

Hydrothermal syntheses, crystal structures and physicochemical properties of 2-D and 3-D inorganic coordination cobalt(II)-sulfite polymers†

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The hydrothermal reaction of $[\text{Co}^{\text{III}}(\text{NH}_3)_6]\text{Cl}_3$ with Na_2SO_3 yields, depending on the concentration of Na_2SO_3 , compounds $\{\text{Na}[\text{Co}^{\text{II}}_2(\text{SO}_3)_2(\mu_3\text{-OH})(\text{H}_2\text{O})]\}_\infty$ (**1**) and $\{\text{Na}_4[\text{Co}^{\text{II}}_2(\text{SO}_3)_4]\}_\infty$ (**2**). When $(\text{NH}_4)_2\text{SO}_3 \cdot \text{H}_2\text{O}$ was substituted for Na_2SO_3 , the trinuclear mixed valence cobalt(II/III) complex $(\text{NH}_4)_4\{\text{Co}^{\text{II}}[\text{Co}^{\text{III}}(\text{SO}_3)_3(\text{NH}_3)_3]_2\} \cdot 2\text{H}_2\text{O}$ (**3**·2H₂O) was isolated. The cobalt-sulfites **1**–**3**·2H₂O were structurally characterized. In **1**, the 1-D chains along the *a*-axis of the subunit $[\text{Co}^{\text{II}}(2)\text{Co}^{\text{II}}(3)(\text{OH})_2(\text{SO}_3)_2]$ are cross-linked with $\text{Co}^{\text{II}}(1)$ atoms via $\text{Co}-\text{O}_{\text{sulfite}}$ and $\text{Co}-\text{O}_{\text{hydroxide}}$ bonds in 2-D sheets, that are further stacked through interlayer hydrogen bonds. In **2**, the $[\text{Co}^{\text{II}}_2(\text{SO}_3)_2]_\infty$ chains along the *b*-axis are cross-linked with tetrahedral cobalts via $\text{Co}^{\text{II}}-\text{O}_{\text{sulfite}}$ bonds in 2-D sheets parallel to the *ab*-plane and the sheets are further bound to sodium atoms via $\text{Na}^+-\text{O}_{\text{sulfite}}$ bonds to form a 3-D structure. The 3-D inorganic coordination polymer, **2**, crystallizes in the non-centrosymmetric space group $P2_12_12_1$. In addition, in compound **2** octahedral and tetrahedral cobalt atoms coexist, which is rather unusual for cobalt clusters. Compound **3**·2H₂O is a 0-D mixed-valence $\{[(\text{NH}_3)_3\text{Co}^{\text{III}}(\mu\text{-SO}_3)_3]\text{Co}^{\text{II}}[(\mu\text{-SO}_3)_3\text{Co}^{\text{III}}(\text{NH}_3)_3]\}^{4-}$ trinuclear cluster and can be considered as an octahedral $\{\text{Co}^{\text{II}}\text{O}_6\}$ complex ligated to two tridentate $[(\text{NH}_3)_3\text{Co}^{\text{III}}(\text{SO}_3)_3]^{3-}$ ligands. The trinuclear clusters are stacked through an extended network of hydrogen bonding into a 3-D structure. Variable temperature magnetic susceptibility studies for **1**–**3**·2H₂O revealed that **1** and **2** are 2-D magnetic systems with strong antiferromagnetic interaction between the Co^{II} atoms leading to an $S = 0$ ground state for **1**, while in compound **2** there is an almost zero interaction between the cobalt(II) atoms leading to a non-zero ground state. The trinuclear compound **3**·2H₂O has two diamagnetic Co^{III} atoms and a high-spin Co^{II} atom with $D = 84(1) \text{ cm}^{-1}$, $E = 6(1) \text{ cm}^{-1}$ and $g = 2.56(1)$. The IR, the solid-state UV-vis spectra and the thermogravimetric analyses of compounds **1**–**3**·2H₂O are also reported.

Introduction

Open-framework and microporous solids, as well as coordination polymers, constitute an important class of materials because of their applications in catalysis, gas sorption, ion exchange and so forth.¹ To date, the most common anions used for the synthesis of these materials are silicates and phosphates. In recent years, other oxyanions such as sulfate, selenate, selenite and tellurite have also been used^{2,3} for the preparation of such species. Currently, work on both metal-sulfites^{4–11} and polyoxometalates,^{12–15} containing the sulfite anion as a templating¹⁶ agent, has been reported. The use of the 3-connected sulfite anion as a basic structural unit for the building of open-framework materials is particularly desirable, since the presence of 3-connected building blocks has been recognized to contribute to large pore sizes and low framework density.¹⁷ The sulfite anion presents the intriguing possibility that all its four atoms can potentially bond to metal atoms and

thus, it can bridge soft (with its sulfur atom)¹⁸ and hard metals (with its oxygens). This possibility differentiates the sulfite anion from other inorganic 3-connected centers, such as $[\text{Se}^{\text{IV}}\text{O}_3]^{2-}$,³ $[\text{Te}^{\text{IV}}\text{O}_3]^{2-}$,³ and $[\text{CO}_3]^{2-}$,¹⁹ which can only bond to metal atoms through their oxygen atoms. In addition, the sulfite ion has C_{3v} symmetry and contains a non-bonding but stereochemically active pair of electrons which may aid in the crystallization of metal-sulfites in non-centrosymmetric space groups with potential non-linear optical properties observed in non-centrosymmetric metal selenites^{3a–e} and metal tellurites.^{3a–e}

The metal-sulfite chemistry is dominated by zinc and copper. In marked contrast, only two cobalt(II)-sulfite clusters have been reported two years ago,¹⁰ though in these compounds the basic building block is $[\text{Cu}^{\text{I}}(\text{SO}_3)_4]^{7-}$. Mononuclear²⁰ cobalt(III)-sulfite compounds of the general formula $[\text{Co}^{\text{III}}(\text{SO}_3)_3\text{N}_3]^{2+}$ and *cis/trans*- $[\text{Co}^{\text{III}}(\text{SO}_3)_2\text{N}_4]^{2+}$ have been well studied from the standpoint of their applications to thermal and photochemical oxidation of sulfite²³ and of their biological relevance.²⁴ Thus, we embarked on an effort to explore the Co(II)-sulfite chemistry. To achieve the goal of the synthesis of cobalt(II)-sulfite compounds, two major strategies are envisaged: (i) the direct reaction of cobalt(II) with SO_3^{2-} in aqueous solution and (ii) the hydrothermal reaction of a cobalt(III) species with monodentate ligands, such as $[\text{Co}^{\text{III}}(\text{NH}_3)_6]^{3+}$, with SO_3^{2-} . Herein, the latter strategy was used in the successful synthesis of cobalt(II)-sulfite compounds, since addition of SO_3^{2-} to aqueous Co^{II} solutions results in the precipitation

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of cobalt oxides. More specifically, this paper reports the synthesis, *via* the hydrothermal reaction (150 °C) of $[\text{Co}^{\text{III}}(\text{NH}_3)_6]\text{Cl}_3$ with Na_2SO_3 , and structural characterization of compounds $\{\text{Na}[\text{Co}^{\text{II}}_2(\text{SO}_3)_2(\mu_3\text{-OH})(\text{H}_2\text{O})]\}_\infty$ (**1**) and $\{\text{Na}_4[\text{Co}^{\text{II}}_2(\text{SO}_3)_4]\}_\infty$ (**2**) which are 2-D and 3-D inorganic coordination polymers, respectively. The 0-D trinuclear mixed-valence $\text{Co}(\text{II/III})$ species, $(\text{NH}_4)_4\{\text{Co}^{\text{II}}[\text{Co}^{\text{III}}(\text{SO}_3)_3(\text{NH}_3)_3]_2\} \cdot 2\text{H}_2\text{O}$ (**3·2H₂O**) was also synthesized, *via* the hydrothermal reaction (110 °C) of $[\text{Co}^{\text{III}}(\text{NH}_3)_6]\text{Cl}_3$ with $(\text{NH}_4)_2\text{SO}_3 \cdot \text{H}_2\text{O}$, and structurally characterized. The physicochemical characterization of **1–3·2H₂O**, [magnetic susceptibility studies, IR and UV-vis spectra as well as thermogravimetric analyses], was also carried out.

