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Cite this: DOI: 10.1039/c0xx00000x

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ARTICLE TYPE

Interaction of 2,4,6-tris(2-pyrimidyl)-1,3,5-triazine (TPymT) with CoX₂ (X = Cl, Br) in water: Trapping of new self-assembled water-chloride/bromide clusters in a [Co(bpca)₂]⁺ host (bpca = bis(2-pyrimidylcarbonyl)amidate anion)

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

2D polymeric water-chloride/bromide sheets comprising a unique pentagon-like dichloride/dibromide-
10 trihydrate cluster in the solid state have been observed as [Co(bpca)₂]⁺ (bpca = bis(2-pyrimidylcarbonyl)amidate anion) counterions. Both compounds were obtained by the reaction of 2,4,6-tris(2-pyrimidyl)-1,3,5-triazine (TPymT) with CoX₂ (X = Cl, Br) in water. Solid-state multinuclear magnetic resonance spectroscopy and XRD provide insight into the structures.

Introduction

15 The important roles played by halide ions in inorganic, organic, and biological materials attract many scientists. This might be explained by the fact that halides are among the most ubiquitous anions in nature. Among the halides, the chloride anion plays a particularly important role, since it is an
20 essential electrolyte located in all body fluids responsible for maintaining acid/base balance, transmitting nerve impulses, and regulating fluid in and out of cells.¹

Water is the most important molecule for every aspect of human life. Noting that the human body contains from 55% to
25 78% water, depending on body size,² it becomes clear that an understanding of water and its interactions with various other chemical moieties is of great importance. Thus, the interaction of chloride anions with water, as well as the understanding of solvation phenomena, are intriguing fields of research.³

30 Only a limited number of water clusters containing inorganic ions are known, such as: [(NO₃)₆(H₂O)₆]⁶⁻, [(NO₃)₄(H₂O)₆]⁴⁻,⁵ [F₂(H₂O)₆]²⁻,⁶ [Br₂(H₂O)₆]²⁻,⁷ and [NH₂(H₂O)₄]⁻.⁸ Monochloride hydrates [Cl(H₂O)_n]⁻ have been extensively investigated by theoretical techniques.⁹ The
35 crystal structures of [Cl(H₂O)₄]⁻¹⁰ and [Cl(H₂O)₃]⁻¹¹ have also been reported. Furthermore, a supramolecular 3D network built from 12-membered [Cl₂(H₂O)₁₀]²⁻ clusters, which are fused together to form 1D chains and linked by additional chloride anions, has been studied.¹² An intriguing
40 rearrangement of the hexameric [Cl₂(H₂O)₆]²⁻ cluster into a helical modification was also reported.¹³ Other examples include: left- and right-handed supramolecular water-chloride helices, formed by hydrogen bonding interactions obtained by Das and co-workers,¹⁴ a 2D anionic network, comprising
45 [Cl₄(H₂O)₂₀]⁴⁻ structural units,¹⁵ and several supramolecular

aggregates of the water-chloride clusters.¹⁶ Additionally, there are two reports on [Cl₂(H₂O)₂]²⁻ clusters linked in 1D chains through the formation of hydrogen bonds either by one¹⁶ or twelve¹⁷ molecules of water. All the aforementioned water-
50 chloride clusters are infinite and templated by metal-containing architectures. There are three water-chloride clusters obtained in a metal free matrix. One of them is a well isolated [Cl₃(H₂O)₄]³⁻ cluster, having a cyclic pentamer [Cl₂(H₂O)₃],¹⁸ and another one is a supramolecular aggregate
55 of the water-chloride clusters.¹⁹ Finally, only one discrete dichloride cluster [Cl₂(H₂O)₆]²⁻, exhibiting a cube-like structure, has been described.²⁰

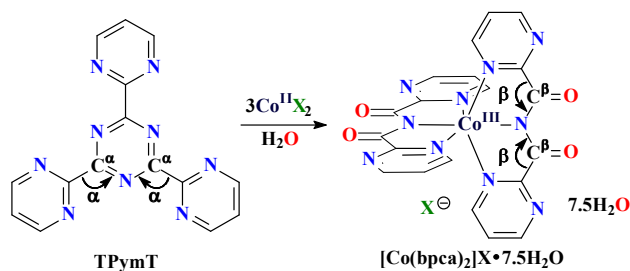
Although 2,4,6-tris(2-pyrimidyl)-1,3,5-triazine (TPymT) has been known for more than 50 years since it was first
60 discovered by Case and Koft,²¹ its coordination chemistry is still poorly explored. Very limited data on the coordination chemistry of TPymT are available, mainly due to the hydrolysis of the triazine fragment of the ligand in the presence of metal cations under mild conditions. In particular,
65 hydrolysis is extensively promoted by Cu^{II} salts with the formation of bis(imino(pyrimidin-2-yl)methyl)amidate²² and bis(2-pyrimidylcarbonyl)amidate (bpca)²³ anions. No direct proof of other metal cation promoted hydrolysis has been established.

