The donor ability of the chelated carbonate ligand: protonation and metallation of [(L)Co(O_2CO)]^+ complexes in aqueous solution†

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Received 24th April 2008, Accepted 6th June 2008
First published as an Advance Article on the web 31st July 2008
DOI: 10.1039/b806981f

The syntheses and X-ray structures of [Co(Me-tpa)O_2COZnCl_3], [Co(pmea)O_2COZnCl_3]·H_2O, [Co(trpyn)O_2COZn(OH_2)Cl_2], [Co(pmea)O_2COH]ZnCl_4·3H_2O, [Co(trpyn)(O_2CO)]ClO_4 and [Co(trpyn)(O_2CO)]ZnCl_4·3H_2O are reported (Me-tpa = [(6-methyl-2-pyridyl)methyl]bis(2-pyridylmethyl)amine, pmea = bis(2-pyridylmethyl)-2-(2-pyridylethyl)amine, trpyn = tris(2-(1-pyrazolyl)ethyl)amine). The chelated bicarbonate complex [Co(trpyn)(O_2COH)]ZnCl_4·3H_2O is isolated as a crystalline solid from an acidic solution of the parent carbonate [Co(trpyn)(O_2CO)]ClO_4, and X-ray structural analysis shows that lengthening of the C=O exo bond and shortening of the C–O endo bond accompanies protonation. The bimetallic complex [Co(Me-tpa)O_2COZnCl_3] results from the unexpected coordination of ZnCl_3 to the exo O atom of a chelated carbonate ligand. This complex is obtained from both acidic and neutral solutions in which [Zn^{2+}] = 1.0 M, while the structurally similar complex [Co(pmea)O_2COZnCl_3]·H_2O is isolated from an analogous neutral solution. The trimetallic complex [Co(trpyn)O_2COZn(OH_2)Cl_2]·H_2O crystallises on prolonged standing of [Co(trpyn)(O_2CO)]ClO_4 in a neutral solution having [Zn^{2+}] = 1.0 M. The Zn–O bond lengths in all three complexes are indicative of bonds of significant strength. DFT calculations show that the nature of the bonding interaction between the Co(III) ion and the endo O atoms of the carbonate ligand remain essentially unaffected by coordination of Zn^{2+} to the exo O atom. They also show that such coordination of Zn^{2+} decreases the C–O exo bond order.

Introduction

The recent reports of structurally characterised metal complexes containing monodentate1–13 chelated14–23 and bridging24–26 bicarbonate bear testament to the current interest in the coordination chemistry of the bicarbonate ligand. While the first structurally characterised complex containing chelated bicarbonate was reported nearly thirty years ago,14 such species are still rare, and their study is of interest as it may lead to a greater understanding of the factors contributing to the stabilisation of what are usually highly unstable species. We have previously shown that chelated carbonate complexes of the type [(L)Co(O_2CO)]^+, (L = tpa, Me-tpa, Me_2-tpa, Me_3-tpa, pmea, pmap, tepa) where L is a pyridyl-based tripodal tetraamine ligand (Figs. 1 and 2), are remarkably stable in aqueous acidic solution, and we have attributed this to the steric effect of the tripodal ligand;22,27 acid-catalysed chelate ring opening and subsequent hydrolysis of the chelated carbonate ligand requires protonation at one of the coordinated endo O atoms (Fig. 1),28 and the trimetallic tetraamine ligands provide sufficient steric hindrance at these positions so as to impede protonation. The unusual stability of these carbonate complexes in aqueous acidic solution has allowed us to isolate and structurally characterise two chelated bicarbonate complexes, [Co(tepa)(O_2COH)]ClO_4·3H_2O and [Co(pmap)(O_2COH)]ZnCl_2·3H_2O, in which the bicarbonate proton is situated on the exo O atom. The fact that such complexes can

† CCDC reference numbers 686136–686140. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b806981f

Fig. 1 Structures of the pyridyl-based tripodal amine ligands, and the general structure of the Co(III) carbonate complexes of these, showing the positions of the exo and endo O atoms.

