl ether, and air-dried.

***N*,*N*-Bis(2-pyridylmethyl)glycine (Hdpg·HCl).** ^{1}H NMR (D_2O): δ 3.75 (s, 2 H, gly CH_2), 4.51 (s, 4 H, picolyl CH_2), 7.99 (t, 2 H), 8.03 (d, 2 H). 8.55 (t, 2 H) and 8.76 (d, 2 H). ^{13}C NMR (D_2O): δ 55.94 (gly α-C), 56.45 (pyridyl CH_2), 127.20, 127.86, 142.15, 148.13, 153.33, 175.30 (CO_2) MS (FAB): *m*/*z* 258 ([H_2dpg]$^+$).

***N*,*N*-Bis(2-pyridylmethyl)-L-alanine (Hdpa·HCl).** L-Alanine was used in the synthesis. ^{1}H NMR (D_2O): δ 1.50 (d, 3 H, CH_3, J = 6.8 Hz), 3.83 (q, 1 H, ala α-H), 4.43 (s, 4 H, picolyl CH_2), 7.93 (t, 2 H), 8.04 (d, 2 H), 8.50 (t, 2 H) and 8.69 (d, 2 H). ^{13}C NMR (D_2O): δ 14.24 (ala CH_3), 54.01 (picolyl CH_2), 60.57 (ala α-C), 127.20, 127.96, 142.08, 148.18, 153.78, 177.31 (CO_2). MS (FAB): *m*/*z* 272 ([H_2dpa]$^+$).

Cyclopropyl-*N*,*N*-bis(2-pyridylmethyl)glycine (Hdpc·HCl). ^{1}H NMR (D_2O): δ 0.46–0.54 (br m, 3 H, cyclopropyl CH_2), 0.62–0.68 (br m, 1 H, cyclopropyl CH_2), 1.03–1.09 (br m, 1 H, cyclopropyl CH), 2.92 (d, 1 H, J = 9.7, α-C), 4.57 (AB, 4 H, J = 16.6 Hz, picolyl CH_2), 7.94 (t, 2 H), 8.08 (d, 2 H), 8.51 (t, 2 H) and 8.71 (d, 2 H). ^{13}C NMR (D_2O): δ 4.47, 5.50, 12.05, 54.90, 70.69 (cpg α-C), 127.15, 127.91, 141.98, 148.13, 154.02, 176.61 (CO_2). MS (FAB): *m*/*z* 298 ([H_2dpc]$^+$).

Preparation of the [Co(dpx)(phen)]$^{2+}$ complexes

General method. $Co(NO_3)_2·6H_2O$ (4.64 g, 16 mmol) and $NaNO_2$ (4.96 g, 70 mmol) were dissolved in a buffer solution of glacial acetic acid (3.5 mL) and NaOH (1.2 g) in water (30 mL). To this was added a solution of Hdpx·HCl (12 mmol), with NaOH (1.44 g, 36 mmol), in water (10 mL). The solution was aerated overnight. An orange-brown precipitate of [Co(dpx)-$(NO_2)_2$] deposited, which was filtered off, washed with ice-cold water, and dried in an oven (50–60 °C). These [Co(dpx)$(NO_2)_2$] complexes were characterised by NMR and mass spectrometry (see below).

[Co(dpx)$(NO_2)_2$] (2.5 mmol) was suspended in 0.2 M NaCl solution (5 mL) with stirring, and a solution of phen (0.49 g, 2.5 mmol) in methanol (5 mL) was added. Stirring was continued at rt for 3 h. Any remaining solid was removed by filtration and the orange filtrate was loaded on to SP Sephadex C25 (H^+ form, 3 × 20 cm). An intense orange band eluted with 0.25 M HCl, and the eluate was reduced in volume on a rotary evaporator. Concentrated $HClO_4$ and ethanol were added, and crystalline [Co(dpx)(phen)][ClO_4]$_2$ formed after standing overnight in a refrigerator. Recrystallisation from dilute $HClO_4$ gave analytically pure products. The yield was generally around 30%.

[Co(dpg)$(NO_2)_2$]. ^{1}H NMR (DMSO-d_6): δ 3.92 (s, 2 H, gly CH_2), 4.77 and 5.09 (AB, 4 H, picolyl CH_2), 7.65 (m, 4 H), 8.15 (t, 2 H) and 8.58 (d, 2 H). ^{13}C NMR (DMSO-d_6): δ 66.46 (gly CH_2), 67.34 (picolyl CH_2), 123.64, 125.61, 140.42, 151.05, 162.31, 176.92 (CO_2). MS (FAB): *m*/*z* 315 ([Co(dpg)]$^+$).

[Co(dpg)(phen)][ClO_4]$_2$ 5. ^{1}H NMR (DMSO-d_6): δ 4.68 (s, 2 H, gly CH_2), 5.32 and 6.19 (AB, 4 H, picolyl CH_2, J = 17.5 Hz), 7.16 (d, 2 H, dpg), 7.31 (t, 2 H, dpg), 7.81 (d, 2 H dpg), 7.99 (t, 1 H, phen), 8.08 (t, 2 H, dpg), 8.38 and 8.57 (AB, 2 H, phen), 8.74 (m, 1 H, phen), 8.92 (d, 1 H, phen), 9.42 (d, 1 H, phen), 9.62 (d, 1 H, phen) and 9.75 (d, 1 H, phen). ^{1}H NMR (D_2O): δ 4.79 (s, partially obscured by HOD peak, gly CH_2), 5.38 and 6.25 (AB, 4 H, J = 17.6, picolyl CH_2), 7.20–7.27 (m, 4 H), 7.80 (d, 2 H), 7.95–8.06 (m, 3 H), 8.25 and 8.45 (AB, 2 H, J = 8.8 Hz), 8.79 (m, 1 H), 8.79 (d, 1 H), 9.30 (d, 1 H), 9.43 (d, 1 H) and 9.89 (d, 1 H). ^{13}C NMR (DMSO-d_6): δ 67.58 (picolyl CH_2), 70.76 (gly CH_2), 125.23 (dpg), 127.52 (dpg), 127.71, 128.07, 128.47, 129.22, 130.63, 131.44, 141.14, 141.55 (dpg), 141.98, 145.16, 146.45, 150.99 (dpg), 153.68, 155.11, 163.50 (dpg) and 177.10 (CO_2). Calc. for [$CoC_{26}H_{22}N_5O_2$][ClO_4]$_2$: C, 44.98; H, 3.19; N, 10.09. Found: C, 44.67; H, 3.04; N, 10.09%. UV-vis: 480 nm (220); λ_{min} 420 nm (71). MS (FAB): *m*/*z* 594 ([Co(dpg)-(phen)(ClO_4)]$^+$, 3) and 495 ([Co(dpg)(phen)]$^+$, 23%).

[Co(dpa)$(NO_2)_2$]. ^{1}H NMR (DMSO-d_6): δ 1.28 (d, 3 H, CH_3, J = 6.8 Hz), 3.57 (m, obscured by H_2O peak), 4.74–4.92 and 5.10–5.16 (picolyl CH_2 overlapping AB quartets, total 4 H), 7.60–7.80 (m, 4 H), 8.14 (br s, 2 H), 8.37 (d, 1 H) and 8.75 (d, 1 H). ^{13}C NMR (DMSO-d_6): δ 13.56 (CH_3), 59.22, 66.70, 67.12, 122.63, 123.89, 125.62, 125.69, 140.47, 140.71, 151.11, 151.26, 162.17, 162.71, 178.05 (CO_2). MS (FAB): *m*/*z* 329 ([Co(dpa)]$^+$).

