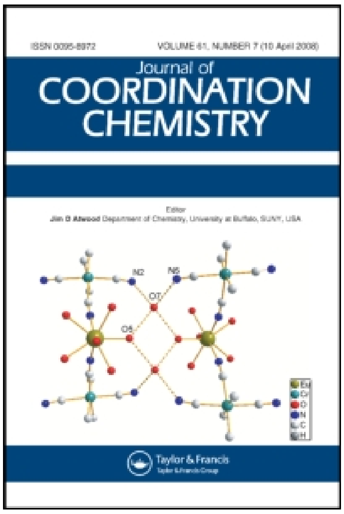

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# CRYSTAL STRUCTURES OF TWO 1:1 COMPLEXES OF MANGANESE(II) WITH 1,10-PHENANTHROLINE, CONTAINING COORDINATED AND UNCOORDINATED SULFATE ANIONS

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# CRYSTAL STRUCTURES OF TWO 1:1 COMPLEXES OF MANGANESE(II) WITH 1,10-PHENANTHROLINE, CONTAINING COORDINATED AND UNCOORDINATED SULFATE ANIONS

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The crystal structures of *fac*-triaqua-(1,10-phenanthroline-*N,N'*)-sulfato-manganese(II) (1) and tetraaqua-(1,10-phenanthroline-*N,N'*)-manganese(II) sulfate dihydrate (2) are described. The coordination polyhedron around the Mn(II) ion displays a distorted octahedral shape and contains the *N,N'*-chelating *phen* ligand. In the first complex the coordination sphere is completed by three water molecules and a monodentate *O*-sulfato ligand ($C_{3v}$), whereas in the second one, an uncoordinated sulfate ion ($T_d$) and four coordinated water molecules have been found. In both structures, the molecular units are extensively 2-D hydrogen bonded, with the 1,10-phenanthroline ligands arranged roughly perpendicular to the sheets; the bidimensional sheets are piled up giving rise to polar layers made by the hydrogen bonded species, the aqua-ions, sulfate anions, and water molecules, alternated with apolar layers formed by the 1,10-phenanthroline ligands.

*Keywords*: Crystal structure; Complexes; Manganese; Phenanthroline

## INTRODUCTION

Coordination compounds of manganese have received great attention because of the possibility of stabilizing different oxidation states of Mn,

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*Corresponding author. e-mail: mmoreno@ujaen.es which play important roles in many biological systems and display diverse applications in catalysis [1]. In this way, the activation of several enzymes and the Mn-containing species occurring in photosynthesis [2], as well as the catalytic disproportionation of hydrogen peroxide [3] in the cell detoxification processes must be cited. Previous studies of the ability of the manganese complexes to work as functional biomimics for manganese enzymes showed that those containing 1,10-phenanthroline (*phen*) as ligand were particularly active [4].

An exhaustive bibliographic research of Mn(II)-phenanthroline compounds showed that there are around twenty-five reported structures, mainly with the $\mathrm{Mn}(phen)_2^{2+}$ moiety [5, 6] although there are also a smaller number of examples of 1 : 3 [7] and 1 : 1 compounds [8], from these, none containing either uncoordinated or coordinated sulfate anions is reported. In this paper, we provide two examples of these situations.

## EXPERIMENTAL

### Preparation of the Complexes

Chemicals were purchased from commercial sources and used without further purification. The syntheses were carried out as follows: an aqueous solution (10 cm$^3$) containing 1 mmol of $MnSO_4 \cdot H_2O$ was added dropwise to another aqueous solution (10 cm$^3$) of 1 mmol of 1,10-phenanthroline. The colourless mixture was stirred for 1 h and left to stand at room temperature. After a day, yellow plates of $[\mathrm{Mn}(phen)(SO_4)(H_2O)_3]$ (**1**) appeared and, some days later, yellow blocks of $[\mathrm{Mn}(phen)(H_2O)_4]SO_4 \cdot 2H_2O$ (**2**) were isolated. Both compounds were filtered off, washed with ethanol and diethylether and air dried. It must be pointed out that a longer time to precipitate does not give a complex with higher *phen*/Mn ratio (*bis*- or *tris*-chelate) but a more soluble compound with uncoordinated sulfate anions; thus, the isolation of the products seems to be mainly controlled by the solubility of the different 1 : 1 species rather than the stability of 1 : 1 complexes if compared with the 2 : 1 or 3 : 1 species, which are quite low [9].