Experimental

Materials, methods and instrumentation

Reagent grade chemicals were obtained from Aldrich and used without further purification. $[\text{Co}^{\text{III}}(\text{NH}_3)_6]\text{Cl}_3$ was prepared by the literature method.²⁵ H, N and S analyses were conducted by the microanalytical service of the Institute of Inorganic and Applied Chemistry, University of Hamburg. Cobalt and sodium were determined by atomic absorption. X-Ray diffraction intensity data for the crystals of **1**, **2** and **3·2H₂O** were collected on an Oxford diffraction CCD²⁶ instrument, 22a using graphite-monochromated $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Cell parameters were determined using up to 2787 (**1**), 2840 (**2**) and 8379 (**3·2H₂O**), highest-intensity reflections. All data were corrected for Lorentz-polarization effects and absorption.²⁶ The structures were solved with direct methods with *SIR92*²⁷ and refined by full-matrix least-squares procedures on *F²* with *SHELXL97*.²⁸ All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located at calculated positions and refined *via* the “riding model” with isotropic thermal parameters fixed at 1.2 times the U_{eq} value of the appropriate carrier atom. Significant crystal data are given in Table 1. Weak restraints were applied to the displacement parameters of some atoms (4 in **1**, 2 in **3·2H₂O**) in

order to avoid them becoming too eccentric (ISOR instruction of SHELX). The *R* factors for compound **3·2H₂O** are relatively high, but we are sure that they do not affect the chemical identity of the model and do not influence the discussion. The high *R* factors may be due to the relatively high residual electron density that suggests some disordered solvent which we were not able to take into the model and to the presence of some strong reflections. The crystal of **2** was a racemic twin. Twin refinement lead to a Flack parameter of 0.45(2). Refinement of the inverted structure lead to a Flack parameter *ca.* 1.5 and it was impossible to refine the structure in a centrosymmetric space group. The origin of the non-centrosymmetry is probably the coordination spheres of both the cobalt atoms which are very distorted or the sodium atoms that connect the cobalt layers. Further details of the crystal structure studies can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: (49) 7247808666; e-mail: drysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD 420815, 420817, 420816 for compounds **1**, **2**, and **3·2H₂O**, respectively. IR spectra of the various compounds dispersed in KBr pellets and were recorded on a Perkin-Elmer Spectrum GX FT-IR spectrometer. Isofield variable-temperature dc magnetic susceptibility measurements were performed at various external fields in the range 0.02–1 Tesla (T) on a Quantum Design Magnetic Phenomena Measurement System (MPMS) Superconducting Quantum Interference Device (SQUID) magnetometer from 1.8 to 300 K using the Field-Cooling (FC) and ZFC zero field-cooling method. Isofield variable-field dc magnetic susceptibility measurements were carried out on a Quantum Design MPMS SQUID magnetometer at 2 K between 0 and 5.5 T. All samples were packed into gelatine capsules and placed in a drinking straw sample holder. All magnetic susceptibility values were corrected with Pascal's constants and corrections were applied for the sample holder (gelatine capsule, and drinking straw). UV-vis diffuse reflectance spectra were obtained at room temperature on a Shimadzu UV-3101PC double-beam, double-monochromator spectrophotometer in the wavelength range 200–1000 nm. BaSO_4 powder was used

Table 1 Summary of crystallographic data and refinement parameters for compounds **1**, **2** and **3·2H₂O**

	1	2	3·2H₂O
Empirical formula	$\text{Co}_2\text{H}_3\text{NaO}_8\text{S}_2$	$\text{Co}_2\text{Na}_4\text{O}_{12}\text{S}_4$	$\text{Co}_3\text{H}_{38}\text{N}_{10}\text{O}_{20}\text{S}_6$
Fw	335.99	530.06	867.55
Crystal system	Triclinic	Orthorhombic	Trigonal
Space group	$P\bar{1}$	$P2_12_12_1$	$R\bar{3}$
<i>a</i> /Å	6.3214(15)	6.6497(7)	9.9242(5)
<i>b</i> /Å	7.827(2)	10.2218(12)	9.9242(5)
<i>c</i> /Å	8.898(2)	17.287(2)	30.2127(18)
α (°)	98.91(2)	90	90
β (°)	109.81(2)	90	90
γ (°)	112.61(2)	90	120
<i>V</i> /Å ³	361.17(19)	1175.0(2)	2577.0(2)
<i>Z</i>	2	4	3
<i>d_c</i> (mg m ^{−3})	3.090	2.996	1.677
μ/mm^{-1}	5.240	3.745	1.873
<i>F</i> (000)	328	1032	1335
Total data collected	4483	3225	8406
Unique data	1264	2124	1012
Data/restraints/params	1264/24/121	2124/0/199	1012/12/67
Final <i>R</i> indices <i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0624, 0.1133	0.0210, 0.0437	0.0547, 0.2255
<i>R</i> indices <i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.1580, 0.1434	0.0247, 0.0448	0.0607, 0.2307

as a reference (100% reflectance) and base material on which the powder sample was coated. Thermogravimetric analyses (TGA) of the samples were performed using a NETZSCH apparatus (model STA 449C, Jupiter) in nitrogen or helium atmosphere (flow rate $\sim 60 \text{ mL min}^{-1}$). The heating program consists of two steps, the dynamic step, from ambient temperature ($\sim 20^\circ \text{C}$) to 1100°C with a heating rate of $\beta = 2^\circ \text{C min}^{-1}$ and the isothermal step (3 h) at 1100°C .

Synthesis of compounds

Preparation of sodium (μ_3 -hydroxido)bis(sulfito)[(μ_6 - η^2 : η^3 : η^3 -O, O, O- SO_3)(μ_6 - η^2 : η^2 : η^2 -O, O, O- SO_3)](aqua)dibaltate(II), $\{\text{Na}[\text{Co}^{\text{II}}(\text{SO}_3)_2(\mu_3\text{-OH})(\text{H}_2\text{O})]\}_\infty$, **1.** To a stirred solution of Na_2SO_3 (5.00 g, 39.5 mmol) in water (23 mL, pH = 9.8), was added aqueous hydrochloric acid 37% ($\sim 3 \text{ mL}$) until its pH value became 5.5. Then, to the above solution was added solid $[\text{Co}^{\text{III}}(\text{NH}_3)_6]\text{Cl}_3$ (0.50 g, 1.87 mmol) in one portion. Upon addition of $[\text{Co}^{\text{III}}(\text{NH}_3)_6]\text{Cl}_3$ to the colorless solution of Na_2SO_3 its colour changed to orange-yellow and the final pH of the solution was 5.5. The resulting solution was sealed in a Teflon-lined stainless steel autoclave (50 mL), kept at 150°C for three days and then slowly cooled, at $5^\circ \text{C min}^{-1}$, to room temperature. Pink crystals of **1** suitable for X-ray structure determination were formed, which were filtered, and dried in air at room temperature ($\sim 20^\circ \text{C}$) to get 0.18 g (57%, based on cobalt) of **1**. Elemental analysis for $\text{H}_3\text{O}_8\text{S}_2\text{Co}_2\text{Na}$, calcd (found)%: H 0.90 (1.13), S 19.09 (19.26), Co 35.08 (34.48), Na 6.84 (6.56). FTIR (KBr, pellets, cm^{-1}): 3511 (m), 1012 (m), 942 (vs), 880 (vs), 703 (m), 530 (m), 469 (m).