[Co(dpa)(phen)][ClO_4]$_2$·H_2O 6. ^{1}H NMR (DMSO-d_6): δ 1.61 (d, 3 H, CH_3, J = 6.8 Hz), 4.40 (m, 1 H, α-H), 5.32 (apparent t, 2 H, picolyl CH_2), 6.03–6.11 (m, 2 H, dpa picolyl CH_2), 7.13 (m, 2 H, dpa), 7.30 (d, 2 H, dpa), 7.72 (d, 1 H, dpa), 7.93–8.12 (m, 4 H, dpa pyridyl H (3 H), and phen (1 H)), 8.38 (d, 1 H, phen), 8.57 (d, 1 H, phen), 8.74 (m, 1 H, phen), 8.92 (d, 1 H, phen), 9.43 (d, 1 H, phen) and 9.75 (m, 2 H, phen). ^{1}H NMR (D_2O): δ 1.80 (d, 3 H, CH_3, J = 7.8), 4.63 (q, partially obscured

by HOD peak), 5.33 and 6.10 (AB, 2 H, J = 16.9), 5.48 and 6.15 (AB, 2 H, J = 18.6 Hz), 7.15–7.28 (m, 3 H), 7.76 (d, 1 H), 7.87 (d, 1 H), 7.97–8.08 (m, 2 H), 8.28 (d, 1 H), 8.46 (d, 1 H), 8.70 (m, 1 H), 8.81 (d, 1 H), 9.32 (d, 1 H), 9.56 (d, 1 H) and 9.92 (d, 1 H). ^{13}C NMR (DMSO-d_6): δ 13.60, 59.03, 66.43, 71.19, 124.28, 125.52, 127.58 (2C), 127.76, 128.08, 128.53, 129.19, 130.64, 131.48, 141.14, 141.57, 142.01 (2C), 145.16, 146.50, 151.18 (2C), 153.54, 155.54, 163.16, 163.90 and 178.08 (CO_2). Calc. for $[CoC_{27}H_{24}N_5O_2][ClO_4]_2 \cdot H_2O$: C, 44.66; H, 3.58; N, 9.64. Found: C, 44.56; H, 3.38; N, 9.66%. UV-vis: 481 (187), 262 (31000), 227 (53200) and 204 nm (58800). MS (FAB): *m*/*z* 608 ([Co(dpa)(phen)(ClO_4)]$^+$, 10) and 509 ([Co(dpa)(phen)]$^+$, 34%).

[Co(dpc)(NO_2)$_2$]. The crude product was rather impure, as shown by its ^{1}H NMR spectrum, but was not further purified before being used in the reaction to give the [Co(dpc)(phen)][ClO_4]$_2$ complex. A ^{13}C NMR spectrum was not acquired due to the small amount of complex which was isolated and the difficulty in recovering it from DMSO. ^{1}H NMR (DMSO-d_6): δ 0.37–0.42 (br m, 1 H), 0.60–0.95 (br m, 4 H), 3.02 (d, obscured by H_2O peak, α-H), 4.66 (d, 1 H), 4.97–5.35 (m, 3 H), 7.58–7.83 (m), 8.10–8.16 (m), 8.45 (d) and 8.63 (d); major unassigned peaks 1.22 (s), 7.50 (m), 8.00 (m), 8.60 (d) and 8.82 (d). MS (FAB): *m*/*z* 355 ([Co(dpc)]$^+$).

[Co(dpc)(phen)][ClO_4]$_2$ 7. ^{1}H NMR (DMSO-d_6): δ 0.60–0.65 (br m, 1 H, cyclopropyl CH_2), 0.82–0.87 (br m, 1 H, cyclopropyl CH_2), 1.02–1.08 (br m, 2 H, cyclopropyl CH and CH_2), 1.14–1.19 (br m, 1 H, cyclopropyl CH_2), 3.85 (d, 1 H, α-H, J = 8.8), 5.17 and 6.15 (AB, 2 H, J = 17.6), 5.80 and 6.19 (AB, 2 H, J = 18.1 Hz), 7.13 (m, 2 H, dpc pyridyl), 7.30 (m, 2 H, dpc pyridyl), 7.75 (d, 1 H, dpc picolyl), 7.99–8.10 (m, 4 H, dpc pyridyl (1 H) and phen (3 H)), 8.39 (d, 1 H), 8.57 (d, 2 H), 8.76 (m, 1 H), 8.93 (d, 1 H), 9.44 (d, 1 H) and 9.78–9.82 (m, 2 H). ^{1}H NMR (D_2O): δ 0.68–0.74 (br m, 1 H), 1.03–1.08 (br m, 1 H), 1.19–1.25 (br m, 3 H), 3.92 (d, 1 H, J = 9.3), 5.21 and 6.20 (AB, 2 H, J = 17.6), 6.03 and 6.24 (AB, 2 H, J = 18.6 Hz), 7.15–7.29 (m, 4 H), 7.72 (d, 1 H), 7.86 (d, 1 H), 7.96–8.07 (t, 3 H), 8.26 (d, 1 H), 8.44 (d, 1 H), 8.68 (m, 1 H), 8.80 (d, 1 H), 9.31 (d, 1 H), 9.58 (d, 1 H) and 9.95 (d, 1 H). ^{13}C NMR (DMSO-d_6): δ 3.42, 5.28, 11.44, 60.25, 67.38, 79.46, 124.31, 125.54, 127.54 (2C), 127.68, 128.04, 128.50, 129.19, 130.63, 131.43, 141.11, 141.39, 141.94 (2C), 145.16, 146.44, 150.85, 151.08, 153.50, 155.44, 163.41, 163.76 and 176.90 (CO_2). UV-vis: 481 nm. MS (FAB): *m*/*z* 634 ([Co(dpc)(phen)(ClO_4)]$^+$) and 535 ([Co(dpc)(phen)]$^+$, 9%).

Photolysis of the [Co(dpx)(phen)]$^{2+}$ complexes 5–7

Method 1: Large scale photolysis and chromatographic isolation of photolysis products. Given the quantity of material required, this technique was only suitable for complex **5**. An aqueous solution (approximately millimolar concentration) was photolysed with an immersible Jelight PS-3004-30 mercury lamp for around 80 min. The solution was kept below 20 °C by flowing ice-cold water through a jacket around the cell. Several 60 mL batches were combined and chromatographed on CM Sephadex C25 (Na^+, 3 × 25 cm). Elution with 0.2 M $NaClO_4$ developed two bands; an orange band of the unchanged starting material and an intense orange-yellow band of the photolysis product. This second eluate was concentrated on a rotary evaporator (<30 °C) until an orange crystalline solid deposited. This solid was filtered off, washed with ethanol and ether, and air dried.

Method 2: NMR scale photolysis. Milligram amounts of the [Co(dpx)(phen)][ClO_4]$_2$ complexes **5**–**7** were dissolved in around 150 μL of deuteriated solvent (D_2O or DMSO-d_6) and placed in 3 mm NMR tubes. They were irradiated with a high-pressure mercury lamp equipped with a 254 nm transmission Pyrex filter (Corning, 7–54). The samples were cooled by immersion in a quartz ice–water bath.

