FULL PAPER

Preparation and photochemistry of cobalt(III) amino and amino acidato complexes containing tripodal polypyridine ligands †

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The photochemical reactivities of cobalt(III)–diamine and cobalt(III)–amino acid compounds have been compared using complexes that also contain polypyridyl ligands. Metallacyclic complexes result from UV-induced photodecarboxylation reactions of the amino acid complexes. UV-irradiation of closely related complexes with amine donors replacing the carboxylate donors does not lead to the production of the same metallacyclic products. The reported UV-induced fragmentation of amine donors and subsequent metallacycle formation appears not to be a general reaction. Nine cobalt(III) complexes of polypyridyl ligands have been structurally characterised, including four that also contain amino acid ligands and one that contains a three-membered metallacyclic ring.

Introduction

Photodecarboxylation of amino acids coordinated to cobalt(III) gives rise to metallacyclic species containing cobalt–carbon bonds.¹ The stepwise mechanistic pathway for this process has been proposed to involve cobalt–ligand bond homolysis, decarboxylation, and then radical trapping by cobalt(II) to form the cobalt–carbon bond. Several such metallacycles have been reported, although those that have been structurally characterised are either part of a polydentate framework or contain good π -acceptor ligands in the coordination sphere.²

Similar chemistry has been postulated for the photolysis of coordinated polyamines (Scheme 1),¹ and we have recently explored the chemistry of some oxime based systems as part of a study of this possibility.³ Identical products have been



Scheme 1

† Electronic supplementary information (ESI) available: Synthetic, spectroscopic and crystallographic details. See http://www.rsc.org/ suppdata/dt/b3/b311809f/

reported (based substantially on spectroscopic studies) from the photolysis of the following pairs of complexes: $[Co(en)_3]^{3^+}$ and $[Co(en)_2(gly)]^{2^+}$, $[Co(bpy)_2(en)]^{3^+}$ and $[Co(bpy)_2(gly)]^{2^+}$, and $[Co(trien)(phen)]^{3^+}$ and $[Co(dtma)(phen)]^{2^+}$ (dtma = 8-amino-3,6-diazaoctanoate).¹ Tris(diamine)cobalt(III) systems have been reported to produce organic material on UV photolysis that is consistent with ligand-based carbon–carbon bond homolysis and decomposition of the complexes.^{4,5}

We are interested in establishing whether cobalt(III) complexes of coordinated amines do indeed exhibit photochemistry that gives the same complexes as those produced from coordinated amino acids. The photochemistry of $[Co(bpg)-(phen)]^{2+}$ (bpg = N,N-bis(2-pyridylmethyl)glycine) has been studied previously in this laboratory, and produces a metallacyclic product when irradiated with UV light.^{2j} The product is stable, has been structurally characterised, and it is possible to follow the reaction using NMR spectroscopy. In this paper we describe the preparation and photochemistry of the related cobalt(III) complex (Scheme 2) containing the ligand N,N-bis(2pyridylmethyl)-1,2-ethanediamine) (bpen), in which a primary amine donor replaces the carboxylate donor of bpg. We also report the results from studies of a new series of complexes containing the tripodal ligand tris(2-pyridylmethyl)amine (tpa).

Experimental

Materials

Reagent grade materials were used without further purification for all syntheses. L-Alanine, 2-aminoisobutyric acid, sarcosine, 1,2-ethanediamine and D₂O were obtained from Aldrich Chem. Co. Glycine, DL-phenyl glycine and 1,10-phenanthroline were obtained from BDH and ion exchange resins from Sigma. The ligands N,N-bis(2-pyridylmethyl)-1,2-ethanediamine (bpen),⁶ N,N-bis(2-pyridylmethyl)-1,3-propanediamine (bptn),⁷ and tris(2-pyridylmethyl)amine perchlorate⁸ were prepared as previously described. [Co(tpa)(NO₂)₂](ClO₄) was prepared according to a literature procedure.⁸

Measurements

The ¹H spectra were taken at 300 MHz and ¹³C spectra at 75 MHz on a Varian Unity-300 spectrometer at 23 °C. D₂O was used as a solvent, unless stated otherwise, and sodium 3-trimethylsilylpropanesulfonate (TMPS, δ 0, singlet) was used as an internal reference. Microanalyses were performed at the University of Otago.