Fig. 2 Structures of the trpyn, pmea and Me-tpa ligands.
be isolated on dissolution of the parent \([\{L\}Co(O-CO)\}^+) carbonate complexes in moderately acidic solution \([H_2O^+] = 1.8–2.7 \text{ M}\) attests to the moderate basicity of the \textit{exo} \(O\) atom (measured \(K_b\), values range from 0.42 to 2.3 \text{ M} for a number of bicarbonate chelates in solution\(^{25}\)) and this therefore makes it not only a site for protonation, but also potential metallation. To our knowledge, there are no examples of \textit{direct} metallation of the \textit{exo} \(O\) atom of a substitutionally inert metal carbonate complex, the result of which would be a complex containing metal ions bridged in an \(\eta^1-\eta^1\) fashion by carbonate. While there are some crystallographically characterised complexes containing this structural motif, they have all been either obtained from self-assembly type reactions with labile metal ions\(^{26–39}\) or resulted from rearrangement of carbon monoxide,\(^{40}\) carbon dioxide\(^{41–43}\) or carbamate\(^{44}\) complexes. In this paper, we report the synthesis and X-ray structural characterisation of the bimetallic complexes \([Co(Me-tpa)O_2CO_2ZnCl]\), \([Co(pmea)O_2CO_2ZnCl_2]·H_2O\), \([Co(trpy)nO_2CO_2ZnCl_3]·H_2O\), \([Co(trpy)nO_2COH)_2ZnCl_2\cdot 3H_2O\), \([Co(trpy)nO_2COH)_2ZnCl_2\cdot 3H_2O\) and its parent complex \([Co(trpy)nO_2COH)_2ZnCl_2\cdot 3H_2O\), \([Co(trpy)nO_2COH)_2ZnCl_2\cdot 3H_2O\), and we detail the structural changes that occur on protonation at the \textit{exo} \(O\) atom. The results of DFT calculations on the complexes containing coordinated Zn\(^{2+}\) are also detailed.

### Experimental

#### General methods

Elemental analyses were performed by the Campbell Microanalytical Laboratory, University of Otago. Reported elemental percentages (C, H, N, Cl) are accurate to within ±0.4%. FT-IR spectra were recorded in the solid state (KBr disk) using a Perkin-Elmer Spectrum BX FT-IR System with Spectrum v. 2.00. \(^1\)H NMR spectra were obtained in D\(_2\)O using a Varian VXR 300 MHz spectrophotometer and were referenced to sodium 3-

### Syntheses

All materials were LR grade and better and were used as received, and all syntheses of complexes were carried out under aerobic conditions. \([Co(Me-tpa)O_2CO_2ClO_4·0.5H_2O]\) and \([Na_2[Co(CO_3)_3]·3H_2O]^{46}\) were prepared as previously described. Trpyn-4HCl was prepared using a modification of a literature procedure,\(^{46}\) in which both ligand purification and conversion to the tetrahydrochloride salt was achieved by passage down a Dowex 50WX2 cation exchange column using 3 M HCl as eluent. Anal. Found: C, 40.49; H, 5.70; N, 21.94; Cl, 31.63. Calc. for C\(_{20}\)H\(_{20}\)N\(_4\)O\(_3\)Cl\(_3\)Co, 40.54; H, 3.55; N, 9.14; Cl, 17.35%. IR (KBr): 1591, 1488, 1438, 1320, 1308 cm\(^{-1}\).

**CAUTION!** Although we have experienced no problems with the perchlorate salts described herein, they should at all times be treated as potentially explosive and handled accordingly.

\[\text{Method } A. \text{ An aqueous solution of } [Co(Me-tpa)O_2CO_2ClO_4·0.5H_2O (0.0218 M, 1.45 mL) was added to an aqueous 2.0 M ZnCl}_2·5.0 M HCl solution (1.45 mL). Refrigeration of the resulting solution gave red X-ray quality crystals of } [Co(Me-tpa)O_2CO_2ClO_4·0.5H_2O], \text{ which were removed by filtration, washed with a small volume of isopropanol and air-dried (11 mg, 29%). Anal. Found: C, 39.60; H, 3.62; N, 9.14; Cl, 17.33. Calc. for C\(_{20}\)H\(_{20}\)N\(_4\)O\(_3\)Cl\(_3\)Co: C, 39.60; H, 3.62; N, 9.14; Cl, 17.33. IR (KBr): 1591, 1488, 1438, 1320, 1308 cm\(^{-1}\). X-Ray crystallographic analysis showed the complex to exist as a monohydrate, and complete desolvation occurred on drying.**

**Method B (hemihydrate).** An aqueous solution of \([Co(Me-tpa)O_2CO_2ClO_4·0.5H_2O (0.0218 M, 1.45 mL) was added to an aqueous 2.0 M ZnCl}_2·5.0 M NaCl solution (1.45 mL). Refrigeration of the resulting solution gave X-ray quality crystals of \([Co(Me-tpa)O_2CO_2ClO_4·0.5H_2O], \text{ which were removed by filtration, washed with small amounts of ice cold water and isopropanol, and air-dried (7 mg, 27%). Anal. Found: C, 39.60; H, 3.51; N, 9.15; Cl, 17.65. Calc. for C\(_{20}\)H\(_{20}\)N\(_4\)O\(_3\)Cl\(_3\)Co·0.5H\(_2\)O: C, 39.76; H, 3.50; N, 9.28; Cl, 17.61%. IR (KBr): 1590, 1473, 1446, 1324 cm\(^{-1}\). X-Ray crystallographic analysis showed the complex to exist as a monohydrate, and partial desolvation occurred on drying.**