Method 3: UV-vis monitoring of the photolysis reaction. Aqueous solutions of the [Co(dpx)(phen)][ClO_4]$_2$ complexes **5**–**7** (concentrations in the range 1.0–1.5 mM) were photolysed in quartz cuvettes. A 200 W high-pressure mercury lamp, equipped with a Pyrex 254 nm transmission filter (Corning 7–54), was used as the light source. Two water-filled 1 cm quartz cuvettes in the irradiation path served as IR filters.

Photolysis of [Co(dpg)(phen)]$^{2+}$ 5: production of [Co(dgm)(phen)]$^{2+}$ 8

Method 1. The crude red-orange precipitate of complex **8** was recrystallised from warm, dilute $HClO_4$. Yield: *ca*. 15% at 70% conversion. ^{1}H NMR (D_2O): δ 4.60 (s, Co–CH_2, partially obscured by HOD peak), 4.80 and 5.59 (AB, the peak at 4.80 was hidden by the HOD signal, J = 17.1 Hz, dgm picolyl CH_2), 5.96 (d, 2 H, dgm), 7.41 (d, 2 H, dgm), 7.66 (m, 2 H, dgm), 8.04–8.09 (m, 1 H, phen), 8.37–8.46 (m, 3 H, phen), 8.83 (d, 1 H, phen), 9.06 (d, 1 H, phen), 10.20 (d, 1 H, phen) and 10.40 (d, 1 H, phen). ^{1}H NMR (DMSO-d_6): δ 4.51 (s, 2 H), 4.50 (s, 2 H, CH_2), 4.73 and 5.75 (AB, 4 H, J = 16.6 Hz), 5.91 (d, 2 H), 6.71 (t, 2 H), 7.53 (d, 2 H), 7.74 (t, 2 H), 8.20 (m, 1 H, phen), 8.43–8.57 (m, 3 H, all phen), 9.00 (d, 1 H, phen), 9.22 (d, 1 H, phen), 10.47 (d, 1 H, phen) and 10.51 (d, 1 H, phen). ^{13}C NMR (DMSO-d_6): δ 46.17 (Co–CH_2), 60.63, 123.13 (dgm), 124.54 (dgm), 126.96, 127.75, 127.99, 128.25, 130.52, 131.08, 139.17, 139.42 (dgm), 140.12, 145.14, 147.22, 148.95 (dgm), 154.71, 157.89 and 159.99 (dgm). Calc. for $[CoC_{25}H_{22}N_5][ClO_4]_2 \cdot H_2O \cdot 0.25NaClO_4$: C, 42.96; H, 3.43; N, 10.02. Found: C, 42.98; H, 3.11; N, 9.74%. UV-vis: 460 (180), 296 (sh, 9000), 274 (25600), 254 (20800) and 222 nm (36000); λ_{min} 422 nm (142). MS (FAB): *m*/*z* 550 ([Co(dgm)(phen)(ClO_4)]$^+$, 25) and ([Co(dgm)(phen)]$^+$, 22%).

Method 2. Samples of [Co(dpg)(phen)]$^{2+}$ **5** were photolysed in both DMSO-d_6 and D_2O. The ^{1}H NMR spectra of the resulting solutions were identical to those described above for chromatographically isolated **8**.

Photolysis of [Co(dpa)(phen)]$^{2+}$ 6: production of [Co(dam)(phen)]$^{2+}$ 9

Method 2. ^{1}H NMR of [Co(dam)(phen)]$^{2+}$ **9** (D_2O, assignments were aided with a COSY spectrum): δ 1.13 (d, 3 H, CH_3, J = 6.4), 4.85 (α-H, obscured by HOD peak), 5.56 (picolyl AB, other half hidden by HOD peak, 1 H, J = 16.6), 5.72 (picolyl AB, other half hidden by HOD peak, 1 H, J = 17.6 Hz), 5.87–5.92 (m, 2 H, dam pyridyl), 6.53–6.65 (m, 2 H, dam pyridyl), 7.36–7.42 (m, 2 H, dam pyridyl), 7.89–7.94 (m, 1 H), 8.00–8.05 (m, 2 H, dam pyridyl and phen), 8.30–8.47 (m, 2 H, phen), 8.81 (d, 1 H, phen), 9.03–9.08 (m, 2 H, phen), 10.17 (d, 1 H, phen) and 10.44 (d, 1 H, phen). ^{1}H NMR (DMSO-d_6): δ 1.02 (d, 3 H, J = 6.3), 4.65–4.79 (m, 3 H, α-H and 2 picolyl CH_2), 5.71 (d, 1 H, CH_2, J = 17.1 Hz), 5.82–5.92 (m, 3 H, 1 picolyl CH_2 and 2 aromatic dam pyridyl), 6.66–6.70 (m, 2 H, dam pyridyl), 7.50–7.56 (m, 2 H, dam pyridyl), 7.71–7.74 (m, 2 H, dam pyridyl), 8.18–8.21 (m, 1 H, phen), 8.42–8.57 (m, 3 H, phen), 8.99 (d, 1 H, phen), 9.22 (d, 1 H, phen) and 10.49 (br m, 2 H, phen). ^{13}C NMR (DMSO-d_6): δ 14.52 (CH_3), 52.71 (Co–CH_2), 57.65, 61.13, 121.31, 123.21, 124.18, 124.87, 126.89, 127.72, 127.96, 128.25, 130.43, 131.07, 139.08, 139.41, 139.74, 139.89, 140.07, 147.28, 148.58, 148.77, 154.19, 157.55, 159.95 and 161.79.

Photolysis of [Co(dpc)(phen)]$^{2+}$ 7: production of [Co(dcm)(phen)]$^{2+}$ 10

Method 2. ^{1}H NMR of [Co(dcm)(phen)]$^{2+}$ **10** (D_2O): δ −0.030 to 0.05 (br m, 1 H, cyclopropyl CH), 0.85 (m, cyclo-

propyl CH_2), 1.09–1.13 (m, 2 H, cyclopropyl CH_2), 1.27–1.31 (m, 1 H, cyclopropyl CH_2), 4.23 (d, 1 H, J = 9.3, α-H), 4.73 and 5.55 (AB, 2 H, J = 16.8), 4.94 and 5.72 (AB, 2 H, J = 17.1 Hz), 5.90–5.96 (m, 2 H, dcm pyridyl), 6.52–6.63 (m, 2 H, dcm pyridyl), 7.34–7.42 (m, 2 H, dcm pyridyl), 7.59–7.68 (m, 2 H, dcm pyridyl), 8.00–8.05 (m, 1 H), 8.30–8.47 (m, 3 H), 8.81 (d, 1 H), 9.05 (d, 1 H), 10.15 (d, 1 H) and 10.50 (d, 1 H). ^{1}H NMR (DMSO-d_6): δ −0.27 to −0.22 (br m, 1 H, CH), 0.72–0.77, 0.95–1.00, 1.18–1.23, 1.38–1.43 (all br m, total 4 H, cyclopropyl CH_2), 4.21 (d, 1 H, J = 9.0, α-H), 4.70 and 5.69 (AB, 2 H, J = 17.1 Hz), 4.74 and 5.90 (AB, downfield doublet obscured by dcm aromatic protons, upfield peak overlapping with other dcm CH_2 peak), 5.90 (m, 2 H, dcm pyridyl), 6.63–6.72 (m, 2 H, dcm pyridyl H), 7.42–7.57 (m, 3 H, dcm pyridyl (2 H) and phen (1 H)), 7.66–7.77 (m, 2 H, dcm pyridyl), 8.17–8.21 (m, 1 H, phen), 8.46–8.57 (m, 2 H), 8.99 (d, 1 H), 9.22 (d, 1 H), 10.39 (d, 1 H) and 10.47 (d, 1 H). ^{13}C NMR (DMSO-d_6): δ 5.75 (2C, cyclopropyl CH_2), 10.24 (cyclopropyl CH), 58.10 (Co–C), 61.09 and 61.21 (dcm picolyl CH_2), 121.4, 123.08, 123.16, 123.59, 124.13, 124.90, 126.87, 127.90, 128.22, 130.38, 137.31, 139.01, 139.23, 139.76, 140.05, 147.31, 148.65, 148.95, 154.03, 157.46, 159.93 and 161.83. Some peaks were assigned to thermal decomposition products (δ 6.50, 50.00).