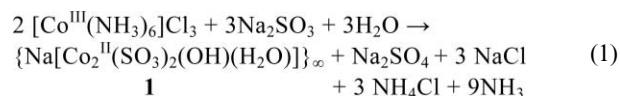
Preparation of sodium tetrakis(sulfito)[(μ_7 - η^2 : η^3 : η^3 -O, O, O- SO_3)(μ_7 - η^2 : η^2 : η^3 -O, O, O- SO_3)(μ_8 - η^3 : η^3 : η^3 -O, O, O- SO_3)(μ_7 - η^2 : η^3 : η^4 -O, O, O- SO_3)]cobaltate(II)](OC-6)cobaltate(II)](T-4)], $\{\text{Na}_4[\text{Co}^{\text{II}}_2(\text{SO}_3)_4]\}_\infty$, **2.** Aqueous hydrochloric acid 37% ($\sim 8 \text{ mL}$) was added dropwise to a stirred suspension of Na_2SO_3 (11.00 g, 86.9 mmol) in water (28 mL). After an additional 30 min of stirring a clear solution was produced (pH = 5.3). To this was added solid $[\text{Co}^{\text{III}}(\text{NH}_3)_6]\text{Cl}_3$ (0.50 g, 1.87 mmol) in one portion and the colourless solution became orange-yellow (pH = 5.3). The resulting reaction mixture was sealed in an autoclave equipped with a Teflon liner (50 mL) and then heated at 150°C for one day, followed by cooling, at $5^\circ \text{C min}^{-1}$, to room temperature. Beautiful violet crystals of compound **2**, suitable for X-ray structure analysis, were formed. The crystals were filtered and dried in air at ambient temperature (25°C) to get 0.25 g (50%, based on cobalt) of **2**. Elemental analysis for $\text{O}_{12}\text{S}_4\text{Co}_2\text{Na}_4$, calcd (found)%: S 24.20 (23.82), Co 22.24 (21.95), Na 17.35 (16.98). FTIR (KBr, pellets, cm^{-1}): 1079 (s), 1060 (s), 1033 (vs), 1008 (w), 960 (vs), 927 (vs), 909 (vs), 874 (vs), 805 (w), 637 (s), 597 (m), 477 (m).

Preparation of ammonium bis[tris(μ_2 - η^1 : η^1 -O, S-sulfito)triamminecobalt(III)]cobaltate(II) dihydrate, $(\text{NH}_4)_4[\text{Co}^{\text{II}}[\text{Co}^{\text{III}}(\text{SO}_3)_3(\text{NH}_3)_3]_2] \cdot 2\text{H}_2\text{O}$, **3.** To a stirred solution of $(\text{NH}_4)_2\text{SO}_3 \cdot \text{H}_2\text{O}$ (10.00 g, 82 mmol) in water (25 mL, pH = 9.5) was added dropwise aqueous hydrochloric acid 37% ($\sim 4 \text{ mL}$) until the pH of the solution became 7. To this, an aqueous solution (10 mL) containing $[\text{Co}^{\text{III}}(\text{NH}_3)_6]\text{Cl}_3$ (1.00 g, 3.74 mmol) was added. The resulting solution sealed in a Teflon-lined stainless steel autoclave (50 mL), kept at 110°C for four days and then, slowly cooled, at $5^\circ \text{C min}^{-1}$, to $\sim 50^\circ \text{C}$. The slight quantity of a brown precipitate which was formed, was filtered and the solution was allowed to slowly cool at room temperature ($\sim 20^\circ \text{C}$). After two to three hours yellow-brown crystals of **3** were formed, which were filtered and dried in air to get 0.25 g (23%, based on cobalt). Elemental analysis for $\text{H}_{38}\text{N}_{10}\text{O}_{20}\text{S}_6\text{Co}_3$, calcd (found)%: H 4.41 (4.22), N 16.15 (15.89), S 22.18 (21.81), Co 20.38 (20.04). FTIR (KBr, pellets, cm^{-1}): 3196 (br), 1641 (m), 1401 (vs), 1317 (w), 1281 (m), 1116 (vs), 1050 (vs), 1003 (vs), 960 (vs), 816 (m), 646 (vs), 531 (m), 435 (m).

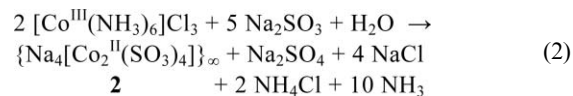
Results and discussion

Syntheses

The synthesis of compounds **1**, **2** and **3** is shown in Scheme 1. Compound **1** was synthesized by reacting $[\text{Co}^{\text{III}}(\text{NH}_3)_6]\text{Cl}_3$ (0.081 M) with Na_2SO_3 ($C = 1.72 \text{ M}$, eqn 1) under hydrothermal conditions (150°C).

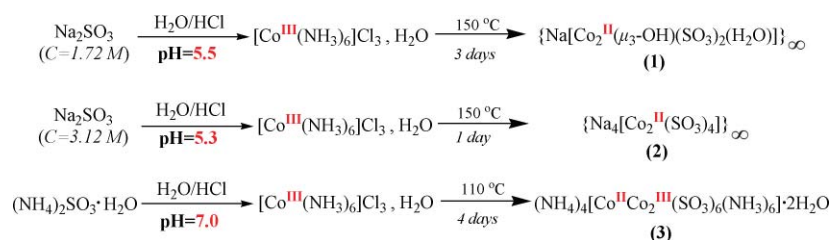


When the concentration of Na_2SO_3 ($C = 3.12 \text{ M}$) was almost doubled and the concentration of $[\text{Co}^{\text{III}}(\text{NH}_3)_6]\text{Cl}_3$ ($C = 0.068 \text{ M}$) was slightly reduced, under the same conditions of temperature (150°C) and pH (5.5) applied for the synthesis of **1**, compound **2** (eqn 2) was formed along with a black-pink precipitate. A slight change of the pH value of the reaction system to 5.3 resulted in the isolation of crystals of compound **2** only.



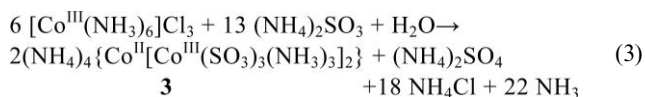
Compound **1** has a $\text{Co}:\text{SO}_3^{2-}$ ratio of 1:1, while **2** has a $\text{Co}:\text{SO}_3^{2-}$ ratio of 1:2. This fact presumably explains why compound **2** is formed when the concentration of Na_2SO_3 is almost doubled.