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

The syntheses and the characterization data for the following compounds are deposited in the ESI: \dagger [Co(bpen)(NO₂)₂]NO₃· H₂O, [Co(bpen)Cl₂](ClO₄), [Co(bpen)(phen)](ClO₄)₃·2H₂O, [Co(bpen)(gly)](ClO₄)₂·2H₂O, [Co(bpen)(gly)][ZnCl₄]·3H₂O, [Co(bptn)(NO₂)₂]NO₃·0.5H₂O, [Co(bptn)Cl₂](ClO₄), [Co(tpa)(en)](ClO₄)₃·0.5H₂O, [Co(tpa)(gly)](ClO₄)₂· H₂O, [Co(tpa)(gly)][ZnCl₄]·1.5H₂O, [Co(tpa)(L-ala)](ClO₄)₂· H₂O, [Co(tpa)(aib)](ClO₄)₂·H₂O, [Co(tpa)(β-ala)](ClO₄)₂·H₂O, [Co(tpa)(gly)](ClO₄)₂·1.5H₂O, [Co(tpa)(sar)](ClO₄)₂·H₂O.

¹H NMR photolysis experiments

Samples of millimolar concentration in D₂O were irradiated in 5 mm NMR tubes using a 500 W high pressure mercury vapour lamp. Solutions of [Co(tpa)(L-ala)](ClO₄)₂·H₂O, [Co(tpa)-(aib)](ClO₄)₂·H₂O and [Co(tpa)(pgly)](ClO₄)₂·2H₂O were irradiated for 75 min. ¹H NMR spectra were recorded at 10, 20, 30, 50 and 75 min. After irradiation, the solutions were acidified with DCl and the spectra rerecorded. The acidified, photolysed solution of [Co(tpa)(pgly)](ClO₄)₂·2H₂O was extracted with CDCl₃, and the ¹H NMR spectrum of the organic phase was recorded. Solutions of [Co(tpa)(gly)](ClO₄)₂·H₂O, [Co(tpa)-(gly)][ZnCl₄]·2H₂O, were irradiated over 17 h and the ¹H NMR spectra were recorded after 6, 10 and 24 h. [Co(bpen)(gly)]-(ClO₄)₂·H₂O and [Co(bpen)(gly)][ZnCl₄]·2H₂O were irradiated over 48 h and the ¹H NMR spectra were recorded after 6, 24 and 48 h. Solutions of [Co(bpen)(phen)](ClO₄)₃·3H₂O and [Co(tpa)(en)](ClO₄)₃·H₂O were irradiated over 4 days, and the NMR spectra were recorded every 24 h.

Preparation of [Co(tpa)(CH₂NH₂)](ClO₄)₂

A solution of $[Co(tpa)(gly)](ClO_4)_2 \cdot H_2O$ (0.2 g, 3 mmol) in water (35 mL) was irradiated over 24 h using an immersible mercury vapour lamp in a jacketed cell. Water was passed through the jacket, cooling the solution to around 10 °C. The crude photosylate was loaded onto a column of CM-25 Sephadex (14 cm × 3.5 cm, Na⁺ form). Elution with water (250 mL) and aqueous NaClO₄ (250 mL, 0.05 M) developed a red band which was collected using aqueous NaClO₄ (0.15 M). The band was concentrated on a rotary evaporator at 35 °C until an intensely coloured orange solid precipitated. The precipitate was collected by filtration and washed with ethanol and diethyl ether. The crude metallacycle was recrystallised from water. Yield 0.05 g. ¹H NMR (D₂O): Two isomers are present in the crystalline material in the ratio of 1 : 1.12. The following signals are assigned to the minor component: δ 10.13 (d, 1H, pyridyl), 5.74 (half of AB system, 2H, CH₂N), 4.91 (half of AB system, 2H, CH₂N), 4.64 (s, H, CH₂N), 4.24 (s, CH₂Co). The following signals are assigned to the major component: δ 9.98 (d, H, pyr-idyl), 6.04 (half of AB system, 2H, CH₂N), 5.61 (half of AB system, 2H, CH₂N), 5.61 (half of AB system, 2H, CH₂N), 5.26 (s, 2H, CH₂N), 4.77 (s, 2H, CH₂Co). ¹³C NMR (D₂O): The following signals were assigned on peak height. Major component: δ 165.60, 165.56, 156.75. 154.92, 142.47, 141.32, 128.58, 128.47, 125.47, 123.99, 71.57, 68.84, 37.56. Minor component: δ 163.75, 163.36, 154.56, 153.22, 142.19, 141.70, 128.94, 128.11, 125.16, 123.92, 73.00, 70.72, 37.73. Anal. Required for C₁₉H₂₂Cl₂CoN₅O₈: C, 39.46; H, 3.83; N, 12.11%. Found: C, 39.22; H, 3.89; N, 12.00%.