Decomposition of the photolysis products 8–10

In neutral solutions. The NMR-scale photolysates were allowed to stand for prolonged periods at room temperature and the appearance of decomposition products was monitored by NMR spectroscopy. The data from the spectra are given in the supplementary material.

*Of complex **8***. This complex has a half-life of around 1 week in D_2O at rt. Bis(2-pyridylmethyl)amine (bpa) and phen were detected.

*Of complex **9***. Acetaldehyde, $[(bpa)(phen)Co(O_2)Co(phen)(bpa)]^{4+}$ (**11**). $[Co(phen)_3]^{3+}$, bpa, and phen were detected.

*Of complex **10***. This complex has a half-life of around 8–9 hours in D_2O at room temperature. Cyclopropanecarbaldehyde and **11** were detected.

In acidic solution. *Of complex **8***. The peaks due to complex **8** disappeared over a period of weeks; Bpa and phen were detected.

*Of complex **9***. The peaks due to complex **9** disappeared with a half-life of around 24 hours. Acetaldehyde, bpa and phen were detected.

X-Ray crystallography

Experimental details are given in the supplementary information. Crystallographic data are given in Table 1.

$[Co(dpg)(phen)][ClO_4]_2$ 5. Crystals suitable for the diffraction study were obtained by the slow cooling of a hot solution of the complex in dilute $HClO_4$. All hydrogen atoms were placed at calculated positions and refined with a riding model.

$[Co(dgm)(phen)][ClO_4]_2 \cdot H_2O$ 8. X-Ray quality crystals were produced by a recrystallisation from water–ethanol (50 : 50). Two independent molecules were present in the asymmetric unit. The hydrogen atoms bound to the carbon atom of the metallacycle (C(13)) were found on a difference electron density map and refined isotropically. Other hydrogen atoms were placed in calculated positions and refined with a riding model.

$[(bpa)(phen)CoO_2Co(phen)(bpa)][ClO_4]_4$ 11. Small orange-brown crystals formed in an NMR tube during the thermal decomposition of complex **10** at room temperature. All hydrogen atoms were included in calculated positions and refined using a riding model. The limited number of reflections that could be used was a consequence of crystal damage during the data collection.

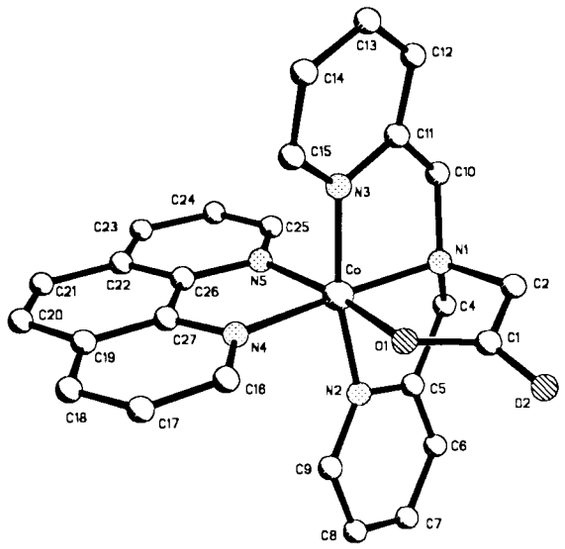


Fig. 1 Crystal structure of complex **5**. All hydrogen atoms have been omitted from the diagram. Selected bond lengths (Å) and angles (°): Co–O(1) 1.880(2); Co–N(1) 1.930(3); Co–N(2) 1.933(3); Co–N(3) 1.921(3); Co–N(4) 1.919(3); Co–N(5) 2.010(3); O(1)–Co–N(1) 87.57(11), N(3)–Co–N(1) 84.73(13); N(3)–Co–N(2) 168.71(12); N(1)–Co–N(2) 84.03(13); N(4)–Co–N(5) 83.01(11); N(1)–Co–N(5) 100.80(11).

CCDC reference number 186/2068.

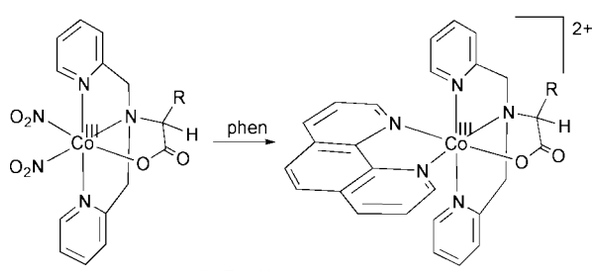
See http://www.rsc.org/suppdata/dt/b0/b003095n/ for crystallographic files in .cif format.

Results

Syntheses

The nucleophilic displacement of chloride from two equivalents of 2-chloromethylpyridine produces *N*,*N*-bis(2-pyridylmethyl)-glycine in good yield, as reported previously.[8] The preparation of $[Co(dpg)(NO_2)_2]$ was based on a published synthesis of $[Co(NO_2)_3(tacn)]$[9] (tacn = 1,4,7-triazacyclononane) and as the desired complex, $[Co(dpg)(NO_2)_2]$, is also a neutral species it too has the attractive property of precipitating out of the aqueous reaction mixture. The Hdpa and Hdpc ligands, and their nitro complexes, were prepared in a similar manner.

The $[Co(dpg)(NO_2)_2]$ complex was characterised by ^{1}H and ^{13}C NMR spectroscopy. It has the pyridyl donor groups arranged in a *trans* fashion (C_s symmetry). This geometry is conserved during the formation of the $[Co(dpg)(phen)]^{2+}$ complex **5**, and the substituted derivatives (Scheme 2), as indicated by examination of ^{1}H and ^{13}C NMR spectra.