C, H, N and S were analyzed on a Fisons EA1108 apparatus. The water content was determined from the TG plots (Shimadzu TGA-50). *Anal.* Calc. for $C_{12}H_{14}N_2O_7SMn$ (**1**) (%): C, 37.41, H, 3.67, N, 7.27, S, 8.32, $H_2O$, 14.02; Found: C, 37.20, H, 3.71, N, 6.95, S, 8.93, $H_2O$, 13.75; Calc. for $C_{12}H_{20}N_2O_{10}SMn$ (**2**) (%): C, 32.80, H, 4.60, N, 6.38, S, 7.30, $H_2O$, 24.58; Found: C, 32.25, H, 4.20, N, 6.25, S, 7.93, $H_2O$, 23.90.

### Crystal Structure Determinations

X-ray diffraction intensity data were collected at 294(1) K using an Enraf-Nonius CAD-4 diffractometer with graphite-monochromatized MoK$\alpha$ radiation ($\lambda = 0.7107$ Å) by the $\theta/2\theta$ scan technique. The resulting crystal data and other relevant details concerning data collection and refinement are quoted in Table I.

The unit cells were determined from 25 random reflections. Three standard reflections were monitored every 120 min with no significative intensity decay. Non-H atoms were located in successive $\Delta F$ maps and refined anisotropically by full-matrix least-squares on $F^2$. All hydrogen atoms were treated as riding atoms (C—H 0.93 to 0.98, O—H 0.82 Å). The absolute configuration of **1** was determined by refining the Flack parameter, which was 0.03(7). The solution and refinement of the structures was carried out with SHELXS97 [10] and SHELXL97 [11] and drawings were performed using the SHELXTL [12] and PLATON [13] system.

TABLE I Crystal data and structure refinement details for *fac*-[Mn(*phen*)(SO$_4$)(H$_2$O)$_3$] (**1**) and [Mn(*phen*)(H$_2$O)$_4$]SO$_4$ · 2H$_2$O (**2**)

| | **1** | **2** |
|---|---|---|
| Empirical formula | $MnC_{12}H_{14}N_2O_7S$ | $MnC_{12}H_{20}N_2O_{10}S$ |
| Formula weight | 385.25 | 439.30 |
| Crystal system | Orthorhombic | Orthorhombic |
| Space group | $P2_12_12_1$ | *Pbca* |
| Unit cell dimensions *a*, Å | 8.0859(9) | 8.8762(6) |
| *b*, Å | 9.690(1) | 18.504(1) |
| *c*, Å | 19.330(1) | 22.095(1) |
| Volume, Å$^3$ | 1514.6(3) | 3629.0(4) |
| *Z* | 4 | 8 |
| $D_c$, mg m$^{-3}$ | 1.690 | 1.608 |
| $\mu$, mm$^{-1}$ | 1.047 | 0.896 |
| *F*(000) | 788 | 1816 |
| Crystal size, mm | 0.35 × 0.25 × 0.05 | 0.44 × 0.40 × 0.22 |
| $\theta$ range for data collection,° | 2.35–26.90 | 2.20–26.90 |
| *h* range | 0–10 | 0–11 |
| *k* range | 0–12 | 0–23 |
| *l* range | 0–24 | 0–28 |
| Reflections collected | 1911 | 3943 |
| Independent reflections | 1906 | 3939 |
| Reflections $I > 2\sigma(I)$ | 1371 | 2730 |
| Absorption correction | Gaussian | $\Psi$-scans |
| Exptl. abs. corr. *T* min., max. | 0.6912, 0.9433 | 0.8919, 0.9679 |
| Weighting scheme: | | |
| $w^{-1} = \sigma^2(F_o^2) + (xP)^2$, $P = 1/3(F_o^2 + 2F_c^2)$ | $x = 0.1619$ | $x = 0.0647$ |
| Data/restrains/parameters | 1906/0/208 | 3939/0/236 |
| G.o.f. on $F^2$ | 1.007 | 1.030 |
| $R[F^2 > 2\sigma(F^2)]$, $R_w(F^2)$ | 0.069, 0.211 | 0.039, 0.109 |
| Max. and min. $\Delta\rho$, e Å$^{-3}$ | 1.507, −1.148 | 0.385, −0.446 |

