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

Lisa F. McClintock,^a Germán Cavigliasso,^b Robert Stranger^b and Allan G. Blackman^{*a}

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 $[Co(Me-tpa)O_2COZnCl_3]$, $[Co(pmea)O_2COZnCl_3] \cdot H_2O$, $[Co(trpyn)O_2COZn(OH_2)_4OCO_2Co(trpyn)](ZnCl_4)_2 \cdot H_2O$, $[Co(trpyn)(O_2COH)]ZnCl_4 \cdot 3H_2O$ and $[Co(trpyn)(O_2CO)]ClO_4$ 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 $[Co(trpyn)(O_2COH)]ZnCl_4 \cdot 3H_2O$ 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 $[Co(pmea)O_2COZnCl_3] \cdot H_2O$ is isolated from an analogous neutral solution. The trimetallic complex $[Co(trpyn)O_2COZn(OH_2)_4OCO_2Co(trpyn)](ZnCl_4)_2 \cdot H_2O$ 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 monodentate^{1–13} chelated^{14–23} and bridging^{24–26} 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, Me₂-tpa, Me₃-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 tripodal 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

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.

bicarbonate complexes, $[Co(tepa)(O_2COH)](ClO_4)_2 \cdot 3H_2O$ ¹⁷ and $[Co(pmap)(O_2COH)]ZnCl_4 \cdot 3H_2O$ ²² in which the bicarbonate proton is situated on the *exo* O atom. The fact that such complexes can

^aDepartment of Chemistry, University of Otago, P.O. Box 56, Dunedin, New Zealand. E-mail: blackman@chemistry.otago.ac.nz; Fax: +64 3 479 7906; Tel: +64 3 479 7931

^bDepartment of Chemistry, Faculty of Science, Australian National University, Canberra, ACT 0200, Australia

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

be isolated on dissolution of the parent $[(L)Co(O_2CO)]^+$ carbonate complexes in moderately acidic solution ($[H_3O^+] = 1.8\text{--}2.7\text{ M}$) attests to the moderate basicity of the *exo* O atom (measured K_a values range from 0.42 to 2.3 M for a number of bicarbonate chelates in solution²⁸) and this therefore makes it not only a site for protonation, but also potential metallation. To our knowledge, there are no examples of *direct* metallation of the *exo* O atom of a substitutionally inert metal carbonate complex, the result of which would be a complex containing metal ions bridged in an $\eta^2:\eta^1$ 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^{29–39} or resulted from rearrangement of carbon monoxide,⁴⁰ carbon dioxide^{41–43} or carbamate⁴⁴ complexes. In this paper, we report the synthesis and X-ray structural characterisation of the bimetallic complexes $[Co(Me-tpa)O_2COZnCl_3]$, (1), $[Co(pmea)O_2COZnCl_3]\cdot H_2O$, (2) and the trimetallic complex $[Co(trpyn)O_2COZn(OH_2)_4OCO_2Co(trpyn)](ZnCl_4)_2\cdot H_2O$, (3), (trpyn = tris(2-(1-pyrazolyl)ethyl)amine,⁴⁵ Fig. 2), all of which were obtained from coordination of Zn^{2+} to the *exo* O atom of the respective parent carbonate complexes $[(L)Co(O_2CO)]^+$ in aqueous media having $[Zn^{2+}] = 1.0\text{ M}$. We also report the synthesis and X-ray structural characterisation of the chelated bicarbonate complex $[Co(trpyn)(O_2COH)]ZnCl_4\cdot 3H_2O$, (4), and its parent complex $[Co(trpyn)(O_2CO)]ClO_4$, (5), and we detail the structural changes that occur on protonation at the *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 $\pm 0.4\%$. 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. 1H NMR spectra were obtained in D_2O using a Varian VXR 300 MHz spectrophotometer and were referenced to sodium 3-(trimethylsilyl)tetrauteriopropionate (NaTSP, 0.00 ppm). ^{13}C NMR spectra were recorded in D_2O and chemical shifts are reported relative to 1,4-dioxane (67.8 ppm). ^{59}Co NMR spectra were recorded in D_2O (10 mm tube) using a Varian Europa 500 MHz spectrophotometer at 118.57 MHz, and chemical shifts are reported relative to an external reference of $K_3[Co(CN)_6]$ (0.00 ppm). Visible spectra were recorded in aqueous solution using a Varian Cary 500 Scan UV-vis NIR spectrophotometer. Mass spectra were obtained using a Shimadzu LCMS-QP8000a system (mass range m/z 10–2000, resolution $R = 2\text{ M}$, 50% valley) with direct infusion *via* a manual Rheodyne injector (5 μL loop). Positive ionisation techniques were used on an ESI probe (H_2O mobile phase, 0.2 mL min^{-1} , CDL temp. 250 $^\circ C$, 4.5 kV).

