Polyhedron 30 (2011) 1927-1934

Contents lists available at ScienceDirect

Polyhedron



journal homepage: www.elsevier.com/locate/poly

A seven membered chelate ring complex of Mn(II) derived from bis(5-phenyl-2H-1,2,4-triazole)-3-yl-disulfane and cleavage of the S-S bond in a Co(II) complex: Synthesis, spectral and structural characterization

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ARTICLE INFO

Article history: Received 4 January 2011 Accepted 18 March 2011 Available online 19 May 2011

Keywords: Seven membered chelate ring Triazole complexes Thermolysis Mn(II) and Co(II) complexes Mixed ligand complexes o-Phenanthroline

1. Introduction

1,2,4-Triazoles and their derivatives represent an interesting class of heterocyclic compounds possessing a wide spectrum of biological activities. A large number of 1,2,4-triazoles are known to exhibit bactericidal, fungicidal, antitubercular, analgesic, antiinflammatory, antitumor, anticonvulsant, antiviral, insecticidal, antidepressant and central nervous system (CNS) activities [1-11]. Derivatives of 1,2,4-triazole were synthesized by intramolecular cyclization of substituted thiosemicarbazides [12]. A series of alkyl/aryl-2,4-dihydro-5-(2-furyl)-3H-1,2,4-triazole-3-thione have been reported [13] and the thione form was proposed as the most stable form in the solid state. The disulfanes behave as bidentate N-donor ligands, although the sulfur atom has additional reactivity [14]. Metal-ligand reactions under thermolysis conditions offer a promising technique for the design and syntheses of novel coordination architectures, especially for those that are inaccessible by direct preparations. In recent years, organic disulfide compounds such as 4,4'-dipyridinedisulfine, 2,2'-dipyridinedisulfine and *bis*((4-pyridin-2-yl)pyrimidin-2-yl) disulfane have received increasing attention since they are capable of displaying different reactions in various circumstances, giving rise to metal organic frameworks with fascinating structures [15,16]. Likewise, under

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ABSTRACT

The reaction of Mn(OAc)₂·4H₂O with *bis*(5-phenyl-2H-1,2,4-triazole)-3-yl-disulfane (H₂ptds 2H₂O) (1) yielded new complex [Mn(ptds)(o-phen)₂] (2). It is observed that under similar conditions the reaction of $Co(OAc)_2$ with $H_2ptds 2H_2O$ (1) leads to thermolysis of the S-S bond of the disulfane to yield [Co(pts)(o-phen)₂]·H₂O·0.5C₂H₅OH, with the newly generated organic ligand 5-phenyl-2H-1,2,4-triazole-3-sulfinate, $(pts)^{2-}$. The ligand H₂ptds·2H₂O (1), $[Mn(ptds)(o-phen)_2]$ (2) and $[Co(pts)(o-phen)_2]$. H₂O·0.5C₂H₅OH (**3**) crystallized into monoclinic, trigonal and triclinic crystal systems, respectively. The triazole ring nitrogen of the bidentate ligand chelates the Mn(II) center forming a seven membered chelate ring, while N, O donor sites of the resulting triazole sulfinate bond Co(II) to form a five membered chelate. The resulting complexes are paramagnetic and have a distorted octahedral geometry.

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different thermolysis conditions with different metal salts, H₂ptds may undergo either S–S bond cleavage or C–S bond scission [17,18] to produce complexes of a newly generated ligand. Additionally even in normal solution reactions, extrusion or insertion of one sulfur atom may take place [19]. Irrespective of increasing research enthusiasm on the reactions of organic disulfide compounds with metal ions, the ambiguous reactivity of disulfides in the presence of different metal ions, to the best of our knowledge, is rarely noticed. Herein, we report our results on the reactivity of a newly synthesized ligand, bis(5-phenyl-2H-1,2,4-triazole)-3-yl-disulfane (H₂ptds)·2H₂O, its Mn(II) complex and the Co(II) complex of the thermolytic product, containing o-phen as a coligand.

2. Experimental

2.1. Materials and methods

Commercial reagents were used without further purification and all experiments were carried out in the open atmosphere. Thiosemicarbazide, benzoyl chloride (SD Fine Chemicals, India) and NaOH (Qualigens, India) were used as received. All the solvents were purchased from Qualigens Chemicals, India and used after purification.