70 With this in mind, in order to understand and gain control of the coordination chemistry of TPymT with first row transition metal ions, we have drawn our attention to the synthesis of Co^{II} complexes.

Results and discussion

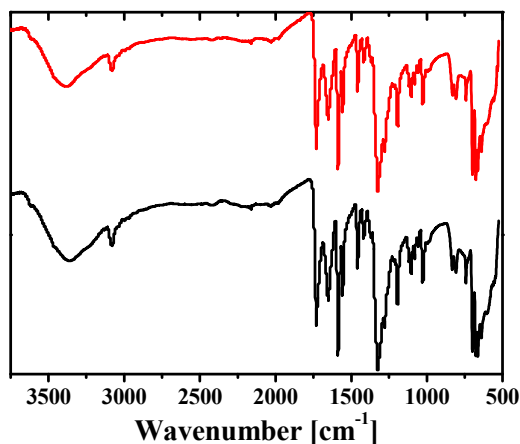
75 Herein we present the isolation of [Co(bpca)₂]₂X·7.5H₂O (X = Cl, Br) complexes (Scheme 1) obtained through metal cation promoted hydrolysis of TPymT. It was found that the TPymT

ligand is hydrolysed under our experimental conditions in the presence of Co^{II} , with the latter cation being oxidized to Co^{III} , which were captured by the formed bpca anions.



5 **Scheme 1** Preparation of $[\text{Co}(\text{bpca})_2]\text{X}\cdot 7.5\text{H}_2\text{O}$ ($\text{X} = \text{Cl}, \text{Br}$).

The FTIR spectra of both complexes are very similar (Fig. 1). The spectra each contain an intense band at about 1730 cm^{-1} , corresponding to the $\text{C}=\text{O}$ groups of the organic ligand. Water molecules show a broad band at about 3370 cm^{-1} . The ^1H NMR spectra in $\text{DMSO-}d_6$ each contain one triplet peak at $7.83\text{--}7.89\text{ ppm}$ and two doublet peaks at $8.32\text{--}8.36$ and $8.87\text{--}8.91\text{ ppm}$, corresponding to the pyrimidine protons.



15 **Fig. 1** FTIR spectra of $[\text{Co}(\text{bpca})_2]\text{Cl}\cdot 7.5\text{H}_2\text{O}$ (black) and $[\text{Co}(\text{bpca})_2]\text{Br}\cdot 7.5\text{H}_2\text{O}$ (red) at 298 K.

In order to study the electronic properties of the coordination complexes, diffuse reflectance spectra were recorded (Fig. 2). The spectra of both complexes are very similar and each exhibit a broad band in the UV region, which is accompanied by a low-energy shoulder in the visible region up to about 600 nm . The former band has been attributed to intraligand $n\text{--}\pi^*$ and $\pi\text{--}\pi^*$ transitions, while the latter shoulder is due to ligand-to-metal or metal-to-ligand transitions. A broad band in the visible region, centered at about 750 nm in the spectra of both complexes, corresponds to the $d\text{--}d$ transitions.

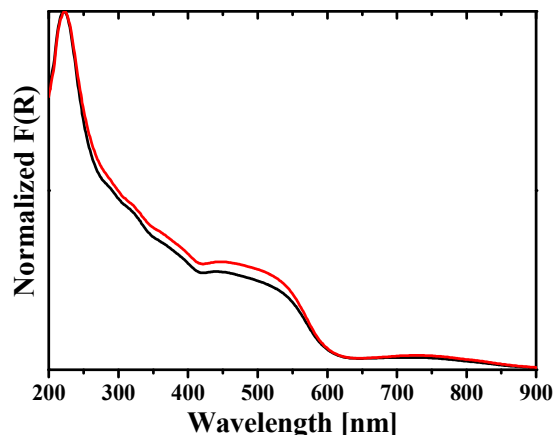


Fig. 2 The normalized Kubelka-Munk spectra of $[\text{Co}(\text{bpca})_2]\text{Cl}\cdot 7.5\text{H}_2\text{O}$ (black) and $[\text{Co}(\text{bpca})_2]\text{Br}\cdot 7.5\text{H}_2\text{O}$ (red) at 298 K.