Syntheses

All materials were LR grade or better and were used as received, and all syntheses of complexes were carried out under aerobic conditions. $[Co(Me-tpa)O_2CO]ClO_4\cdot 0.5H_2O$,²⁷

$[Co(pmea)O_2CO]ClO_4$ ²² and $Na_3[Co(CO_3)_3]\cdot 3H_2O$ ⁴⁶ were prepared as previously described. Trpyn-4HCl was prepared using a modification of a literature procedure,⁴⁵ 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 $C_{15}H_{21}N_7\cdot 4HCl$: C, 40.45; H, 5.62; N, 22.02; Cl, 31.91%. 1H NMR (D_2O): δ 7.72 (6H, dd, pyz-H), 6.49 (3H, t, pyz-H), 4.65 (6H, t, CH_2), 3.79 (6H, t, CH_2). ^{13}C NMR (D_2O): δ 139.34 (3 $\times$ pyz-C), 133.46 (3 $\times$ pyz-C), 107.37 (3 $\times$ pyz-C), 53.28 (3 $\times$ CH_2), 45.76 (3 $\times$ CH_2).

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.

$[Co(Me-tpa)O_2COZnCl_3]$ (1). *Method A.* An aqueous solution of $[Co(Me-tpa)O_2CO]ClO_4\cdot 0.5H_2O$ (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 $[Co(Me-tpa)O_2COZnCl_3]$, which were removed by filtration, washed with a small volume of isopropanol and air-dried (11 mg, 29%). Anal. Found: C, 40.37; H, 3.55; N, 9.23; Cl, 17.87. Calc. for $CoC_{20}H_{20}N_4O_3Cl_3Zn$: C, 40.31; H, 3.38; N, 9.40; Cl, 17.85%. IR (KBr): 1590, 1473, 1446, 1324 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 $[Co(Me-tpa)O_2CO]ClO_4\cdot 0.5H_2O$ (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 red crystals of $[Co(Me-tpa)O_2COZnCl_3]\cdot 0.5H_2O$, 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 $CoC_{20}H_{20}N_4O_3Cl_3Zn\cdot 0.5H_2O$: 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.

$[Co(pmea)O_2COZnCl_3]\cdot H_2O$ (2). An aqueous solution of $[Co(pmea)O_2CO]ClO_4$ (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 $[Co(pmea)O_2COZnCl_3]\cdot H_2O$, 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 $C_{20}H_{20}N_4O_3Cl_3CoZn\cdot H_2O$: C, 39.18; H, 3.62; N, 9.14; Cl, 17.35%. IR (KBr): 1591, 1488, 1438, 1320, 1308 cm^{-1} .

$[Co(trpyn)O_2CO]ClO_4$ (5). A solution of trpyn-4HCl (1.56 g, 4.40 mmol) in water (10 mL) was added to a suspension of $Na_3[Co(CO_3)_3]\cdot 3H_2O$ (2.50 g, 4.40 mmol) in H_2O (40 mL). The solution was heated for 10 min at 65 $^\circ C$, then filtered through Celite. The filtrate was diluted to 1 L with H_2O and loaded onto a Sephadex SP C-25 cation-exchange column. Elution with 0.1 M $NaClO_4$ following washing with water removed a purple band which was reduced in volume (rotavap) until crystallisation just started to occur. Storage in the refrigerator overnight gave the

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, 7.00. Calc. for $C_{16}H_{21}N_7O_7ClCo$: C, 37.10; H, 4.06; N, 18.94; Cl, 6.86%. ESI-MS: calc. for $CoC_{16}H_{21}N_7O_3^+$ 418; found 418 $[M^+]$. UV-vis (H_2O) [λ_{max}/nm , ($\epsilon/M^{-1} cm^{-1}$): 510 (93). 1H NMR (D_2O): δ 8.49 (1H, d, pyz-H), 7.98 (2H, d, pyz-H), 7.91 (1H, d, pyz-H), 7.70 (2H, d, pyz-H), 6.80 (1H, t, pyz-H), 6.55 (2H, t, pyz-H), 4.86 (4H, m, CH_2), 4.41 (2H, m, CH_2), 3.98 (2H, m, CH_2), 3.57 (2H, m, CH_2), 3.41 (2H, m, CH_2). ^{13}C NMR (D_2O): δ 144.31 (2 C, pyz-C), 143.04 (1 C, pyz-C), 138.61 (2 C, pyz-C), 138.52 (1 C, pyz-C), 110.64 (1 C, pyz-C), 109.60 (2 C, pyz-C), 58.69 (CH_2), 55.10 (CH_2), 45.87 (CH_2), 45.71 (CH_2). While there was no signal corresponding to the carbonate C atom in D_2O , one was observed in d_6 -DMSO (162.1 ppm). ^{59}Co NMR (D_2O): δ 9561.

