Two New Mn(II) and Co(II) Complexes with the Tridentate 2,4,6-Tris(2-pyridyl)-1,3,5-triazine Ligand

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Two new complexes of manganese(II) and cobalt(II), $[Mn(tptz)(OCH_3CO)(H_2O)_2]ClO_4$ (**1**) and $[Co(tptz)\ (OSO_3)\ (H_2O)_2](H_2O)_2$ (**2**) {where tptz = 2,4,6-tris(2-pyridyl)-1,3,5-triazine}, have been prepared and characterised by elemental analyses, spectroscopic, electrochemical studies and single crystal X-ray diffraction. Single crystal X-ray analysis reveals complexes of Mn(II) and Co(II), where tptz remains intact and behaves as a tridentate ligand and forms heptacoordinated Mn(II) and hexacoordinated Co(II) complexes for **1** and **2**, respectively.

Key words: Heptacoordinated Mn(II), Hexacoordinated Co(II), Tptz

Introduction

Organic bridging ligands such as pyrazine (pyz) [1], pyrimidine (pym) [2], and 4,4'-bipyridine (bipy) [3] containing nitrogen donor atoms have been used extensively to organise ions, particularly transition metal ions, into a variety of architectures. Among these types of ligands more complex species which feature three or more potentially coordinating nitrogen atoms are known, such as 2,2'-bipyrimidine (bpym) [4], hexaazatriphenylene (hat) [5] and purine (pur) [6]. It is noteworthy to point out that the aforementioned ligands typically form chelates with metal cations. In the case of non-chelating ligands, multiple bonding modes are often possible. This requires assessments of geometrical considerations, especially when the N atoms are in reasonably close proximity to one another.

Another interesting molecule having polydentate nitrogen donor sites that has been currently utilised in crystal engineering is 2,4,6-tris(2-pyridyl)-1,3,5-triazine (tptz) shown in Fig. 1. Tptz was first prepared by Case and Koft [7]. It has gained considerable importance because of its use as a spacer for the design of supramolecular complexes [8]. It has been used in spectrophotometric determination of transition metal ions and as an analytical reagent for various metal ions [9]. It has been shown that polydentate nitrogen ligands can separate actinides from the lanthanides which is essential in the partition step for the safe long term treatment and management of radioactive wastes [10]. The tptz complexes can be used in a variety of electrochemical / photocatalytic reactions. Thorp *et al.* synthesised some derivatives of complexes based on $[Ru(tpy)(bpy)OH_2]^+$ which were found to have unusual DNA binding or cleavage properties [11]. A number of transition metal and lanthanide complexes of the same ligand have also been reported [12, 13]. Tptz can also function simultaneously as a tridentate and a bidentate ligand and has been used to prepare dicobalt, dimercury and diruthenium complexes [14]. The possibility of this ligand to form complexes with the metals through terpyridine- and bipyridine-like sites simultaneously has also been well characterised [9]. Tptz is a planar molecule and

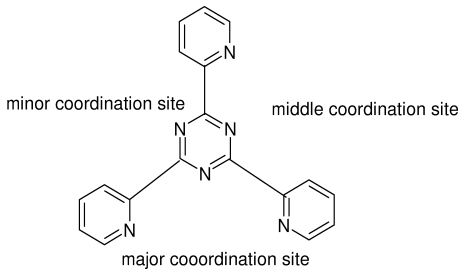

Fig. 1. Coordination sites in 2,4,6-tris(2-pyridyl)-1,3,5-triazine.

has three "coordination sites" (major, middle and minor) according to the number of donor nitrogen atoms (three, two and one, respectively). The major coordination site contains three nitrogen atoms (Fig. 1) and can form complexes with both cations and anions. The middle coordination site contains two nitrogen atoms – one in a pyridine and one in a triazine ring but also a C–H bond which may hinder ions to coordinate to the nitrogen atoms. The minor coordination site contains only one nitrogen atom from the triazine ring which makes it unlikely to form complexes with any ions. The complexing ability of tptz depends in part upon the size of the metal cations, because it normally coordinates as a tridentate (chelating) ligand to give a metal:ligand ratio of 1:1 [15]. The described possibilities render this ligand particularly amenable to the design and construction of multidimensional arrays.