## RESULTS AND DISCUSSION

Fractional atomic coordinates and equivalent isotropic thermal parameters for all non-H atoms are listed in Tables II and III. A view of the molecular units showing the labelling scheme is shown in Figures 1 and 2. Bond distances and angles around the metal centres and in the sulfate ions are given in Table IV.

The coordination polyhedron around the Mn(II) ion contains the *N*,*N′*-chelating *phen* ligand. In the first complex the coordination sphere is completed by three water molecules, in a *facial* arrangement, and a monodentate *O*-sulfato ligand ($C_{3v}$), whereas in the second one, an uncoordinated sulfate ion ($T_d$) and four coordinated water molecules have been found. In each structure, the manganese atom is six-coordinate but the geometry is far removed from octahedral, mainly due to the 'bite' of the phenanthroline ligand. Thus, the O—Mn—O and N—Mn—O angles defined by contiguous metal-ligand bonds are between 83° and 103°, whereas the N—Mn—N angles are ca. 74°. Both compounds exhibit Mn—N distances ranging from 2.25 to 2.27 Å, shorter than those found in the compound

TABLE II Fractional atomic coordinates and equivalent isotropic displacement parameters for *fac*-[Mn(*phen*)($SO_4$)($H_2O$)$_3$]

| *Atom* | *x/a* | *y/b* | *z/c* | $U_{eq}$ (Å $^2$) |
|---|---|---|---|---|
| Mn | −0.1410(2) | −0.0395(1) | −0.68410(7) | 0.0234(4) |
| S | 0.2550(3) | −0.0725(2) | −0.7281(1) | 0.0257(5) |
| O(1) | 0.0928(8) | −0.1376(6) | −0.7091(3) | 0.025(1) |
| O(2) | 0.3696(9) | −0.1829(7) | −0.7464(4) | 0.036(2) |
| O(3) | 0.320(1) | 0.0035(9) | −0.6698(4) | 0.045(2) |
| O(4) | 0.226(1) | 0.0197(9) | −0.7864(4) | 0.046(2) |
| O(5) | −0.2913(9) | −0.1996(7) | −0.7294(5) | 0.041(2) |
| O(6) | −0.099(1) | 0.0738(7) | −0.7802(4) | 0.036(2) |
| O(7) | −0.3663(9) | 0.0798(7) | −0.6755(4) | 0.036(2) |
| N(1) | −0.043(1) | 0.1175(8) | −0.6074(4) | 0.030(2) |
| C(2) | 0.005(1) | 0.247(1) | −0.6209(5) | 0.037(2) |
| C(3) | 0.051(2) | 0.341(1) | −0.5695(7) | 0.053(3) |
| C(4) | 0.049(2) | 0.299(1) | −0.5025(6) | 0.055(4) |
| C(4A) | 0.000(2) | 0.164(1) | −0.4854(6) | 0.047(3) |
| C(5) | −0.000(2) | 0.111(2) | −0.4168(6) | 0.065(5) |
| C(6) | −0.052(2) | −0.019(1) | −0.4016(6) | 0.054(3) |
| C(6A) | −0.097(2) | −0.109(1) | −0.4576(5) | 0.044(3) |
| C(7) | −0.142(2) | −0.247(1) | −0.4442(6) | 0.056(3) |
| C(8) | −0.184(2) | −0.328(1) | −0.5000(7) | 0.055(3) |
| C(9) | −0.185(1) | −0.274(1) | −0.5663(7) | 0.044(3) |
| N(10) | −0.144(1) | −0.1435(8) | −0.5801(4) | 0.028(2) |
| C(10) | −0.100(1) | −0.063(1) | −0.5251(5) | 0.029(2) |
| C(1A) | −0.046(1) | 0.076(1) | −0.5413(5) | 0.028(2) |