\[\text{Method C (hemihydrate). An aqueous solution of } [Co(pmea)O_2CO_2ClO_4·0.5H_2O (0.0218 M, 2.00 mL) was added to an aqueous 2.0 M ZnCl}_2·5.0 M NaCl solution (2.00 mL). Refrigeration of the resulting solution gave X-ray quality crystals of } [Co(pmea)O_2CO_2ClO_4·0.5H_2O], \text{ which were removed by filtration, washed with small amounts of ice cold water and isopropanol, and air-dried (7 mg, 18%). Anal. Found: C, 39.18; H, 3.70; N, 9.02; Cl, 17.33. Calc. for C\(_{20}\)H\(_{20}\)N\(_4\)O\(_3\)Cl\(_3\)Co·0.5H\(_2\)O: C, 39.18; H, 3.62; N, 9.14; Cl, 17.35%. IR (KBr): 1591, 1488, 1438, 1320, 1308 cm\(^{-1}\). X-Ray crystallographic analysis showed the complex to exist as a monohydrate, and complete desolvation occurred on drying.**

\[\text{Method D (hemihydrate). An aqueous solution of } [Co(trpy)nO_2CO_2ClO_4·0.5H_2O (0.0218 M, 2.00 mL) was added to an aqueous 2.0 M ZnCl}_2·5.0 M NaCl solution (2.00 mL). Refrigeration of the resulting solution gave X-ray quality red crystals of } [Co(trpy)nO_2CO_2ClO_4·0.5H_2O], \text{ which were removed by filtration, washed with small amounts of ice cold water and isopropanol, and air-dried (7 mg, 18%). Anal. Found: C, 39.18; H, 3.70; N, 9.02; Cl, 17.33. Calc. for C\(_{20}\)H\(_{20}\)N\(_4\)O\(_3\)Cl\(_3\)Co·0.5H\(_2\)O: C, 39.18; H, 3.62; N, 9.14; Cl, 17.35%. IR (KBr): 1591, 1488, 1438, 1320, 1308 cm\(^{-1}\). X-Ray crystallographic analysis showed the complex to exist as a monohydrate, and partial desolvation occurred on drying.**
product as purple X-ray quality crystals, which were removed by filtration, washed with isopropanol, and air-dried. (0.553 g, 24%). Anal. Found: C, 37.35; H, 4.11; N, 18.84; Cl, 6.84%. ESI-MS: calc. for \( \text{Co}_{16}\text{H}_{22}\text{Cl}_{4}\text{CoN}_{7}\text{O}_{3}\text{Zn} \), 55%). Anal. Found: C, 37.35; H, 4.11; N, 18.84; Cl, 7.00. Calc. for \( \text{Co}_{16}\text{H}_{21}\text{Cl}\text{CoN}_{7}\text{O}_{7} \), 37.10; H, 4.06; N, 18.94; Cl, 6.86%. ESI-MS: calc. for \( \text{Co}_{16}\text{H}_{21}\text{Cl}_{3}\text{CoN}_{4}\text{O}_{4}\text{Zn} \), 595.05; 626.51; 517.78.

X-Ray crystallography

X-ray crystal data for 1, 2, 3, 4 and 5 were collected at 85 K on a Bruker Kappa APEX-II⁴⁸ system using graphite-monochromated Mo-Kα radiation with exposure times over 0.5°, and they were corrected for Lorentz and polarization effects using SAI⁴⁸. All structures were solved using SIR-97⁴⁸ or SIR-2004⁴⁸ running within the WinGX package,⁴⁸ and weighted full-matrix refinement on \( F^2 \) was carried out using SHELXL-97.⁵² Hydrogen atoms attached to carbon and nitrogen were included in calculated positions and were refined as riding atoms with individual (or group, where appropriate) isotropic displacement parameters. Hydrogen atoms on the O atoms of solvent water molecules, coordinated aqua ligands or chelated bicarbonate ligands were located in searches of the Fourier map where possible, and were allowed to refine freely. The SQUEEZE option in PLATON was used to investigate the presence of disordered solvent molecules in 2 and 4, as outlined in the respective CIFs. Crystal data and structure refinement details for complexes 1–5 are reported in Table 1.