[Co(tpa)(CH₂NH₂)](BPh₄)₂·(CH₃)₂CO

To a solution of $[Co(tpa)(CH_2NH_2)](ClO_4)_2$ (0.04 g, 7×10^{-6} mol) in water (1.5 mL) and methanol (10 mL), a solution of NaBPh₄ (0.5 g, 15 mmol) in methanol (10 mL) was added. The solution was refrigerated and after 4 h a crude tetraphenylborate salt of the metallacycle precipitated, was collected by filtration and air dried. Yield 0.03 g. X-Ray quality crystals were obtained from the vapour diffusion of diethyl ether into a solution of the crude salt in acetone at 4 °C. Microanalytical data was not obtained as the crystalline material loses solvent in air.

Preparation of [Co(tpa)(CH₂NHMe)](ClO₄)₂·H₂O

A solution of $[Co(tpa)(sar)](ClO_4)_2 \cdot H_2O$ (0.2 g, 3 mmol) in water (35 mL) was irradiated over 13 h using an immersible mercury vapour lamp in a jacketed cell. Water was passed through the jacket, cooling the solution to around 10 °C. The crude photosylate was loaded onto a column of CM-25 Sephadex (14 cm \times 3.5 cm, Na⁺ form). Elution with water (250 mL) and aqueous NaClO₄ (250 mL, 0.05 M) developed a red band which was collected using aqueous NaClO₄ (0.15 M). The band was concentrated on a rotary evaporator at 35 °C to approximately 10 mL and placed in a fridge overnight. Red microcrystalline material formed over this time that was collected by filtration and washed with ethanol and diethyl ether. Yield 0.02 g. ¹H NMR (D₂O): δ 9.95 (d, H, pyridyl), 8.13 (d, H, pyridyl), 8.03 (d, H, pyridyl), 7.80-7.69 (m, 3H, pyridyl), 7.55-7.49 (m, 3H, pyridyl), 7.25-7.18 (m, 3H, pyridyl), 6.10-6.00 (m, 2H, CH2N), 5.68-5.61 (m, 2H, CH2N), 5.26 (s, 2H, CH₂N), 4.92 (s, H, CoCH), 4.59 (s, H, CoCH). ¹³C NMR (D₂O): 165.56, 165.33, 165.26, 156.58, 155.39, 154.63, 142.77, 142.64, 141.41, 128.74, 128.72, 128.69, 126.10, 125.67, 123.99, 71.77, 71.73, 69.27, 45.96, 38.04. ESMS: *m*/*z* 394 (M⁺ + H), 349 (M⁺ - CH₂NHCH₃). Anal. Required for C₂₀H₂₄Cl₂CoN₅O₈: C, 40.56; H, 4.08; N, 11.82%. Found: C, 40.31; H, 3.99; N, 11.73%.

Crystal structure determinations

Experimental details are provided in the ESI. † Crystallographic data are shown in Table 1.

CCDC reference numbers 220354-220362.

See http://www.rsc.org/suppdata/dt/b3/b311809f/ for crystallographic data in CIF or other electronic format.

Results

Complex syntheses

The reaction of $Co(NO_3)_2$ ·6H₂O with bpen or bptn using standard conditions⁹ afforded good yields of the [Co(bpen)-(NO₂)₂]NO₃ and [Co(bptn)(NO₂)₂]NO₃ complexes. The dinitro complex of the bpen system is the more symmetrical *trans* isomer. In the case of bptn, however, the reaction produces major and minor products that both contain the less symmetrical *cis*-coordinated bptn. We suspect that the material is a mixture of linkage isomers in which both the nitro and nitrito coordination modes are present. An incomplete X-ray structure analysis of poor quality crystals revealed that the nitro group *trans* to the pyridine donor was disordered, and the residual electron density in the area was consistent with the presence of O-bound nitrito ligands in some molecules.