Crystals of $[\text{Co}(\text{bpca})_2]\text{X}\cdot 7.5\text{H}_2\text{O}$ ($\text{X} = \text{Cl}, \text{Br}$) suitable for single-crystal X-ray analysis were obtained after slow evaporation for 2 days. According to the X-ray data, the complexes are isostructural and crystallize in the monoclinic space group $P2_1/c$. Each structure contains seven and a half crystal water molecules per coordination complex. Two organic ligands are coordinated to a metal center in a $\kappa^3\text{-}N,N',N''$ -coordination mode with the two $\text{C}=\text{O}$ functions remaining uncoordinated (Fig. 3). The coordination sphere of the Co^{III} atom is best described as a slightly distorted octahedron. The $\text{Co}\text{--}N$ and $\text{C}=\text{O}$ bond lengths are very similar in both compounds and are 1.9 and 1.2 \AA , respectively (Tables S1 and S2 in ESI†). The $N_{\text{imide}}\text{--Co}\text{--}N_{\text{imide}}$ angles are almost linear (178°), while the $N_{\text{Pym}}\text{--Co}\text{--}N_{\text{Pym}}$ angles are 166° . The endocyclic angles around the metal cation are 83° , while their corresponding supplementary angles are $96\text{--}98^\circ$. The remaining exocyclic angles around the metal center are close to 90° .

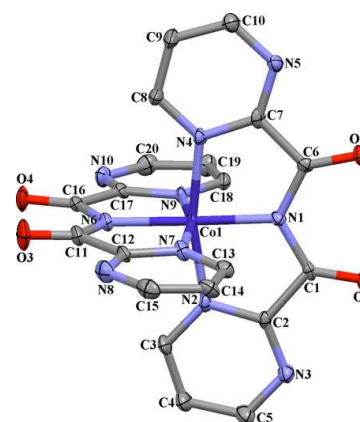


Fig. 3 Molecular structure of the cation $[\text{Co}(\text{bpca})_2]^+$ in $[\text{Co}(\text{bpca})_2]\text{X}\cdot 7.5\text{H}_2\text{O}$ ($\text{X} = \text{Cl}, \text{Br}$). Thermal ellipsoids are shown in the 30% probability level.

Alkyl and aryl substituted triazines are known to hydrolyze,²⁴ but these reactions generally require vigorous conditions.²⁵ This is also true for TPymT, where one known method of purification involves dissolving it in 6 N HCl.^{23a} Furthermore, TPymT was found to be stable upon reacting with CdSO₄²⁶ and Pb(NO₃)₂²⁷ in hot water. Thus, the Co^{II} atom likely assists the hydrolysis of the TPymT triazine ring. It seems improbable that the hydrolysis is being caused by the metal acting solely as a Schiff acid since TPymT is stable in mineral acids. Destabilization of the triazine ring upon coordination is likely the main reason. When Co^{II} binds in one of the tridentate terpyridine-like sites of TPymT, it induces an angular strain at the carbon atoms of the triazine ring which allows for nucleophilic attack by OH⁻ or H₂O. The angles, α , at the carbon atoms C ^{α} are of 120° for *sp*² hybridization, which seems to be consistent with the free ligand (Scheme 1). These values range between 115–118° in the known crystal structures of complexes with TPymT^{26–28} and very close to the ideal value. Within the chelate rings in [Co(bpca)₂]X·7.5H₂O the angles, α , are compressed to 110°. The angles, β , at the carbon atoms C ^{β} are very close to the values expected for the tetrahedral intermediate or transition state of the hydrolysis by the nucleophilic attack of OH⁻ or H₂O at C ^{α} atoms. As a result of the carbon-nitrogen bond cleavage, the coordinated imide is formed. After hydrolysis, C ^{β} are no longer in the triazine ring and β angles are significantly decreased. This allows the pyrimidine fragment to come closer to the metal center, which results in shorter Co–N distances. Although the ionic radii of Co^{II} and Cu^{II} are the same (0.72 Å), allowing an efficient coordination with the bpca anion as was found for Cu^{II},²³ the former cation is further oxidized to Co^{III}. This might be explained by the coordination of two bpca anions with the subsequent oxidation of the metal center similar to that of the hexamminecobalt(III) salts upon reacting cobalt(II) salts with NH₃.²⁹ Alternatively, the hexamminecobalt(III) salts might be formed directly from the reaction of cobalt(II) salts with NH₃. The latter compound was found to be released during the hydrolysis of TPymT.³⁰ The hexamminecobalt(III) salts might further react with bpca.