The Na^+ cation, which is present in compounds **1** and **2** is clearly structurally noninnocent. Thus, replacing Na^+ by NH_4^+



Scheme 1 Synthetic routes to compounds **1**, **2** and **3**·2H₂O

{using $(\text{NH}_4)_2\text{SO}_3 \cdot \text{H}_2\text{O}$ instead of Na_2SO_3 } compound $3 \cdot 2\text{H}_2\text{O}$ was isolated (eqn 3) at 110°C and pH 7.



At temperatures higher than 110°C (110 – 150°C) a black precipitate was always formed. Thus, it is evident that the sodium cations play a crucial role in the thermal stability of **1** and **2** which were isolated at 150°C . The thermogravimetric analysis (*vide infra*) verified this conclusion. When the pH of the reaction system was in the range $5.5 < \text{pH} < 7.0$ a pink precipitate, which was not further characterized, was formed after mixing $[\text{Co}^{\text{III}}(\text{NH}_3)_6]\text{Cl}_3$ with $(\text{NH}_4)_2\text{SO}_3 \cdot \text{H}_2\text{O}$. When this reaction system was heated at 110 , 120 , 130 , 140 and 150°C a black precipitate was always formed. To avoid the formation of the pink precipitate the pH 7 was chosen for the synthesis of $3 \cdot 2\text{H}_2\text{O}$.

Compound $[\text{Co}^{\text{III}}(\text{SO}_3)(\text{NH}_3)_5]_4\{\text{Co}^{\text{II}}[\text{Co}^{\text{III}}(\text{SO}_3)_3(\text{NH}_3)_3]_2\} \cdot 16\text{H}_2\text{O}$ ($4 \cdot 16\text{H}_2\text{O}$)^{20b} contains the same trinuclear mixed valence cobalt(II/III) anion, $\{\text{Co}^{\text{II}}[\text{Co}^{\text{III}}(\text{SO}_3)_3(\text{NH}_3)_3]_2\}^{4-}$, as compound $3 \cdot 2\text{H}_2\text{O}$ and it was prepared^{20b} by subsequent treatment of a solution of concentrated aqueous ammonia containing $\text{Co}^{\text{II}}\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{CO}_3$ with air (8 h) and then $\text{Na}_2\text{S}_2\text{O}_4$, in a very small yield (2.5%). The time for the synthesis of $4 \cdot 16\text{H}_2\text{O}$ is approximately twelve days.

From eqn (1), (2) and (3) it is clear that the sulfite anion plays a dual role; of the ligand and of the reducing agent.

Crystal structures

The asymmetric unit of **1** contains three crystallographically distinct Co^{2+} ions [Co(1), Co(2) and Co(3)], two SO_3^{2-} ions, one Na^+ cation, one OH^- anion, and one water molecule. The Co(2) and Co(3) atoms are symmetry related and have an occupation factor of 0.5. All the cobalt(II) atoms have distorted $[\text{Co}^{\text{II}}\text{O}_6]$ octahedral geometry (Fig. 1). More specifically, the Co(1) is ligated to four sulfite oxygen atoms from four different sulfite ions, as well as to two *cis*-oxygen atoms from a μ_3 -OH[−] group and a water molecule (Fig. 1). The Co(2) and Co(3) centers are also ligated to four oxygen atoms from four different sulfites as well as to two *trans*-oxygen atoms from two μ_3 -hydroxyl groups (Fig. 1). The three cobalt atoms form an almost ideal isosceles triangle with $d[\text{Co}(1) \dots \text{Co}(2)]$, $d[\text{Co}(2) \dots \text{Co}(3)]$ and $\angle[\text{Co}(2) \dots \text{Co}(1) \dots \text{Co}(3)]$, $\angle[\text{Co}(1) \dots \text{Co}(2) \dots \text{Co}(3)]$ being 3.589 , 3.161 \AA and 52.29° , 63.77° , respectively. The three cobalt atoms are bridged by a μ_3 -OH[−] and a μ_3 - $\eta^1:\eta^1:\eta^1$ -(O, O, O) sulfite

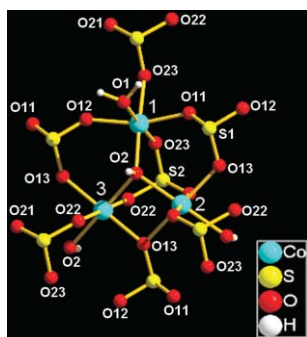


Fig. 1 The triangular configuration of cobalt atoms in **1**.

group, which lie above and below the Co_3 plane. $[\text{Co}(2)\text{O}_6]$ and $[\text{Co}(3)\text{O}_6]$ octahedrons form chains along the a -axis, through a μ_3 -OH[−] and oxygens from the sulfite anions. The hydroxide groups are in alternating positions in the chains and bind to $[\text{Co}(1)\text{O}_6]$ octahedrons to create an undulating two dimensional layer parallel to the ac -plane (Fig. 2). The Co(1) atoms are bridged by two sulfite oxygen atoms. The sodium cations fill the empty space in the layer through bonds to sulfite oxygens. The layers are hydrogen bonded to the water molecules along the b -axis forming a three-dimensional hydrogen bonded network (Fig. 3). The BVS (bond valence sum)^{29,30} analysis for the oxygen atoms O(2) and O(1) (Fig. 1) gave values 1.011 and 0.304 respectively, indicating that the O(2) is singly protonated and the O(1) is doubly protonated. BVS calculations^{29,30} indicate that the cobalt atoms are in the +2 oxidation state and this is confirmed by the O -ligation of the sulfite groups [cobalt(III) is always S -bonded to the SO_3^{2-}] and the sulfur atoms in oxidation state +4.

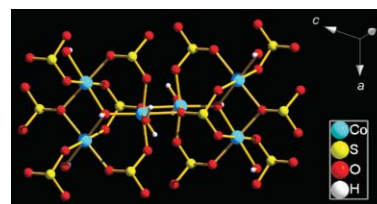


Fig. 2 The two-dimensional layer of **1**. Sodium atoms are omitted for clarity.

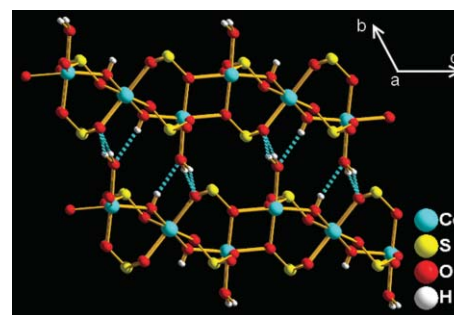
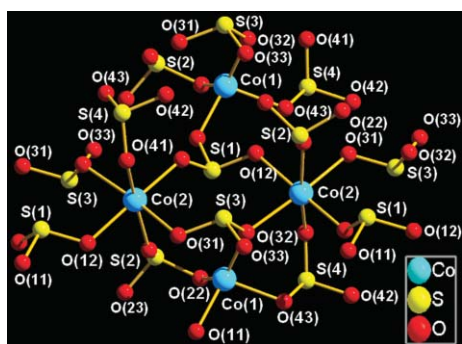


Fig. 3 The three-dimensional framework of **1**, looking along the a -axis. (Blue lines; hydrogen bonds). Sodium atoms are omitted for clarity.