[Co(trpy)nO₂COH]ZnCl₄·3H₂O (4). An aqueous solution of **5** (0.016 M, 1.00 mL) was added to a 2.0 M ZnCl₂/5.0 M HCl solution (1.00 mL) and refrigerated. Purple X-ray quality crystals of [Co(trpy)nO₂COH]ZnCl₄·3H₂O deposited over 48 h, and these were filtered off and washed with isopropanol (6 mg, 55%). Anal. Found: C, 28.31; H, 4.22; N, 14.40. Calc. for $CoC_{16}H_{22}N_7O_3Cl_4Zn\cdot 3H_2O$: C, 28.23; H, 4.15; N, 14.41%.

[Co(trpy)nO₂COZn(OH)₂·4OCO₂Co(trpy)n](ZnCl₄)₂·H₂O (3). An aqueous solution of **5** (0.0218 M, 2.00 mL) was added to an aqueous 2.0 M ZnCl₂/5.0 M NaCl solution (2.00 mL). Refrigeration of the resulting solution for approximately 2 months gave purple X-ray quality crystals of [Co(trpy)nO₂COZn(OH)₂·4OCO₂(trpy)nCo](ZnCl₄)₂·H₂O which were removed by filtration, washed with small volumes of ice cold water and isopropanol, and then air dried (14 mg, 23%). Anal. Found: C, 27.26; H, 3.98; N, 13.76; Cl, 19.86. Calc. for $C_{32}H_{50}N_{14}O_{10}Cl_8Co_2Zn_3\cdot H_2O$: C, 27.32; H, 3.73; N, 13.95; Cl, 20.16%. IR (KBr): 3474, 1656, 1617, 1519, 1444, 1419. X-Ray crystallographic analysis showed the complex to exist as a trihydrate, and partial desolvation occurred on drying.

X-Ray crystallography

X-ray crystal data for **1**, **2**, **3**, **4** and **5** were collected at 85 K on a Bruker Kappa APEX-II⁴⁷ system using graphite-monochromated Mo-K α radiation with exposures over 0.5°, and they were corrected for Lorentz and polarization effects using SAINT.⁴⁸ All structures were solved using SIR-97⁴⁹ or SIR-2004⁵⁰ running within the WinGX package,⁵¹ 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.^{53–55} 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.^{53–55} Relativistic effects were included by means of the Zero Order Regular Approximation (ZORA).^{57–59} The Conductor-like Screening Model (COSMO) was used for the treatment of solvation effects.⁶⁰ Plots of the molecular orbitals were generated with the MOLEKEL program^{61,62} using data in MOLDEN format^{63,64} 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

Table 1 Crystal data and structure refinement for complexes **1–5**

Complex	1	2	3	4	5
Empirical formula	$C_{20}H_{22}Cl_3CoN_4O_4Zn$	$C_{20}H_{20}Cl_3CoN_4O_3Zn$	$C_{32}H_{54}C_{18}Co_2N_{14}O_{13}Zn_3$	$C_{16}H_{22}Cl_4CoN_7O_3Zn$	$C_{16}H_{21}ClCoN_7O_7$
M_r	613.07	595.05	1440.46	626.51	517.78
T/K	85(2)	85(2)	85(2)	85(2)	85(2)
$\lambda/\text{\AA}$	0.71073	0.71073	0.71073	0.71073	0.71073
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$Pbca$	$P2_1/n$
$a/\text{\AA}$	8.2809(8)	8.2916(7)	20.9731(9)	18.182(5)	12.2764(4)
$b/\text{\AA}$	11.2581(10)	11.0966(11)	17.371(5)	14.726(4)	11.9332(3)
$c/\text{\AA}$	13.7533(11)	14.0994(13)	15.764(5)	19.634(7)	27.9535(8)
$\alpha/^\circ$	95.303(4)	95.851(4)			
$\beta/^\circ$	103.086(4)	102.607(4)	111.376(5)		100.082(1)
$\gamma/^\circ$	107.175(5)	108.600(4)			
$V/\text{\AA}^3$	1175.59(18)	1179.04(19)	5348(2)	5257(3)	4031.9(2)
Z	2	2	4	8	8
$D_c/Mg\ m^{-3}$	1.732	1.676	1.789	1.583	1.706
μ/mm^{-1}	2.102	2.090	2.403	1.981	1.042
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0348$, $wR2 = 0.0735$	$R1 = 0.0347$, $wR2 = 0.0770$	$R1 = 0.0235$, $wR2 = 0.0515$	$R1 = 0.0405$, $wR2 = 0.1034$	$R1 = 0.0435$, $wR2 = 0.1130$
R indices (all data)	$R1 = 0.0491$, $wR2 = 0.0783$	$R1 = 0.0521$, $wR2 = 0.0815$	$R1 = 0.0339$, $wR2 = 0.0548$	$R1 = 0.0476$, $wR2 = 0.1067$	$R1 = 0.0506$, $wR2 = 0.1181$

and gradient-corrected functionals, showed that some structural parameters, particularly those associated with the $[\text{COZnCl}_3]$ moiety, could not be satisfactorily reproduced by the calculations. The computationally determined bond distances and angles for the Co–O, Co–N, and C–O interactions are in reasonably good agreement with the observed results, but significant discrepancies are found in the parameters describing the interaction between the $[\text{ZnCl}_3]$ and $[\text{CO}_3]$ units, namely, the Zn–O distance and Zn–O–C angle.