5 R = H
6 R = CH_3
7 R = cyclopropyl

Scheme 2

The solid state structure of $[Co(dpg)(phen)][ClO_4]_2$ **5** was determined by X-ray crystallography (Fig. 1). The geometry

Table 1 Crystallographic data for complexes **5**, **8** and **11**

Formula	$C_{26}H_{22}Cl_2CoN_5O_{10}$	$C_{25}H_{24}Cl_2CoN_5O_9$	$C_{48}H_{42}Cl_4Co_2N_{10}O_{18}$
M	694.32	666.31	1306.58
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/c$	*Pbcm*	*C*2/*m*
a/Å	11.620(8)	18.158(5)	21.652(10)
b/Å	24.487(13)	8.978(2)	11.320(5)
c/Å	10.296(6)	34.173(9)	12.352(6)
β/°	114.54(3)		114.142(6)
V/Å^3	2665(3)	5571(2)	2763(2)
Z	4	8	2
T/K	293(2)	159(2)	168(2)
μ/mm^{-1}	0.687	0.870	0.875
Reflections	26963	42616	6574
Independent	3873	11940	2287
R [$I > 2\sigma(I)$]	0.0351	0.0431	0.0497
R' [$I > 2\sigma(I)$]	0.0888	0.1006	0.1017

around the cobalt centre is approximately octahedral. There is a marked difference in the Co–N_{phen} bond lengths (2.01 Å *trans* to the carboxylate group, and 1.92 Å *trans* to the tertiary nitrogen donor) which is presumably indicative of the greater *trans* influence of the more basic amine donor. The five-membered picolylamine chelate adopts the common envelope motif, with the picolyl methylene unit slightly out of the plane of the other four atoms. The metal–ligand bond lengths are marginally shorter than those found in a related tetranuclear cobalt(III) complex of *N*-(2-pyridylmethyl)glycinate.[10]

The assignment of the stereochemistry of the *N*,*N*-bis(2-pyridylmethyl)alaninato (**6**) and cyclopropyl-*N*,*N*-bis-(2-pyridylmethyl)glycinato (**7**) complexes from NMR data was less straightforward than for the parent complex, as the alkyl substituent breaks the C_s symmetry. However, the chemical shifts of the protons of the two pyridine rings and those of the picolyl methylene groups in both complexes are similar to those observed for **5**. This implies that **6** and **7** also have a *trans*-pyridyl geometry. Furthermore, the UV-vis spectra of these complexes are very similar to that of **5**.

Photochemistry of [Co(dpx)(phen)]$^{2+}$ complexes 5–7

The UV photolysis reaction of complex **5** was examined by three different methods: (i) large-scale photolysis with separation of the product by ion-exchange chromatography; (ii) ^{1}H NMR spectroscopy; and (iii) UV-vis spectroscopy.

Photolysis of an aqueous solution of complex **5** with broad spectrum light from an immersible mercury lamp induced a change from orange-red to yellow. Chromatography of this photolysate produced two closely spaced bands. The band which eluted first was orange-red, and identified as unchanged **5**. The similar chromatographic behavior of the second band implied that it also had a 2+ charge. This eluate was noticeably more yellow than the starting material and, upon concentration of the solution, orange crystals that contained some sodium perchlorate deposited. Recrystallisation furnished crystals suitable for X-ray crystallography. The solid state structure of the photolysis product **8** is shown in Fig. 2.

The X-ray diffraction study revealed that carbon dioxide had been eliminated from the amino acidato chelate to leave a three-membered Co–C–N ring (Scheme 3). The bite angle of the new chelate is 43.5°, with bond lengths Co–C 1.93 Å and Co–N 1.90 Å. Both hydrogen atoms attached to the co-ordinated carbon atom (C13) were found on a electron density difference map during the refinement. The C13–N13 bond length (1.42 Å) is of particular interest (see Discussion). The Co–N_{py} bond lengths fall between 1.92 and 1.94 Å and the chelate bite angles are all clustered around 84–85°. The picolylamine chelate rings retain their envelope configurations in the photolysis product.

Comparison of the solid state structures of complexes **5** and **8** indicates that there are significant changes in the orientation of the pyridylmethyl arms of the tetradentate ligand upon

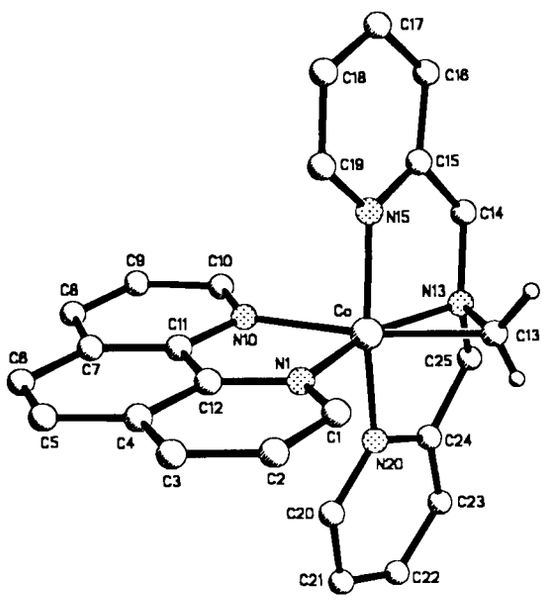
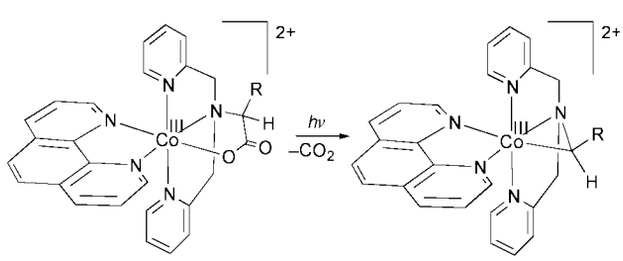


Fig. 2 Crystal structure of one of the two cations of complex **8** found in the asymmetric unit. Most hydrogen atoms have been omitted from the diagram. Selected bond lengths (Å) and angles (°): Co–N(13) 1.898(4); Co–C(13) 1.924(6); Co–N(15) 1.931(4); Co–N(20) 1.940(4); Co–N(1) 1.970(4); C(13)–N(13) 1.417(7); Co–N(10) 2.044(4); N(13)–Co–C(13) 43.5(2); N(13)–Co–N(15) 84.31(18); N(13)–Co–N(20) 84.12(17); N(13)–Co–N(1) 157.79(18); N(13)–Co–N(10) 119.13(17); N(1)–Co–N(10) 83.07(17).



5 R = H
6 R = CH_3
7 R = cyclopropyl

8 R = H
9 R = CH_3
10 R = cyclopropyl

Scheme 3

photoelimination of CO_2. This has major ramifications for the appearance of the ^{1}H NMR spectra of **8**, as the pyridine rings have been rotated around their Co–N axis, moving the *ortho* protons closer to the π electrons of the phen ligand. These protons now resonate at δ 5.96, which is an unusually low value for aromatic protons. Another notable shift occurs for two of the phen resonances (probably the two *ortho* protons) which move downfield, to beyond 10 ppm. The methylene groups

attached to the pyridyl arms remain as an AB system, one half of which was found under the HOD peak through collection of a COSY spectrum.

^{1}H NMR spectra of complex **8** obtained *directly after* photolysis of a D_2O or DMSO-d_6 sample of **5** were identical to spectra of the photolysis product which had been isolated following column chromatography. The results of the NMR scale photolyses indicated that the photochemical conversion is very clean. A ^{13}C NMR spectrum in DMSO-d_6 showed that, as expected, the signal for the carboxylate carbon had disappeared.