The substitution reaction of $[Co(bpen)Cl_2]ClO_4$ with 1,10phenanthrolene gave $[Co(bpen)(phen)]^{3+}$. Only a moderate yield was obtained since $[Co(phen)_3]^{3+}$ is also produced under the reaction conditions. $[Co(bpen)(gly)]^{2+}$ was prepared from $[Co(bpen)Cl_2]ClO_4$, and a similar route was used to prepare tpa-amino acid complexes, $[Co(tpa)(aa)]^{2+}$.

Following the reactions of $[Co(tpa)Cl_2]ClO_4$ and $[Co(bpen)-Cl_2](ClO_4)$ with amino acids, ion exchange chromatography of the reaction mixtures affords one major product band. In each case, ¹H NMR spectra of the dried eluates were consistent with the formation of only one diastereoisomer. Several of these amino acid complexes were structurally characterised, either as their perchlorate or tetrachlorozincate salts, while studies of a number of others did not produce structural solutions of publishable standard. In the $[Co(tpa)(aa)]^{2+}$ complexes prepared under these conditions, the amino acid is coordinated with the carboxylate group *trans* to the tertiary amine of tpa. Similarly, in $[Co(bpen)(gly)]^{2+}$, the glycine ligand is coordinated with the carboxylate group *trans* to the tertiary amine of bpen.

Photolysis experiments

The effect of UV irradiation on samples of $[Co(bpen)(gly)]^{2+}$, $[Co(bpen)(phen)]^{3+}$, $[Co(tpa)(en)]^{2+}$ and $[Co(tpa)(aa)]^{2+}$ dissolved in D₂O was followed by NMR spectroscopy. Generally, the amino acid containing complexes required less irradiation than their amine analogues before a change in the NMR spectrum was noticeable.

¹H NMR spectra recorded during the photolysis of [Co-(tpa)(gly)]²⁺ show the gradual appearance of pairs of new peaks. The most obvious new peaks in the downfield region are a pair of doublets that appear at 10.12 and 9.98 ppm, reproducibly integrating with a ratio of 1 : 1.1. The aromatic region between 7.50 and 8.50 ppm rapidly becomes complicated, and three new AB systems appear between 5.58 and 6.07 ppm. A fourth AB system is mostly obscured by a broad HOD peak in the crude photolysate. Two new singlets appear at 4.32 and 4.72 ppm and these also integrate at 1 : 1.1. After 24 h of irradiation, starting material is still present in the photolysate (approx. 60% conversion).

Two isomers of the metallacyclic complex are possible (with the amine bound *cis* or *trans* to the tertiary amine of the tpa ligand) and we believe, based on these NMR results, that both are present in the isolated material. The relative yield of these two isomers appears not to depend on temperature.

From a larger scale photolysis of a sample of $[Co(tpa)(gly)]^{2+}$

and subsequent ion-exchange chromatography, we were able to isolate the metallacyclic species $[Co(tpa)(CH_2NH_2)](ClO_4)_2$. The metallacycle co-elutes with unreacted starting material, but when the eluted band is concentrated on a rotary evaporator, the perchlorate salt of the metallacyclic complex precipitates from the solution before that of the unreacted starting material. Both isomers are present in this isolated material. A reaction time of 17 h was found to provide the optimum yield from the bulk photolyses. Using a similar procedure, we were able to isolate a metallacyclic species from the photolysis of $[Co(tpa)(sar)]^{2+}$.

Complexes containing amino acids substituted at the α -carbon were more reactive. After 75 min of irradiation, only a small amount of starting material could be detected by NMR spectroscopy in the photolysates of $[Co(tpa)(L-ala)]^{2+}$ and $[Co(tpa)(pgly)]^{2+}$ and none was present in the photolysate of $[Co(tpa)(aib)]^{2+}$. In general, the loss in intensity of resonances assigned to starting material was accompanied by the growth of new resonances assigned to the metallacyclic product.