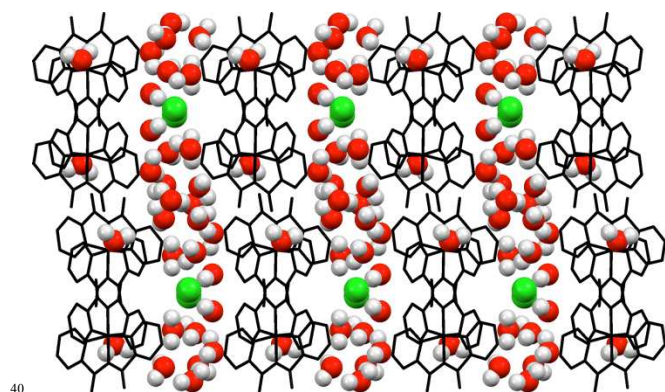


Fig. 4 Stick and space fill crystal packing of water-chloride/bromide clusters and cations [Co(bpca)₂]⁷⁺ in [Co(bpca)₂]X·7.5H₂O (X = Cl, Br).

The structures of both complexes are stabilized by a

number of intermolecular hydrogen bonds formed between: C=O groups, one of the non-coordinated nitrogen atoms of the pyrimidine functions, water molecules and halide anions. (Table S3 in ESI†). As a result of two latter functions, the formation of 2D polymeric sheets is observed (Fig. 4). These sheets comprise polymeric 1D chains, constructed from water-chloride/bromide pentagonal [(Cl/Br)₂(H₂O)₃]²⁻ clusters (Fig. 5), separated from each other by a wide network of hydrogen bonded water molecules. Each halogen atom in [(Cl/Br)₂(H₂O)₃]²⁻ is linked by two water molecules and separated from each other either by one or two water molecules, respectively. The O···O and Cl/Br···O separations in these clusters are 2.69–2.71 and 3.11–3.35 Å, respectively (Table S3 in ESI†). These values together with the values for the O–H and H···O/Cl/Br distances, and O–H···O/Cl/Br angles are in accordance with strong/medium hydrogen bonds based on established criteria.³¹

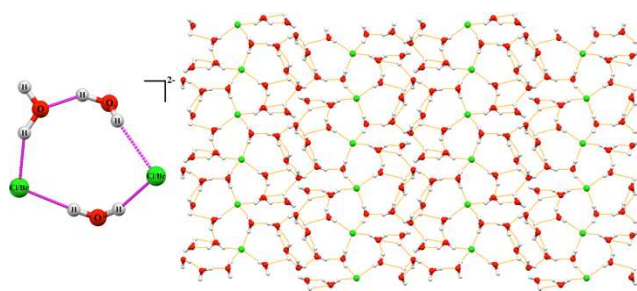


Fig. 5 Hydrogen bonded ball and stick [(Cl/Br)₂(H₂O)₃]²⁻ cluster (left) and 2D sheets (right), constructed from water and chloride/bromide molecules in [Co(bpca)₂]X·7.5H₂O (X = Cl, Br).

⁵⁹Co solid-state NMR spectra were acquired for both compounds at 9.4 T and 21.1 T using a solid-echo experiment and fitted to yield unique sets of NMR parameters (Fig. 6 and Table 1). As higher applied magnetic fields increase the effects of chemical shift anisotropy (CSA), substantially different spectra were obtained in both fields. The higher-field spectra are dominated by CSA. In order to clearly discriminate the high-frequency low intensity region of these spectra, WURST-QCPMG experiments were performed (data not shown). The simulated line shapes were sensitive to small parameter changes, thus providing confidence in the results obtained.

