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FULL PAPER

Formation of *trans*(N)-bis(amino acidato)(2,2′-bipyridine)cobalt(III) complexes following the UV irradiation of amino acidatobis(2,2′-bipyridine)cobalt(III) complexes in dimethyl sulfoxide

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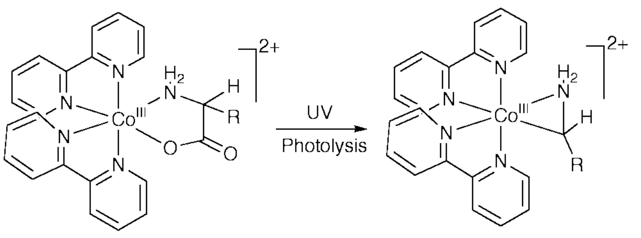
The products from the steady state photolysis of $[Co(aa)(2,2'\text{-bpy})_2]^{2+}$ (aa = glycinate (gly), alaninate (ala) or 2-aminoisobutyrate (aib)) complexes in dmso have been identified, and include the *trans*(N)-$[Co(aa)_2(2,2'\text{-bpy})]^+$ complex ions. This contrasts with photolyses in aqueous solution where the $[Co(2,2'\text{-bpy})_3]^{3+}$ ion is produced. This solvent dependence can be attributed to the secondary reactions of the photolysis products, rather than to different photochemistry. Electrochemical data have been gathered on a range of $[Co(aa)_x(2,2'\text{-bpy})_y]^{(3-x)+}$ compounds and are used to help rationalise the observed selectivity. Two of the products have been characterised by X-ray crystallography: (Δ-*SS*/Λ-*RR*)-*trans*(N)-$[Co(ala)_2(2,2'\text{-bpy})]ClO_4\cdot H_2O$ and *trans*(N)-$[Co(aib)_2(2,2'\text{-bpy})]ClO_4\cdot NaClO_4\cdot 0.5H_2O$.

Introduction

Recently we have been exploring the mechanism of some of the reactions which occur during the photolysis of amino acidatocobalt(III) complexes. UV Irradiation of aqueous solutions of these complexes induces decarboxylation of the amino acid and formation of complexes which contain a cobalt–carbon–nitrogen metallacycle (Scheme 1). These reactions were first reported by Poznyak and co-workers,[1] and more recently other groups have taken an interest.[2] In most cases the metallacyclic product is not very stable and decomposition products, such as a carbonyl compound, are observed instead.[3] The aqueous photolysate also contains Co^{II}, free 2,2′-bipyridine, free amino acid and $[Co(2,2'\text{-bpy})_3]^{3+}$.



Scheme 1

The mechanism by which the metallacycle is formed is still unclear, but we have established, through the use of a cyclopropylglycine based substrate, that any intermediate that involves a radical on what was the α-carbon atom of the amino acid has a very short lifetime.[3a] This result may have implications for the mechanism of the reaction, and we are presently gathering data with the aim of being able to propose a mechanism.

During the course of these mechanistic studies we conducted some of the photochemical reactions in non-aqueous solvents. This paper describes the results obtained through performing steady state photolysis reactions on $[Co(aa)(2,2'\text{-bpy})_2]^+$ (aa = glycinate (gly), alaninate (ala) or 2-aminoisobutyrate (aib)) complexes in dmso. A range of spectroscopic, electrochemical, and synthetic techniques have been employed in order to identify the complex ions which are produced, and to help understand the role that the solvent plays in their formation.

Experimental

Materials

Reagent grade compounds were used without further purification for all syntheses. DL-Alanine, 2-aminoisobutyric acid, ferrocene, D_2O, and dimethyl-d^6 sulfoxide were obtained from Aldrich Chem. Co, glycine and 2,2′-bipyridine from BDH and ion-exchange resins from Sigma.

Measurements

The ^1H NMR spectra were obtained at 300 MHz on a Varian Unity-300 spectrometer at 23 °C. For those recorded in dimethyl-d^6 sulfoxide (dmso-d^6), the dmso-d^5 multiplet at δ 2.50 was used as a reference. An internal reference was used for spectra recorded in D_2O or DCl solutions (sodium 3-trimethylsilylpropanesulfonate (TMPS), δ 0 (singlet)). The signals are described as singlets (s), doublets (d), triplets (t), or multiplets (m), and broad (br) where appropriate. A Varian XL-300 spectrometer was employed to obtain the ^{13}C NMR spectra at 75 MHz, and all spectra were proton decoupled. The spectra were recorded at 23 °C and referenced to the dmso-d^6 peak at δ 39.5 or, in D_2O, to an internal standard; 1,4-dioxane at 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} ($\varepsilon_{max}/M^{-1}\ cm^{-1}$). Microanalyses were performed by the University of Otago Microanalytical Service.

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

Photochemistry of $[Co(aa)(2,2'\text{-bpy})_2]^{2+}$ complexes in dmso: General procedure

The $[Co(aa)(2,2'\text{-bpy})_2]^{2+}$ complexes were prepared by the general method of Tatehata,[4] isolated as the perchlorate salts and characterised by NMR methods. A solution of each complex in dmso-d^6 was irradiated in an NMR tube, or quartz cuvette, which was submerged in a quartz ice-bath. The concentration was typically ≈1 mM. A 200 W high pressure mercury lamp was used as the light source. After about one hour, portions of the photolysates were added to 0.025 M DCl/D$_2$O solutions for the recording of ^{1}H NMR spectra. In some cases, reasonable quality NMR spectra of the photolysate could be obtained after standing the photolysate for about 48 h. Better results were usually obtained if ^{13}C NMR spectra were acquired in this manner. In the quantitative experiments the dmso-d^5 line was used to standardise the NMR integrals. All products were identified by spiking the NMR solutions with authentic samples.

(a) [Co(gly)(2,2′-bpy)$_2$][ClO$_4$]$_2$. ^{1}H NMR (D$_2$O/DCl): free glycine, δ 3.92; *trans*(N)-[Co(gly)$_2$(2,2′-bpy)]$^+$, δ 3.48–3.55 (m) and 3.71–3.79 (m) (the 2,2′-bipyridine peaks coincide with those of free 2,2′-bipyridine); free 2,2′-bipyridine, δ 7.93 (t), 8.41–8.52 (m) and 8.87 (d). ^{13}C NMR (dmso): glycine, δ 45.2 and 179.4; free 2,2′-bipyridine, δ 122.9, 126.8, 140.9, 150.3 and 156.3; *trans*(N)-[Co(gly)$_2$(2,2′-bpy)]$^+$ was not detected, due to its relatively low concentration.

(b) [Co(ala)(2,2′-bpy)$_2$][ClO$_4$]$_2$. ^{1}H NMR (D$_2$O/DCl): free alanine, δ 1.59 (d) and 4.17 (q); acetaldehyde and hydrated acetaldehyde, δ 1.18–1.34 (m, CH$_3$ of both), 5.23 (q, hydrated form, partially obscured by HOD peak) and 9.67 (q, aldehyde); (Δ-*SS*/Λ-*RR*)-*trans*(N)-[Co(ala)$_2$(2,2′-bpy)]$^+$, δ 1.52 (d), 3.60 (m) and 5.79–5.90 (br m) (the 2,2′-bpy peaks were obscured by free 2,2′-bipyridine); (Δ-*RR*/Λ-*SS*)-*trans*(N)-[Co(ala)$_2$(2,2′-bpy)]$^+$, δ 1.33 (d), 3.90 (m) and 6.50 (br m) (the 2,2′-bpy peaks were obscured by free 2,2′-bipyridine); free 2,2′-bipyridine, δ 7.93 (t), 8.41–8.52 (m) and 8.87 (d). ^{13}C NMR (dmso): free alanine, δ 19.1, 51.9 and 179.6; free 2,2′-bipyridine, δ 122.9, 126.8, 140.9, 150.3 and 156.3; *trans*(N)-[Co(ala)$_2$(2,2′-bpy)]$^+$ complexes were not detected due to their relatively low concentration.