Compound $\{\text{Na}_4[\text{Co}_2^{\text{II}}(\text{SO}_3)_4]\}_\infty$, **2**, is a 3-D inorganic polymer, crystallizing in the noncentrosymmetric space group $P2_12_12_1$. The asymmetric unit of **2** contains two crystallographically distinct Co^{2+} ions [Co(1) and Co(2)], four sodium ions [Na(1), Na(2), Na(3) and Na(4)] and four SO_3^{2-} ions [S(1), S(2), S(3) and S(4)]. As shown in Fig. 4, Co(1) atom is tetrahedrally coordinated to four oxygens from four different sulfite anions. The Co(1)–O bond lengths range from $1.989(3)$ to $2.013(3) \text{ \AA}$ (Table 2). The Co(2) has a distorted octahedral geometry and is ligated to six oxygens from six different sulfites. The Co(2)–O bond distances range from $2.054(3)$ to $2.220(3) \text{ \AA}$ (Table 2). Co(2) atoms are connected together through two μ_3 - SO_3^{2-} ions (S1 and S3) leading to the formation of chains along the b -axis. The tetrahedral Co(1) atoms are connected to these “Co(2) chains”, through $\text{O}_{\text{sulfite}}$ oxygen atoms (Fig. 4), forming a two-dimensional layer, which is a combination of “Co(2) chains” cross-linked with Co(1) atoms, parallel to the ab -plane (Fig. 5). Sodium cations [Na(1) and Na(2)]

Table 2 Selected bond distances in compounds **1**, **2** and **3·2H₂O**

Bond	Distance/Å	Bond	Distance/Å
Compound 1			
Co(1)–O(11)#1	2.037(9)	Co(3)–O(13)#6	2.094(8)
Co(1)–O(12)#2	2.051(9)	Co(3)–O(13)	2.094(8)
Co(1)–O(2)	2.053(9)	Co(3)–O(2)#2	2.130(9)
Co(1)–O(23)#2	2.113(9)	Co(3)–O(2)#3	2.130(9)
Co(1)–O(1)	2.132(10)	Co(3)–O(22)	2.156(9)
Co(1)–O(23)	2.163(9)	Co(3)–O(22)#6	2.156(9)
Co(2)–O(2)#3	2.105(8)	Na(1)–O(11)#1	2.389(11)
Co(2)–O(2)#1	2.105(8)	Na(1)–O(13)	2.470(11)
Co(2)–O(13)	2.123(8)	Na(1)–O(21)#5	2.514(11)
Co(2)–O(13)#4	2.123(8)	Na(1)–O(12)#1	2.529(11)
Co(2)–O(21)#5	2.168(9)	Na(1)–O(11)	2.622(11)
Co(2)–O(21)#6	2.168(9)	Na(1)–O(22)	2.740(11)
Compound 2			
Co(1)–O(22)	1.989(3)	Na(2)–O(11)#1	2.395(3)
Co(1)–O(11)#1	2.001(2)	Na(2)–O(23)	2.454(3)
Co(1)–O(32)	2.002(3)	Na(2)–O(22)	3.015(3)
Co(1)–O(43)#1	2.013(3)	Na(3)–O(12)#9	2.320(3)
Co(2)–O(41)#3	2.054(3)	Na(3)–O(13)	2.378(3)
Co(2)–O(13)#4	2.099(3)	Na(3)–O(31)#9	2.388(3)
Co(2)–O(21)	2.104(2)	Na(3)–O(11)	2.490(3)
Co(2)–O(12)	2.125(2)	Na(3)–O(33)#12	2.509(3)
Co(2)–O(31)	2.184(3)	Na(3)–O(43)#9	2.616(3)
Co(2)–O(32)#5	2.220(3)	Na(3)–O(32)#12	2.616(3)
Na(1)–O(42)#6	2.355(3)	Na(3)–O(21)#9	2.819(3)
Na(1)–O(23)#7	2.388(3)	Na(4)–O(42)#9	2.305(3)
Na(1)–O(43)	2.400(3)	Na(4)–O(33)#9	2.310(3)
Na(1)–O(41)#3	2.407(3)	Na(4)–O(13)	2.342(3)
Na(1)–O(31)	2.571(3)	Na(4)–O(23)	2.364(3)
Na(1)–O(42)	2.954(4)	Na(4)–O(21)	2.739(3)
Na(2)–O(33)#9	2.355(3)	Na(4)–O(12)	2.738(3)
Compound 3·2H₂O			
Co(1)–S(1)	2.2213(11)	Co(2)–O(13)	2.079(3)
Co(1)–N(1)	2.000(4)	Co(1)···Co(2)	3.874(3)

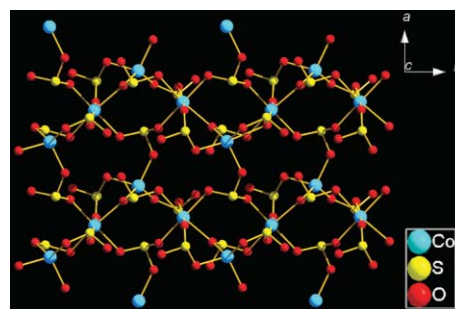
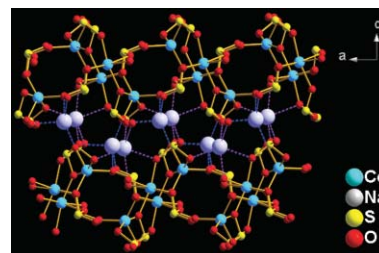
**Fig. 4** Coordination environment of the cobalt atoms in **2**.

bind to the layers through the oxygens of the sulfite ions, forming a three-dimensional framework, as shown in Fig. 6, whilst Na(3) and Na(4) cations fill the empty space between the layers. BVS calculations^{29,30} indicate that the cobalt and sulfur atoms are in the oxidation states +2 and +4, respectively. It is worth noting at this point the coexistence of octahedral and tetrahedral cobalt atoms in **2**. This is quite unusual for cobalt clusters,^{31–36} and in any case the first example to be reported with inorganic-only ligands.

As shown in Fig. 7, the anion of **3·2H₂O** is $\{[(\text{NH}_3)_3\text{Co}^{\text{III}}(\mu\text{-SO}_3)_3]\text{Co}^{\text{II}}[(\mu\text{-SO}_3)_3\text{Co}^{\text{III}}(\text{NH}_3)_3]\}^{4-}$, structurally identical to the anion in $[\text{Co}^{\text{III}}(\text{SO}_3)(\text{NH}_3)_5]_4\{\text{Co}^{\text{II}}[\text{Co}^{\text{III}}(\text{SO}_3)_3(\text{NH}_3)_3]_2\}\cdot 16\text{H}_2\text{O}$ (4.16H₂O).^{20b} The cobalt(III) atoms possess a $[\text{Co}^{\text{III}}\text{S}_3\text{N}_3]$ octahedral coordination and are ligated to three sulfite sulfur atoms, as well as three ammonia nitrogen atoms. The Co–S and Co–N bond