Calculation details

All density-functional calculations reported in this article were carried out with the Amsterdam Density Functional (ADF 2006) package.⁵¹–⁵⁵ A Generalized-Gradient-Approximation (GGA) functional consisting of the exchange and correlation expressions proposed by Perdew, Burke, and Ernzerhof, labelled PBE, was utilized.⁵⁶ Basis sets of triple-zeta quality and one polarization function (TZP or type IV), incorporating frozen cores (Zn 2p, Co 2p, Cl 2p, O 1s, N 1s, C 1s), were employed.⁵⁶–⁵⁸ Relativistic effects were included by means of the Zero Order Regular Approximation (ZORA).⁵⁵–⁵⁶ The Conductor-like Screening Model (COSMO) was used for the treatment of solvation effects.⁵⁸ Plots of the molecular orbitals were generated with the MOLEKEL program⁵³–⁵⁵ using data in MOLDEN format⁵³–⁵⁵ derived from the ADF TAPE21 files.

All results reported in this work correspond to single-point calculations on the experimentally characterized structures, as a number of geometry optimisation tests, carried out using local

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**Table 1**

<table>
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<tr>
<th>Complex</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
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<td>( \text{C}<em>{32}\text{H}</em>{50}\text{N}<em>{14}\text{O}</em>{10}\text{Cl}<em>{8}\text{Co}</em>{2}\text{Zn}_{3} )</td>
<td>( \text{C}<em>{32}\text{H}</em>{50}\text{N}<em>{14}\text{O}</em>{10}\text{Cl}<em>{8}\text{Co}</em>{2}\text{Zn}_{3} )</td>
<td>( \text{C}<em>{32}\text{H}</em>{50}\text{N}<em>{14}\text{O}</em>{10}\text{Cl}<em>{8}\text{Co}</em>{2}\text{Zn}_{3} )</td>
<td>( \text{C}<em>{32}\text{H}</em>{50}\text{N}<em>{14}\text{O}</em>{10}\text{Cl}<em>{8}\text{Co}</em>{2}\text{Zn}_{3} )</td>
<td>( \text{C}<em>{32}\text{H}</em>{50}\text{N}<em>{14}\text{O}</em>{10}\text{Cl}<em>{8}\text{Co}</em>{2}\text{Zn}_{3} )</td>
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<td><strong>M, Da</strong></td>
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<td>1440.46</td>
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<td>85(2)</td>
<td>85(2)</td>
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<td><strong>γ/Å</strong></td>
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<td>95.851(4)</td>
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<td><strong>b/Å</strong></td>
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<td>102.607(4)</td>
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<td><strong>D, Mg m⁻³</strong></td>
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<td><strong>Final R indices [I &gt; 2σ(I)]</strong></td>
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<td>( R_1 = 0.0347, ) ( wR_2 = 0.0770 )</td>
<td>( R_1 = 0.0325, ) ( wR_2 = 0.0515 )</td>
<td>( R_1 = 0.0405, ) ( wR_2 = 0.1034 )</td>
<td>( R_1 = 0.0435, ) ( wR_2 = 0.1130 )</td>
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<td><strong>R indices (all data)</strong></td>
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<td>( R_1 = 0.0521, ) ( wR_2 = 0.0815 )</td>
<td>( R_1 = 0.0339, ) ( wR_2 = 0.0548 )</td>
<td>( R_1 = 0.0476, ) ( wR_2 = 0.1067 )</td>
<td>( R_1 = 0.0506, ) ( wR_2 = 0.1181 )</td>
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and characterisation of the bicarbonate complex of stable bicarbonate complexes. This is evidenced by the isolation of a complex containing tripodal ligand trpyn·HCl with \(\text{Na}_3[\text{Co}(\text{O}_2\text{CO})_3]\) · 3\(\text{H}_2\text{O}\) at 65 °C in aqueous solution. Purification was effected by cation exchange chromatography and the product was crystallised as the \(\text{ClO}_4^-\) salt. The complex exhibits a UV/vis maximum at 510 nm and a \(\text{^57}{\text{Co}}\) NMR resonance at 9561 ppm, both of which are consistent with trpyn being a slightly stronger-field ligand than tepa (\(\delta = 10121\) ppm for \([\text{Co}(\text{tepa})(\text{O}_2\text{CO})]^+\)),\textsuperscript{17,22} and of comparable strength to both pmap (\(\delta = 9096\) ppm for \([\text{Co}(\text{pmap})(\text{O}_2\text{CO})]^+\))\textsuperscript{27} and Me\textsubscript{2}-tpa (\(\delta = 9162\) ppm for \([\text{Co}(\text{Me}_2\text{-tpa})(\text{O}_2\text{CO})]^+\))\textsuperscript{27} (the shorter wavelength band expected around 350 nm is obscured by an intense charge-transfer band, meaning that \(\Delta\epsilon\) cannot be calculated as this requires the values of \(\lambda_{\text{max}}\) for both d-d transitions\textsuperscript{60}). The X-ray structure of one of the two independent \([\text{Co}(\text{trpyn})(\text{O}_2\text{CO})]^+\) cations in the asymmetric unit is shown in Fig. 3. The Co–N bonds to the aromatic N atoms are significantly shorter than those found in \([\text{Co}(\text{tepa})(\text{O}_2\text{CO})]^+\), the average lengths being 1.929 and 1.990 Å, respectively, while the Co–N bonds to the tertiary N atom are almost identical in both complexes (2.0113(17) and 2.008(3) Å, respectively). The two Co–O bond lengths are essentially the same in 5, in contrast to the asymmetric coordination found in the tepa complex, while the analogous C–O\textsubscript{endo} and C–O\textsubscript{exo} bonds of the carbonate ligands are the same in both complexes. Inspection of a space filling diagram (Fig. 4) shows that the carbonate ligand is ‘buried’ to a certain extent in the ancillary ligand, and as a result of this, both endo O atoms experience significant steric hindrance, an apparently necessary condition for the formation of stable bicatecarbonate complexes. This is evidenced by the isolation and characterisation of the bicatecarbonate complex 4, obtained as X-ray quality crystals following treatment of an aqueous solution of 5 with an equal volume of aqueous 2.0M \(\text{ZnCl}_2\)/5.0M HCl solution. This solution provides not only the necessary acidic medium, but also the \(\text{ZnCl}_2^2-\) anion, which has been used as a counterion in many structurally characterised Co(III) complexes.\textsuperscript{68} The crystal structure of 4 is shown in Fig. 5. The presence of a bicarbonate ligand is confirmed on the basis of charge considerations, the single \(\text{ZnCl}_2^2-\) counterion requiring a single 2+ charged cation for charge neutrality. The bicarbonate proton was also located in a search of the Fourier map. Protonation of the \(\text{exo}\) O atom of the chelated carbonate ligand leads to a shortening of the C=O\textsubscript{endo} bond (1.269(2) vs. 1.230(2), 1.229(3) Å for the two independent molecules of 5) and shortening of the C–O\textsubscript{exo} bonds (1.291(3), 1.290(2) Å in 4, vs. 1.326(2), 1.319(2); 1.327(2), 1.318(2) Å in the two independent molecules of 5). Similar changes in the C=O and C–O bond lengths were also found on protonation of \([\text{Co}(\text{tepa})(\text{O}_2\text{CO})]^+\)\textsuperscript{17} and \([\text{Co}(\text{pmap})(\text{O}_2\text{CO})]^+\)\textsuperscript{22} Significant shortening of the Co–O\textsubscript{endo} bond (O\textsubscript{endo} is \textit{trans}-disposed towards the bicarbonate proton) is also observed (1.9310(15) Å in 4 vs. 1.8958(14), 1.8896(15) Å in 5) on protonation of the \(\text{exo}\) O atom. Table 2 lists bond lengths for the carbonate regions of complexes 1, 2, 3 and 4 and their corresponding carbonate complexes.