2.2. Preparation of 1-(2-phenyl)-3-thiosemicarbazide

Thiosemicarbazide (2.73 g, 20 mmol) was dissolved in aqueous sodium hydroxide (10%, 20 ml) and the resulting solution was



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filtered off. Benzoyl chloride (4.0 ml) was added dropwise to the above solution, shaken continuously for 15 min, cooled in ice and acidified with dil. HCl. A white precipitate was obtained which was filtered, washed with water and air dried. Yield 87% ; m.p. 440 K.

2.3. Synthesis of bis(5-phenyl-2H-1,2,4-triazole)-3-yl-disulfane (H₂ptds·2H₂O) (**1**)

Bis(5-phenyl-2H-1,2,4-triazole)-3-yl-disulfane was synthesized by dissolving the freshly prepared 1-(2-phenyl)-3-thiosemicarbazide (3.9 g, 20 mmol) in aqueous NaOH (10%, 10 ml) and refluxing the solution for 2–3 h until it turned green due to evolution of H₂S gas. The solution was cooled in ice and acidified with conc. HCl. The white precipitate so obtained was filtered, washed with water, air dried and crystallized from ethanol. Yield 70%; m.p. 538 K. *Anal.* Calc. for C₁₆H₁₆N₆S₂O₂ (388.46): C, 49.46; H, 4.11; N, 21.62; S, 16.50. Found: C, 49.50; H, 4.05; N, 21.55; S, 16.45%. IR (*v*/cm⁻¹, KBr): *v*(OH) 3430; *v*(NH) 3363s; *v*(N–N) 1078; *v*(C=N) 1608s; *v*(C=S) 972. ¹H NMR (300 MHz, DMSO-d6; δ ppm): 7.51–7.95 (m, 5H, -C₆H₅), 13.66–13.83 (d, 2H, -NH). ¹³C NMR (DMSO-d₆; δ ppm): 167.06 (>C=S), 150.32 (>C=N), 125.5–130.70 (phenyl ring carbons). UV–Vis (λ_{max}, Nujol mull, nm): 324, 314, 304, 258, 231.

2.4. Preparation of $[Mn(ptds)(o-phen)_2]$ (2)

A methanolic solution of $Mn(OAc)_2 \cdot 4H_2O(0.244 \text{ g}, 1 \text{ mmol})$ was added to a methanol solution of *bis*(5-phenyl-2H-1,2,4-triazole)-3yl-disulfane (0.384 g, 1 mmol) with continuous stirring for 30 min. The resulting precipitate was filtered and washed with ethanol and air dried. The precipitate was suspended in methanol and heated for 30 min with a methanolic solution of *o*-phen (0.400 g, 2 mmol), whereupon it changed into a clear solution which was filtered and kept for crystallization. After slow evaporation of the solution for 10 days, yellow crystals of **2** suitable for X-ray analyses were obtained. Yield 55%; m.p. 573 K. *Anal.* Calc. for $C_{40}H_{26}MnN_{10}S_2$ (765.79): C, 62.73; H, 3.42; N, 18.28; S, 8.37. Found: C, 62.55; H, 3.50; N, 18.36; S, 8.30%. IR (ν /cm⁻¹, KBr): ν (C=N) 1578s; ν (N–N) 1098; ν (C–S) 982. UV–Vis (λ_{max} , Nujol mull, nm): 450, 427, 362, 339, 306, 271.

2.5. Preparation of $[Co(pts)(o-phen)_2] \cdot H_2O \cdot 0.5C_2H_5OH$ (3)

A methanolic solution of Co(OAc)₂ (0.178 g, 1 mmol) was added to a methanol solution of *bis*(5-phenyl-2H-1,2,4-triazole)-3-yldisulfane (0.384 g, 1 mmol) with continuous stirring for 30 min. The resulting green color precipitate was filtered and washed with ethanol and air dried. The precipitate was suspended in methanol and refluxed with a methanolic solution of *o*-phen (0.400 g, 2 mmol). The suspension changed to a reddish-brown clear solution which was filtered and kept for crystallization. Orange crystals of **3** suitable for X-ray analyses were obtained by slow evaporation of its MeOH solution over a period of 14 days. Yield 60%; m.p. 579 K. *Anal.* Calc. for C₆₆H₅₂Co₂N₁₄O₇S₂ (1335.20): C, 59.31; H, 3.89; N, 14.67; S, 4.79. Found: C, 59.25; H, 4.00; N, 14.75; S, 4.70%. IR (ν/cm^{-1} , KBr): $\nu(C=N)$ 1625s; $\nu(N-N)$ 1101; $\nu_{assy}(SO_2)$ 1295; $\nu_{sym}(SO_2)$ 1101; $\nu(C-S)$ 987. UV–Vis (λ_{max} , Nujol mull, nm): 540, 480, 420, 374, 335, 307.