2,4,6-Triaryltriazines are usually stable towards hydrolysis and concentrated mineral acid and temperatures above 150 °C are required for their hydrolytic reaction [16]. However, Lerner and Lippard found that Cu(II) ions in aqueous media promoted the hydrolysis of tptz to the bis-(2-pyridylcarbonyl)amide anion [17] and crystallographic characterisation of Cu(II) complexes with hydrolysed tpmtz and tptz were also reported [9, 18].

In the present paper, we report the synthesis, crystal structure and spectral characterisation of two complexes $[Mn(tptz)(OCH_3CO)(H_2O)_2]ClO_4$ (**1**) and $[Co(tptz)\ (OSO_3)(H_2O)_2](H_2O)_2$ (**2**), where tptz remains intact and behaves as a tridentate ligand.

Results and Discussion

Complex **1** was synthesised by refluxing an ethanolic solution of $Mn(CH_3COO)_2$ with tptz followed by the addition of excess $NaClO_4$, and complex **2** was prepared by refluxing a mixture of $CoSO_4$ and tptz in water-ethanol medium.

Infrared spectra

The infrared spectra of the two complexes **1** and **2** are very much consistent with the structural data presented in this paper. Peaks at 3650 – 3300 cm^{-1} (**1**) and 3550 – 3480 cm^{-1} (**2**) are attributable to O-H stretching vibrations of water molecules and indicate the presence of hydrogen bonding. Strong bands at 1560 and 1520 cm^{-1} for **1** and 1572 and 1524 cm^{-1} for **2** correspond to the coordinated tptz ligand. Peaks at 1625, 1593, 1530, 1479, 1461, 1443, 1369 and 973 cm^{-1} present in both **1** and **2** can be assigned for the C=C and C=N ring stretching vibrations. Peaks at 766 cm^{-1} (C-H stretching) and 586 cm^{-1} (pyridyl out-of-ring deformation) is also observed for both the complexes [19]. Bands in agreement with coordinated perchlorate anions could also be observed for compound **1** at 1150, 1150, 1115, 1090 cm^{-1}. The characteristic strong bands of carboxylate groups appeared at 1560 (for asymmetric stretching) and 1416 cm^{-1} (for symmetric stretching) [19]. The difference ($\Delta\nu = 144$ cm^{-1}) between $\nu_{asym}(COO^-)$ and $\nu_{sym}(COO^-)$ bands suggests the presence of chelating acetate group linked with the metal centre for complex **1** [19]. Peaks due to a monodentate SO_4^{2-} group are observed at 1012 and 1118 cm^{-1} [19]. Bands appearing at 465, 355, 456 and 378 cm^{-1} correspond to ν(Mn-N), ν(Mn-O), ν(Co-N), and ν(Co-O), respectively.

Electronic spectra

The electronic spectrum of **1** was recorded in dimethylformamide and showed two strong bands at about 240 and 265 nm which are clearly charge transfer in origin and the absorption band observed at 295 nm can be assigned to the charge transfer from the coordinated ligand to the Mn(II). The complex does not show any *d-d* transition [20].

The electronic spectrum of **2** was recorded in methanol and displayed two strong absorption bands at about 205 and 210 nm. These are clearly charge transfer in origin and the absorption band observed at 302 nm can be assigned to the charge transfer from the coordinated ligand to the Co(II). Complex **2** also does not show any *d-d* transition [20].