The photolysis of an aqueous solution of complex **5** was also monitored by UV-vis spectroscopy. The 480 nm ligand field band shifts to shorter wavelengths upon irradiation of the complex is consistent with the replacement of a carboxylate donor by a strongly basic carbon donor. There is a significant rise in absorption in the 400–425 nm region. The final spectrum was identical to that obtained from a solution of an isolated sample of **8**. These spectral changes are similar to those noted by Poznyak and Pavlovskii during the photolysis of $[Co(gly)(phen)_2]^{2+}$.[11]

The photolysis of a D_2O solution of the alaninato analogue **6** was monitored by ^{1}H NMR spectroscopy. Many of the spectral changes observed during the photolysis of complex **5** were repeated in this instance. For example, two of the phen resonances were observed downfield of 10 ppm, and a multiplet appeared at δ 5.95. In addition, the doublet assigned to the methyl group was seen to move from δ 1.80 to 1.13. Examination of molecular models reveals that, upon formation of **9**, the methyl group would be expected to move into a shielded region over a pyridine ring, and its ^{1}H NMR signal should therefore be observed at higher field.

The photolysis of the dpa complex **6** in aqueous solution was also monitored by UV-vis spectroscopy. The ligand field band, initially centred at 481 nm, shifted to 462 nm, and absorption in the 400–430 nm region rose significantly. These changes are consistent with the formation of **9** during the photolysis.

Unfortunately complex **9** could not be isolated as a crystalline solid. This has prevented a full characterisation of the photolysis product as neither elemental analysis nor X-ray crystallography was possible.

Upon irradiation of the cyclopropyl derivative **7** with 254 nm light a clean reaction takes place to form complex **10**. The changes that occur in the ^{1}H NMR spectrum are similar to those seen in the photolyses of **5** and **6**. For instance, two of the phen signals shift downfield to δ 10.50 and 10.15, and two protons which can be assigned to the pyridyl rings move upfield to around δ 5.95. Thus it appears likely that a similar metallacycle has been formed. A broadened set of signals centered at around δ 1 is seen for **7**, which is characteristic of a cyclopropyl group. The cyclopropyl methine proton of the photolysis product resonates at δ 0. Examination of a molecular model reveals that this proton is likely to lie directly over a pyridine ring. Similar spectral changes were observed when the photolysis was carried out in DMSO-d_6.

The UV-vis spectra of complexes **7** and **10** are shown in Fig. 3. The shift of the d–d absorption peak to shorter wavelengths (462 nm), accompanied by a rise in absorption in the 400–430 nm region, is also consistent with **10** being the expected metallacyclic photolysis product.

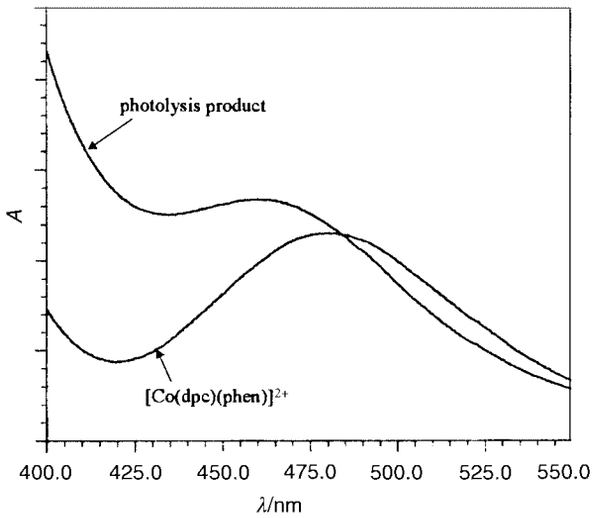
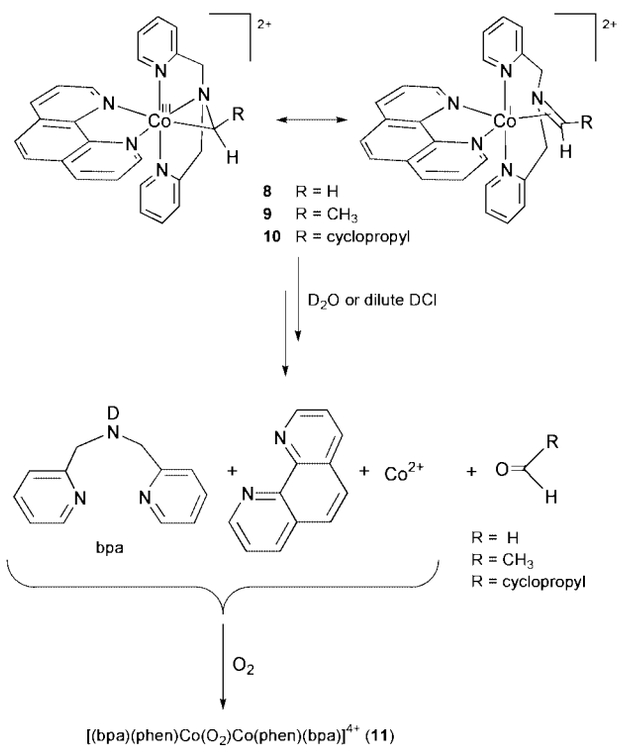


Fig. 3 A portion of the visible spectrum of $[Co(dpc)(phen)]^{2+}$ **7** and its photolysis product **10**, in aqueous solution.



Scheme 4

Thermal decomposition of the metallacycles 8–10

The complexes **9** and **10** decomposed on standing to give aldehydes (acetaldehyde and cyclopropanecarbaldehyde respectively) in both D_2O and DMSO-d_6 (Scheme 4). These complexes have half-lives at room temperature in D_2O of 5 days and 7–9 hours respectively. Extraction of the resulting D_2O solutions with $CDCl_3$ followed by NMR spectroscopy established the presence of free phen and bis(2-pyridylmethyl)amine (bpa) in both cases. These products were also observed following the thermal decomposition of **5**, although this complex had a relatively long half-life in D_2O (<1 week).

If the D_2O solutions of the (decomposing) complexes **9** or **10** were allowed to stand at room temperature for prolonged periods a new grouping of eight aromatic protons appeared in the ^{1}H NMR spectra. Clearly the growth of these signals was due to the formation of a new compound. We were rather fortunate in that crystals of it formed in a NMR sample. X-Ray crystallography revealed the structure shown in Fig. 4.

The complex is a peroxo-bridged dinuclear complex, $[(bpa)(phen)CoO_2Co(phen)(bpa)]^{4+}$ **11**. The geometry around each cobalt is identical, with the peroxo ligand occupying a coordination site *trans* to the secondary nitrogen of the facially co-ordinated bpa ligand. This gives a highly symmetrical structure (the atoms which are labeled in Fig. 4 comprise the asymmetric unit). The remainder of the complex is generated by a mirror plane which contains the two cobalt ions and the peroxo ligand (bisecting the phen ligands), and a centre of inversion, which is located at the midpoint of the O–O bond. The geom-

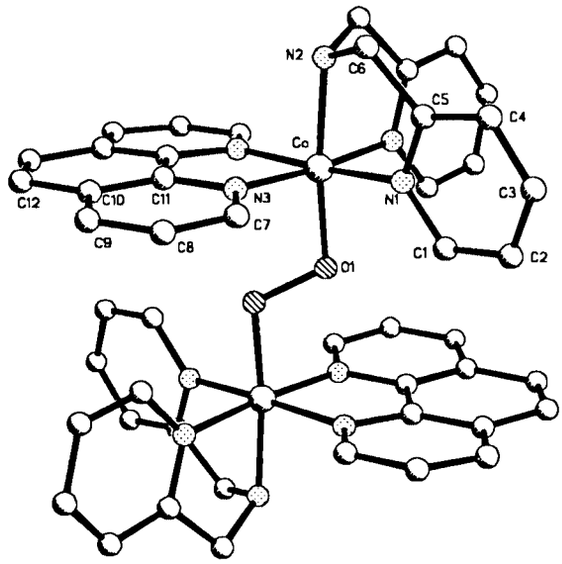


Fig. 4 Crystal structure of the complex ion **14**. All hydrogen atoms have been omitted from the diagram. Selected bond lengths (Å) and angles (°): Co–O(1) 1.833(5); Co–N(1) 1.925(4); Co–N(2) 2.004(6); Co–N(3) 1.943(4); N(1)–Co–N(2) 84.20(18); N(3)′–Co–N(3) 84.2(3); N(1)′–Co–N(1) 88.9(2); O(1)′–O(1)–Co 113.0(4).