**Results and discussion**

**Syntheses and structures of 4 and 5**

Our previous work with Co(III) carbonate complexes containing pyridyl-based tripodal amine ligands showed that these complexes were remarkably resistant to acid hydrolysis, an observation we attributed to the steric effect of the pyridyl groups.\textsuperscript{17,22,27} We have now extended this work to complexes containing the pyrazole-containing tripodal ligand trpyn\textsuperscript{65,66} (Fig. 2). No Co(III) complexes of trpyn have been reported, and there are only two structurally characterised complexes containing this ligand.\textsuperscript{65,66} Trpyn can be thought of as the pyrazole analogue of tepa, as both ligands form a devianate six-membered chelate ring with \(\text{Na}_3[\text{Co}(\text{O}_2\text{CO})_3]\) and can be considered as the pyrazole analogue of tepa, as both ligands form a six-membered chelate ring with \(\text{Na}_3[\text{Co}(\text{O}_2\text{CO})_3]\) and can be considered as the pyrazole analogue of tepa, as both ligands form a six-membered chelate ring with \(\text{Na}_3[\text{Co}(\text{O}_2\text{CO})_3]\).
Table 2 Bond lengths (Å) for the carbonate regions of complexes 1, 2, 3 and 4 and their corresponding carbonate complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>Co–O₁</th>
<th>Co–O₂</th>
<th>O₁–C</th>
<th>O₂–C</th>
<th>C–O₁</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.8896(12)</td>
<td>1.9195(12)</td>
<td>1.304(2)</td>
<td>1.298(2)</td>
<td>1.246(2)</td>
</tr>
<tr>
<td>[Co(Me-tpa)(O₂CO)]⁺</td>
<td>1.8853(12)</td>
<td>1.9262(15)</td>
<td>1.312(2)</td>
<td>1.317(2)</td>
<td>1.237(2)</td>
</tr>
<tr>
<td>2</td>
<td>1.9034(10)</td>
<td>1.9167(11)</td>
<td>1.2951(19)</td>
<td>1.3052(17)</td>
<td>1.2536(18)</td>
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<tr>
<td>[Co(pmea)(O₂CO)]⁺</td>
<td>1.893(3)</td>
<td>1.912(3)</td>
<td>1.312(5)</td>
<td>1.324(5)</td>
<td>1.22(5)</td>
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<tr>
<td>3</td>
<td>1.8990(12)</td>
<td>1.9171(11)</td>
<td>1.3112(19)</td>
<td>1.3149(19)</td>
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<tr>
<td>5</td>
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<td>1.8977(14)</td>
<td>1.326(2)</td>
<td>1.319(2)</td>
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<tr>
<td>4</td>
<td>1.9310(15)</td>
<td>1.9062(15)</td>
<td>1.327(2)</td>
<td>1.318(2)</td>
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<tr>
<td>5</td>
<td>1.8955(14)</td>
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<td>1.326(2)</td>
<td>1.319(2)</td>
<td>1.230(2)</td>
</tr>
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</table>