Electrochemical study

The electrochemical studies of complexes **1** and **2** were performed using dimethylformamide and methanol, respectively, as solvent and tetrabutylammonium perchlorate as supporting eletrolyte at a scan rate of 50 mV sec^{-1}. For complex **1**, one irreversible reductive response at -1.05 V *vs.* SCE was observed which is attributed to ligand-centered reduction. For complex **2**, one reductive response at -0.7 V *vs.* SCE was observed and tentatively assigned to the reduction of coordinated ligand [21]. For both the complexes, no oxidation response was found on the positive side of SCE.

Magnetic study

The effective magnetic moment at 20 °C for complex **1** and **2** are 5.98 and 3.94 B. M., respec-

Table 1. Crystallographic data for complexes **1** and **2**.

	1	**2**
Chemical formula	$C_{20}H_{15}MnN_6ClO_8$	$C_{18}H_{20}CoN_6O_8S$
Formula weight	557.77	539.39
Crystal system	triclinic	triclinic
Space group	*P*-1	*P*-1
a [Å]	9.9120(4)	7.6948(15)
b [Å]	10.8770(4)	11.662(2)
c [Å]	11.7830(5)	12.385(3)
α [°]	78.739(2)	84.92(3)
β [°]	72.044(2)	75.16(3)
γ [°]	70.973(3)	74.94(3)
V [Å^3]	1136.10(8)	1037.10(4)
Z	2	2
Reflections collected	10264	9684
Independent reflections	3824	3507
Density (calculated)	1.630 Mg/m^3	1.727 Mg/m^3
Absorption coefficient	6.358 mm^{-1}	0.991 mm^{-1}
$F(000)$	566	554
Crystal size [mm^3]	$0.06 \times 0.08 \times 0.25$	$0.83 \times 0.50 \times 0.32$
θ Range for data coll.	4.00 to 73.20°	1.70 to 24.71°
R Indices (all data)	$R_1 = 0.0508$	$R_1 = 0.0883$
	$wR2 = 0.0769$	$wR2 = 0.1288$
Final *R* indices	$R_1 = 0.0349$	$R_1 = 0.0620$
$[I > 2\sigma(I)]$	$wR2 = 0.0745$	$wR2 = 0.1192$
Largest diff. peak and hole [eÅ^{-3}]	0.14, −0.11	0.58, −0.60

tively, which are nearer to the spin-only value of manganese(II) and cobalt(II) ion relative to mercury(tetrathiocyanato)cobaltate as the standard.

Crystal structures

$[Mn(tptz)(OCH_3CO)(H_2O)_2]ClO_4$ (**1**): A perspective view of complex **1** with atom numbering scheme is shown in Fig. 2 and selected bond lengths and angles are summarised in Table 2. Here, tptz acts as a tridentate ligand through its major coordination site. The cental manganese atom adopts the common coordination geometry for seven coordinated manganese(II) complexes – distorted pentagonal-bipyramidal. The basal plane is formed by the three nitrogen atoms N1, N2 and N3 from the triazine ligand and the two oxygen atoms from the acetate group and axial sites are occupied by the oxygen atoms of the two coordinated water molecules yielding O3-Mn1-O4 as the *trans-axial* angle (172.4(2)°). The deviation from ideal pentagonal-bipyramidal geometry is indicated by the difference in the basal angles which vary from 57.1(2) to 80.7(2)°. The source of distortion primarily comes from the bites taken by the ligand. The bite angles N1-Mn1-N2 and N2-Mn1-N3 are 68.5(2)° and 69.3(2)°, respectively, significantly smaller than the ideal value of 72°, because of the constraint imposed in the five-membered

Table 2. Selected bond distances (Å) and angles (°) for complex **1**.