(c) [Co(aib)(2,2′-bpy)$_2$][ClO$_4$]$_2$. ^{1}H NMR (D$_2$O/DCl): acetone, δ 2.22 (s); free aib, δ 1.61 (s); *trans*(N)-[Co(aib)$_2$(2,2′-bpy)]$^+$, δ 1.21 (s), 1.58 (s), 5.40 (d, NH) and 6.14 (d, NH) (the 2,2′-bpy peaks are obscured by free 2,2′-bipyridine); free 2,2′-bipyridine, δ 7.93 (t), 8.41–8.52 (m) and 8.87 (d). ^{13}C NMR (dmso): acetone, δ 30.2 and 206.0; free aib, δ 30.1, 55.8 and 179.3; *trans*(N)-[Co(aib)$_2$(2,2′-bpy)]$^+$, δ 27.0, 27.4, 57.8, 122.7, 126.0, 140.5, 150.0, 157.2 and 187.2.

Preparation and spectroscopy of [Co(aa)$_2$(2,2′-bpy)]$^+$ complexes in aqueous solution

The method of Yasui[5] was followed to prepare the [Co(aa)$_2$(2,2′-bpy)]$^+$ complexes which were separated on SP-Sephadex, desalted on G-10 Sephadex, and isolated by the addition of concentrated NaClO$_4$ solution. The crude complexes were recrystallised from the minimum volume of hot, dilute HClO$_4$ and the precipitate was filtered off and dried. The NMR spectra are reported here for the first time.

(a) (i) *trans*(N)-[Co(gly)$_2$(2,2′-bpy)]ClO$_4$·1.5H$_2$O. ^{1}H NMR: (dmso-d$_6$) δ 3.08–3.27 (m, 4 H), 5.65 (br m, 2 H, NH), 6.04 (br, m, 2 H, NH), 7.88 (t, 2 H), 8.37 (m, 4 H) and 8.71 (d, 2 H); (D$_2$O) δ 3.48–3.56 (m, 2 H, CH), 3.71–3.79 (m, 2 H, CH), 5.28–5.37 (br m, 2 H, NH), 5.99–6.05 (br m, 2 H, NH), 7.90 (t, 2 H), 8.42 (t, 2 H) and 8.51–8.56 (m, 4 H). ^{13}C NMR: (dmso-d$_6$) δ 45.8, 123.8, 127.4, 141.4, 150.9, 157.0 and 182.2; (D$_2$O) δ 47.0 (α-C), 125.1, 129.0, 143.2, 151.7, 157.5 and 187.0 (COO). Calc. for [C$_{14}$H$_{16}$CoN$_4$O$_4$]ClO$_4$·1.5H$_2$O: C, 34.33; H, 3.88; N, 11.44. Found: C, 34.03; H, 3.51; N, 11.39%. The UV-VIS spectrum agreed quantitatively with that previously reported for *trans*(N)-[Co(2,2′-bpy)(gly)$_2$]Cl;[5] 481 (110), 309 (19000), 300 (sh, 23000) and 221 nm (63000) M^{-1} cm^{-1}.

(ii) *cis*(O)*cis*(N)-[Co(gly)$_2$(2,2′-bpy)]ClO$_4$. ^{1}H NMR: (D$_2$O) δ 3.18–3.30 (br m, 1 H), 3.42–3.55 (br m, 1 H), 3.75–3.92 (br m, 1 H), 4.89–4.97 (br m, 1 H), 5.02 (br m, 1 H, NH), 5.62 (br m, 1 H, NH), 6.04 (br m, 1 H, NH), 6.38 (br m, 1 H, NH), 7.88 (t, 1 H), 8.00 (t, 1 H), 8.39 (t, 1 H), 8.50 (t, 1 H), 8.58–8.63 (m, 2 H), 8.73 (d, 1 H) and 8.82 (d, 1 H). ^{13}C NMR: (D$_2$O) δ 46.4, 46.9 (both α-C), 125.3, 125.5, 129.4, 129.5, 143.2, 143.3, 151.0, 152.9, 157.8, 158.2, 185.2 and 185.5 (both COO); (dmso-d$_6$) δ 44.6, 46.2 (both α-C), 123.5, 123.6, 126.9, 127.0, 141.1 (2C), 149.4, 153.5, 156.7, 156.8, 180.6 and 181.6 (both COO). A satisfactory microanalysis could not be obtained for this compound, however the UV-VIS spectrum was in qualitative agreement with that reported earlier for the *cis*(O)*cis*(N)-[Co(gly)$_2$(2,2′-bpy)]Cl compound.[5]

(b) (i) (Δ-*SS*/Λ-*RR*)-*trans*(N)-[Co(ala)$_2$(2,2′-bpy)]ClO$_4$·H$_2$O. ^{1}H NMR: (dmso-d$_6$) δ 1.33 (d, 3 H, CH$_3$, $J = 4$ Hz), 3.11 (quartet, 1 H, α-H), 5.72 (br m, 1 H, NH), 5.96 (br m, 1 H, NH), 7.90 (d), 8.40 (m) and 8.70 (d); (D$_2$O) δ 1.52 (d, 3 H, CH$_3$), 3.60 (br m, 1 H, α-H), 5.75–5.90 (br m, NH), 7.87 (m) and 8.36–8.53 (m). ^{13}C NMR (dmso-d$_6$): δ 19.0 (CH$_3$), 32.2 (α-C), 123.4, 127.1, 141.2, 150.8, 157.2 and 183.3 (COO).

(ii) (Δ-*RR*/Λ-*SS*)-*trans*(N)-[Co(ala)$_2$(2,2′-bpy)]ClO$_4$·H$_2$O. ^{1}H NMR: (dmso-d$_6$) δ 1.15 (d, 3 H, CH$_3$, $J = 6.9$ Hz), 3.48 (quartet, 1 H, α-H), 5.14 (br m, 1 H, NH), 6.46 (br m, 1 H, NH), 7.90 (d), 8.40 (m) and 8.70 (d); (D$_2$O) δ 1.33 (d, 3 H, CH$_3$), 3.88–3.96 (br m, 1 H, α-H), 5.02–5.08 (br m, NH), 6.44–6.55 (br m, NH), 7.87 (m) and 8.36–8.53 (m). ^{13}C NMR (dmso-d$_6$): δ 18.9 (CH$_3$), 52.5 (α-C), 123.3, 127.2, 141.2, 150.6, 156.9 and 183.4 (COO). Calc. for [C$_{16}$H$_{20}$CoN$_4$O$_4$]ClO$_4$·H$_2$O: C, 38.09; H, 4.36; N, 11.01. Found: C, 38.02; H, 4.32; N, 10.91%. The microanalysis was performed on a mixture of *trans*(N)-[Co(ala)$_2$(2,2′-bpy)]ClO$_4$ isomers.