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.^{17,22,27} We have now extended this work to complexes containing the pyrazole-containing tripodal ligand trpy⁴⁵ (Fig. 2). No Co(III) complexes of trpy have been reported, and there are only two structurally characterised complexes containing this ligand.^{65,66} Trpy can be thought of as the pyrazole analogue of tepa, as both ligands form three six-membered chelate rings on coordination of all donor atoms to a metal ion. **5** was prepared by reaction of trpy $\cdot$ 4HCl with $\text{Na}_3[\text{Co}(\text{O}_2\text{CO})_3]\cdot 3\text{H}_2\text{O}$ at 65 °C in aqueous solution. Purification was effected by cation exchange chromatography and the product was crystallised as the ClO_4^- salt. The complex exhibits a UV/vis maximum at 510 nm and a ^{59}Co NMR resonance at 9561 ppm, both of which are consistent with trpy being a slightly stronger-field ligand than tepa ($\delta = 10121$ ppm for $[\text{Co}(\text{tepa})(\text{O}_2\text{CO})]^+$),²² and of comparable strength to both pmap ($\delta = 9096$ ppm for $[\text{Co}(\text{pmap})(\text{O}_2\text{CO})]^+$)²² and $\text{Me}_2\text{-tpa}$ ($\delta = 9162$ ppm for $[\text{Co}(\text{Me}_2\text{-tpa})(\text{O}_2\text{CO})]^+$)²⁷ (the shorter wavelength band expected around 350 nm is obscured by an intense charge-transfer band, meaning that λ_{max} cannot be calculated as this requires the values of λ_{max} for both d–d transitions⁶⁷). The X-ray structure of one of the two independent $[\text{Co}(\text{trpy})(\text{O}_2\text{CO})]^+$ 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 $[\text{Co}(\text{tepa})(\text{O}_2\text{CO})]\text{ClO}_4$, 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_{endo} and C=O_{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 bicarbonate complexes. This is evidenced by the isolation and characterisation of the bicarbonate complex **4**, obtained as X-ray quality crystals following treatment of an aqueous solution of **5** with an equal volume of aqueous 2.0M ZnCl_2 /5.0M HCl solution. This solution provides not only the necessary acidic medium, but also the ZnCl_4^{2-} anion, which has been used as a counterion in many structurally characterised Co(III) complexes.⁶⁸ The crystal structure of **4** is shown in Fig. 5. The presence of a bicarbonate

Fig. 3 View of one of the two independent cations of **5**, with thermal ellipsoids drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): Co1–O11 1.8955(14), Co1–O12 1.8977(14), Co1–N1 2.0113(17), Co1–N11 1.9254(17), Co1–N21 1.9391(17), Co1–N31 1.9224(17), O11–C1 1.326(2), O12–C1 1.319(2), O13–C1 1.230(2); O11–Co1–O12 69.50(6), O11–Co1–N1 97.68(6), N11–Co1–N1 97.28(7), O12–Co1–N11 95.54(7).

Fig. 4 Space filling diagram of one of the two independent cations of **5**.

ligand is confirmed on the basis of charge considerations, the single ZnCl_4^{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 *exo* O atom of the chelated carbonate ligand leads to a lengthening of the C=O_{exo} 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_{endo} 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 $[\text{Co}(\text{tepa})(\text{O}_2\text{CO})]^+$,¹⁷ and $[\text{Co}(\text{pmap})(\text{O}_2\text{CO})]^+$.²² Significant lengthening of the Co–O₁ bond (O₁ is *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 *exo* O atom. Table 2 lists bond lengths for the carbonate regions of complexes **1**, **2**, **3** and **4** and their corresponding carbonate complexes.

Table 2 Bond lengths (Å) for the carbonate regions of complexes **1**, **2**, **3** and **4** and their corresponding carbonate complexes

Complex	Co–O ₁	Co–O ₂	O ₁ –C	O ₂ –C	C–O ₃
1	1.8896(12)	1.9195(12)	1.304(2)	1.298(2)	1.246(2)
[Co(Me-tpa)(O ₂ CO)] ⁺	1.8853(12)	1.9262(15)	1.312(2)	1.317(2)	1.237(2)
2	1.9034(10)	1.9167(11)	1.2951(19)	1.3052(17)	1.2536(18)
[Co(pmea)(O ₂ CO)] ⁺	1.893(3)	1.912(3)	1.312(5)	1.324(5)	1.220(5)
3	1.8990(12)	1.9171(11)	1.3112(19)	1.3149(19)	1.2346(19)
	1.8905(11)	1.9292(11)	1.3061(18)	1.3074(18)	1.2438(18)
5	1.8955(14)	1.8977(14)	1.326(2)	1.319(2)	1.230(2)
	1.8895(15)	1.9062(14)	1.327(2)	1.318(2)	1.229(3)
4	1.9310(15)	1.9096(15)	1.291(3)	1.290(2)	1.269(2)
5	1.8955(14)	1.8977(14)	1.326(2)	1.319(2)	1.230(2)
	1.8895(15)	1.9062(14)	1.327(2)	1.318(2)	1.229(3)

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.