Mn1-O3	2.212(5)	Mn1-O4	2.189(5)
Mn1-O1	2.307(4)	Mn1-O2	2.267(5)
Mn1-N1	2.399(5)	Mn1-N2	2.279(5)
Mn1-N3	2.375(5)		
C5-C6	1.483(9)	C8-C9	1.485(8)
C7-C14	1.497(8)		
O1-Mn1-O2	57.10(15)	O1-Mn1-N1	84.44(16)
O2-Mn1-N3	80.74(16)	N1-Mn1-N2	68.53(17)
N3-Mn1-N2	69.32(17)	O3-Mn1-O4	172.44(16)

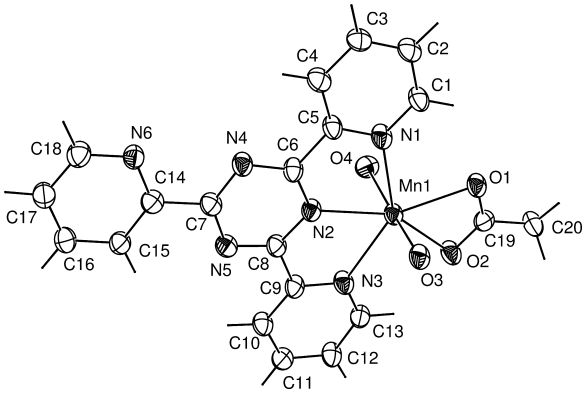

Fig. 2. Perspective view of complex **1** with atom numbering scheme. Lattice water and perchlorate molecules are omitted for clarity.

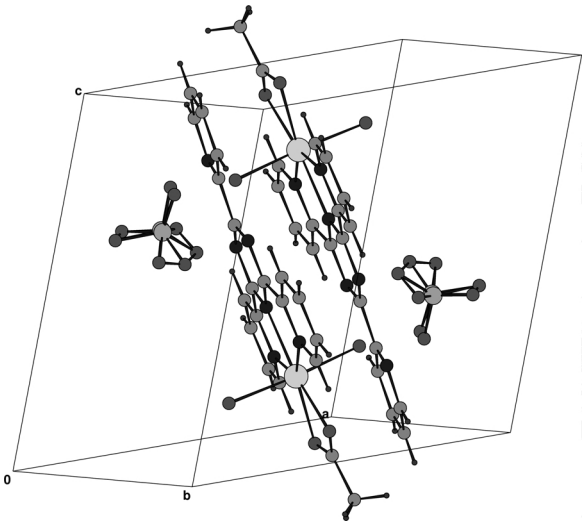

Fig. 3. Packing diagram of complex **1**.

chelate rings. The two axial distances are shorter (Mn1-O3, 2.212(5) and Mn1-O4, 2.189(5) Å) than the equatorial bond distances (Mn1-O1, 2.307(4); Mn1-O2, 2.267(5); Mn1-N1, 2.399(5); Mn1-N2, 2.279(5); Mn1-N3, 2.375(5) Å) which are more or less compa-

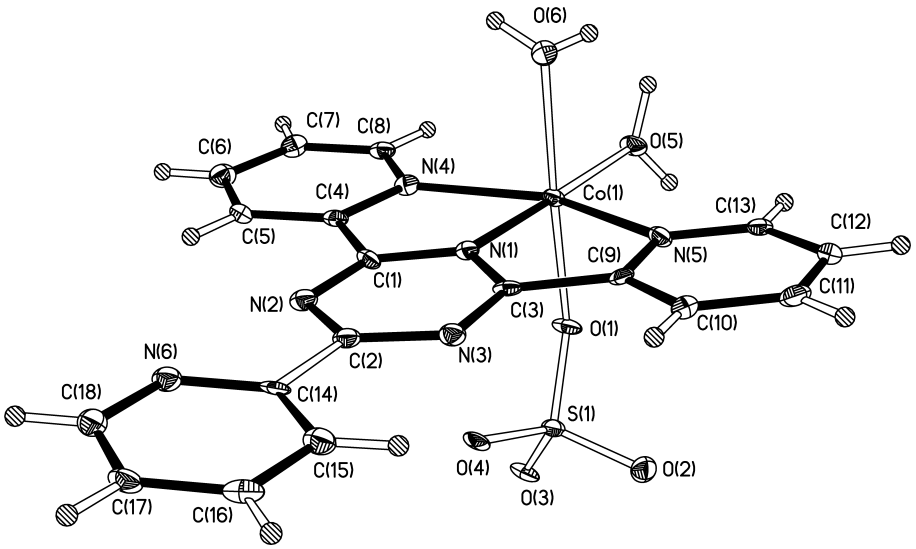

Fig. 4. Perspective view of complex **2** with atom numbering scheme. Lattice water molecules are omitted for clarity.