The fitted parameters validate the high-symmetry structure around cobalt observed in the crystal structures. The measured chemical shift tensor span in [Co(bpca)₂]Cl·7.5H₂O (2550 ppm) is slightly superior to that of [Co(bpca)₂]Br·7.5H₂O (2300 ppm), which can be attributed to the differences in the bond angles between both crystal structures surrounding cobalt. The isotropic chemical shift, quadrupolar coupling constant (55.5 MHz for both samples), and asymmetry parameter for both complexes are consistent with data known for previously reported octahedral complexes with six nitrogen atoms coordinated to cobalt.³²

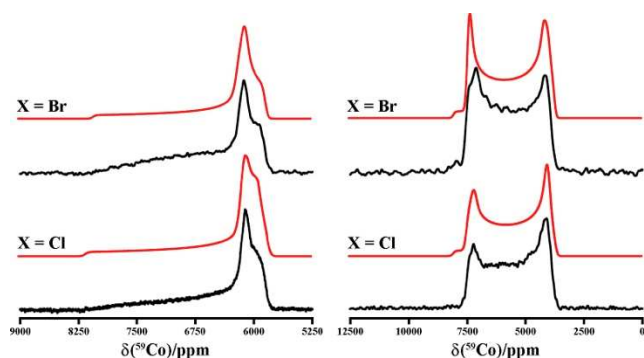


Fig. 6 Experimental (black) and simulated (red) ^{59}Co solid-state NMR of $[\text{Co}(\text{bpca})_2]\text{X}\cdot 7.5\text{H}_2\text{O}$ ($\text{X} = \text{Cl}, \text{Br}$) acquired at 21.1 T (left) and 9.4 T (right).

Table 1 ^{59}Co fitted NMR parameters for $[\text{Co}(\text{bpca})_2]\text{X}\cdot 7.5\text{H}_2\text{O}$ ($\text{X} = \text{Cl}, \text{Br}$)

^{59}Co parameter	$[\text{Co}(\text{bpca})_2]\text{Cl}\cdot 7.5\text{H}_2\text{O}$	$[\text{Co}(\text{bpca})_2]\text{Br}\cdot 7.5\text{H}_2\text{O}$
δ_{iso} (ppm)	6540 ± 20	6555 ± 20
C_Q (MHz)	55.5 ± 1.5	55.5 ± 0.2
η	0.03 ± 0.01	0.020 ± 0.003
Ω (ppm)	2550 ± 50	2300 ± 30
κ	-0.80 ± 0.04	-0.95 ± 0.03
α	40 ± 10	160 ± 40
β	88.0 ± 2	84.5 ± 1.5
γ	1.0 ± 1	3.0 ± 1

A ^{35}Cl solid-state NMR signal was acquired for $[\text{Co}(\text{bpca})_2]\text{Cl}\cdot 7.5\text{H}_2\text{O}$ at 21.1 T (Fig. 7). The spectrum obtained under stationary conditions has a narrow asymmetric line shape which could suggest a slight distribution of chemical environments. The ^{35}Cl magic-angle spinning (MAS) NMR spectrum, however, shows the presence of a single narrow peak with a chemical shift of 13.1 ppm, consistent with the presence of one crystallographic site in the X-ray structure.

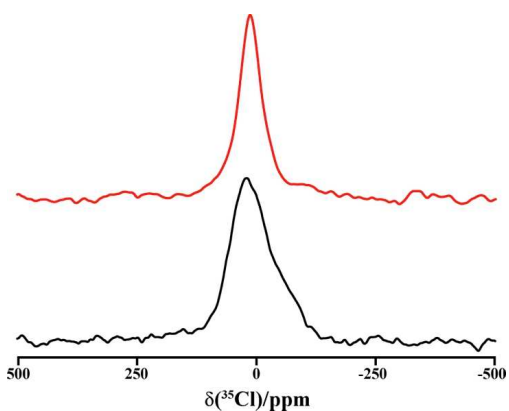


Fig. 7 Static ^{35}Cl solid-state NMR spectrum under stationary conditions (black) and 18 kHz MAS spectrum (red) of $[\text{Co}(\text{bpca})_2]\text{Cl}\cdot 7.5\text{H}_2\text{O}$ acquired at 21.1 T using a solid echo.

^{13}C CP/MAS NMR spectra of the powdered samples of both complexes confirm their structure, crystallinity, and phase purity (Fig. 8). Peaks for the pyrimidine and carbonyl carbon atoms are shown at 160.03–165.38 and 125.49–129.03 ppm, respectively.