Fig. 5 View of the cation of **4**, with thermal ellipsoids drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): Co1–O1 1.9310(15), Co1–O2 1.9096(15), Co1–N1 1.9887(17), Co1–N11 1.9050(16), Co1–N21 1.9305(17), Co1–N31 1.9239(17), O1–C7 1.291(3), O2–C7 1.290(2), O3–C7 1.269(2); O1–Co1–O2 68.84(6), O1–Co1–N1 99.51(7), N1–Co1–N11 97.08(7), N11–Co1–O2 94.57(6).

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,²⁷ 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 ZnCl₂–5.0 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 ZnCl₃[–] unit is observed, leading to formation of a neutral bimetallic complex through formal donation of an electron pair on the *exo* O atom to ZnCl₃[–]. The geometry about the Zn²⁺ ion is approximately tetrahedral, and the ZnCl₃[–] 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

Fig. 6 View of **1** with thermal ellipsoids drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): Co1–O1 1.8896(12), Co1–O2 1.9195(12), Co1–N1 1.9296(15), Co1–N2 1.9601(15), Co1–N3 1.9116(14), Co1–N4 1.9126(14), O1–C20 1.304(2), O2–C20 1.298(2), O3–C20 1.246(2), Zn1–O3 1.9954(13), Zn1–Cl1 2.2423(6), Zn1–Cl2 2.2654(6), Zn1–Cl3 2.2597(6); O1–Co1–O2 69.03(5), O1–Co1–N1 95.33(6), N1–Co1–N2 87.03(6), O2–Co1–N2 108.61(6), C20–O3–Zn1 122.17(12), O3–Zn1–Cl1 110.59(4), O3–Zn1–Cl2 107.93(4), O3–Zn1–Cl3 101.15(4), Cl1–Zn1–Cl2 112.17(2), Cl1–Zn1–Cl3 113.13(2), Cl3–Zn1–Cl2 111.23(2).

those of the starting material [Co(Me-tpa)(O₂CO)]ClO₄·0.5H₂O, with only a slight lengthening of the C=O_{exo} bond on coordination of the ZnCl₃[–] unit (1.246(2) 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 ZnCl₂–5.0 M NaCl solution again resulted in crystallisation of the [Co(Me-tpa)O₂COZnCl₃] complex, thus showing that the ZnCl₃[–] unit coordinates to the *exo* O atom regardless of the solution acidity. Indeed, formation of [Co(Me-tpa)O₂COZnCl₃] in neutral solution is even preferred over the simple crystallisation of [Co(Me-tpa)(O₂CO)]₂(ZnCl₄), the ZnCl₄^{2–} salt of the carbonate complex.

Syntheses and structures of **2** and **3**

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 $[\text{Co}(\text{pmea})\text{O}_2\text{CO}]\text{ClO}_4$ with an equal volume of aqueous 2.0M ZnCl_2 –5.0 M HCl solution results in crystallisation of $6\text{-}[\text{Co}(\text{pmea})\text{O}_2\text{COZnCl}_3]\cdot 2\text{H}_2\text{O}$,⁶⁹ 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 $\text{C}=\text{O}_{\text{exo}}$ 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.

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–C20 1.2951(19), O2–C20 1.3052(17), O3–C20 1.2536(18), Zn1–O3 1.9889(12); O1–Co1–O2 69.06(5), O1–Co1–N1 93.67(5), N1–Co1–N4 98.73(6), O2–Co1–N4 98.52(5), C20–O3–Zn1 122.57(10), O3–Zn1–Cl1 112.02(4), O3–Zn1–Cl2 108.20(4), O3–Zn1–Cl3 102.05(3), Cl2–Zn1–Cl1 112.066(17), Cl3–Zn1–Cl1 109.716(19), Cl3–Zn1–Cl2 112.388(18).

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 $[\text{Co}(\text{trpy})\text{(O}_2\text{CO)}]^+$ units bridged by a $\text{Zn}(\text{OH})_4^{2-}$ 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.³⁹ 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

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), N11–Co1–N1 97.73(6), O11–Co1–N1 97.15(5), O21–Co2–O22 68.80(4), N21–Co2–O22 97.06(5), N21–Co2–N2 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).

chelated carbonate ligand gives only a slight lengthening of the $\text{C}=\text{O}_{\text{exo}}$ 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 oximes⁷⁰ and carboxylates^{71–73} in Co(III) complexes, and to a ligand C atom of a Co(III) cage,⁷⁴ 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_4^{2-} salts of the carbonate complexes are subtle; $[\text{Co}(\text{trpy})\text{(O}_2\text{CO)}]^+$ forms the bicarbonate complex **4** in acidic solution but gives the trimetallic complex **3** in neutral solution, while $[\text{Co}(\text{Me-tpa})\text{(O}_2\text{CO)}]^+$ 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 $[\text{Co}(\text{tepa})\text{(O}_2\text{CO)}]_2\text{ZnCl}_4\cdot 3\text{H}_2\text{O}$, 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.⁷⁵ 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 $\text{Zn}-\text{O}_{\text{exo}}$ 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 $\text{Zn}-\text{O}_{\text{exo}}$ and $\text{Zn}-\text{O}_{\text{water}}$ distances in **3** are comparable, suggesting bonds of similar strength.