2.6. Physical measurements

Carbon, hydrogen and nitrogen contents were determined on a Carlo Erba 1108 model microanalyser. Magnetic susceptibility measurements were performed at room temperature on a Cahn



Scheme 1. Synthesis of the ligand and the complexes.

Table	1
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Crystallographic data for H₂ptds·2H₂O (1), [Mn(ptds)(o-phen)₂] (2), [Co(pts)(o-phen)₂]H₂O·0.5C₂H₅OH (3).

Compound	1	2	3
Empirical formula	$C_{16}H_{12}N_6O_2S_2$	$C_{40}H_{26}MnN_{10}S_2$	C66H52C02N14O7S2
Formula weight	384.46	765.79	1335.20
T (K)	293	293	298
λ (Å)	0.71073	0.71073	0.71073
Crystal system	monoclinic	trigonal	triclinic
Space group	C2/c	P 31 2 1	ΡĪ
Unit cell dimensions			
a (Å)	12.4335(10)	9.8038(3)	10.4590(5)
b (Å)	14.7236(9)	9.8038(3)	12.7063(5)
c (Å)	10.3007(9)	31.7523(9)	12.8046(5)
β(°)	103.990(9)	90.000(0)	85.016(4)
<i>V</i> (Å ³)	1829.8(3)	2642.98(1)	1542.83(11)
Ζ	4	4	1
$\rho_{\rm calc} ({\rm g}{\rm cm}^{-3})$	1.396	1.95	1.437
$\mu (\mathrm{mm}^{-1})$	0.314	0.721	0.673
F(0 0 0)	792.0	1611.6	688
Crystal size (mm)	$0.66 \times 0.41 \times 0.29$	$0.30\times0.28\times0.25$	$0.29 \times 0.27 \times 0.25$
Number of reflections collected	2084	3794	11257
Number of independent reflections (R_{int})	2438 (0.0236)	3794 (0.0176)	6841 (0.0230)
Number of data/restraints/parameters	2084/0/118	3794/0/240	6841/6/447
Goodness-of-fit (GOF) on F^2	1.051	0.893	0.932
$R_1, w R_2^{a,b} [(I > 2\sigma(I))]$	0.060, 0.162	0.031, 0.055	0.050, 0.1267
R_1 , $wR_2^{a,b}$ (all data)	0.077, 0.174	0.047, 0.058	0.089, 0.1405
Largest difference in peak and hole ($e A^{-3}$)	0.583, -0.690	0.223, -0.250	0.223, -0.250

^a
$$R_1 = \Sigma ||F_0| - |FC||\Sigma |F_0|.$$

^b
$$R_2 = \left[\sum_{w} (|F_0^2| - |F_c^2|)^2 / \sum_{w} |F_0^2|^2\right]^{1/2}.$$

Faraday balance using Hg[Co(NCS)₄] as the calibrant. Electronic spectra were recorded on a Shimadzu 1700 UV–Vis spectrophotometer as Nujol mulls. IR spectra were recorded in the 4000–400 cm⁻¹ region as KBr pellets on a Varian 3100- FT IR spectrophotometer. ¹H and ¹³C NMR spectra were recorded in DMSO-d₆ on a JEOL AL 300 FT NMR spectrometer using TMS as an internal reference.

3. Crystal structure determination

Data for the structures **1–3** were obtained at 296(2) K on an Oxford Diffraction Gemini diffractometer equipped with CrysAlis Pro., using a graphite mono-chromated Mo K α (λ = 0.71073 Å) radiation source. The structures were solved by direct methods (SHELXL-2008) and refined against all data by full matrix least-squares on F^2 using anisotropic displacement parameters for all non-hydrogen atoms. All hydrogen atoms were included in the refinement at geometrically ideal positions and refined with a riding model [20]. The MER-CURY package and ORTEP-3 for Windows program were used for generating molecular graphics [21,22]. In complex **3**, the solvent molecules are not at full occupancy, therefore the occupancy was tested and the best value was near 0.5. So the occupancy of the solvent was fixed at 0.5.