(c) (i) *trans*(N)-[Co(aib)$_2$(2,2′-bpy)]ClO$_4$·NaClO$_4$·0.5H$_2$O. ^{1}H NMR: (dmso-d$_6$) δ 1.01 (s, 3 H, CH$_3$), 1.39 (s, 3 H, CH$_3$), 5.41 (d, 2 H, NH), 6.07 (d, 2 H, NH), 7.88 (t, 2 H), 8.35–8.40 (m, 4 H) and 8.69 (d, 2 H); (D$_2$O) δ 1.22, 1.58 (both s, 3 H, CH$_3$), 5.32 (d, NH, 2 H), 6.15 (d, 1 H, NH), 7.87 (t, 2 H) and 8.36–8.53 (m, 6 H). ^{13}C NMR: (dmso-d$_6$) δ 27.5 (CH$_3$), 27.9 (CH$_3$), 58.2 (*C*(CH$_3$)$_2$), 123.1, 126.5, 141.0, 150.5, 157.7 and 185.5 (COO); (D$_2$O) δ 27.5 (CH$_3$), 27.9 (CH$_3$), 61.3 (*C*(CH$_3$)$_2$), 125.0, 128.9, 143.2, 151.5, 157.8 and 191.3 (COO). Calc. for [C$_{18}$H$_{24}$CoN$_4$O$_4$]ClO$_4$·NaClO$_4$·0.5H$_2$O: C, 33.25; H, 3.84; N, 8.61. Found: C, 33.51; H, 3.76; N, 8.34%. UV-VIS: 478 (126), 308 (1300), 258 (1190) and 238 nm (sh, 1060 M^{-1} cm^{-1}).

(ii) *cis*(O)*cis*(N)-[Co(aib)$_2$(2,2′-bpy)]ClO$_4$·2H$_2$O. ^{1}H NMR: (dmso-d$_6$) δ 0.83, 1.38, 1.42, 1.45 (all s, 3 H, CH$_3$), 5.22 (br d, NH, 1 H), 5.38–5.52 (br m, 2 H, NH), 5.66 (br d, NH, 1 H), 7.89 (t, 1 H), 8.03 (t, 1 H), 8.42 (t, 1 H), 8.51 (t, 1 H), 8.62 (d, 1 H) and 8.75–8.83 (m, 3 H); (D$_2$O) δ 1.03 (s, 3 H, CH$_3$), 1.50 (s, 3 H, CH$_3$), 1.60 (s, 3 H, CH$_3$), 1.63 (s, 3 H, CH$_3$), 7.88 (t, 1 H), 8.00 (t, 1 H), 8.40 (t, 1 H), 8.49 (t, 1 H), 8.57–8.64 (m, 2 H), 8.70 (d, 1 H) and 8.78 (d, 1 H). ^{13}C NMR: (dmso-d$_6$) δ 27.1, 28.0, 28.1, 28.6 (all CH$_3$), 58.2, 59.6 (both α-C), 123.9, 124.1, 127.4, 127.4, 141.6, 141.8, 150.4, 152.6, 157.7, 157.8 and 184.7 (2 COO); (D$_2$O) δ 27.2, 27.9, 28.0, 28.6 (all CH$_3$), 60.7, 62.1 (both α-C), 125.6, 125.9, 129.5 (2C), 143.6, 143.8, 151.4, 152.8, 158.2, 158.5 and 189.3 (2 peaks, COO). Calc. for [C$_{18}$H$_{24}$CoN$_4$O$_4$]ClO$_4$·2H$_2$O: C, 38.96; H, 5.05; N, 10.09. Found: C, 38.69; H, 5.08; N, 10.10%. UV-VIS: 518 (171), 307 (17000) and 224 nm (54000 M^{-1} cm^{-1}).

Preparation of [Co(aib)$_2$(2,2′-bpy)]$^+$ in dmso

Sodium 2-aminoisobutyrate (50 mg, 0.40 mmol, prepared by mixing one equivalent of each of 2-aminoisobutyric acid and NaOH and recrystallised from methanol–water (10:1)), was dissolved in dry dmso (50 ml) with warming and stirring. (The solubility of sodium 2-aminoisobutyrate in dmso is about 1 g l^{-1} at room temperature.) To this was added, after cooling to room temperature, 2,2′-bipyridine (31 mg, 0.20 mmol) and blue anhydrous $CoCl_2$ (26 mg, 0.20 mmol) to give a yellow-brown solution. Air, dried by passing through concentrated H_2SO_4 and 4 Å molecular sieves, was slowly bubbled through the stirred solution overnight. The red-orange reaction mixture was then diluted with distilled water and quickly loaded on to SP-Sephadex (H^+, 3 × 20 cm). A red band eluted with 0.1 M HCl and was identified as *trans*(N)-$[Co(aib)_2(2,2'\text{-bpy})]^+$. A small amount of the *cis*(O)*cis*(N) isomer followed closely. A pink band, Co^{II}, was eluted with 0.5 M HCl, and a yellow band with 1 M HCl, subsequently identified as $[Co(2,2'\text{-bpy})_3]^{3+}$. UV-VIS Spectroscopy was used to quantify all the products.

Electrochemistry

Non-aqueous solvents. Cyclic voltammograms in CH_3CN and dmso were recorded with an EG&G Princeton Applied Research 173 potentiostat driven by a EG&G PAR 175 Universal Programmer. A standard three-electrode set-up was used: a glassy carbon working electrode, a platinum wire auxiliary electrode and an Ag–AgCl reference electrode. A scan rate of 0.1 V s^{-1} was used in all experiments. The salt Bu_4NPF_6 (0.1 M) was added as the supporting electrolyte and ferrocene was added as an internal reference. The solvents were dried over molecular sieves and deoxygenated by bubbling with N_2 prior to use. All voltammograms were recorded under an N_2 atmosphere. The concentration of the complexes was typically ≈1 mM. Solutions of anhydrous $CoCl_2$ (0.65 mg, 5 μM), 2,2′-bipyridine (0.78 mg, 5 μM) and sodium 2-aminoisobutyrate (1.25 mg, 10 μM) in dry, degassed dmso (freshly distilled from CaH_2) were employed for the oxidation experiments. An oxidation scan in the range −1400 to +500 mV was taken before a reduction scan in the same range.

Aqueous solution. The voltammograms of $[Co(2,2'\text{-bpy})_3]^{3+}$ and $[Co(aib)(2,2'\text{-bpy})_2]^{2+}$ and the cobalt(II) complexes were recorded at a glassy carbon electrode and employed an SCE reference electrode and the same hardware as above. A dropping mercury electrode was employed in order to record voltammograms of the $[Co(aib)(2,2'\text{-bpy})_2]^{2+}$ and *trans*(N)- and *cis*(O)*cis*(N)-$[Co(aib)_2(2,2'\text{-bpy})]^{2+}$ complexes (EG&G PAR 303A drop generator equipped with an EG&G PAR 174A Polarographic Analyser and an Ag–AgCl reference electrode). A scan rate of 0.1 V s^{-1} was used in all experiments. The salt $NaClO_4$ (0.1 M) was used as the supporting electrolyte for all the solutions. To enable the reporting of data with respect to a common reference system, a voltammogram of the Fc–Fc^+ couple was recorded with the glassy carbon set-up. The results were extrapolated to the mercury electrode system *via* the potentials measured for $[Co(aib)(2,2'\text{-bpy})_2]^{2+}$ at both electrodes. For the oxidation experiments, a solution of $CoCl_2\cdot 6H_2O$ (1.19 mg, 5 μM), 2,2′-bipyridine (0.78 mg, 5 μM) and 2-aminoisobutyric acid (1.03 mg, 10 μM) were combined in deoxygenated water. An oxidation scan in the range −1150 to +350 mV was taken before a reduction scan in the same range.