$U_{eq}$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

TABLE III Atomic coordinates and equivalent isotropic displacement parameters for $[Mn(\textit{phen})(H_2O)_4]SO_4 \cdot 2H_2O$

| *Atom* | *x/a* | *y/b* | *z/c* | $U_{eq}$ (Å$^2$) |
|---|---|---|---|---|
| Mn | 0.13428(4) | 0.41199(2) | 0.08525(2) | 0.0293(1) |
| S | 0.08879(7) | 0.15591(3) | 0.03205(3) | 0.0313(2) |
| O(1) | 0.1874(2) | 0.1054(1) | −0.0006(1) | 0.0465(5) |
| O(2) | −0.0444(2) | 0.1170(1) | 0.05437(9) | 0.0441(5) |
| O(3) | 0.0400(2) | 0.2141(1) | −0.00957(9) | 0.0435(5) |
| O(4) | 0.1711(2) | 0.1877(1) | 0.08324(9) | 0.0431(5) |
| O(5) | 0.2845(2) | 0.32055(9) | 0.07533(8) | 0.0375(4) |
| O(6) | −0.0256(2) | 0.3538(1) | 0.03000(9) | 0.0446(5) |
| O(7) | −0.0134(2) | 0.5061(1) | 0.07499(8) | 0.0399(5) |
| O(8) | 0.2628(2) | 0.46315(9) | 0.01114(8) | 0.0403(5) |
| O(9) | 0.7043(2) | 0.2035(1) | 0.0968(1) | 0.0574(6) |
| O(10) | 0.0544(2) | 0.6307(1) | 0.12977(9) | 0.0474(5) |
| N(1) | 0.0467(2) | 0.3576(1) | 0.1706(1) | 0.0364(5) |
| C(2) | −0.0434(3) | 0.3008(2) | 0.1737(1) | 0.0488(7) |
| C(3) | −0.0898(4) | 0.2695(2) | 0.2281(2) | 0.064(1) |
| C(4) | −0.0412(4) | 0.2984(2) | 0.2804(2) | 0.062(1) |
| C(4A) | 0.0530(3) | 0.3586(2) | 0.2802(1) | 0.0524(8) |
| C(5) | 0.1062(4) | 0.3939(3) | 0.3335(1) | 0.071(1) |
| C(6) | 0.1962(4) | 0.4508(3) | 0.3304(1) | 0.071(1) |
| C(6A) | 0.2441(4) | 0.4806(2) | 0.2736(1) | 0.0525(8) |
| C(7) | 0.3387(4) | 0.5402(2) | 0.2678(2) | 0.069(1) |
| C(8) | 0.3819(4) | 0.5640(2) | 0.2125(2) | 0.066(1) |
| C(9) | 0.3306(3) | 0.5269(1) | 0.1608(1) | 0.0492(8) |
| N(10) | 0.2392(2) | 0.4705(1) | 0.1639(1) | 0.0359(5) |
| C(10) | 0.1954(3) | 0.4475(1) | 0.2199(1) | 0.0369(6) |
| C(1A) | 0.0958(3) | 0.3867(1) | 0.2234(1) | 0.0361(6) |

$U_{eq}$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

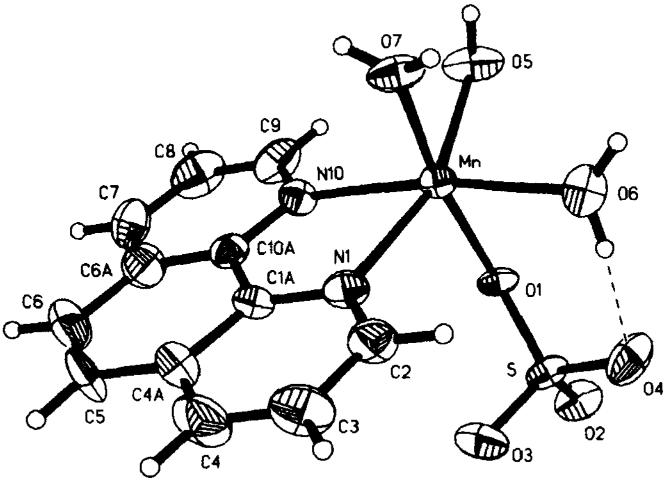

FIGURE 1 Molecular drawing and numbering scheme of the complex *fac*-$[Mn(\textit{phen})(SO_4)(H_2O)_3]$, with the non-hydrogen atoms represented by 50% probability ellipsoids.