DFT calculations

We have previously carried out DFT calculations on the Co(III) carbonate complexes $[\text{Co}(\text{L})\text{O}_2\text{CO}]^+$ ($\text{L} = \text{tpa}, \text{Me-tpa}, \text{Me}_2\text{-tpa}, \text{Me}_3\text{-tpa}, \text{pmea}, \text{pmap}, \text{tepa}$) 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 CO_3^{2-} moiety.⁷⁷ 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 $[\text{ZnCl}_3]^-$ 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.

Fig. 9 Highest occupied and lowest unoccupied energy levels and corresponding molecular orbitals for **1**.

For the cation of **3**, each “ e_g ” and “ t_{2g} ” level occurs in pairs of orbitals due to the presence of two $[\text{Co}(\text{trpy})\text{(O}_2\text{CO)}]^+$ 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

Fig. 10 Highest occupied and lowest unoccupied energy levels and corresponding molecular orbitals for anhydrous **2**.

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 $d_{x^2-y^2}$ and O and N p-type functions, and Co d_{z^2} and N p-type functions. The “ t_{2g} ” levels can be divided into two groups. The two highest-lying orbitals represent π -antibonding interactions involving Co d_{xz} or d_{yz} and O p-type functions, whereas the third orbital possesses almost exclusively Co d_{xy} 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 $[\text{Zn}(\text{OH})\text{Cl}_3]^{2-}$ 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 $\text{C}=\text{O}_{\text{exo}}$ interaction possesses significant multiple-bond character, whereas the $\text{C}-\text{O}_{\text{endo}}$ interactions can be described as single bonds. In the complexes considered in this work, the binding of the $[\text{ZnCl}_3]^-$ unit to the *exo* carbonate oxygen atom appears to reduce the multiple-bond character of the $\text{C}=\text{O}_{\text{exo}}$ 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 Zn^{2+} ions in aqueous solution. While it appears that

Fig. 11 Highest occupied and lowest unoccupied energy levels and corresponding molecular orbitals for the cation of 3.

Fig. 12 Spatial plots of Zn-OCO₂ orbital interactions in the cation of 3.

such interactions do occur in all acidic and neutral solutions containing ZnCl₄²⁻, the range of complexes (carbonate complex as the ZnCl₄²⁻ 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 *exo* O atom of chelated carbonate is in fact peculiar to Zn²⁺ and, with this in mind, we are currently studying the reactivity of other MCl₄²⁻ 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.

References

- 1 R. J. Crutchley, J. Powell, R. Faggiani and C. J. L. Lock, *Inorg. Chim. Acta*, 1977, **24**, L15.
- 2 S. F. Hossain, K. M. Nicholas, C. L. Teas and R. E. Davis, *J. Chem. Soc., Chem. Commun.*, 1981, 268.
- 3 L. Latos-Grazynski, J. Lisowski, M. M. Olmstead and A. L. Balch, *J. Am. Chem. Soc.*, 1987, **109**, 4428.
- 4 S. Ganguly, J. T. Mague and D. M. Roundhill, *Inorg. Chem.*, 1992, **31**, 3831.
- 5 D. J. Darensbourg, M. L. M. Jones and J. H. Reibenspies, *Inorg. Chem.*, 1993, **32**, 4675.
- 6 M. Ito, M. Ebihara and T. Kawamura, *Inorg. Chim. Acta*, 1994, **218**, 199.
- 7 D. J. Darensbourg, M. L. M. Jones and J. H. Reibenspies, *Inorg. Chem.*, 1996, **35**, 4406.
- 8 S. Iglesias, O. Castillo, A. Luque and P. Roman, *Inorg. Chim. Acta*, 2003, **349**, 273.
- 9 C. Roy Choudhury, S. K. Dey, S. Mitra and V. Gramlich, *Dalton Trans.*, 2003, 1059.
- 10 R. F. R. Jazzar, P. H. Bhatia, M. F. Mahon and M. K. Whittlesey, *Organometallics*, 2003, **22**, 670.
- 11 J. C. Kim, J. Cho, H. Kim and A. J. Lough, *Chem. Commun.*, 2004, 1796.
- 12 Z.-L. You, W.-S. Liu, H.-L. Zhu and H.-K. Fun, *Transition Met. Chem.*, 2005, **30**, 1.
- 13 N. F. Curtis and H. Puschmann, *Polyhedron*, 2005, **24**, 281.
- 14 T. Yoshida, D. L. Thorn, T. Okano, J. A. Ibers and S. Otsuka, *J. Am. Chem. Soc.*, 1979, **101**, 4212.
- 15 H. Ito and T. Ito, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1985, **41**, 1598.
- 16 M. Doering, M. Meinert, E. Uhlig, L. Dahlenburg and R. Fawzi, *Z. Anorg. Allg. Chem.*, 1991, **598–599**, 71.