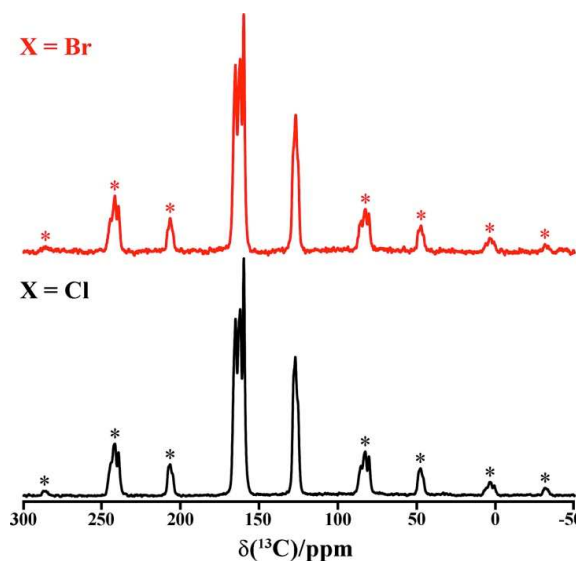


Fig. 8 ^{13}C solid-state NMR spectrum of $[\text{Co}(\text{bpca})_2]\text{X}\cdot 7.5\text{H}_2\text{O}$ ($\text{X} = \text{Cl}, \text{Br}$) acquired at 500 MHz with a spinning speed of 10 kHz. Asterisks denote spinning sidebands.

Conclusions

In summary, we have established that the reaction of TPymT with CoX_2 ($\text{X} = \text{Cl}, \text{Br}$) in water leads to the formation of Co^{III} mononuclear, homoleptic complexes $[\text{Co}(\text{bpca})_2]\text{X}\cdot 7.5\text{H}_2\text{O}$ ($\text{X} = \text{Cl}, \text{Br}$), where two bis(2-pyrimidylcarbonyl)amidate anions each are coordinated to the metal center through the amide and two pyrimidine nitrogen atoms. The C=O groups remained uncoordinated. ^{59}Co , ^{35}Cl , and ^{13}C solid-state NMR spectra have been used to provide structural insight, as well as confirming the crystallinity and phase purity of the samples in powdered form.

Additional counter anions Cl^-/Br^- were trapped in the structures in the form of unprecedented water-chloride/bromide pentagonal $[(\text{Cl}/\text{Br})_2(\text{H}_2\text{O})_3]^{2-}$ clusters. To the best of our knowledge, such clusters have not been previously observed.

Experimental

Physical measurements

Infrared spectra were recorded with a Varian 640 FTIR spectrometer equipped with an ATR in the 500–4000 cm^{-1} range. ^1H NMR spectra in $\text{DMSO}-d_6$ were obtained on a Bruker Avance 300 MHz spectrometer at 25 °C. Chemical shifts are reported with respect to SiMe_4 . Diffuse reflectance spectra were obtained with a Varian Cary 100 spectrometer using polytetrafluoroethylene (PTFE) as a reference. Kubelka-

Munk spectra were normalized to allow meaningful comparisons. Elemental analyses were performed on a Perkin Elmer 2400 CHN analyzer.

Synthesis

5 An aqueous (10 mL) solution of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ or CoBr_2 (0.66 mmol; 0.157 or 0.144 g) was added to a suspension of TPymT (0.2 mmol, 0.063 g) in the same solvent (20 mL). The resulting red solution was left for slow evaporation of the solvent yielding red block-like crystals.

10 **[Co(bpca)₂]Cl·7.5H₂O**. Yield: 0.060 g (87%). ¹H NMR, δ : 7.89 (t, ³J_{H,H} = 8.2 Hz, 4H, *p*-CH, pyrimidine), 8.32 (d, ³J_{H,H} = 8.2 Hz, 4H, *m*-CH, pyrimidine), 8.87 (d, ³J_{H,H} = 8.2 Hz, 4H, *m*-CH, pyrimidine) ppm. *Anal. Calc.* for $\text{C}_{20}\text{H}_{27}\text{ClCoN}_{10}\text{O}_{11.5}$ (685.88): C 35.02, H 3.97, N 20.42. Found: C 35.15, H 4.04, N 20.36%.