X-Ray crystallography

X-Ray crystallographic data were collected on a Siemens P4 four circle diffractometer with graphite monochromated Mo-Kα (λ = 0.71073 Å) radiation. The solution and refinement procedures made use of the SHELXTL software package.[6]

(i) (Δ-*SS*/Λ-*RR*)-*trans*(N)-$[Co(ala)_2(2,2'\text{-bpy})]ClO_4\cdot H_2O$. Suitable crystals were grown by slow cooling of a hot solution of the complex in dilute $HClO_4$. The data were corrected for Lorentz-polarisation effects. An absorption correction was applied using the ψ-scan method.[7] The structure was solved by the Patterson method and refined anisotropically for all non-hydrogen atoms with full-matrix least-squares calculations.

(ii) *trans*(N)-$[Co(aib)_2(2,2'\text{-bpy})]ClO_4\cdot NaClO_4\cdot 0.5H_2O$. Orange crystals were grown by slowly cooling a hot aqueous solution of the crude complex. The data were corrected for Lorentz-polarisation effects but not for absorption. The structure was solved by direct methods and refined anisotropically for all non-hydrogen atoms with full-matrix least-squares calculations.

CCDC reference number 186/1598.

See http://www.rsc.org/suppdata/dt/1999/3217/ for crystallographic files in .cif format.

Results

Steady state photolysis of $[Co(aa)(2,2'\text{-bpy})_2]^{2+}$

UV Irradiation of $[Co(aib)(2,2'\text{-bpy})_2]^{2+}$ in dmso was found to produce (i) *trans*(N)-$[Co(aib)_2(2,2'\text{-bpy})]^+$, (ii) acetone, (iii) uncomplexed amino acid, (iv) uncomplexed 2,2′-bipyridine, and (v) cobalt(II) species. The products, except for the cobalt(II) species, were detected either by measurement of the ^1H NMR spectrum of a sample of the dmso-d^6 photolysate, or by obtaining a ^1H NMR spectrum after adding a portion of the photolysate to a solution of DCl. The latter method was found to be of superior utility for quantification of the products, as poor signal to noise ratios were generally encountered when NMR spectra of the dmso photolysates were obtained directly. This difficulty, probably caused by interactions of the proton containing species with paramagnetic cobalt(II) ions in solution, was far less significant in acidified D_2O. The identities of the products were confirmed by spiking the NMR samples with authentic samples. The relative product yields were ascertained by integration of ^1H NMR resonances. Ion exchange chromatography was used in order to confirm the presence of cobalt(II) ions in solution.

The most notable contrast with the product distribution seen in the photolysis of these complexes in aqueous solution is the absence of the $[Co(2,2'\text{-bpy})_3]^{3+}$ ion. This is the only complex product seen in the aqueous photolysate. Spiking experiments demonstrated that it could have been detected in the dmso solution if it had been formed in any significant amount. This was in spite of the paramagnetic broadening that affected the spectra obtained in dmso-d^6. It was noted, however, that small amounts of $[Co(2,2'\text{-bpy})_3]^{3+}$ were rapidly formed when the dmso photolysates were added to DCl, and that its concentration increased over time.

A typical one hour irradiation of $[Co(aib)(2,2'\text{-bpy})_2]^{2+}$ in dmso gave the following product distribution (percentages calculated as a fraction of starting material employed): acetone, 25%; aib (both complexed as *trans*(N)-$[Co(aib)_2(2,2'\text{-bpy})]^+$ and uncomplexed), 40%. Neither the *cis*(O)*cis*(N) nor *trans*-(O) isomers were detected by ^1H NMR spectroscopy. The amount of *trans*(N)-$[Co(aib)_2(2,2'\text{-bpy})]^+$ was initially small, but increased over the period after the photolysis at the expense of free amino acid. Uncomplexed 2,2′-bipyridine typically accounted for 65–70% of the 2,2′-bipyridine contained in the starting material.

In general, it was difficult to obtain a reliable mass balance following photolysis of the $[Co(aib)(2,2'\text{-bpy})_2]^{2+}$ ion. The samples were ice-cooled during the photolysis, and NMR spectra promptly recorded, to prevent the evaporation of volatile products. It is possible that the paramagnetic cobalt(II) ions in solution continued to interact with the 'uncomplexed' amino acid and 2,2′-bipyridine, despite the addition of DCl to the NMR samples. This may cause a reduction of intensity for NMR resonances of these species.

It should be noted that the product ratios stated above do not represent solely the photoproducts of the $[Co(aib)(2,2'\text{-bpy})_2]^{2+}$ ion. The *trans*(N)-$[Co(aib)_2(2,2'\text{-bpy})]^+$ ion, which is formed in small amounts during the irradiation, is also photoactive, and will itself yield acetone and free amino acid upon photolysis. For example, a one hour irradiation of the *trans*(N)-$[Co(aib)_2(2,2'\text{-bpy})]^+$ ion, under the same conditions, decomposed 30% of the complex with 5% being found as acetone and 25% as free amino acid. The influence of this process on the observed product distribution is likely to be small, however, as the complex is present in relatively low concentration, and these experiments indicate that it reacts more slowly than the $[Co(aib)(2,2'\text{-bpy})_2]^{2+}$ complex.

Similar studies were conducted on solutions of other $[Co(aa)(2,2'\text{-bpy})_2]^{2+}$ complexes, where aa = glycinate (gly) or *R*,*S*-alaninate (ala). In all cases, resonances due to uncomplexed amino acid and uncomplexed 2,2′-bipyridine could be seen in the ^1H NMR spectra of the photolysates. In the glycinate case, the expected complex, $[Co(gly)_2(2,2'\text{-bpy})]^+$, was seen, but formaldehyde was not detected. For the alaninato complex, the signals due to acetaldehyde were evident in the ^1H NMR spectrum. Although we are confident that *trans*(N)-$[Co(ala)_2(2,2'\text{-bpy})]^+$ complexes are formed in the photolysate, the congested ^1H NMR spectra made it difficult to rule out the possibility that other geometrical isomers are also present.

Synthesis and crystallography of $[Co(aa)_2(2,2'\text{-bpy})]^+$ complexes

The initial photochemical experiments in dmso solution led us to the conclusion that photolysis of the $[Co(aa)(2,2'\text{-bpy})_2]^{2+}$ complexes was giving rise to a single but different complex of the amino acids. The ^1H and ^{13}C NMR data were consistent with the compounds being of the type $[Co(aa)_2(2,2'\text{-bpy})]^+$. A number of isomers are possible for such complexes, and we therefore prepared some of these complexes *via* a previously published route to use as authentic samples to aid in the identification of components of the photolysates.

Following the preparative method of Yasui,[5] we were able to synthesize the $[Co(gly)_2(2,2'\text{-bpy})]^+$, $[Co(ala)_2(2,2'\text{-bpy})]^+$, and $[Co(aib)_2(2,2'\text{-bpy})]^+$ complexes *via* the PbO_2 oxidation of Co^{II}, amino acid, and 2,2′-bipyridine in water. Ion-exchange chromatography was used to separate the various components of reaction mixture, and all complexes were characterised by NMR techniques and UV-VIS spectroscopy.