- 17 K. E. Baxter, L. R. Hanton, J. Simpson, B. R. Vincent and A. G. Blackman, *Inorg. Chem.*, 1995, **34**, 2795.
- 18 M. A. McLoughlin, N. L. Keder, W. T. A. Harrison, R. J. Flesher, H. A. Mayer and W. C. Kaska, *Inorg. Chem.*, 1999, **38**, 3223.
- 19 L. Broge, I. Sotofte, C. E. Olsen and J. Springborg, *Inorg. Chem.*, 2001, **40**, 3124.
- 20 A. Tutass, M. Klopfer, H. Huckstadt, U. Cornelissen and H. Homborg, *Z. Anorg. Allg. Chem.*, 2002, **628**, 1027.
- 21 D. W. Lee, C. M. Jensen and D. Morales-Morales, *Organometallics*, 2003, **22**, 4744.
- 22 P. M. Jaffray, L. F. McClintock, K. E. Baxter and A. G. Blackman, *Inorg. Chem.*, 2005, **44**, 4215.
- 23 A. Romero, A. Santos and A. Vegas, *Organometallics*, 1988, **7**, 1988.
- 24 P. K. Nanda, M. Bera, G. Aromi and D. Ray, *Polyhedron*, 2006, **25**, 2791.
- 25 A. Graham, S. Meier, S. Parsons and R. E. P. Winpenny, *Chem. Commun.*, 2000, 811.
- 26 D. J. Darensbourg, M. W. Holtcamp, B. Khandelwal and J. H. Reibenspies, *Inorg. Chem.*, 1995, **34**, 5390.
- 27 S. E. Cheyne, L. F. McClintock and A. G. Blackman, *Inorg. Chem.*, 2006, **45**, 2610.
- 28 D. A. Buckingham and C. R. Clark, *Inorg. Chem.*, 1994, **33**, 6171.
- 29 C. Bergquist, T. Fillebeen, M. M. Morlok and G. Parkin, *J. Am. Chem. Soc.*, 2003, **125**, 6189.
- 30 Y. Dussart, C. Harding, P. Dalgaard, C. McKenzie, R. Kadirvelraj, V. McKee and J. Nelson, *J. Chem. Soc., Dalton Trans.*, 2002, 1704.
- 31 Z.-W. Mao, F. W. Heinemann, G. Liehr and R. van Eldik, *J. Chem. Soc., Dalton Trans.*, 2001, 3652.
- 32 D. L. Bond, D. L. Clark, R. J. Donohoe, J. C. Gordon, P. L. Gordon, D. W. Keogh, B. L. Scott, C. D. Tait and J. G. Watkin, *Inorg. Chem.*, 2000, **39**, 3934.
- 33 A. Escuer, F. A. Mautner, E. Penalba and R. Vicente, *Inorg. Chem.*, 1998, **37**, 4190.
- 34 C. Pariya, V. G. Puranik and N. R. Chaudhuri, *Chem. Commun.*, 1997, 1307.
- 35 A. Escuer, R. Vicente, S. B. Kumar, X. Solans and M. Font-Bardia, *J. Chem. Soc., Dalton Trans.*, 1997, 403.
- 36 J. L. Schneider, V. G. Young, Jr. and W. B. Tolman, *Inorg. Chem.*, 1996, **35**, 5410.
- 37 N. Kitajima, S. Hikichi, M. Tanaka and Y. Morooka, *J. Am. Chem. Soc.*, 1993, **115**, 5496.
- 38 N. Ehlers and R. Mattes, *Inorg. Chim. Acta*, 1995, **236**, 203.
- 39 B. F. Abrahams, A. Hawley, M. G. Haywood, T. A. Hudson, R. Robson and D. A. Slizys, *J. Am. Chem. Soc.*, 2004, **126**, 2894.
- 40 L. Contreras, M. Paneque, M. Sellin, E. Carmona, P. J. Perez, E. Gutierrez-Puebla, A. Monge and C. Ruiz, *New J. Chem.*, 2005, **29**, 109.
- 41 J. Chatt, M. Kubota, G. J. Leigh, F. C. March, R. Mason and D. J. Yarrow, *J. Chem. Soc., Chem. Commun.*, 1974, 1033.
- 42 T. Herskovitz and L. J. Guggenberger, *J. Am. Chem. Soc.*, 1976, **98**, 1615.
- 43 R. Alvarez, E. Carmona, J. M. Marin, M. L. Poveda, E. Gutierrez-Puebla and A. Monge, *J. Am. Chem. Soc.*, 1986, **108**, 2286.
- 44 F. Ozawa, T. Ito and A. Yamamoto, *Chem. Lett.*, 1979, 735.
- 45 T. N. Sorrell and D. L. Jameson, *Inorg. Chem.*, 1982, **21**, 1014.
- 46 H. F. Bauer and W. C. Drinkard, *Inorg. Synth.*, 1966, **8**, 202.
- 47 APEXII, Version 1.0-27, Bruker AXS Inc., Madison, WI, USA, 2004.