N.B. O₁ is positioned cis to the tertiary N atom of the tripodal ligand in all cases. O₁ and O₂ are the endo O atoms, while O₃ is the exo O atom of the chelated carbonate ligand.

Isolation and characterisation of 1

We have previously shown that the [Co(Me-tpa)O₂CO]⁺ cation hydrolyses a factor of 25 times more slowly than [Co(tpa)(O₂CO)]⁺ in 6 M HCl solution, and this relatively slow rate of hydrolysis therefore made the bicarbonate complex [Co(Me-tpa)(O₂COH)]ZnCl₄ a viable candidate for isolation. However, mixing an aqueous solution of [Co(Me-tpa)(O₂CO)]ClO₄ with an equal volume of aqueous 2.0 M ZnCl₃·5.0 M HCl solution as described above for 5 gave X-ray quality crystals not of the expected bicarbonate complex, but the bimetallic complex 1, the X-ray structure of which is shown in Fig. 6. Instead of protonation occurring at the exo O atom, coordination of a ZnCl₄⁻ unit is observed, leading to formation of a neutral bimetallic complex through formal donation of an electron pair on the exo O atom to ZnCl₄⁻. The geometry about the Zn²⁺ ion is approximately tetrahedral, and the ZnCl₄⁻ unit is coordinated to the exo O atom such that it lies cis to the methyl group of the Me-tpa ligand. The bond lengths around the Co(III) ion and within the carbonate ligand are very similar to those of the starting material [Co(Me-tpa)(O₂CO)]ClO₄·0.5H₂O, with only a slight lengthening of the C=O bond on coordination of the ZnCl₄⁻ unit (1.246(2) Å vs. 1.237(2) Å in the starting material). The positioning of the methylated pyridine ring is the same in both the starting material and product; in both complexes, the methyl group lies in the same plane as the carbonate ligand.

Carrying out the reaction in the absence of acid by mixing an aqueous solution of [Co(Me-tpa)O₂CO]ClO₄ with an equal volume of a neutral aqueous 2.0 M ZnCl₃·5.0 M NaCl solution again resulted in crystallisation of the [Co(Me-tpa)O₂COZnCl₄] complex, thus showing that the ZnCl₄⁻ unit coordinates to the exo O atom regardless of the solution acidity. Indeed, formation of [Co(Me-tpa)O₂COZnCl₄] in neutral solution is even preferred over the simple crystallisation of [Co(Me-tpa)(O₂CO)](ZnCl₄), the ZnCl₄⁻ salt of the carbonate complex.
Isolation and X-ray structural characterisation of 2 shows that coordination of ZnCl$_3^-$ to the exo O atom of chelated carbonate is not unique to 1. Mixing an aqueous solution of [Co(pmea)O$_2$CO]ClO$_4$ with an equal volume of aqueous 2.0 M ZnCl$_2$–5.0 M HCl solution results in crystallisation of 6-[Co(pmea)O$_2$COZnCl$_3$]·2H$_2$O, the X-ray structure of which is shown in Fig. 7. A ZnCl$_3^-$ unit is again coordinated to the exo O atom of the chelated carbonate ligand, with the ZnCl$_3^-$ unit lying cis to the equatorial pyridine ligand, as also found for 1.

In this case, coordination to the exo O atom causes significant lengthening of the C=O$_{\text{cis}}$ bond relative to the parent carbonate complex, as shown by distances of 1.220(5) Å (starting material) and 1.2536(18) Å (2). However, all other bond distances within the carbonate ligand remain the same within 3 esds.