4. Results and discussion

The ligand *bis*(5-phenyl-2H-1,2,4-triazole)-3-yl-disulfane (H₂ptds·2H₂O) (**1**) reacted with Mn(OAc)₂·4H₂O and Co(OAc)₂ to form yellow and green precipitates respectively, which dissolved in a methanolic solution of *o*-phen under hot conditions yielding [Mn(ptds)(*o*-phen)₂] (**2**) and [Co(pts)(*o*-phen)₂]·H₂O·0.5C₂H₅OH (**3**). Complex **3** is formed after S–S bond cleavage and aerial oxidation of sulfur, whereas such cleavage did not occur in the case of complex **2** in which only mild heating was required to dissolve the binary complex of manganese(II). These complexes are stable towards air and moisture. Scheme 1 depicts the formation of the ligand and its complexes which contain ptds^{2–} and (pts)^{2–} as

Table 2Selected bond lengths (Å) and angles (°) for $H_2ptds \cdot 2H_2O$.

Bond lengths	Bond angles

S(1)-C(1)	1.7574(1)	$C(1)-S(1)-S(1_2)$	101.17(10)
N(1)-C(1)	1.3202(1)	C(2)-N(3)-C(1)	103.0(2)
$S(1)-S(1_2)$	2.0585(2)	N(3)-C(2)-C(3)	125.9(2)
N(3)-C(2)	1.3329(1)	N(1)-N(2)-C(2)	109.6(2)
N(3)-C(1)	1.3545(1)	C(2)-C(3)-C(8)	120.0(3)
N(1)-N(2)	1.3499(1)	S(1)-C(1)-N(3)	124.3(2)
N(2)-C(2)	1.3424(1)	N(3)-C(2)-N(1)	109.8 (2)
C(3) - C(2)	1.4700(1)	C(8)-C(3)-C(4)	119.1(3)
C(3) - C(8)	1.3762(1)	S(1)-C(1)-N(2)	121.4(2)
		N(2)-N(1)-C(1)	103.3(2)

Table 3

Selected bond lengths (Å) and angles (°) for [Mn(H₂ptds)(o-phen)₂].

Bond lengths		Bond angles	
Mn-N(1)	2.190(15)	N(1)-Mn-N(1)	102.93(8)
Mn-N(4)	2.290(16)	N(1)-Mn-N(4)	97.89(6)
Mn-N(5)	2.309(17)	N(1)-Mn-N(4)	92.41(6)
S(1)-C(1)	1.749(2)	N(4)-Mn-N(4)	163.44(9)
S(1) - S(1)	2.041(13)	N(1)-Mn-N(5)	88.65(5)
N(1)-C(1)	1.345(2)	N(1)-Mn-N(5)	162.07(6)
N(1)-N(2)	1.381(2)	N(4) - Mn - N(5)	72.23(6)
N(2)-C(2)	1.327(2)	N(4)-Mn-N(5)	95.20(6)
N(3)-C(1)	1.333(2)	C(1)-S(1)-S(1)	103.90(8)
N(3)-C(2)	1.356(2)	C(1)-N(1)-N(2)	104.91(15)
C(2) - C(3)	1.473(2)	C(1)-N(1)-Mn	135.72(13)
C(3) - C(4)	1.377(3)	C(2)-N(2)-N(1)	105.47(15)
C(3)-C(8)	1.390(3)	C(1)-N(3)-C(2)	101.47(16)
N(5)-C(18)	1.320(3)	N(2)-C(2)-C(3)	123.34(18)
N(5)-C(19)	1.350(3)	N(3)-C(2)-C(3)	122.64(17)
		N(3)-C(1)-N(1)	114.15(17)
		N(1)-C(1)-S(1)	124.56(14)

ligands and *o*-phen as the coligand. The ligand is soluble in methanol and ethanol, while the complexes are insoluble even in DMF and DMSO. The ligand **1** and the complexes **2** and **3** melt at 535, 573 and 578 K, respectively.



Fig. 1. ORTEP plot of H2ptds-2H2O (1) with the atomic numbering scheme at the 30% probability level. Hydrogen atoms and solvent molecules are omitted for clarity.