Table 3 S–O bond distances (Å) in compounds **1**, **2** and **3·2H₂O**

Compound	S–O	Distance
1	S(1)–O(11)	1.545(10)
	S(1)–O(12)	1.481(10)
	S(1)–O(13)	1.564(9)
	S(2)–O(21)	1.551(9)
	S(2)–O(22)	1.540(9)
	S(2)–O(23)	1.521(9)
	S(1)–O(11)	1.543(3)
	S(1)–O(12)	1.523(2)
	S(1)–O(13)	1.543(3)
	S(2)–O(21)	1.554(3)
2	S(2)–O(22)	1.552(3)
	S(2)–O(23)	1.494(3)
	S(3)–O(31)	1.523(3)
	S(3)–O(32)	1.581(3)
	S(3)–O(33)	1.501(3)
	S(4)–O(41)	1.524(3)
	S(4)–O(42)	1.480(3)
	S(4)–O(43)	1.554(3)
	S–O(11)	1.477(4)
	S–O(12)	1.474(4)
3·2H₂O	S–O(13)	1.498(3)

**Fig. 5** The two-dimensional layer of **2**, looking along the *c*-axis. Sodium atoms are omitted for clarity.**Fig. 6** The three-dimensional structure of **2**, looking along the *b*-axis. Na(3) and Na(4) atoms omitted for clarity.

distances are 2.2213(11) and 2.000(4) Å respectively. The cobalt(II) atom possesses an octahedral $[\text{CoO}_6]$ coordination and is ligated to six sulfite oxygen atoms. The Co^{II}–O bond distance is 2.079(3) Å. The $[\text{Co}^{\text{II}}\text{O}_6]$ octahedron is coordinated to two $[\text{Co}^{\text{III}}\text{S}_3\text{N}_3]$ octahedrons, through six $[\mu_2\text{-}\eta^1\text{-}\eta^1\text{-(S,O)}]$ sulfite ions, forming a linear trinuclear cluster $\{\text{Co}^{\text{II}}[(\text{O}_3\text{S})_3\text{Co}^{\text{III}}(\text{NH}_3)_3]_2\}^{4-}$ and thus, both Co^{II}···Co^{III} distances are identical, being 3.874(3) Å. All the Co^{III}–S, Co^{III}–N, and Co^{II}–O bond lengths in **3·2H₂O** are identical, which is not the case in **4·16H₂O**.^{20b} Compound **3·2H₂O** joins a handful of structurally characterized linear, valence-trapped Co^{III}–Co^{II}–Co^{III} clusters.^{20b,37–46} The hydrogen atoms of the

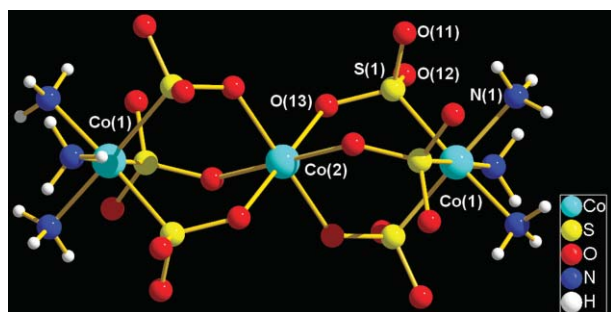


Fig. 7 Ball and stick representation of the anion of the $3 \cdot 2\text{H}_2\text{O}$.

ammonia molecules ligated to Co(III) as well as the ammonium and water hydrogen atoms form an extensive intermolecular hydrogen-bonded network with the sulfite and water oxygens, leading to the formation of a three-dimensional structure. BVS calculations^{29,30} indicate that the sulfur atoms are in oxidation state +4, the central cobalt atom in the +2 oxidation state and the outer cobalts in the +3 oxidation state. The latter is confirmed by the *O*- and the *S*-ligation of the sulfite groups to the central and outer cobalts, respectively.

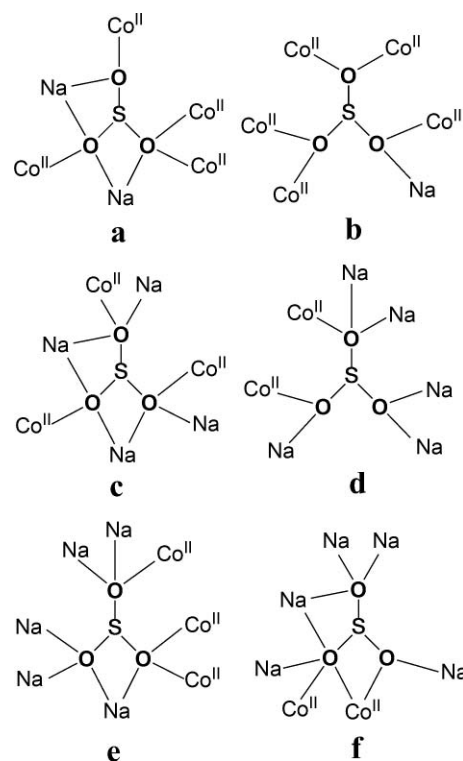
At this point, it is worth noting that the sulfite anion binds to cobalt(II) through its oxygen atoms and through its sulfur atom to cobalt(III). Zinc(II) binds to the oxygen atoms of the sulfite group, while copper(I) binds to the sulfur atom of it. In the Co/Cu/Zn -sulfites, the cobalt(III) is always six-coordinate, the cobalt(II) is four/six-coordinate, the zinc(II) is four/five-coordinate and the copper(I) is four-coordinate.

Infrared spectroscopy

The FT-IR spectra of cobalt-sulfite compounds **1**, **2** and $3 \cdot 2\text{H}_2\text{O}$ are shown in Fig. S1.† The differences between the spectra of **1**– $3 \cdot 2\text{H}_2\text{O}$ are quite compelling (Fig. S1†) and are due to the different coordination modes of the sulfite groups (Scheme 2) in these compounds. IR spectra of metal-sulfites provide a very sensitive indicator of their bonding. It has been reported⁴⁷ that the free pyramidal (C_{3v}) sulfite anion in aqueous solution has four fundamentals (ν_1 – ν_4) at wavenumbers: $\nu_1(A_1) = 967 \text{ cm}^{-1}$, $\nu_2(A_1) = 620 \text{ cm}^{-1}$, $\nu_3(E) = 933 \text{ cm}^{-1}$, and $\nu_4(E) = 469 \text{ cm}^{-1}$. The ν_1 and ν_3 bands are stretching vibrations, whereas ν_2 and ν_4 are bending vibrations. However, coordination of the sulfite anion and interactions with other ions in the crystal lattice are expected to reduce the symmetry, shift the fundamentals and lift the degeneracy of the sulfite modes. In addition, sulfur ligation gives at least one very strong peak,^{5,12g,20a} at ~ 1170 – 1145 cm^{-1} and since in all cobalt(III)-sulfite compounds reported thus far,^{5,12g,20–22} the sulfite group is always S-bonded to Co^{III} , the existence of a peak(s) at such wavenumbers confirms the existence of Co^{III} center(s) in a compound. It is worth noting that compound **2** has two strong peaks at 1079 and 1061 cm^{-1} (Fig. S1,B†) which is unexpected for *O*-binding of the SO_3^{2-} group. Compound **1** shows a very strong and sharp peak at 3509 cm^{-1} which was assigned to the $\nu(\text{O-H})$ group.