rable to similar systems [22a]. The Mn-O3, O4(water) distances are somewhat shorter than the average Mn-O1,O2 (acetate) distances, probably due to the limited O1-C1-O2 bite angle of acetate. The bond distance of Mn(II) to the middle nitrogen N(2) is significantly shorter than the Mn1-N(1) and Mn1-N(3) distances, which is usually observed in tptz-type ligands [22, 23]. There are two asymmetric molecules in one unit cell and they are stacked in the alternate fashion. One perchlorate anion is present in the lattice for each molecule. The tptz ligand is almost planar; the angles between the central triazine ring and the attached pyridyl rings are 3.2(2)°, 3.4(2)°, 3.9(2)° [13e] and the tptz plane is inclined by an angle of 3.8(6)° to the bidentate acetate plane. In the tptz, $C(sp^2)$ – $C(sp^2)$ distances within the ring are normal (1.378 Å) and the exterior bonds (C(5)-C(6), 1.483(9) Å; C(8)-C(9), 1.485(8) Å; C(7)-C(14), 1.497(8) Å) are also normal. The manganese atom is 0.013(2) Å out of the basal pentagonal plane. The deviations of the atoms N1, N2, N3, O1, O2 from the mean basal plane are −0.06, −0.05, −0.01, 0.06, −0.04. There exist several weak hydrogen bondings involving the perchlorate anions, pyridyl hydrogen atoms and the oxygen atom from the acetate group. The packing diagram of complex **1** is shown in Fig. 3.

$[Co(tptz)(OSO_3)(H_2O)_2](H_2O)_2$ (**2**): A perspective view of the complex **2** with an atom numbering scheme is shown in Fig. 4 and selected bond lengths and angles are summarised in Table 3. In the present structure, the cobalt(II) atom is covalently bound within the major coordination site. The tptz acts as a tridentate ligand. One nitrogen from triazine and two from pyridyl moieties along with the two water molecules and one sulphate anion form the distorted octahedral geometry around Co(II). Three nitrogen atoms (N(4), N(1) and N(5)) from the tptz ligand and O(5) (water) form the mean equatorial base, while O(6) from water and O(1) from unidentate sulphate occupy the axial positions. There are four asymmetric units in one unit cell, where each two pairs are in staggered orientation. The deviation from ideal octahedral geometry is indicated by the difference in *cisoid* (73.89(16)° to 106.64(16)°) and *transoid* angles (148.98(15)° to 178.05(17)°). The deviations of the atoms N(4), N(1), N(5) and O(5) from the mean basal plane are 0.004, 0.005, 0.004, 0.003 Å. The source of distortion primarily comes from the bites taken by the ligand; the bite angles N(4)-Co(1)-N(1) and N(1)-Co(1)-N(5) are 73.89(16)° and 75.13(16)°, respectively, significantly smaller than the ideal value of 90°. The bond distance of Co(II) to the middle nitrogen N(1) (2.048(4) Å) is significantly shorter than the Co(1)-N(4) (2.201(4) Å) and Co(1)-N(5) (2.170(4) Å)

Table 3. Selected bond distances (Å) and angles (°) for complex **2**.