The UV-VIS spectra of the *trans*(N)- and *cis*(O)*cis*(N)-$[Co(gly)_2(2,2'\text{-bpy})]^+$ complexes were consistent with published data,[8] and these complexes were further characterised by ^1H and ^{13}C NMR spectroscopy. The characterisation of the aminoisobutyrato complexes was relatively straightforward. The first band which eluted from the ion exchange column exhibited a ^1H NMR spectrum indicative of C_2 symmetry. The UV-VIS spectrum was similar to that of the glycinato complex with *trans*(N) geometry, and this configuration was confirmed by an X-ray crystallographic study. The complex was further characterised by ^{13}C NMR spectroscopy and microanalysis. The second, crimson, band was assigned the *cis*(O)*cis*(N) configuration based on analysis of its ^1H and ^{13}C NMR spectra, and by comparison of its UV-VIS spectrum with that of the analogous glycinato complex. The *trans*(N)- to *cis*(O)*cis*(N)-$[Co(aib)_2(2,2'\text{-bpy})]^+$ ratio was approximately 5.5 : 1 (the combined yield of these complexes was around 40%). This indicates that the *trans*(N)-$[Co(aib)_2(2,2'\text{-bpy})]^+$ isomer may be slightly more favoured in comparison to the analogous glycinato and serinato (ser) complexes.[5] The failure to observe any *trans*(O)-$[Co(aa)_2(2,2'\text{-bpy})]^+$ complexes contrasts with analogous 1,2-diaminoethane and oxalato complexes, $[Co(aa)_2(en)]^+$ [9] and $[Co(aa)_2(ox)]^-$ [10] where all three geometrical isomers have been isolated and characterised.

The numerous isomers of the alaninato complexes made separation and characterisation of these complexes somewhat more difficult. The $[Co(ala)_2(2,2'\text{-bpy})]^+$ complexes were prepared using DL-alanine and the reaction mixture was chromatographed on SP-Sephadex. A red band was eluted with 0.1 M NaCl, and had a UV-VIS spectrum which was consistent with the complex having the *trans*(N) geometry. Analysis of the ^1H NMR spectrum indicated that a mixture of diastereoisomers was present, and a COSY spectrum supported this conclusion, showing at least two compounds.

Small red crystals formed upon recrystallisation from hot, dilute $HClO_4$. A ^1H NMR spectrum of this solid indicated that the ratio of the components had changed from that present in the crude solid. The component which was now present in the greatest amount, presumably the least soluble diastereoisomer, was assigned the Δ-*SS*/Λ-*RR* configuration on the basis of the ^1H NMR chemical shift of the protons on the amino acid ligands. From an inspection of a molecular model it can be seen that, for this configuration, the methyl groups are directed away from the 2,2′-bipyridine ligand, and would not therefore be expected to be strongly affected by its anisotropic magnetic field. These methyl protons resonate at δ 1.33. On the other hand, the Δ-*RR*/Λ-*SS* configuration has the methyl groups located in a shielded environment out of the plane of the aromatic rings, thereby resonating at higher field (δ 1.15). This conclusion is supported by the reversal of the relative positions of the amino acid α-protons in the ^1H NMR spectrum. In the case of the Δ-*SS*/Λ-*RR* isomers this proton is somewhat shielded and resonates downfield (δ 3.11) from that of the Δ-*RR*/Λ-*SS* diastereoisomer (δ 3.48).

It is possible that some Δ-*RS*/Λ-*SR* diastereoisomer is also formed. Although this complex is unsymmetrical it would be difficult to detect by ^1H NMR in the presence of the other diastereoisomers as the spectrum of this complex is likely to be similar to a superposition of the spectra of the other diastereoisomers. Although the separation of these diastereoisomers has precedent,[5] this was not pursued.

The solid state structures of two of the complex products, $[Co(ala)_2(2,2'\text{-bpy})]^+$ and $[Co(aib)_2(2,2'\text{-bpy})]^+$, were determined by X-ray crystallography. The *trans*(N) geometry which was proposed for both of these complexes, on the basis of UV-VIS and ^1H NMR spectroscopy, was confirmed by this study. The structure determined for the $[Co(ala)_2(2,2'\text{-bpy})]^+$ complex proved to be that of the Δ-*SS*/Λ-*RR* diastereoisomer. The data collection and refinement parameters are summarised in Table 1.

The co-ordination sphere of the C_2-symmetric Δ-*SS*/Λ-*RR*-*trans*(N)-$[Co(ala)_2(2,2'\text{-bpy})]^+$ complex cation has a distorted octahedral geometry (Fig. 1, Table 2). The most significant deviations are the chelate bite angles of the amino acid (85.7°), and the 2,2′-bipyridine (83.2°). This contraction allows the amine donors of the amino acid ligands to adopt an angle of 172.1° around the cobalt atom. The Co–O (1.89 Å) and Co–N bond lengths (1.94 Å) are similar to those previously found for the $[Co(aa)_2(phen)]^+$ (phen = 1,10-phenanthroline) complexes of glycinate,[11] alaninate[12] and L-prolinate.[13] A water molecule was found in the crystal lattice for the bis(alaninato) complex. Short contacts between this water molecule and the carbonyl oxygen of one amino acid ligand (2.9 Å) and to two oxygen atoms of the perchlorate counter ion (2.9 Å) are indicative of hydrogen bonding interactions. In addition, another short contact (3.3 Å) links the perchlorate anion with the amine nitrogen atom of the other amino acid ligand.

The structure of *trans*(N)-$[Co(aib)_2(2,2'\text{-bpy})]^+$ ion is rather similar to that of the alaninato analogue (Fig. 2, Table 3). Sodium perchlorate was found to co-crystallise with the complex, and this observation was consistent with the elemental analysis results. The sodium ion is positioned closer to the two carbonyl oxygen atoms of the amino acid ligands (2.2–2.4 Å) than to the perchlorate oxygen atoms (2.4–2.6 Å). One of the perchlorate anions is disordered over two sites (2 : 3) which differ by rotation about one of the Cl–O bonds.

Table 1 Crystallographic data for *trans*(N)-[Co(aa)$_2$(2,2′-bpy)]ClO$_4$ complexes

	(Δ-*SS*/Λ-*RR*)-[Co(ala)$_2$(2,2′-bpy)]ClO$_4$·H$_2$O	[Co(aib)$_2$(2,2′-bpy)]ClO$_4$·NaClO$_4$·0.5H$_2$O
Formula	$C_{16}H_{22}ClCoN_4O_9$	$C_{18}H_{26}Cl_2CoNaN_4O_{12.5}$
M	508.76	650.24
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
a/Å	10.556(7)	8.776(3)
b/Å	10.345(7)	11.218(2)
c/Å	18.62(3)	14.186(3)
α/°		76.90(1)
β/°	99.06(8)	79.31(3)
γ/°		79.08(2)
V/Å^3	2008(3)	1320.6(6)
Z	4	2
T/°C	−129	−105
μ/mm^{-1}	1.047	0.937
No. reflections collected	3531	6367
No. observed reflections ($>2\sigma I$)	2250	3392
R (for $I > 2\sigma I$)	0.0595	0.0704
R′ (for $I > 2\sigma I$)	0.1116	0.1096

Table 2 Selected bond lengths (Å) and angles (°) for (Δ-*SS*/Λ-*RR*)-*trans*(N)-[Co(ala)$_2$(2,2′-bpy)]$^+$

Co–N(1)	1.940(5)	Co–O(3)	1.891(4)
Co–N(2)	1.939(5)	N(1)–C(1)	1.478(7)
Co–N(3)	1.917(5)	C(1)–C(3)	1.529(8)
Co–N(4)	1.912(4)	C(3)–O(1)	1.221(6)
Co–O(2)	1.889(4)	C(3)–O(2)	1.290(7)
N(1)–Co–O(2)	85.7(2)	N(1)–Co–N(4)	93.7(2)
N(2)–Co–N(3)	94.3(2)	N(1)–Co–O(3)	88.7(2)
N(3)–Co–N(4)	83.1(2)	N(1)–Co–N(2)	172.1(2)
N(4)–Co–N(2)	92.1(2)	Co–O(2)–C(3)	115.2(3)