[Co(bpca)₂]Br·7.5H₂O. Yield: 0.066 g (91%). ¹H NMR, δ : 7.83 (t, ³J_{H,H} = 8.2 Hz, 4H, *p*-CH, pyrimidine), 8.36 (d, ³J_{H,H} = 8.2 Hz, 4H, *m*-CH, pyrimidine), 8.91 (d, ³J_{H,H} = 8.2 Hz, 4H, *m*-CH, pyrimidine) ppm. *Anal. Calc.* for $\text{C}_{20}\text{H}_{27}\text{BrCoN}_{10}\text{O}_{11.5}$ (730.33): C 32.89, H 3.73, N 19.18. Found: C 32.77, H 3.65, N 19.29%.

Solid-state NMR spectroscopy

Samples were ground and packed in a 4 mm rotor. The ¹³C spectra were acquired using a 500 MHz spectrometer (11.7 T, ¹³C ν = 125.758 MHz) using a CP-MAS pulse sequence, and referenced to 176.5 ppm using glycine. The ⁵⁹Co spectra were acquired using a 400 MHz spectrometer (9.4 T, ⁵⁹Co ν = 94.95 MHz) using a solid-echo pulse sequence with proton decoupling (P1 = 1 μ s) at variable offsets. ⁵⁹Co spectra were also acquired at 21.1 T (⁵⁹Co ν = 213.50 MHz) using a solid-echo pulse sequence with proton decoupling (P1 = 1 μ s) and WURST-QCPMG (P1 = 25 μ s). All ⁵⁹Co were referenced using a 0.56 M $\text{K}_3[\text{Co}(\text{CN})_6]$ solution to 0 ppm (Table 1). The ³⁵Cl spectrum was acquired at 21.1 T (³⁵Cl ν = 88.194 MHz) using a solid-echo pulse sequence (P1 = 3 μ s) with proton decoupling. The ³⁵Cl MAS spectrum was obtained using the same pulse lengths and proton decoupling, with the echo delay synchronized with the rotor spinning rate of 18 kHz. The ³⁵Cl chemical shift was referenced using solid NaCl to -41.11 ppm.

Single-crystal X-ray diffraction

The X-ray data were collected at 200(2) K on a Bruker AXS SMART single crystal diffractometer with a sealed Mo tube APEX II CCD detector. The Mo radiation wavelength, ⁴⁵ 0.71073 Å, was used. Data collection and processing were performed with APEX software from Bruker AXS.³³ The crystal structures were solved by direct methods and refined using the SHELX program.³⁴ All non-hydrogen atoms were refined anisotropically and the positions of all hydrogen atoms were obtained from the Fourier map analysis. Figures were generated using the Mercury program.³⁵

[Co(bpca)₂]Cl·7.5H₂O. $\text{C}_{20}\text{H}_{27}\text{ClCoN}_{10}\text{O}_{11.5}$, M_r = 685.89 g mol⁻¹, monoclinic, space group $P2_1/c$, a = 11.727(3), b = 24.744(6), c = 9.764(3) Å, β = 98.883(5)°, V = 2799.2(13) Å³,

⁵⁵ Z = 4, ρ = 1.628 g cm⁻³, $\mu(\text{Mo-K}\alpha)$ = 0.787 mm⁻¹, reflections: 14262 collected, 4029 unique, R_{int} = 0.1078, $R_1(\text{all})$ = 0.1222, $wR_2(\text{all})$ = 0.1468.

[Co(bpca)₂]Br·7.5H₂O. $\text{C}_{20}\text{H}_{27}\text{BrCoN}_{10}\text{O}_{11.5}$, M_r = 730.35 g mol⁻¹, monoclinic, space group $P2_1/c$, a = 11.7712(5), b = 24.6598(11), c = 9.8817(5) Å, β = 99.559(2)°, V = 2828.6(2) Å³, Z = 4, ρ = 1.715 g cm⁻³, $\mu(\text{Mo-K}\alpha)$ = 2.097 mm⁻¹, reflections: 70326 collected, 6960 unique, R_{int} = 0.0548, $R_1(\text{all})$ = 0.0761, $wR_2(\text{all})$ = 0.1370.

CCDC 994355 (**[Co(bpca)₂]Cl·7.5H₂O**) and 994356 (**[Co(bpca)₂]Br·7.5H₂O**) contain the supplementary crystallographic data. This data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Acknowledgements

This work was financially supported by the NSERC-DG, CFI, ORF, and ERA.

Notes and references

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† Electronic Supplementary Information (ESI) available: Tables S1–S3. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x

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