etry around the cobalt atom is approximately octahedral, with the largest deviations appearing in the chelate bite angles. The O(1)′–O(1)-Co bond angle (113.0°), and the O(1)–O(1)′ bond length (1.436 Å) are similar to those seen for other dinuclear, monobridged peroxo complexes of Co(III).[12,13] The relatively long Co–N(2) bond (2.004 Å) is in keeping with other μ-peroxo dimers which have similar donor sets.[14]

The effect of acid conditions on the decomposition was probed by monitoring DCl solutions ([DCl] ≈ 0.5 M) of complexes **8** and **9** by ^{1}H NMR spectroscopy. In the case of **9** the methyl group of the amino acid fragment was incorporated into acetaldehyde, however the fate of the remainder of the complex was initially less clear due to the crowding in the aromatic region of the spectra. However, free bpa and phen were found for both complexes following extraction of alkaline solutions with chloroform.

Discussion

The preparation of complexes **5**–**7** was quite straightforward. The observed lability of the nitro ligands is rather remarkable. Nitro complexes are common intermediates in cobalt(III) chemistry. Typically they are treated with acid (HCl) solutions to generate intermediate (chloro) complexes which readily undergo substitution reactions. For the [Co(dpx)(NO_2)$_2$] complexes, reaction *via* this two step route is also possible but results in a diminished yield. It is possible that a trace cobalt(II) impurity may have been catalysing the direct reactions of the nitro complexes with phen, however we did not pursue evidence for this hypothesis.

Irradiation of complexes **5**–**7** resulted in decarboxylation and formation of complexes that contain Co–C–N metallacycles. The metallacyclic complex **8** that results from photolysis of the **5** has fully been characterised. Characterisation of the analogous complexes **9** and **10** was based on their NMR and UV-vis spectra, and the structural assignments are supported by the similarities of their spectra to those observed for the fully characterised complex.

The structural and spectroscopic data for complex **8** raise a question about the nature of the bonding in the metallacycle. In particular, the C–N bond length (1.42 Å) is rather short, which may imply that the bond order that is greater than one. This bond length is midway between that expected for a C–N single bond (1.50 Å) and the C–N bond length found in pyridine[15] (1.34 Å). Thus we may conclude that the C–N bond order is about 1.25.

Four other complexes that contain a Co–C–N chelate ring have been characterised by X-ray crystallography. Two of these were synthesized by photochemical decarboxylation of an amino acidato chelate,[2g,16g] whilst the other two[17,18] resulted from intramolecular reactions of macrocyclic complexes. The range of C–N bond lengths in these molecules (1.35–1.45 Å) brackets that revealed in our structure.

The downfield chemical shift changes that we observed for the phen resonances are also consistent with the idea that the C–N bond of the metallacycle has some π character, with the *ortho* protons in particular being influenced by the resulting magnetic anisotropy.

Taking all these data together, we believe that the structure of these complexes may best be represented as a combination of the resonance forms shown in Scheme 4. The complex can be viewed as a combination of a distorted octahedral cobalt(III) complex and a trigonal bipyramidal cobalt(I) complex (in which the C(13)–N(13) fragment is a π-bound η^2 imine ligand). We believe that this imine character in the metallacyclic fragment of these molecules may be significant in the context of the decomposition reactions that we observed.

The metallacyclic complexes **8**–**10** decompose with time, with those derived from alanine and cyclopropylglycine giving the related carbonyl compounds, acetaldehyde and cyclopropanecarbaldehyde respectively. These same products were observed following photolysis of the related bidentate amino acid complexes **1**.[5] This study establishes a direct link between the decomposition of the metallacyclic complexes and the formation of the carbonyl compounds. This supports the contention that the unsubstituted amino acid complexes do indeed react *via* metallacyclic species.

Formation of the amine fragment of the metallacycle was also observed, both directly and through isolation of a dimeric μ-peroxo complex. The most common method of synthesis of μ-peroxo complexes is the air oxidation of neutral solutions of Co^{II} and the required ligands.[13] Thus, the discovery of the dimer **11** in the decomposing photolysates is not surprising given that bpa, phen and (probably) Co^{II} are all by-products from the decomposition reactions of **9** and **10**. Of the nine possible geometrical isomers for the dimeric complex **11**, the observed isomer is one with the same conformation around each cobalt centre, and with the peroxo ligand *trans* to the secondary nitrogen of the bpa ligand. This *trans* configuration may be favoured because the Co–peroxo ligand bonding interaction, *i.e.* the filling of the O_2 π* orbitals with electron density from the metal d orbitals, is maximised.[13]

Cobalt–carbon bond cleavage can occur in three ways during the decomposition of the metallacycle. They differ according to how the bonding electrons are shared between the alkyl fragment and the cobalt centre;[19] eqns. (1)–(3). Reaction *via* path (1)

$$Co^{III}–R \longrightarrow Co^{III} + R^- \quad (1)$$

$$Co^{III}–R \longrightarrow Co^{II} + R^\bullet \quad (2)$$

$$Co^{III}–R \longrightarrow Co^{I} + R^+ \quad (3)$$

would lead to an α-amino carbanion, which would be expected to acquire a deuteron from the solvent (D_2O or DMSO-d_6) generating a substituted methylamine. Alternatively, a cobalt(II) complex and an α-amino radical may be formed *via* heterolytic cleavage of the Co–C bond (path 2). This radical could abstract a hydrogen atom from a species in solution or from the solvent, generating an amine, or react with another odd-electron species (*e.g.* self-termination, or reaction with O_2) to give a diamine or a carbonyl compound (see below). The third possibility is the production of a cobalt(I) complex and a carbocation (path 3).

A carbocation with an adjacent amine group is a canonical form of an imine, and hydrolysis of this imine would give an amine and a carbonyl compound. These are the products that we observed in both neutral and acidic solution, and this decomposition pathway would seem to be a reasonable way for them to be produced. It should be noted however that a one electron oxidation of the aminoalkyl radical that results from the second pathway would also generate the imine and could therefore also explain the products we observe. Aminoalkyl radicals are known to be strong reductants.[20] Indeed, if the oxidant were the cobalt(II) ion, the combination of the second pathway and electron transfer from the radical to cobalt(II) would be the equivalent of the third path.

We favour the third decomposition path, with production of cobalt(I) and an imine, since there is evidence for π character in the C–N bond of the metallacyclic complex. Cobalt(I) would likely react further to give cobalt(II) species in aqueous solution. Metallacycle decomposition could be envisaged as occurring through structures which had increasing contributions from the imine canonical form (Scheme 4). This mechanism can also account for the observation of formaldehyde in the photolysis of related complexes.[21]

Decomposition pathway (1) has been observed previously for a cyclam-based Co–C–N metallacycle in dilute HCl whereby the metallacycle is (presumably) opened by electrophilic attack of a proton at the co-ordinating carbon.[2g] A chloro ligand filled the vacant co-ordination site with no apparent change of the cobalt oxidation state. If complexes **8**–**10** had followed this pathway in acidic solution, deuteriated bis(2-pyridylmethyl)-methylamine, free or complexed, would have been observed.