Decomposition of the metallacycles resulted, ultimately, in formation of the carbonyl compounds derived from the amino acid, presumably via the related imines. In some cases, the decomposition was sufficiently rapid that metallacyclic complex resonances had only rather low intensity. The carbonyl compounds could usually be detected in the photolysate, but in the case of the phenylglycine complex, the benzaldehyde was detected following extraction into CDCl₃. The complexity of the aromatic region and the low stability of the metallacyclic complexes limited the degree to which resonances could be assigned to the metallacyclic complexes, but some could be assigned by analogy to the stable complex derived from the glycinato complex (Table 2). Resonances due to free tpa and free amino acid could also be identified, along with another set of resonances for an unidentified compound that was formed, in small amounts, from all of these substrates.

 $[Co(bpen)(phen)]^{3+}$ is reasonably stable to UV irradiation, and a significant amount of starting material is present even after 4 days. New peaks do appear in the spectrum; the most abundant species in the solution after this time is $[Co(phen)_3]^{2+}$. A new AB system appears at 5.11 and 5.43 ppm, and several singlets appear at 4.49, 4.14 and 3.97 ppm. The singlet at 3.97 ppm is much larger than the other two after four days of photolysis. A large singlet is also present at 0.16 ppm. We are unable to identify the compounds giving rise to these peaks, but it is clear that they are not the metallacyclic complex that is obtained on photolysis of $[Co(bpg)(phen)]^{2+}$.

The complex $[Co(tpa)(en)](ClO_4)_3$ is comparatively stable toward UV radiation. After 4 days of photolysis there are few changes in the ¹H NMR spectrum. The only significant new peak is a singlet appearing at 3.40 ppm. Free en was identified in the photolysate, following spiking experiments. A dark material begins to precipitate from the solution after 24 h. We note also that, when the solution has stood for 7 days following the photolysis, the ¹H and ¹³C NMR spectra show that the picolyl protons on the starting material have exchanged. Similar observations have proven significant in a recent study of ligand substitution mechanism.¹⁰ There is no indication of any peaks that can be assigned to the metallacyclic complex, $[Co(tpa)-(CH_2NH_2)]^{2+}$.

Photolyses on bulk samples of the amine complexes were performed in a similar manner to those of the related amino acid complexes. No metallacyclic complexes could be detected following use of the chromatographic procedures that were developed for their isolation from photolysates of the amino acid based systems.

Description of structures

The complex cations $[Co(bpen)(NO_2)_2]^+$, $[Co(bpen)(ghen)]^{3+}$, $[Co(bpen)(gly)]^{2+}$ and $[Co(bptn)Cl_2]^+$ all have near octahedral