Table 3 Selected bond lengths (Å) and angles (°) for *trans*(N)-[Co(aib)$_2$(2,2′-bpy)]$^+$

Co–N(1)	1.940(4)	Co–O(3)	1.894(3)
Co–N(2)	1.947(4)	N(1)–C(1)	1.497(6)
Co–N(3)	1.930(4)	C(1)–C(4)	1.534(7)
Co–N(4)	1.916(4)	C(4)–O(1)	1.291(6)
Co–O(1)	1.869(3)	C(4)–O(2)	1.223(6)
N(1)–Co–O(1)	86.2(2)	N(2)–Co–N(3)	94.5(2)
N(2)–Co–O(3)	85.9(2)	N(1)–Co–N(3)	91.9(2)
N(3)–Co–N(4)	83.2(2)	N(2)–Co–O(1)	87.7(2)
Co–O(1)–C(4)	117.1(3)	N(1)–Co–N(2)	171.8(2)

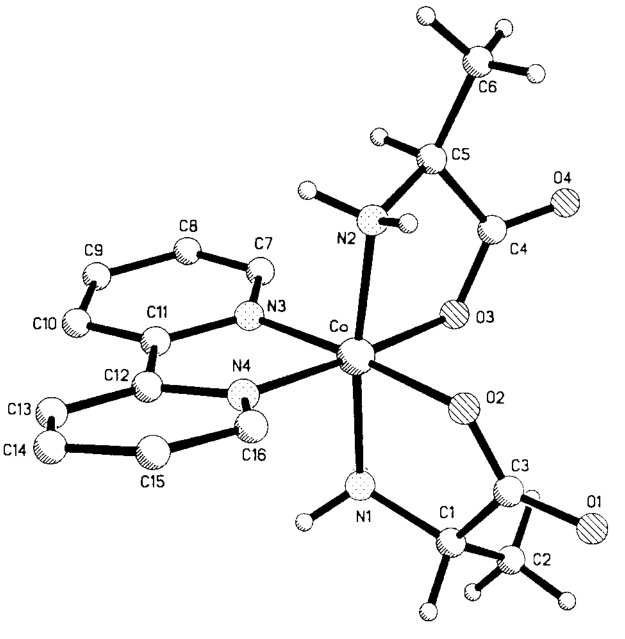


Fig. 1 Crystal structure of the (Δ-*SS*/Λ-*RR*)-*trans*(N)-[Co(ala)$_2$(2,2′-bpy)]$^+$ complex ion. Hydrogen atoms have been omitted for clarity.

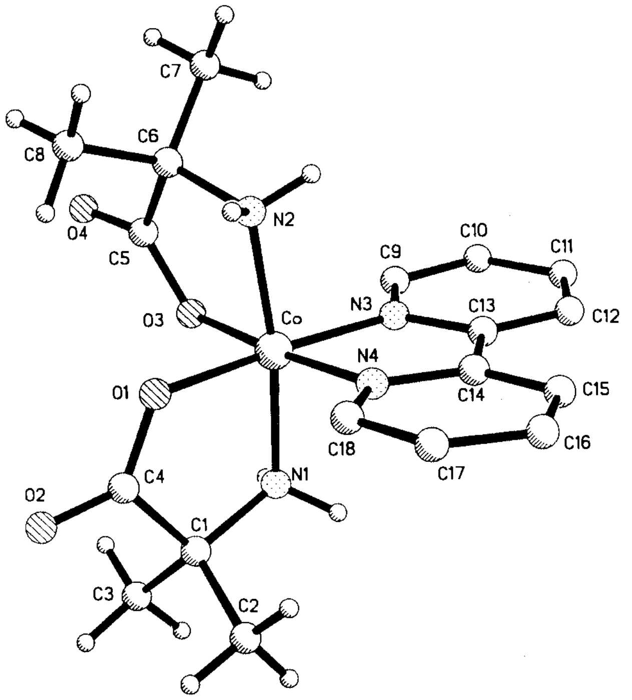


Fig. 2 Crystal structure of the *trans*(N)-[Co(aib)$_2$(2,2′-bpy)]$^+$ cation. Hydrogen atoms have been omitted for clarity.

Preparation of *trans*(N)-[Co(aa)$_2$(2,2′-bpy)]$^+$ complexes in dmso

The dmso photolysate of [Co(aib)(2,2′-bpy)$_2$]$^{2+}$ contains Co^{II}, free 2,2′-bipyridine and free, anionic amino acid. This mixture was simulated on a preparative scale by combining anhydrous CoCl$_2$, sodium 2-aminoisobutyrate, and 2,2′-bipyridine in dry dmso. Dry air was bubbled through this solution and the reaction mixture chromatographed on an SP-Sephadex ion-exchange resin. Similar reactions were also performed in which the aib : 2,2′-bpy ratio was 2 : 1. The products were characterised by ^{1}H NMR spectroscopy, and the yields from the latter reactions ascertained by UV-VIS spectroscopy.

We found that this synthetic procedure did indeed lead to the formation of the [Co(aib)$_2$(2,2′-bpy)]$^+$ ion, predominantly as the *trans*(N) isomer (approximately 40% based on Co). However, some [Co(2,2′-bpy)$_3$]$^{3+}$ (as much as 25%) and *cis*(O)*cis*(N)-[Co(aib)$_2$(2,2′-bpy)]$^+$ (3%) complexes were also

Table 4 Potentials for reduction of [Co(aib)$_x$(2,2′-bpy)$_y$]$^{(3-x)+}$ to [Co(aib)$_x$(2,2′-bpy)$_y$]$^{(2-x)+}$ [a]

Complex	Water		dmso		CH_3CN	
	E_{pc}	$E_{pc} - E_{pa}$	E_{pc}	$E_{pc} - E_{pa}$	E_{pc}	$E_{pc} - E_{pa}$
[Co(2,2′-bpy)$_3$]$^{3+}$	−125	70	−230	160	−100	110
[Co(aib)(2,2′-bpy)$_2$]$^{2+}$	−280	[b]	−575	[b]	−380	120
trans(N)-[Co(aib)$_2$(2,2′-bpy)]$^+$	−535	[b]	−1210	[b]	−935	[b]
cis(O,N)-[Co(aib)$_2$(2,2′-bpy)]$^+$	−605	[b]	−990	[b]	−770	[b]

[a] All data are reported in millivolts *versus* Fc–Fc$^+$. [b] No anodic peak observed.

detected, and occasionally a small amount of a violet, uncharged material (possibly [Co(aib)$_3$]) was seen during the chromatography. The remainder of the cobalt was found as cobalt(II) species. Reactions performed in CH_3CN gave similar results to the dmso experiments although a change of solvent to 50:50 dmso–water dramatically reduced the yield of *trans*(N)-[Co(aib)$_2$(2,2′-bpy)]$^+$.

Electrochemistry of [Co(aib)$_x$(2,2′-bpy)$_y$]$^{z+}$ complexes

Cyclic voltammograms of a series of [Co(aib)$_x$(2,2′-bpy)$_y$]$^{(3-x)+}$ complexes were obtained in both aqueous and non-aqueous solvents. The data obtained from these experiments are summarised in Table 4. All potentials are reported *versus* the ferrocene–ferrocenium (Fc–Fc$^+$) couple. For the electrochemistry in aqueous solution, both glassy carbon and mercury working electrodes had to be used as, unfortunately, neither was compatible with all the complexes studied. It should be stressed that the data in Table 4 refer to the peak cathodic currents, that is the potential for reductions of [Co(aib)$_x$(2,2′-bpy)$_y$]$^{(3-x)+}$ to [Co(aib)$_x$(2,2′-bpy)$_x$]$^{(2-x)+}$. Where distinct anodic current peaks could be observed, the anodic and cathodic peak separations are given.