The difference in the decomposition pathways of this complex and our pyridine-based systems can perhaps be ascribed to the nature of the bonding in the complexes and the auxiliary ligands. The cyclam-based complex was found to have a C–N bond length of 1.447 Å, longer than the 1.417 Å found in **8**. This may imply that there is somewhat more π character in the C–N bond in the complex we have isolated than in the cyclam complex. This would render the carbon atom less susceptible to electrophilic attack (since the electrons will be shared with the nitrogen atom). Furthermore, the π-acidic co-ligands on this complex would favour the cobalt(I) canonical form to a greater degree, and would stabilise any cobalt(I) products that might be formed. The strongly σ-donating co-ordination sphere of the cyclam complex would stabilise cobalt(III) species and this in turn would favour the decomposition pathway that generates the carbanion.

Conclusion

A series of cobalt(III) complexes which contain amino acidato chelates which are incorporated into tetradentate frameworks have been synthesized and characterised. UV photolysis of these complexes leads to elimination of CO_2, as observed for related bidentate amino acidato complexes. However, in this case the resulting Co–C–N three-membered chelates are relatively stable, even with alkyl groups on the co-ordinated carbon atom, and can be characterised by conventional methods.

Studies of a cyclopropyl containing substrate have shown that the cyclopropane ring is retained in both the metallacyclic product of photodecarboxylation and its decomposition products. This demonstrates that any intermediates in the formation and decomposition of the metallacyclic compound that have a radical centre on what was the α-carbon of the amino acid must be very short-lived.

This study has opened the door to the synthesis of a range of other complexes by similar photochemical methods. Furthermore, the chemistry of such complexes is as yet unexplored and may itself lead to novel and interesting compounds along with shedding light on the nature of the bonding in the Co–C–N metallacycle.

Acknowledgements

S. G. T. acknowledges the University of Canterbury for the provision of a doctoral scholarship. We are also indebted to the members of the X-ray crystallography laboratory. We particularly thank Dr P. J. Steel for his help with the structure determination of the dinuclear complex.

References

1 For reviews of early work see: (*a*) V. I. Pavlovskii and A. L. Poznyak, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 789; (*b*) J. Sykora and J. Sima, *Coord. Chem. Rev.*, 1990, **107**, 1; (*c*) V. I. Pavlovskii and A. L. Poznyak, *Z. Chem.*, 1989, **29**, 6.
2 For recent examples see: (*a*) V. V. Pansevich and A. L. Poznyak, *Russ J. Inorg. Chem.*, 1991, **36**, 1425; (*b*) A. L. Poznyak and V. E. Stelímashok, *Metallorg. Khim.*, 1992, **5**, 611; (*c*) A. L. Poznyak and L. V. Stopolyanskaya, *Russ. J. Inorg. Chem.*, 1995, **40**, 1080; (*d*) T. Ama, H. Kawaguchi, K. Okamoto, T. Yasui, T. Yonemura and M. Yoshida, *Bull. Chem. Soc. Jpn.*, 1995, **68**, 874; (*e*) T. Yonemura, H. Kawaguchi, K. Shibuya, K. Murakami, T. Yasui, K. Okamoto and J. Hidaki, *Bull. Chem. Soc. Jpn.*, 1995, **68**, 2287; (*f*) M. Kojima, F. M. D. Akhter, K. Nakajima and Y. Yoshikawa, *Bull. Chem. Soc. Jpn.*, 1996, **69**, 2889; (*g*) D. M. Tonei, L. J. Baker, P. J. Brothers, G. R. Clark and D. C. Ware, *Chem. Commun.*, 1998, 2953; (*h*) T. Yonemura, K. Shibuya, T. Ama, H. Kawaguchi, K. Okamoto, J. Hidaka and T. Yasui, *Inorg. Chem.*, 1999, **38**, 3244; (*i*) R. M. Hartshorn and S. G. Telfer, *J. Chem. Soc., Dalton Trans.*, 1999, 3217.
3 V. I. Pavlovskii and A. L. Poznyak, *Z. Anorg. Allg. Chem.*, 1982, **485**, 225.
4 E. B. Chuklanova, V. I. Pavlovskii, T. V. Polynova, M. A. Porai-Koshits and A. L. Poznyak, *Monatsh Chem.*, 1982, 113.
5 R. M. Hartshorn and S. G. Telfer, *J. Chem. Soc., Dalton Trans.*, 1999, 3565.
6 E. Natarajan and P. Natarajan, *Inorg. Chem.*, 1992, **31**, 1215.
7 P. J. Lawson, M. J. McCarthy and A. M. Sargeson, *J. Am. Chem. Soc.*, 1982, **104**, 1734.
8 H. Iikura and T. Nagata, *Inorg. Chem.*, 1998, **37**, 4702.
9 M. S. Okamoto and E. K. Barefield, *Inorg. Chim. Acta*, 1976, **17**, 91.
10 T. Ama, K. Okamoto, T. Yonemura, H. Kawaguchi, A. Takeuchi and T. Yasui, *Chem. Lett.*, 1997, 1189.
11 A. L. Poznyak and V. I. Pavlovskii, *Russ. J. Inorg. Chem.*, 1981, **26**, 292.
12 E. C. Niederhoffer, J. H. Timmons and A. E. Martell, *Chem. Rev.*, 1984, **84**, 137.
13 D. A. Buckingham and C. R. Clark, in *Comprehensive Coordination Chemistry*, ed. G. Wilkinson, Pergamon Press, Oxford, 1987, vol. 4, ch. 47, pp. 775–789.
14 J. H. Timmons, R. H. Niswander, A. Clearfield and A. E. Martell, *Inorg. Chem.*, 1979, **18**, 1042; *Inorg. Chem.*, 1979, **18**, 2977.
15 A. Albert, *Heterocyclic Chemistry*, 2nd edn., Athlone Press, London, 1968.
16 E. B. Chuklanova, T. N. Polynova, M. A. Porai-Koshits, A. L. Poznyak and V. I. Pavlovskii, *Koord. Khim.*, 1986, **14**, 103.
17 C.-K. Poon, W.-K. Wan and S. S. T. Liao, *J. Chem. Soc., Dalton Trans.*, 1997, 1247.
18 S. M. Polson, L. Hansen and L. G. Marzilli, *J. Am. Chem. Soc.*, 1996, **118**, 4804.
19 P. J. Toscano, L. G. Marzilli in *Prog. Inorg. Chem.*; S. J. Lippard (Ed); Interscience, New York, 1984.
20 D. A. Armstrong, A. Rauk and D. Yu, *J. Am. Chem. Soc.*, 1993, **115**, 660.
21 V. Balzani, V. Cassarati, L. Moggi and F. Scandola, *Inorg. Chem.*, 1964, **4**, 1247; A. L. Poznyak and V. E. Stelmashok, *Inorg. Chim. Acta*, 1984, **83**, L59; C. H. Langford and G. W. Quance, *Can. J. Chem.*, 1977, **55**, 133.