Hole I of jotanographic date	Table 1	Crystallographic data
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Formula $C_{18}H_{18}Cl_3CoN_4O_4$ $C_{20}H_{26}Cl_4CoN_5O_4Zn$ $C_{21}H_{26}Cl_2CoN_5O_{11}$ $C_{22}H_{28}Cl_2CoN_5O_{11}$	$C_{15}H_{20}Cl_3CoN_4O_4$
	405 (3
$M_{\rm r}$ 319.04 000.50 034.30 008.32	485.03
Crystal system Orthornombic Orthornombic Orthornombic Orthornombic	Monoclinic D2 /
space group $P_{2_12_12_1}$ $P_{2_12_{1_22_1}}$ $P_{2_12_{1_22_1}}$ $P_{2_12_{1_22_1}}$ $P_{2_12_{1_22_1}}$	$P Z_1/n$ 12 402(4)
d/A 8.59/(10) 8.580(2) 11.51(4) 11.51/(5)	12.493(4)
D/A 15.162(13) 12.014(3) 15.70(3) 13.70(5) 13.490(6)	12.111(4)
c/A 15.214(1/) 25.633(6) 16.721(6) 17.594(7)	13.068(4)
ν_{μ}^{ρ} $\nu_{\lambda}^{A^{3}}$ 1983(4) 2580.8(12) 2600.5(17) 2733(2)	1882 7(11)
7 4 4 4 4 4	4
T/K 168(2) 168(2) 168(2) 168(2)	168(2)
u/mm^{-1} 1305 2024 0935 0891	1 368
Reflections collected 24201 15466 33700 17782	23580
Independent reflections 4039 5019 5301 531	3851
Observed 2240 4813 4942 4858	3397
Parameters refined 271 316 398 416	244
$R[I > 2\pi(I)]$ 0.043 0.029 0.023 0.030	0.034
$R_{1} [I \ge 2\pi (I)]$ 0.050 0.020 0.055 0.070	0.091
	0.071
Compound $[Co(bpen)(NO_2)_2](NO_3) \cdot H_2O$ $[Co(bpen)(phen)](ClO_4)_3 \cdot 3H_2O$ $[Co(bpen)(gly)][ZnCl_4] \cdot 3H_2O$ $[Co(tpa)(CH,NH_2)](BP)$	$h_{4}_{2} \cdot (CH_{3})_{2} CO$
Formula $C_{14}H_{20}CoN_7O_8$ $C_{26}H_{32}Cl_3CON_6O_{15}$ $C_{16}H_{28}Cl_4CoN_4O_5Zn C_{12}H_{23}CoN_4O_7$ $C_{70}H_{68}B_2CoN_5O$	
M _r 473.30 833.86 636.53 1075.84	
Crystal system Monoclinic Monoclinic Monoclinic Triclinic	
Space group $P_{2_1/n}$ $P_{2_1/n}$ $P_{2_1/n}$ $P_{\overline{1}}$	
alÅ 15.77(3) 12.010(9) 9.5884(19) 11.338(3)	
b/Å 8.229(13) 15.139(11) 14.168(3) 13.516(4)	
c/Å 15.77(3) 18.554(12) 18.429(5) 18.982(6)	
a/° 83.967(4)	
β° 106.93(4) 98.70(2) 102.541(4) 84.605(5)	
y/° 88.122(4)	
$V/Å^3$ 1959(6) 3335(4) 2443.9(10) 2879.1(15)	
Z 4 4 2	
<i>T</i> /K 168(2) 168(2) 168(2) 168(2)	
μ/mm^{-1} 0.935 0.836 2.135 0.347	
Reflections collected 8674 23349 19602 36499	
Independent reflections 3694 6689 4732 11492	
Observed 2797 3112 3876 7084	
Parameters refined271532309726	
$R[I > 2\sigma(I)]$ 0.026 0.047 0.030 0.057	
$R_{\rm w}[I > 2\sigma(I)]$ 0.059 0.083 0.070 0.100	

Table 2 Results from photolyses of $[Co(tpa)(aa)]^{2+}$	complexes
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Coordinated amino acid	L-Alanine	Aminoisobutyric acid	DL-Phenylglycine	Sarcosine
¹ H NMR resonances assigned to metallacyclic species	10.15 (d), 5.09–5.80 (2 × AB), 4.20 (m), 0.83 (d)	10.19 (d), 5.6 (AB), 0.72 (s)	10.01, 5.2–5.8 (AB systems)	10.19 (d), 6.3 (m), 5.9 (m), 4.8 (s), 1.8 (s)
C=O Compound detected in photolysate	Acetaldehyde	Acetone	Benzaldehyde ^{<i>a</i>}	

^{*a*} Following extraction into CDCl₃.



Fig. 1 Structures of some complex cations containing the bpen or bptn ligands: $[Co(bpen)(NO_2)_2]^+$, top left; $[Co(bpen)(phen)]^{3+}$, top right; $[Co(bpen)(gly)]^{2+}$, bottom left; and $[Co(bptn)Cl_2]^+$, bottom right.

geometry (Fig. 1), as do the tpa complexes, $[Co(tpa)Cl_2]^+$, $[Co(tpa)(gly)]^{2+}$, $[Co(tpa)(L-ala)]^{2+}$ and $[Co(tpa)(aib)]^{2+}$ that are shown in Fig. 2. The largest distortion from a perfect octahedron arises from accommodation of the fused five-membered rings containing the *trans* pyridine donors.

A satisfactory structure of the metallacyclic complex, [Co-(tpa)(CH₂NH₂)]²⁺, was finally obtained for the tetraphenylborate salt (Fig. 3). This complex cation also adopts a distorted octahedral geometry. The distortions can again be attributed to the constraints put on the structure by the chelate rings. The three five-membered chelate rings subtend angles at cobalt of 83-87°, and the angle in the three-membered metallacyclic ring, 43.5°, is much smaller than the 90° angle of the perfect octahedron. The carbon-nitrogen bond of the metallacycle is of similar length (1.432(4) Å) to those observed in other similar structures (1.35-1.45 Å), and is indicative of a bond order somewhat greater than one, as has been noted previously.^{2j} The refinement was marginally better for the isomer shown than for the structure where N5 and C19 are exchanged but, given that both isomers were observed by NMR techniques, we consider it very likely that there is some disorder and both isomers are present in the crystal. We do not believe that the data and refinement are sufficiently good to make a meaningful determination of C/N partial occupancy at each site.