In water and dmso, oxidation scans of a 1:1:2 mixture of Co^{II}, 2,2′-bpy, and aib$^-$ were recorded, along with a subsequent reduction scan. In both cases clear anodic (oxidation) peaks were not observed, however distinct cathodic (reduction) current peaks were evident (at −145 mV in water, and at −1200 mV in dmso).

Discussion

Pavlovskii and Poznyak [1a] have isolated a complex containing a Co–C–N metallacycle following the photolysis of [Co(gly)(2,2′-bpy)$_2$]$^{2+}$ in aqueous solution. Substitution of an alkyl group on the α-C of the amino acid appears significantly to destabilise the metallacyclic products derived from the other amino acidato complexes, as they have only been characterised spectrophotometrically at low temperature.[14] We have shown that the eventual products, presumably from decomposition of the metallacyclic species, are Co^{II}, the related carbonyl compound, and uncomplexed 2,2′-bipyridine.[3a] Free amino acid and [Co(2,2′-bpy)$_3$]$^{3+}$ are also found in the aqueous photolysate.

In dmso, *trans*(N)-[Co(aa)$_2$(2,2′-bpy)]$^+$ complexes are formed in addition to Co^{II}, free amino acid, free 2,2′-bipyridine, and a carbonyl compound derived from the α-C–N fragment of the amino acid. Apart from the complex ion that was isolated, the products from photolyses in dmso are the same as those seen for the aqueous photolyses. We were not able to isolate any metallacyclic products following photolysis of the [Co(aa)(2,2′-bpy)$_2$]$^{2+}$ complexes in dmso.

We employed 2-aminoisobutyrate to make a detailed study of this system as: (i) the uncomplexed photolysis products, acetone, aib, and 2,2′-bipyridine, are easily detected by NMR spectroscopy; (ii) the diastereoisomers of the [Co(aib)$_2$(2,2′-bpy)]$^+$ complex differ only in the co-ordination environment around the cobalt ion; and (iii) the *trans*-(N) and *cis*-(O)*cis*-(N) isomers are easily prepared and characterised for use as authentic samples.

Both the aqueous and dmso photolysates contained the 'starting materials' for the formation of [Co(aa)$_x$(2,2′-bpy)$_y$]$^{(3-x)+}$ complexes: Co^{II}, amino acid, 2,2′-bipyridine and an oxidant (dissolved molecular oxygen, or other species derived from it). When replicated on a synthetic scale, air oxidation of these mixtures gave product distributions similar to those obtained in the photochemical experiments, *viz.* predominantly *trans*(N)-[Co(aa)$_2$(2,2′-bpy)]$^+$ in dmso (with the small amount of remaining material being a mixture of [Co(aa)$_x$(2,2′-bpy)$_y$]$^{(3-x)+}$ complexes), but almost exclusively [Co(2,2′-bpy)$_3$]$^{3+}$ in water. These results allow us to infer immediately that the different product distributions in the photochemical experiments are due to secondary reactions rather than to different photochemistry. This is consistent with the observation that formation of the *trans*(N)-[Co(aa)$_2$(2,2′-bpy)]$^+$ complexes in the photochemical experiments is slow, and continues after the photolysis has ceased.

The dmso syntheses also produced some [Co(2,2′-bpy)$_3$]$^{3+}$ and *cis*(O)*cis*(N)-[Co(aa)$_2$(2,2′-bpy)]$^+$, although neither was detected in the dmso photolysate. One possible reason for the appearance of [Co(2,2′-bpy)$_3$]$^{3+}$ may lie in the method of isolation. The products from the synthetic reactions were separated and isolated by ion exchange chromatography in aqueous solution. The ion [Co(2,2′-bpy)$_3$]$^{3+}$ forms rapidly in aqueous solutions containing cobalt(II), 2,2′-bipyridine and an oxidant, such as dissolved oxygen, and the observed [Co(2,2′-bpy)$_3$]$^{3+}$ complex may therefore result from reactions that occur after the reaction mixture is diluted with water. Some support for this hypothesis can be drawn from the observation that small amounts of this complex were observed by ^{1}H NMR spectroscopy in the photochemical experiments only after addition of DCl/D_2O solution. Spiking experiments showed that the complex could have been detected if it was present in the photolysate prior to the addition of DCl/D_2O solution, leading to the inference that its formation is linked to the addition of the DCl/D_2O solution.

The *trans*-(N) complex is easily synthesized for a variety of amino acids by the PbO_2 oxidation of Co^{II}, amino acid and 2,2′-bipyridine, in the presence of charcoal, but needs to be separated from a range of other [Co(aa)$_x$(2,2′-bpy)$_y$]$^{(3-x)+}$ complexes, usually by ion exchange chromatography.[5] From a practical perspective, the dmso method we have developed is probably an inferior preparative route to *trans*(N)-[Co(aa)$_2$(2,2′-bpy)]$^+$ complexes, as it is somewhat less convenient to set up and ion exchange chromatography is still required in order to isolate the product. In spite of the selectivity observed, the yields of complex products obtained from the dmso aeration reactions are not much better than those obtained from the PbO_2 oxidations, even at rather long reaction times.

Rationalising the observed product distributions in dmso and water

Given that the dmso photolysate of [Co(aib)(2,2′-bpy)$_2$]$^{2+}$ contains more than twice as much free 2,2′-bipyridine as free amino acid, it was somewhat surprising that the *trans*(N)-$[Co(aib)_2(2,2'\text{-bpy})]^{2+}$ complex is the predominant secondary product. The synthetic experiments demonstrate that secondary chemistry of species present in the photolysate can give rise to the product complex, and this is consistent with the observation that the complex is seen to form slowly during the period after photolysis has ceased. Similarly, $[Co(2,2'\text{-bpy})_3]^{3+}$, which is seen in the aqueous photolysate, is the major product from air oxidation of the same mixture in water. Therefore, the selectivity appears to originate in the solvent dependent air oxidation reactions of a mixture of Co^{II}, amino acid and 2,2′-bipyridine.

In order to explore this in more detail, it is necessary to consider the solvent dependent shifts in the equilibria that will exist between the substitutionally labile cobalt(II) complexes, $[Co(aib)_x(2,2'\text{-bpy})_y]^{(2-x)+}$, the solvent dependence of the ease of oxidation of such complexes, and the ability of the oxidant to perform the oxidation reactions in aqueous and non-aqueous solvents. We have performed a range of electrochemical experiments in order to shed some light on these issues.

Most of the complexes under investigation did not exhibit reversible redox behaviour. Indeed, anodic waves were not observed for a number of the complexes studied. The potentials at which the $[Co(aib)_x(2,2'\text{-bpy})_y]^{(3-x)+}$ complexes are reduced to $[Co(aib)_x(2,2'\text{-bpy})_y]^{(2-x)+}$ follow a distinct pattern in all three solvents, as can be seen from Table 4.