4.1. IR spectra

The IR spectrum of the ligand *bis*(5-phenyl-2H-1,2,4-triazole)-3-yl-disulfane dihydrate, H_2 ptds·2H₂O (**1**) shows absorptions (cm^{-1}) due to the stretching modes of OH (3430), NH (3363), N-N (1078) and C–S (972). A band at 3430 cm^{-1} shows the presence of a water molecule in the ligand. The IR spectra of complexes 2 and **3** are devoid of any peak in the region $3367-3300 \text{ cm}^{-1}$, and show positive shifts of 20–23 cm⁻¹ for v(N–N), indicating the removal of the NH proton of triazole and bonding of the triazole nitrogen atom to the metal ion. The IR spectrum of [Co(pts)(ophen)₂]·H₂O·0.5C₂H₅OH (**3**) shows a broad band at 3404 cm^{-1} for v(OH). Thus, it is clear from the IR data that the ligand acts as dinegative bidentate in complex 2, bonding through both triazole nitrogen atoms, and as dinegative bidentate in complex 3 bonding through the triazole nitrogen and sulfinate oxygen atoms. The presence of bands at 1295 and 1101 cm^{-1} in complex **3** may be assigned to v_{assy} and v_{sym} respectively for O-bonded SO₂ [23].

4.1.1. ¹H and ¹³C NMR spectra

The ¹H NMR spectrum of H₂ptds·2H₂O (1) exhibits a signal at δ 13.66–13.83 ppm for the proton of the triazole ring and the five protons of the phenyl ring appear as a multiplet between 7.51

and 7.95 ppm. The ¹³C spectrum of H_2 ptds·2 H_2 O shows signals at δ 167.06, 150.32 and 125.5–130.70 ppm due to C–S, C=N and phenyl ring carbons, respectively.

4.2. Electronic spectra and magnetic moments

 $[Mn(H_2ptds)(o-phen)_2]$ (2) shows a magnetic moment of 5.9 BM which indicates the presence of five unpaired electrons. The complex shows absorption bands at 450 and 427 nm attributed to ${}^{6}A_{1g} \rightarrow 4A_{1g}$ and ${}^{4}E_g(G)$ transitions respectively for the distorted octahedral geometry of Mn(II). Other bands at 362, 339, 306 and 271 nm may be assigned to intraligand/charge transfer transitions [24]. Complex **3** shows a magnetic moment of 5.01 B.M., indicating its octahedral geometry. It shows two bands at 540 and 480 nm which may be attributed to d–d transitions of octahedrally coordinated cobalt(II). Other bands at 420, 374, 335 and 307 nm may be assigned to charge transfer/intraligand transitions.

4.3. Crystal structure description of H₂ptds·2H₂O (**1**)

The crystallographic data and structural refinement details are given in Table 1 and selected bond distances and bond angles are given in Table 2. Hydrogen bonding parameters of the ligand are



Fig. 2. N-H···O hydrogen bonding by the H₂O molecule leading to a linear chain structure.



Fig. 3. ORTEP plot of [Mn(ptds)₂(o-phen)₂] with the atomic numbering scheme at the 30% probability level. Hydrogen atoms are omitted for clarity.

given in Table 3. Fig. 1 shows the ORTEP diagram of H₂ptds·2H₂O (1) with the atomic numbering scheme. The structure of H₂ptds·2H₂O (1) is stabilized by intermolecular N-H···O hydrogen bonding, responsible for producing a linear chain structure (Fig. 2). The N-H···O hydrogen bonds are formed between the triazole hydrogen and oxygen of a water molecule. The C-S bond distance of 1.7574(1) Å in H₂ptds agrees well with those in related compounds, being a C-S single bond [25].

4.4. Crystal structure description of $[Mn(ptds)(o-phen)_2]$ (2)

Fig. 3 shows the ORTEP diagram of [Mn(ptds)(o-phen)₂] (**2**) with the atomic numbering scheme. The structural refinement data

related to complex **2** are listed in Table 1 and selected bond distances and bond angles are given in Table 3. The metal centre in complex **2** is coordinated in a N6 core by one dinegative bidentate ligand using both triazole nitrogens (N1 after loss of a proton). The N donor sites of the dinegative bidentate ligand chelate the Mn(II) centre to form a seven membered $C_2N_2S_2Mn$ ring. The average bond lengths in complex **2** are: S1–C1 = 1.7882(1) (L), C1–N1 = 1.3351(1) (L), C1–N3 = 1.3249(1) (S), N(2)–N(1) = 1.3813 (L), N(2)–C(2) = 1.3269 (S) Å (L, longer and S, shorter) (Table 3) which are longer or shorter than those of the corresponding distances in the free ligand due to bonding of Mn(II) with the ligand. The resulting complex has a distorted octahedral geometry. The Mn–N bond lengths in (**2**) are 2.190 and 2.290 Å for Mn–N (triazole)



Fig. 4. Intermolecular C-H...C interactions leading to a linear chain structure.