Discussion

The intention of this work was to compare the photochemistry of coordinated primary amines with the photochemistry of coordinated amino acids. First, study of the $[Co(bpen)(phen)]^{3+}$ cation would allow a direct comparison with photochemistry of the $[Co(bpg)(phen)]^{2+}$ that we have studied previously. Second, we sought to compare the photochemistry of the new complexes $[Co(tpa)(en)]^{3+}$ and $[Co(tpa)(gly)]^{2+}$. We have also examined a variety of $[Co(tpa)(aa)]^{2+}$ complexes to establish that their photochemistry is the same decarboxylation chemistry as seen for other amino acid systems.

Structural studies

In the complexes $[Co(tpa)(gly)]^{3+}$, $[Co(tpa)(L-ala)]^{3+}$, $[Co(tpa)-(aib)]^{3+}$ and $[Co(bpen)(gly)]^{3+}$ the observed coordination mode



Fig. 2 Structures of some complex cations containing the tpa ligand: $[Co(tpa)Cl_2]^+$, top left; $[Co(tpa)(gly)]^{2+}$, top right; $[Co(tpa)(L-ala)]^{2+}$, bottom left; and $[Co(tpa)(aib)]^{2+}$, bottom right.



Fig. 3 The structure of the $[Co(tpa)(CH_2NH_2)]^{2+}$ complex cation.

of the amino acids, with the carboxylate donor *trans* to the tertiary amine, is different to that observed in the $[Co(tren)-(aa)]^{2+}$ systems (tren = tris(2-aminoethyl)amine), where the amine donor is coordinated *trans* to the tertiary amine.

In the tren systems, the relative stabilities of the two isomers have been discussed previously in relation to possible non-bonding interactions between hydrogen atoms on the glycine nitrogen atom and nearby hydrogen atoms on the tren nitrogen atom and carbon backbone. In the less stable isomer, the amine hydrogen atoms are predicted to lie only 2.13 Å from the adjacent primary amine hydrogen atoms of the tren ligand, based on the results of a molecular mechanics study.¹²

A similar argument may be considered for the [Co(tpa)(aa)]²⁺ complexes, but with a change in isomer preference due to the different structures of the tetradentate ligands. The closest hydrogen atoms to the hydrogen atoms on N(5) of the amino acid lie 2.206 Å away, on the picolyl arms of the pyridine rings that are also cis to the amino acid nitrogen atom (and trans to each other). However, if the glycinato amine occupied the position of the carboxylate oxygen (i.e. trans to the tertiary nitrogen atom, as is seen in the tren systems), its hydrogen atoms would lie close to the hydrogen atoms in the 6-position of those pyridine rings that are trans to each other. The torsion angles between the vertical Co-N(1) bond and the pyridine rings are approximately 16° for the trans pyridine groups. These pyridine hydrogen atoms are forced to occupy that region of space because of geometrical restrictions imposed by coordination of the tripodal ligand (and formation of three fused fivemembered rings).

Photochemical studies

From the photolysis experiments with the complex pairs $[Co(bpen)(phen)]^{3+}$, $[Co(bpg)(phen)]^{2+}$ and $[Co(tpa)(gly)]^{2+}$, $[Co(tpa)(en)]^{3+}$ it is clear that the amino acid based systems and the analogous amine systems give different products. Stable metallacycles are produced from photolyses of $[Co(bpg)-(phen)]^{2+}$ and $[Co(tpa)(gly)]^{2+}$, and these have been isolated and fully characterised.

The presence of metallacyclic products is easily recognised in ¹H NMR spectra as a downfield chemical shift is observed for the resonance assigned to the 6-proton on the pyridyl ring *trans* to the metallacycle. This type of downfield shift has been observed on photolysis of $[Co(bpg)(phen)]^{2+}$. Spectra obtained following photolysis of $[Co(tpa)(gly)]^{2+}$ contain two such peaks, which is indicative of the presence of two such compounds, while $[Co(tpa)(sar)]^{2+}$ and $[Co(tpa)(L-ala)]^{2+}$ produce only one metallacyclic complex.