Co(1)-O(5)	2.028(4)	Co(1)-N(1)	2.048(4)
Co(1)-O(1)	2.081(3)	Co(1)-O(6)	2.145(4)
Co(1)-N(5)	2.170(4)	Co(1)-N(4)	2.201(4)
O(5)-Co(1)-N(1)	178.05(17)	O(5)-Co(1)-O(6)	89.23(18)
O(5)-Co(1)-N(5)	104.26(16)	N(1)-Co(1)-N(5)	75.13(16)
O(5)-Co(1)-N(4)	106.64(16)	N(1)-Co(1)-N(4)	73.89(16)
N(5)-Co(1)-N(4)	148.98(15)		

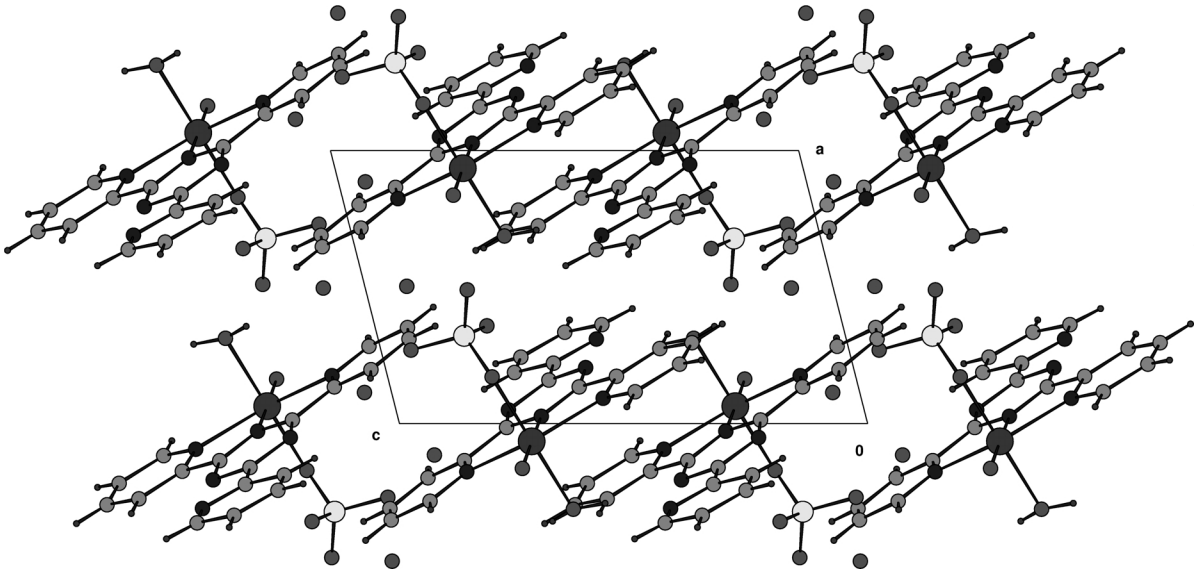

Fig. 5. Packing diagram of complex **2**.

distances, a pattern usually observed in this type of three point attachment of tptz-type ligands [24]. The Co(1)-O (water) distances vary from 2.028(4) Å to 2.145(4) Å and Co(1)-O(SO_3^{2-}) is 2.028(4) Å. In the ligand tptz, the C(sp^2) - C(sp^2) distances within the ring are normal (in the range 1.364(8) to 1.389(8) Å) and the exterior bond distances C(1)-C(4), 1.489(7) Å; C(2)-C(14), 1.480(7) Å and C(3)-C(9), 1.471(7) Å are also normal. The tptz ligand deviates not much from planarity [13b, 13e]; the three pyridyl rings are twisted with respect to the central triazine ring by angles of 4.22°, 2.96° and 8.11° with the non-coordinating ring displaying the highest degree of twisting. There are extensive arrays of hydrogen bonds involving the coordinated sulphate ion, coordinated water as well as lattice water molecules and the pyridyl hydrogen atoms. The packing diagram of complex **2** is shown in Fig. 5.