More surprising still is the isolation of the trimetallic complex 3 from the reaction of an aqueous solution of 5 with an equal volume of aqueous 2.0 M ZnCl$_2$–5.0 M NaCl solution and prolonged standing. The X-ray crystal structure of this complex, shown in Fig. 8, shows two [Co(trpyn)(O$_2$CO)]$^+$ units bridged by a Zn(OH)$_2$$_3$ unit through coordination of the Zn$^{2+}$ ion to both exo O atoms of the chelated carbonate ligands. Such a structure appears rare in the literature, with the only previous examples being found in a series of coordination polymers prepared by Robson and co-workers. The exo O atoms are trans-disposed about the octahedral Zn$^{2+}$ ion and the mean planes of the carbonate ligands lie at approximately 62° to each other. As found for complex 1, coordination of Zn$^{2+}$ to the exo O atom of the chelated carbonate ligand gives only a slight lengthening of the C=O$_{\text{cis}}$ bond in 3 relative to the starting material 5.

The ZnCl$_3^-$ unit has previously been found to undergo coordination to deprotonated ligand O atoms of oximes and carboxylates in Co(III) complexes, and to a ligand C atom of a Co(III) cage, but the examples presented here are, we believe, the first involving coordination of Zn$^{2+}$ to a coordinated carbonate oxygen atom of a substitutionally inert metal complex. Obviously the factors governing the isolation of the bi- and trimetallic complexes in favour of both the bicarbonate complexes and the ZnCl$_2^-$ salts of the carbonate complexes are subtle; [Co(trpyn)(O$_2$CO)]$^+$ forms the bicarbonate complex 4 in acidic solution but gives the trimetallic complex 3 in neutral solution, while [Co(Me-tpa)(O$_2$CO)]$^+$ gives the bimetallic ZnCl$_3$ adduct 1 in both acidic and neutral solution. However, it appears that coordination of Zn$^{2+}$ to the exo O atom is not a general phenomenon, as the crystal structure of the carbonate complex [Co(tepa)(O$_2$CO)]ZnCl$_3$·3H$_2$O, which was crystallised from neutral solution in the same manner as 1 and 3, shows no interaction of the Zn$^{2+}$ ion with either of the exo O atoms of the two cations.

While solubility undoubtedly plays a role in determining the nature of the product that crystallises from the reaction mixture, the results presented here confirm that the Zn$^{2+}$ ion, at the relatively modest concentration of 1M, does show an unexpected affinity for the exo O atom of chelated carbonate in both acidic and neutral aqueous solution. The Zn–O$_{\text{exo}}$ bond distances in 1 (1.9954(13) Å) and 2 (1.9889(12) Å) indicate Zn–O bonds of significant strength—a search of the Cambridge Structural Database gives the mean Zn–O bond length in all complexes as 2.049 Å (SD = 0.110 Å)$^{76}$, while those in 3 (2.0897(11) Å and 2.0601(11) Å) also lie well within one standard deviation of the mean. Indeed, the Zn–O$_{\text{exo}}$ and Zn–O$_{\text{trans}}$ distances in 3 are comparable, suggesting bonds of similar strength.

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**Fig. 7** View of 2 with thermal ellipsoids drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): Co1–O1 1.9034(10), Co1–O2 1.9167(11), Co1–N1 1.9391(14), Co1–N2 1.9049(13), Co1–N3 1.9244(13), Co1–N4 1.9458(12), O1–Co1 2.951(19), O2–Co2 1.3052(17), O3–Co2 1.2536(18), Zn1–O3 1.9889(12); O1–Co1–O2 69.06(5), O1–Co1–N4 98.73(6), O1–Co1–N1 93.67(5), N1–Co1–N4 98.52(5), N1–Co1–N2 106.57(10), N1–Co1–N3 122.02(4), O3–Zn1–O2 108.20(4), O3–Zn1–C13 102.05(3), C12–Zn1–C13 112.066(17), C13–Zn1–Cl1 109.716(19), C13–Zn1–Cl2 112.388(18).

**Fig. 8** View of the cation of 3 with thermal ellipsoids drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): Co1–O11 1.8990(12), Co1–O12 1.9171(11), Co1–N1 2.0038(13), Co1–N11 1.9327(14), Co1–N12 1.9447(14), Co1–N13 1.9285(15), Co2–O21 1.8905(11), Co2–O22 1.9291(11), Co2–N2 2.0092(13), Co2–N21 1.9279(14), Co2–N22 1.9124(14), Co2–N23 1.9470(14), O11–C13 1.3112(19), O12–C13 1.3149(19), O13–C13 1.2346(19), O21–C14 1.3061(18), O22–C14 1.3074(18), O23–C14 1.2438(18), Zn3–O1 2.0957(14), Zn3–O2 2.1019(14), Zn3–O3 2.0689(13), Zn3–O4 2.0812(14), Zn3–O13 2.0897(11), Zn3–O23 2.0601(11), O11–Co1–O12 68.89(5), O12–Co1–N11 96.23(5), O11–Co1–N13 97.73(6), O11–Co1–N1 97.15(5), O21–Co2–O22 68.80(4), N21–Co2–O22 97.06(5), N21–Co2–N21 97.11(5), O21–Co2–N2 97.01(5), O23–Zn3–O13 178.07(4), O4–Zn3–O1 176.50(6), O3–Zn3–O2 175.07(5).
DFT calculations