Thermal analysis

The thermal decomposition of compound **2** occurs in two main steps (Fig. S2,† curve 2). The first step takes place at ~ 120 – $420 \text{ }^\circ\text{C}$ and is attributed to the removal of two sulfur dioxide



Scheme 2 Coordination modes of the sulfite anion in compound **1** (a and b) and **2** (c, d, e, f).

molecules. The second weight loss starts at $850 \text{ }^\circ\text{C}$ in a dynamic heating step and continues in the isothermal one with a slight mass loss and corresponds to the release of the other two molecules of sulfur dioxide resulting in the formation of the mixed metal oxides $2\text{Na}_2\text{OCo}^{\text{II}}\text{O}$. The experimental (calculated) percentage weight loss for the two stages is 22.06 (24.18) and 23.27 (24.18), respectively. The decrease of the sodium content in **1** in comparison with **2** results in a sharper first step (Fig. S2,† curve 1) at ~ 200 – $370 \text{ }^\circ\text{C}$ and is attributed to the removal of the ligated water molecule and of 1.25 molecules of sulfur dioxide, as well as to the dehydroxylation ($0.5\text{H}_2\text{O}$) of **1**. The removal of the remaining 0.75 molecules of sulfur dioxide also starts at $850 \text{ }^\circ\text{C}$ in a dynamic heating step and continues in the isothermal one with a slight mass loss resulting in the formation of the mixed metal oxides $0.5\text{Na}_2\text{OCo}^{\text{II}}\text{O}$. The experimental (calculated) percentage weight loss for the two stages is 31.93 (31.88) and 14.95 (14.35), respectively. The substitution of NH_4^+ ions for Na^+ ions in $3 \cdot 2\text{H}_2\text{O}$, and maybe the presence of the ligated ammonia molecules and of two crystalline water molecules, results in the decomposition of $3 \cdot 2\text{H}_2\text{O}$ at much lower temperatures in comparison with compounds **1** and **2**. The thermal decomposition of $3 \cdot 2\text{H}_2\text{O}$ occurs also in two main steps. The first step takes place at 40 – $450 \text{ }^\circ\text{C}$ (Fig. S2,† curve 3), and is attributed to the loss of the two crystalline water molecules, ten ammonia molecules [from four NH_4^+ counterions and the ligated six ammonia molecules to cobalt(III)] and three and a half sulfur dioxide molecules, as well as the dehydroxylation of $3 \cdot 2\text{H}_2\text{O}$. The second step takes place at 620 – $980 \text{ }^\circ\text{C}$ and is attributed to the removal of 2.5 sulfur dioxide molecules resulting in the formation of $\text{Co}^{\text{II}}\text{O Co}_2^{\text{III}}\text{O}_3$. The experimental (calculated) percentage weight loss for the two steps is 52.70 (50.62) and 18.58 (18.46), respectively.

UV-vis spectroscopy-NLO properties

The solid-state (diffuse reflectance) UV-vis spectra of compounds **1**–**3**·2H₂O are shown in Fig. S3.† The spectrum of **3**·2H₂O (Fig. S3,† C) is dominated by the bands due to the low-spin octahedral Co^{III} subunits.⁴⁸ The low-spin octahedral ground term is ¹A_{1g} and there are two relatively low lying spin allowed transitions, with lower lying spin triplet partners, all derived from (*t*_{2g})⁶(*e*_g). Under this scheme, the bands at ~430 and 650 nm are assigned⁴⁸ to the ¹A_{1g} → ¹T_{2g} and ¹T_{1g} transitions, respectively. The expected bands due to the ⁴T_{1g} → ⁴T_{1g}(P), ⁴A_{2g} transitions of the high-spin octahedral Co^{II}O₆ subunit (under *O*_h symmetry) may be hidden under the broad band covering the whole 600–700 nm range. In the spectrum of **1** (Fig. S3,† A), the multiple structure band at ~530 nm is assigned to the ⁴T_{1g} → ⁴T_{1g}(P) [under *O*_h] transition.⁴⁸ The multiple structure arises primarily from the admixture of spin forbidden transitions to doublet states mainly derived from ²G and ²H. The shoulder at ~670 nm is most probably due to the transition to ⁴A_{2g}. The interpretation of the spectrum of **2** (Fig. S3,† B) is difficult; the large number of maxima reflects the two different stereochemistries of the Co^{II} centers (tetrahedral and high-spin octahedral), with the ⁴A₂ → ⁴T₁(P) transition of the tetrahedral ligand field contributing to the multiple nature of the absorption in the visible region.⁴⁸ The NLO properties of compound **2** were studied in the solid state. Under laser irradiation at 590 nm, with a 5 ns pulse duration, the NLO properties of **2** were found to be limited; experiments using lasers in the picosecond time domain are underway.

Magnetism

Magnetic susceptibility measurements of compound **3**·2H₂O were carried out at different magnetic fields and in the temperature range 2–300 K. Fig. 8A shows the $\chi_M T$ versus *T* susceptibility

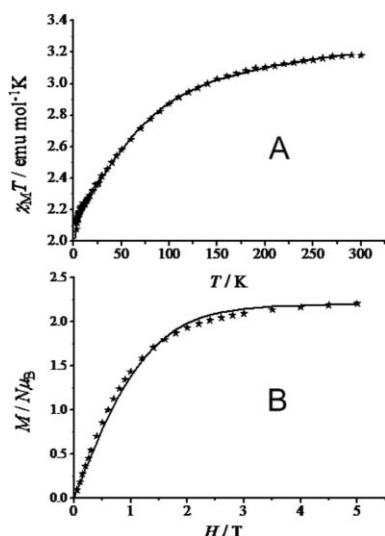


Fig. 8 Temperature dependence of the magnetic susceptibility of **3**·2H₂O, in the form of $\chi_M T$ vs. *T*, in the temperature range 2.0–300 K using an external magnetic field of 0.5 T. The solid line represents the fitting results (A). Magnetization of **3**·2H₂O, in the form of $M/N\mu_B$ vs. H/T , at 2 K and in the field range 0–5 T. The solid line represents the theoretical Brillouin function for an isolated $S = 1/2$ system with a $g_{\text{eff}} = 4.4$ (B).

data at 0.5 T of compound **3**·2H₂O, while the solid line represents the fit according to the following general Hamiltonian:

$$H = D \left[S_z^2 - \frac{1}{3} S(S+1) \right] + E(S_x^2 - S_y^2) + g\mu_B H \cdot S \quad (4)$$

All the parameters in eqn (4) have their usual definitions, and $S = 3/2$.

The $\chi_M T$ values decrease smoothly from 3.2 emu mol^{−1} K at 300 K to 3.0 emu mol^{−1} K at 150 K and then more steeply to a minimum value of 2.2 emu mol^{−1} K at 9 K. After that an abrupt decrease takes place to a value of 2.04 emu mol^{−1} K at 2 K. The high-temperature value of $\chi_M T$ is higher than 1.875 emu mol^{−1} K, the value which would be expected for a cobalt(II) system with an $S = 3/2$. This behavior is consistent with the presence of a significant orbital contribution to the anisotropic nature of the cobalt(II) system investigated. The employed fitting model for the susceptibility data is shown in eqn 4. The model takes into account: i) both the axial and rhombic parts of distortion of the crystal field (*D*, *E*), ii) an isotropic *g*-value, and iii) the mean field correction due to the intermolecular interactions with the fitting results yielding the following parameters: $D = 84(1)$ cm^{−1}, $E = 6(1)$ cm^{−1} $g = 2.56(1)$. The theoretical curve is shown as a solid line in Fig. 8A. It must be pointed out that the signs of the parameter *D* along with the parameter *E* are not resolved from the magnetic measurements, while introduction of an axial symmetry to the *g*-parameter (g_{\perp} , g_{\parallel}) leads to no improvement of the fit. The large value of the parameter *D* (and/or the small value of *E*) is in accordance with an octahedral cobalt(II) atom, where the ground state doublet is well-isolated from the excited ones.⁴⁹ The magnetization data for **3**·2H₂O in the form of $M/N\mu_B$ versus H/T , is shown in Fig. 8B, for 2 K and in the field range 0–5 T. The solid line represents the theoretical magnetization curve for a system having a ground state with an effective spin $S = 1/2$ and an effective *g* value equal to 4.4 at 2 K. The ground state of the free high-spin Co(II) atom in an octahedral environment is ⁴F, but the orbital degeneracy is removed in an octahedral crystal field yielding one ⁴A and two ⁴T levels, with the lowest-lying state being a ⁴T_{1g}. The degeneracy of the ⁴T_{1g} level is removed through the action of axial and rhombic distortions of the crystal field as well as through spin–orbit coupling. The overall effect of the low symmetry crystal-field components and spin–orbit coupling produces six Kramers' doublets and results in a doublet ground state. Taking into account that: i) the same doublet energy level remains lower in energy for all values of the applied field strength, and ii) the energy difference between the two lower lying doublets is relatively large with respect to the thermal energy present at low temperatures (<30 K), one could claim that the cobalt(II) system may be described as one having a ground state with an effective spin of $S = 1/2$.