Fig. 5. ORTEP plot of [Co(pts)(o-phen)₂]-H₂O-0.5C₂H₅OH with the atomic numbering scheme at the 30% probability level. Hydrogen atoms and solvent molecules are omitted for clarity.

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and Mn–N (*o*-phen), respectively. The shorter Mn–N (triazole) bond length as compared to Mn–N (*o*-phen) indicates that the triazole nitrogen bonds more strongly than the *o*-phen nitrogen. The bond angles N(1)–Mn–N(1) 102.94(7)° and N(4)–Mn–N(4) 72.20(7)° indicate distortion from an ideal octahedral geometry [26]. In the complex the chelate rings and the triazole rings lie nearly in the same plane forming a dihedral angle of 20.46°. The bond distances for Mn–N and Mn–N(o-phen) are 2.1904, 2.2902(1) and 2.3094(1) Å, respectively, which are comparable to the bond lengths reported for [Mn(Hpchce)₂(*o*-phen)] and {2[Mn(pchcm)(*o*-phen)₂]}·7H₂O [27]. Compound **2** is quite stable in the solid state due to weak intermolecular C–H···C interactions between the carbons of triazole and the phenyl ring and the hydrogen atom of the *o*-phen ring (Fig. 4) forming a linear chain structure.

4.5. Crystal structure description of [Co(pts)(o-phen)₂]·H₂O·0.5C₂H₅OH (3)

5 shows Fig. the ORTEP diagram of [Co(pts)(ophen)₂] \cdot H₂O \cdot O.5C₂H₅OH (**3**), together with the atomic numbering scheme. The crystallographic data and structural refinement details are given in Table 1 and selected bond distances and bond angles are presented in Table 4. The elements of the structure are joined to each other in the crystal packing by means of an extended system of H-bonds, where the hydrogen belonging to the *o*-phen participates in the structure. In complex **3** the crystallographic asymmetric unit consists of [Co(pts)(o-phen)₂], one water and half an ethanol molecule. The ethanol is near a symmetry element and this has distorted its geometry so that the O-C-C angle is not 109°. However, the C–O 1.480(11) Å and C–C 1.329(11) Å bond lengths are reasonable. The bonding of the ligand via Co-N(1) and

Co–O(2) gives the distances 2.056(18) and 2.106(15) Å, (Table 4) forming a five membered NCSOCo chelate ring with a bite angle of 81.01(7)° which represents a major deviation from an octahedral geometry. In complex **3** the –S–S– bond breaks and gives a cobalt(II) complex with a newly generated ligand, pts^{2-} (Scheme 1). The cobalt(II) ion is octahedrally coordinated by four nitrogen atoms of two *o*-phen, one nitrogen of triazole and one oxygen atom of the newly generated ligand. Thus, the newly generated ligand, containing a sulfinate group, acts as a dinegative bidentate ligand. The average bond lengths in complex **3** are: N(2)–N(1) = 1.371(3), N(1)–C(1) = 1.30(3), N(2)–C(2) = 1.343(3), S(1)–C(1) = 1.800(2) and S(1)–O(2) = 1.507(16) Å, and these are normal for triazole complexes. The Co–N and Co–N(phen) bond distances are 2.056(18), 2.137(15) and 2.163(18) Å, respectively, and these val-

Table 4				
Selected bond	lengths (Å) and	angles (°) for	[Co(pts)(o-pher	$h_{2}] \cdot H_{2}O \cdot 0.5C_{2}H_{5}OH.$