We have previously carried out DFT calculations on the Co(III) carbonate complexes [Co(L)O₂CO]⁺ (L = tpa, Me-tpa, Me₂-tpa, Me₃-tpa, pmea, pmap, tepa) in order to obtain a detailed description and analysis of the electronic structures of the complexes, particularly the nature of the interaction between the Co atom and the CO₃²⁻ moiety. The results showed that the HOMOs in the complexes contained contributions from the carbonate O atoms, implying that facile interaction with Lewis acids should be possible at these sites. We have now carried out calculations on the three complexes in which Zn is bound to the exo O atom of chelated carbonate, namely 1, anhydrous 2 and the cation of 3. The general results and conclusions from our previous work are applicable to the systems considered in the present article, as the binding of the [ZnCl₃]⁻ unit to the exo oxygen atom does not lead to significant changes in the overall character and properties of the interaction between the Co and the endo carbonate oxygen atoms.

This observation can be illustrated by considering the highest occupied and lowest unoccupied energy levels and corresponding molecular orbitals, which are given in Figs. 9–11. The five levels and orbitals shown for 1 (Fig. 9) and anhydrous 2 (Fig. 10) can be associated with the e_g (upper set) and t_2g (lower set) levels of a regular transition metal octahedral system, but some splitting is caused by the lower symmetry about the Co(III) ions. The splittings are approximately 900–1400 and 1100–1800 cm⁻¹ for the “e_g” and “t_2g” levels, respectively.

For the cation of 3, each “e_g” and “t_2g” level occurs in pairs of orbitals due to the presence of two [Co(trpyn)(O₂CO)]⁺ units in the molecule. The four orbitals in the “e_g” set and the six orbitals in the “t_2g” set are spread within a range of approximately 1100 and 3600 cm⁻¹, respectively. Fig. 11 contains plots of one orbital from each distinct level.

The “e_g” orbitals primarily correspond to σ-antibonding interactions between Co dₓ²₋ᵧ² and O and N p-type functions, and Co dₓz and N p-type functions. The “t_2g” levels can be divided into two groups. The two highest-lying orbitals represent p-antibonding interactions involving Co dₓz or dᵧz and O p-type functions, whereas the third orbital possesses almost exclusively Co dₓz character with no significant contributions from the ligands, and is therefore largely nonbonding in nature.

The basis function populations and the orbital compositions indicate that bonding between the Zn and O or Cl atoms occurs through a combination of the metal s, p and d orbitals. An analogous result has been obtained from calculations on a model [Zn(OH)Cl₃]⁻ system. A molecular orbital plot for an interaction between Zn and carbonate oxygen atoms in the cation of 3, which involves metal d-type functions, is presented in Fig. 12.

Bonding interactions have also been studied using Mayer bond order analysis. These results suggest that the Zn–O bonds should be somewhat weaker than the Co–O bonds. In the case of the C–O interactions, results from our previous study indicate that the C=O endo interaction possesses significant multiple-bond character, whereas the C–O exo interactions can be described as single bonds. In the complexes considered in this work, the binding of the [ZnCl₃]⁻ unit to the exo carbonate oxygen atom appears to reduce the multiple-bond character of the C=O exo interaction, and all three C–O bond orders lie between 1.15 and 1.31.

Conclusions

The results presented herein confirm that the exo O atom of chelated carbonate has a significant donor ability towards both protons and Zn²⁺ ions in aqueous solution. While it appears that
such interactions do occur in all acidic and neutral solutions containing ZnCl$_4^{2-}$, the range of complexes (carbonate complex as the ZnCl$_4^{2-}$ salt, bicarbonate complex, or bi- and trimetallic Zn complexes) isolated from these solutions suggest that solubility is the most important factor in determining the identity of the solid obtained from such reactions. We are interested to see if coordination to the \textit{exo} O atom of chelated carbonate is in fact peculiar to Zn$^{2+}$ and, with this in mind, we are currently studying the reactivity of other MCl$_4^{2-}$ ions towards the carbonate chelates.

**Acknowledgements**

We thank the Department of Chemistry, University of Otago for supporting this research. We thank Dr David McMorran for assistance with figures, and Dr Christophe Bucher for assistance with CSD searches. L. F. M. thanks the Foundation of Research, Science and Technology for the award of a Bright Futures Ph.D scholarship. G. C. and R. S. gratefully acknowledge the Australian Research Council for financial support, and the Australian National University for access to the APAC (Australian Partnership for Advanced Computing) facilities.

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