Compounds **1** and **2** represent 2-D magnetic systems (**1** is crystallographically a 3-D network through hydrogen bonding and **2** is also crystallographically a 3-D network through Na⁺ ions), where the repeating unit is a dimer. The $\chi_M T$ values decrease from 7.4 and 6.0 emu mol^{−1} K at 300 K for **1** and **2**, respectively, to a value close to zero emu mol^{−1} K at 2 K for **1**, while the corresponding value for **2** is 0.9 emu mol^{−1} K (Fig. 9A and 10A, respectively). The difference in the magnetic behavior of compounds **1** and **2** is due to two major reasons: i) the fact that the crystal field

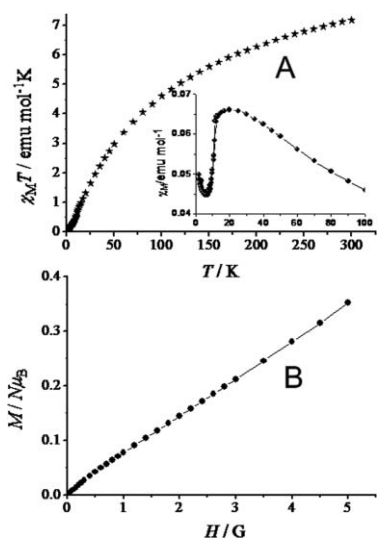


Fig. 9 Temperature dependence of the magnetic susceptibility of **1**, in the form of $\chi_M T$ vs. T , in the temperature range 2.0–300 K using an external magnetic field of 0.5 T. In the inset, it is shown the χ_M vs. T , in the temperature range 2.0–100 K, where the Curie tail is well resolved as well as the low temperature peak of the susceptibility data due to the low-dimensional character of the system (A). Magnetization of **1**, in the form of $M/N\mu_B$ vs. H/T , at 2 K and in the field range 0–5 T (B).

environment is different in these systems. In compound **1** there are two octahedral cobalt(II) atoms, while in compound **2** there are one octahedral and one tetrahedral cobalt(II) atoms, and ii) there is strong antiferromagnetic interaction leading to an $S = 0$ ground state in **1**, while in compound **2** there is an almost zero interaction leading to non-zero ground state (addition of the two non-interacting monomers). In addition, in the inset of Fig. 9A is shown the χ_M vs. T for compound **1**, where there is a pronounced peak denoting the 2-D magnetic character of the system, while at very low temperatures (< 4 K) there is a Curie tail due to a paramagnetic impurity. The above findings are further verified from the magnetization data (Fig. 9B and Fig. 10B) where

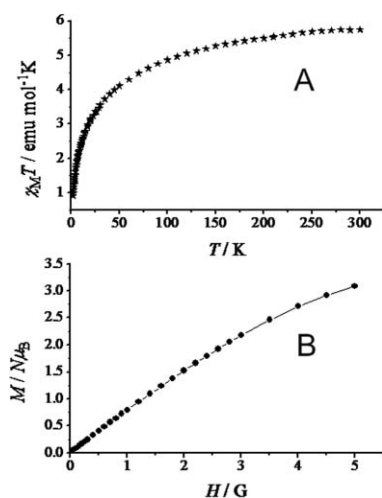


Fig. 10 Temperature dependence of the magnetic susceptibility of **2**, in the form of $\chi_M T$ vs. T , in the temperature range 2.0–300 K using an external magnetic field of 0.5 T (A). Magnetization of **2**, in the form of $M/N\mu_B$ vs. H/T , at 2 K and in the field range 0–5 T (B).

the ground state of **1** is zero (the small non-zero values are due to the paramagnetic impurity observed in the low temperature susceptibility data), while in compound **2** the two cobalt(II) atoms lead to a magnetization curve which is simply the addition of two almost not interacting cobalt(II) atoms with different crystal fields.

Conclusions

The strategy of hydrothermal reaction of $[\text{Co}^{\text{III}}(\text{NH}_3)_6]\text{Cl}_3$ with Na_2SO_3 led to the successful synthesis of the cobalt(II)-sulfite 2-D and 3-D inorganic coordination polymers $\{\text{Na}[\text{Co}^{\text{II}}_2(\text{SO}_3)_2(\mu_3\text{-OH})(\text{H}_2\text{O})]\}_\infty$ (**1**) and $\{\text{Na}_4[\text{Co}^{\text{II}}_2(\text{SO}_3)_4]\}_\infty$ (**2**), respectively. The sodium cation, which is present in compounds **1** and **2**, is structurally non-innocent and indeed substitution of $(\text{NH}_4)_2\text{SO}_3 \cdot \text{H}_2\text{O}$ for Na_2SO_3 resulted in the isolation of the 0-D trinuclear mixed-valence species $(\text{NH}_4)_4\{\text{Co}^{\text{II}}[\text{Co}^{\text{III}}(\text{SO}_3)_3(\text{NH}_3)_2]\}_2 \cdot 2\text{H}_2\text{O}$ (**3**·2H₂O). Compounds **1**–**3**·2H₂O were structurally and physico-chemically characterized. Variable temperature magnetic susceptibility studies for **1**–**3**·H₂O revealed that **1** and **2** are 2-D magnetic systems with antiferromagnetic interactions between cobalt(II) atoms, while the trinuclear **3**·2H₂O has two diamagnetic cobalt(III) atoms and a high spin cobalt(II) atom with $D = 84(1) \text{ cm}^{-1}$, $E = 6(1) \text{ cm}^{-1}$ and $g = 2.56(1)$. The compounds **1**–**3**·2H₂O reported here in parallel with other sulfite compounds,^{4–15} reveal that the sulfite anion is capable of simultaneously binding many metal atoms (Scheme 2); the short bridges generated in this way allow facile electronic communication between the metal centers, possibly leading to useful cooperative electronic/magnetic effects. In addition, this capability of SO_3^{2-} to simultaneously bind many metal atoms usually results in the formation of inorganic polymers such as compounds **1** and **2**, which hold a great promise as a source of new solids with useful properties. On the basis of the present study, it is clear that the field of metal-sulfite chemistry is quite a fruitful one, and new metal-sulfite coordination polymers and open-framework compounds, with novel physical properties, will appear in the near future.

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