	Bond lengths		Bond angles	
1	Co-N(1)	2.056(18)	O(2)-Co-N(1)	81.01(7)
	Co-N(4)	2.137(15)	O(2)-Co-N(6)	92.80(6)
	Co-N(5)	2.146(18)	O(2)-Co-N(5)	169.46(6)
	Co-N(6)	2.163(18)	O(2)-Co-N(7)	96.11(7)
	Co-N(7)	2.121(17)	N(1)-Co-N(5)	96.33(7)
	Co-O(2)	2.106(15)	N(1)-Co-N(4)	95.68(7)
	N(2)-N(1)	1.371(3)	N(4)-Co-N(7)	167.87(7)
	N(2)-C(2)	1.343(3)	N(6)-Co-N(7)	77.15(7)
	N(1)-C(1)	1.330(3)	Co-N(1)-N(2)	136.06(14)
	N(3)-C(1)	1.334(3)	O(1)-S(1)-C(1)	103.93(10)
	N(3)-C(2)	1.356(3)	Co-N(1)-C(1)	117.69(15)
	S(1)-C(1)	1.800(2)	N(2)-N(1)-C(1)	106.24(17)
	S(1)-O(2)	1.507(16)	N(1)-N(2)-C(2)	104.57(17)
	S(1) - O(1)	1.481(18)	S(1)-C(1)-N(1)	119.28(16)
	C(33)-C(34)	1.329(11)	O(2)-S(1)-C(1)	98.66(9)
	C(33)-O(5)	1.480(11)	O(1)-S(1)-O(2)	109.69(11)
			C(34)-C(33)-O(5)	152.0(8)



Fig. 6. O-H···O, C-H···O and C-H···S interactions leading to a supramolecular architecture.

ues are comparable to the bond lengths reported for [CoCl(ophen)₂(H₂O)]Cl·2·5H₂O [28], $[Co(L_1)_2(NCS)_2(H_2O)_2]$ ·2H₂O and $[Co_3(L_2)_6(NCS)_4(H_2O)_2](NCS)_2 \cdot H_2O$ $(L_1 = 4 - [3 - (1, 2, 4 - triazolyl) -$ 1,2,4-triazole] and L_2 = 4-aminotriazole) [29]. Due to deprotonation of triazole ring nitrogen, N-H-...O intermolecular hydrogen bonding present between the hydrogen atom of the triazole ring and the oxygen of water molecule in the free ligand disappears in complex 3. One ethanol molecule present between two complex units is linked to the two water molecules of both units and in turn both hydrogens of the water molecule are hydrogen bonded to the sulfinite oxygen of the complex unit (Fig. 6). A C-H...O interaction occurs between the CH₃ hydrogen and OH₂ oxygen and O-H···O interactions exist between the H₂O hydrogen and sulfinite oxygen, and the oxygen of ethanol is linked to the other hydrogen of H₂O molecule forming a supramolecular structure. In addition to this there is a weak intermolecular $C-H\cdots S$ interaction between the sulfinite sulfur and the hydrogen atom of the o-phen ring.

5. Conclusion

A new ligand, *bis*(5-phenyl-2H-1,2,4-triazole)-3-yl-disulfane (H₂p·tds·2H₂O) (**1**), and the complexes $[Mn(ptds)(o-phen)_2]$ (**2**) and $[Co(pts)(o-phen)_2]\cdot H_2O\cdot 0.5C_2H_5OH$ (**3**) have been synthesized. A S–S bond cleavage and aerial oxidation of sulfur was observed in complex **3**, whereas such cleavage did not occur in the case of complex **2**. Complex **2** is stabilized through weak intermolecular C–H···C interactions between the carbon atoms of the triazole and the phenyl ring hydrogen atom of the *o*-phen ring, forming a linear chain structure. Complex **3** is stabilized by a weak intermolecular C–H···S interaction between the sulfinite sulfur atom and the hydrogen atom of the *o*-phen ring, and C–H···O hydrogen bonding between the oxygen of the water molecule and the hydrogen atom of the *o*-phen ring, forming a supramolecular architecture.

Acknowledgment

One of the authors (Aarti Singh) is thankful to the University Grant Commission, New Delhi for financial support.

Appendix A. Supplementary data

CCDC 796493, 796494 and 796495 contain the supplementary crystallographic data for $(H_2ptds)\cdot 2H_2O(1)$, $[Mn(ptds)(o-phen)_2](2)$ and $[Co(pts)(o-phen)_2]\cdot H_2O\cdot 0.5C_2H_5OH(3)$. These 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.

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