Experimental Section

Materials

All the chemicals and solvents used for the synthesis were of reagent grade. $Mn(CH_3COO)_2 \cdot 4H_2O$, $NaClO_4$, $CoSO_4 \cdot 7H_2O$ (Fluka), 2,4,6-tris(2-pyridyl)-1,3,5-triazine (Aldrich) were used as received.

Caution! Although no problems were encountered in this work, perchlorate salts are potentially explosive. They should be prepared in small quantities and handled with care.

Physical techniques

The infrared spectra of complex **1** and **2** were recorded on a Perkin-Elmer FT-IR spectrometer with a KBr disc. The electronic spectra were recorded on a Perkin-Elmer Lambda 40 (UV-vis) spectrophotometer in dimethylformamide and methanol. Elemental analyses were carried out using a Perkin-Elmer 2400 II elemental analyser. Electrochemical studies were performed on a CH 600A cyclic voltammeter instrument using dimethylformamide and methanol as solvents for complex **1** and **2**, respectively, and using tetrabutylammonium perchlorate as the supporting electrolyte. Magnetic susceptibilities were measured on a powder sample in a vibrating sample magnetometer using mercury(tetrathiocyanato)cobaltate as the standard.

*Synthesis of [Mn(tptz)(OCH_3CO)(H_2O)$_2$]ClO_4 (**1**)*

$Mn(CH_3COO)_2 \cdot 4H_2O$ (0.246 g, 1.0 mmol) and tptz (0.312 g, 1.0 mmol) were dissolved in 20 ml of ethanol and the reaction mixture was refluxed for 3 h. The light yellow coloured solution was cooled to 20 °C and an excess of sodium perchlorate was added. Slow evaporation of the solvent at 20 °C afforded yellow single crystals after 2 days. Yield: 0.39 g (70%). Analysis for $C_{20}H_{15}MnN_6ClO_8$: calcd. C 43.03, H 2.69, N 15.06, Mn 9.85; found C 43.10, H 2.66, N 15.01, Mn 9.81.

*Synthesis of [Co(tptz)(H_2O)$_2$(OSO_3)](H_2O)$_2$ (**2**)*

$CoSO_4 \cdot 7H_2O$ (0.281 g, 1.0 mmol) and tptz (0.312 g, 1.0 mmol) were dissolved in 20 ml of water-ethanol and the

reaction mixture was refluxed for 3 h. The orange coloured solution was cooled to 20 °C. Slow evaporation of the solvent at 20 °C afforded red single crystals after 1 day. Yield: 0.35 g (65%). Analysis for $C_{18}H_{20}CoN_6O_8S$: calcd. C 40.04, H 3.71, N 15.57, Co 10.93; found C 40.01, H 3.66, N 15.55, Co 10.89.

X-ray crystallography

The X-ray single crystal data for the compound **1** were collected on a MacScience DIP-Labo diffractometer using graphite-monochromatised Cu-K_α radiation (λ = 1.54184 Å). Crystallographic data and some features of the structure refinements are listed in Table 1. Calculations were performed using maXus [25a] crystallographic software package. The structure was solved by direct methods using the SHELXS97 [25b] system and refined by a full-matrix least-squares methods based on F^2 using SHELXL97 [25c]. Disorder of a perchlorate anion was observed. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms of water molecules were omitted, and other hydrogen atoms were placed at idealised geometry.

The X-ray single crystal data for the compound **2** were collected on a Bruker SMART APEX CCD diffractometer using graphite-monochromatised Mo-K_α radiation (λ = 0.71073 Å), and the ω scan technique was used to collect the data sets. Crystallographic data and some features of the structural refinements are listed in Table 1. The data were corrected for absorption effects with SAINT [26a] and SADABS [26b], respectively. The structures were solved by direct methods SHELXTL [26c] and refined by full-matrix least-squares method SHELXL97 [26d]. All the non-hydrogen atoms were refined anisotropically.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 233904 and 233905 for **1** and **2** respectively. Copies of this information may be obtained free of charge from The Director, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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