- 48 SAINT, Bruker AXS Inc., Madison, WI, USA, 2001.
- 49 A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori and R. Spagna, *J. Appl. Crystallogr.*, 1999, **32**, 115.
- 50 M. C. Burla, R. Caliendo, M. Camalli, B. Carrozzini, G. L. Cascarano, L. De Caro, C. Giacovazzo, G. Polidori and R. Spagna, *J. Appl. Crystallogr.*, 2005, **38**, 381.
- 51 L. J. Farrugia, *J. Appl. Crystallogr.*, 1999, **32**, 837.
- 52 G. M. Sheldrick and T. R. Schneider, *Methods Enzymol.*, 1997, **277**, 319.
- 53 Amsterdam Density Functional, SCM, Vrije Universiteit, Amsterdam, The Netherlands (<http://www.scm.com>).
- 54 C. Fonseca Guerra, J. G. Snijders, G. Te Velde and E. J. Baerends, *Theor. Chem. Acc.*, 1998, **99**, 391.
- 55 G. Te Velde, F. M. Bickelhaupt, E. J. Baerends, C. Fonseca Guerra, S. J. A. Van Gisbergen, J. G. Snijders and T. Ziegler, *J. Comput. Chem.*, 2001, **22**, 931.
- 56 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.
- 57 E. van Lenthe, E. J. Baerends and J. G. Snijders, *J. Chem. Phys.*, 1993, **99**, 4597.
- 58 E. van Lenthe, E. J. Baerends and J. G. Snijders, *J. Chem. Phys.*, 1994, **101**, 9783.
- 59 E. van Lenthe, A. Ehlers and E. J. Baerends, *J. Chem. Phys.*, 1999, **110**, 8943.
- 60 C. C. Pye and T. Ziegler, *Theor. Chem. Acc.*, 1999, **101**, 396.
- 61 MOLEKEL: An interactive molecular graphics tool (<http://www.cscs.ch/molekel>).
- 62 S. Portmann and H. P. Luthi, *Chimia*, 2000, **54**, 766.
- 63 MOLDEN: A Pre and Post Processing Program for Molecular and Electronic Structures (<http://www.cmbi.ru.nl/molden/molden.html>).
- 64 G. Schaftenaar and J. H. Noordik, *J. Comput. Aided Mol. Des.*, 2000, **14**, 123.
- 65 M. Di Vaira, P. Stoppioni and F. Mani, *J. Organomet. Chem.*, 1983, **247**, 95.
- 66 A. Bencini and F. Mani, *Inorg. Chim. Acta*, 1984, **87**, L9.
- 67 R. Bramley, M. Brorson, A. M. Sargeson and C. E. Schaeffer, *J. Am. Chem. Soc.*, 1985, **107**, 2780.
- 68 The CSD shows over 100 instances of Co(III) complexes having ZnCl₄²⁻ counterions.
- 69 6 refers to the positioning of the 6-membered chelate ring with respect to the plane of the chelated carbonate ligand. See ref. 22.
- 70 C. A. Otter and R. M. Hartshorn, *Aust. J. Chem.*, 2003, **56**, 1179.
- 71 K. Panneerselvam, T.-H. Lu, T.-Y. Chi, F.-L. Liao and C.-S. Chung, *Anal. Sci.*, 2000, **16**, 1105.
- 72 K. Panneerselvam, T.-H. Lu and T.-Y. Chi, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 2000, **56**, e128.
- 73 R. Barfod, J. Eriksen, B. T. Golding, A. Hammershoi, T. A. Jacobsen, A. Langkilde, S. Larsen, O. Monsted, A. M. Sargeson and H. O. Sorensen, *Dalton Trans.*, 2005, 491.
- 74 I. I. Creaser, J. D. Lydon, A. M. Sargeson, M. R. Snow and E. Horn, *J. Am. Chem. Soc.*, 1984, **106**, 5729.
- 75 L. F. McClintock and A. G. Blackman, unpublished results.
- 76 CSD Version 5.29 with November 2007 updates. The search specified Zn–O bonds in structures which were not disordered, contained no errors and were not powder structures, with an *R* factor of <5%.
- 77 G. Cavigliasso, R. Stranger, L. F. McClintock, S. E. Cheyne, P. M. Jaffray, K. E. Baxter and A. G. Blackman, *Dalton Trans.*, 2008, 2433.