The two isomeric metallacyclic products that are produced from the $[Co(tpa)(gly)]^{2+}$ system presumably arise because the amine end of the metallacyclic ligand can be coordinated either *cis* or *trans* to the tertiary amine donor of the tpa ligand. There is little preference for either isomer on steric (or any other) grounds until a methyl group is introduced, as in the sarcosine and alanine systems; in which case only one isomer is detected. One might predict, on steric grounds, that the opposite isomer preference might be observed in the sarcosine and alanine systems, and that the methyl-substituted end of the ligand would be bound at the less hindered site, which is *cis* to the tertiary amine and *trans* to a pyridine donor (see Fig. 3).

The downfield resonances assigned to the 6-proton on the pyridyl ring *trans* to the metallacycle occur at 10.13 and 9.98 ppm in the two isomers of the glycine derived system. The difference in chemical shift will result from this proton being close to either the coordinated methylene group or the coordinated amine group of the metallacyclic complex, depending on the isomer. If the methyl substituent is introduced *cis* to the tertiary amine, the pyridine 6-proton resonance should not be greatly affected, and the chemical shift should depend principally upon whether the pyridine proton is close to an amine group (as it would be in the alanine derived metallacycle) or a methylene group (as it would be in the sarcosine derived metallacycle) of a metallacycle. The observation of resonances at 10.15 and 9.95 ppm for the alanine and sarcosine derived metallacycles, respectively, is consistent with this proposal.

Variable-temperature NMR experiments provided no evidence of fluxionality at temperatures up to 80 °C, and the initial isomeric ratio was retained on cooling the sample to 23 °C. The results do, however, demonstrate the stability of the metallacyclic isomers that were present, as there was no evidence of any decomposition of the sample following this treatment. In the absence of any fluxionality in the system, the two isomers must be formed during the photochemical reaction. The lability of the cobalt(II) intermediates that have been proposed for such systems¹ would presumably allow sufficient configurational flexibility in the formation of these isomers.

The photochemistry of $[Co(tpa)(L-ala)]^{2+}$, $[Co(tpa)(aib)]^{2+}$ and $[Co(tpa)(pgly)]^{2+}$ is consistent with photodecarboxylation followed by reasonably rapid decomposition of the metallacyclic species, as has been seen before for related systems.²ⁱ,^{j,11} Only small amounts of metallacyclic complexes could be detected in photolysed solutions of these complexes. The complexes decompose through a similar route giving the appropriate aldehyde or ketone. The same complex product appears to be formed in all these cases when the photolysed solutions are allowed to stand following decomposition.

 $[Co(bpen)(phen)]^{3+}$ and $[Co(tpa)(en)]^{3+}$ require longer periods of irradiation before significant changes are present in their NMR spectra. New species are produced which do not have NMR spectra that correspond to the metallacyclic product that would be predicted based on the literature (which we have independently synthesised). We were unable to identify any of the new complex products with any certainty, other than the $[Co(phen)_3]^{3+}$ which is produced on photolysis of [Co(bpen)- (phen)]³⁺. It is possible that the amine systems are simply very much less reactive, but no metallacycle was detected (by NMR) in the photolysates, even over long periods of time. Bulk photolyses using an immersion lamp gave similarly negative results. Given the observed stability of the metallacycles, it seems unlikely that the amine systems are producing the same product as the glycine derived systems.

Conclusion

We have established that if amine ligands are photochemically cleaved, as is reported in the literature, the formation of metallacyclic species is not a general reaction. Indeed, our attempts to characterise metallacycles following photolyses of amine complexes, as described in the literature, have proven unsuccessful as well. We have prepared the metallacyclic complexes *via* the photodecarboxylation of chelated amino acids, shown they are relatively stable under the conditions of the experiments, and established that the products from the irradiation of the amine complexes are different. We have also isolated and structurally characterised nine cobalt(III) complexes of polypyridyl ligands, including four that also contain amino acid ligands and one containing a three-membered metallacyclic ring.

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