The ease of reduction of these complexes correlates with the charge on the complex and the number of 2,2′-bipyridine ligands. That is, $[Co(2,2'\text{-bpy})_3]^{3+}$ is most easily reduced and *trans*(N)-$[Co(aib)_2(2,2'\text{-bpy})]^{+}$ is hardest to reduce. This seems reasonable, as an electron is likely to be more easily added to a higher charged complex, and the presence of more π-acidic 2,2′-bipyridine ligands should also favour the lower oxidation state. The potentials which we observed for the $[Co(2,2'\text{-bpy})_3]^{3+/2+}$ couple in water and CH_3CN agree well with those found by Maki[15] and Anson and co-workers.[16]

Although anodic peaks were not observed for all the complexes, we believe that it is reasonable to infer that, of the related cobalt(II) complexes that we are interested in, $[Co(2,2'\text{-bpy})_3]^{2+}$ is the hardest to oxidise, and that *trans*(N)-$[Co(aib)_2(2,2'\text{-bpy})]$ is the easiest.

The difference in the spread of reduction potentials in the various solvents was also rather noticeable. For example, the difference between the potentials at which $[Co(2,2'\text{-bpy})_3]^{3+}$ and *trans*(N)-$[Co(aib)_2(2,2'\text{-bpy})]^{+}$ are reduced in dmso (780 mV) is much greater than that seen in water (480 mV). The differences in the ease of oxidation of the related cobalt(II) complexes will therefore be greater in the organic solvents than in water, and might be expected to lead to enhanced selectivity under the appropriate conditions.

The absence of anodic current peaks in the cyclic voltammograms of many of the complexes studied implies that the cobalt(II) species formed at the electrode may be undergoing ligand exchange reactions. Indeed, the observation, in the reverse scan, of oxidation waves which can be assigned to other $[Co(aib)_x(2,2'\text{-bpy})_y]^{(3-x)+/(2-x)+}$ complexes provides evidence that ligand exchange reactions are occurring following reduction. Of most note in this context were peaks that could be seen following the reduction of *trans*(N)-$[Co(aib)_2(2,2'\text{-bpy})]^{+}$ in water (which could be assigned to the $[Co(2,2'\text{-bpy})_3]^{3+/2+}$ couple), and the appearance of a cathodic peak in the voltammogram following repeated cycling of the $[Co(aib)(2,2'\text{-bpy})_2]^{2+}$ ion dissolved in dmso (which could be assigned to reduction of *trans*(N)-$[Co(aib)_2(2,2'\text{-bpy})]^{+}$). Similar behaviour has been observed previously for the bis(iminodiacetato)-cobaltate(III) ion, $[Co(ida)_2]^{-}$, and was interpreted in terms of isomerisation of the complex.[17]

In aqueous solution the $[Co(2,2'\text{-bpy})_3]^{3+}$ complex is produced in the air oxidation reactions, despite the fact that $[Co(2,2'\text{-bpy})_3]^{2+}$ is harder to oxidise than any of the mixed ligand complexes. If the equilibria involving $[Co(aib)_x(2,2'\text{-bpy})_y]^{(2-x)+}$ species in aqueous solution lie heavily in favour of the $[Co(2,2'\text{-bpy})_3]^{2+}$ ion, however, production of the $[Co(2,2'\text{-bpy})_3]^{3+}$ complex may be favoured due to the high concentration of $[Co(2,2'\text{-bpy})_3]^{2+}$ ion. This contention is supported by the stability constant data for cobalt(II) complexes of 2,2′-bpy ($\log \beta_3 = 17.6$) and gly ($\log \beta_3 = 10.8$).[18]

Some experimental evidence has been gathered in support of the equilibrium favouring the $[Co(2,2'\text{-bpy})_3]^{2+}$ ion. Cyclic voltammetry experiments were performed on solutions containing cobalt(II), 2-aminoisobutyrate, and 2,2′-bipyridine. In water, only the $[Co(2,2'\text{-bpy})_3]^{3+/2+}$ reduction is seen (−145 mV), presumably because the $[Co(2,2'\text{-bpy})_3]^{2+}$ complex dominates the distribution of cobalt(II) complexes and is the only one oxidised in the oxidation scan. If any significant amount of the other cobalt(II) complexes were present, they would have been oxidised before the $[Co(2,2'\text{-bpy})_3]^{2+}$ ion, and should have been observed in the return scan.

On the other hand, although no anodic waves are seen distinctly in the electrochemical oxidation experiments in dmso; a subsequent large cathodic wave (at −1200 mV) can be assigned to reduction of the *trans*(N)-$[Co(aib)_2(2,2'\text{-bpy})]^{+}$ complex. No redox activity of the $[Co(2,2'\text{-bpy})_3]^{3+/2+}$ couple is observed in the non-aqueous solvent, which may indicate that there is little $[Co(2,2'\text{-bpy})_3]^{2+}$ in solution to be oxidised. It is reasonable to expect that in the less polar solvent the equilibria between the cobalt(II) complexes will be shifted towards the neutral species, $[Co(aib)_2(2,2'\text{-bpy})]$, which will be oxidised to give the observed *trans*(N)-$[Co(aib)_2(2,2'\text{-bpy})]^{+}$. The interconversion of *trans*(N)-$[Co(aib)_2(2,2'\text{-bpy})]^{+}$ and *cis*(O)*cis*(N)-$[Co(aib)_2(2,2'\text{-bpy})]^{+}$ is not observed under the conditions of the synthesis, which suggests that the *trans*(N) complex is the predominant geometrical isomer of $[Co(aib)_2(2,2'\text{-bpy})]^{+}$. This is supported by the absence of any peaks corresponding to the *cis*(O)*cis*(N) complex in the electrochemical oxidation.

It may also be important that dioxygen is a more powerful oxidant in protic solvents, such as water, than in aprotic solvents.[19] Our results are consistent with the idea that, in aqueous solution, dioxygen provides (directly or indirectly) a sufficiently strong oxidant to remove an electron from any of the possible $[Co(aib)_x(2,2'\text{-bpy})_y]^{(2-x)+}$ species, and the product distribution may reflect the fact that the $[Co(2,2'\text{-bpy})_3]^{2+}$ ion dominates the equilibria. In dmso the weaker oxidant(s) may only be able to remove an electron from $[Co(aib)_2(2,2'\text{-bpy})]$ complexes (and possibly $[Co(aib)_3]^{-}$ if there is any present).

It follows that reactions which give rise to mixtures of the various stereoisomers of the $[Co(aib)_x(2,2'\text{-bpy})_y]^{(3-x)+}$ complexes are likely to be performed under kinetic control, under conditions where mixtures of the cobalt(II) complexes will be present, and employing relatively strong oxidants, so that the differences in ease of oxidation of the various cobalt(II) precursors become less significant. The literature methods which were used to prepare the various isomer mixtures use PbO_2 for this purpose. Oxidation by dioxygen, however, is likely to proceed at a rate which allows equilibration of the cobalt(II) complexes, favouring oxidation of the dominant cobalt(II) species in solution, especially at low conversion. The difference in ease of oxidation of the cobalt(II) complexes will also play some role in determining the product distribution and as such may also play a role in the selectivity of oxidations in dmso.

Conclusion

The solvent dependence of the observed products from photolysis of $[Co(aa)(2,2'\text{-bpy})_2]^{2+}$ complexes is the result of secondary reactions between the by-products of the photochemical reactions. The selective production of *trans*(N)-$[Co(aib)_2(2,2'\text{-bpy})]^{+}$ in dmso (rather than the $[Co(2,2'\text{-bpy})_3]^{3+}$ ion which is produced in water) appears to result from the different concentrations and electrochemical properties of the various cobalt(II) complexes in solution, combined with the reduced strength of the oxidant when it is employed in non-aqueous solvents. The larger differences between the reduction potentials of the complexes that exist in non-aqueous solvents may also exert significant influence on the product distribution.

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Paper 9/04486H