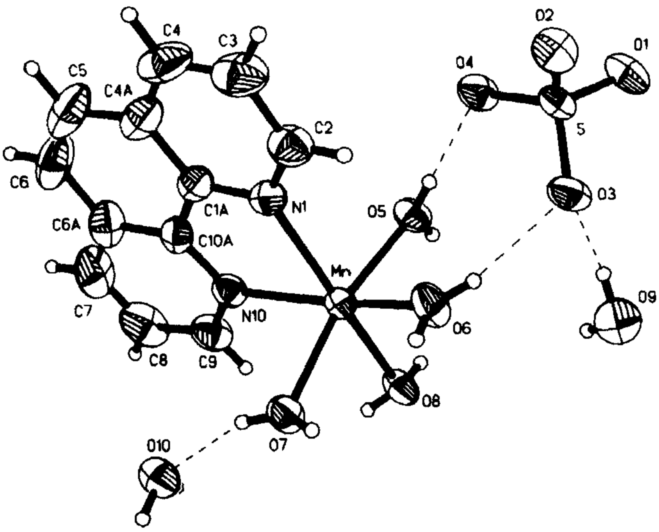

FIGURE 2 View of the complex $[Mn(phen)(H_2O)_4]SO_4 \cdot 2H_2O$, showing the labelling scheme (ellipsoids at 50% probability).

*cis*-$[MnCl_2(phen)_2]$ [6] (2.28–2.37 Å), in which the *trans* influence of the chloride ligands is evident. The molecular units are clearly magnetically dilute since the distance between the nearest metal centres is 5.9 (**1**) and 5.5 Å (**2**).

The phenanthroline ligands are planar, having only very small differences in the dihedral angles defined by the three conjugated rings, which range from 1.1° to 2.9°. Also, the five-membered chelate ring is *quasi*-coplanar with the *phen* mean plane, the manganese atom being distanced by 0.140 Å (**1**) and 0.059 Å (**2**).

There are two different sulfate ions in these compounds. Compound **1** contains a monodentate *O*-coordinated sulfato ligand, whereas in the structure of **2** an uncoordinated sulfate anion has been found. The corresponding geometrical data (see Tab. IV) are in good accord with the different symmetry displayed. In the compound **2**, the uncoordinated sulfate anion posseses *quasi*-ideal $T_d$ symmetry, as indicated by the mean values of bond lengths and angles which are 1.472(4) Å and 109.5(1)°, respectively. The coordinated sulfato group found in the compound **1** seems to have $C_{3v}$ symmetry, since there is a S—O(1) bond length quite different from the other three S—O ones, these distances being, respectively, larger and shorter than the mean S—O bond length found in the structure of **2**; in addition to this, the standard deviation of the values of bond angles with respect to the

TABLE IV Bond lengths (Å) and angles (°) around the manganese and in the sulfate anions

*fac*-[Mn(*phen*)($SO_4$)($H_2O$)$_3$] (1)

| | | | |
|---|---|---|---|
| Mn—N(1) | 2.266(8) | O(1)—Mn—O(6) | 84.0(3) |
| Mn—N(10) | 2.249(7) | O(5)—Mn—N(10) | 91.9(3) |
| Mn—O(1) | 2.171(7) | O(7)—Mn—N(10) | 99.2(3) |
| Mn—O(5) | 2.156(7) | O(1)—Mn—N(10) | 90.8(3) |
| Mn—O(6) | 2.184(7) | O(6)—Mn—N(10) | 170.8(3) |
| Mn—O(7) | 2.164(7) | O(5)—Mn—N(1) | 160.9(3) |
| O(5)—Mn—O(7) | 86.6(3) | O(7)—Mn—N(1) | 83.4(3) |
| O(5)—Mn—O(1) | 94.9(3) | O(1)—Mn—N(1) | 97.8(3) |
| O(7)—Mn—O(1) | 169.8(3) | O(6)—Mn—N(1) | 99.5(3) |
| O(5)—Mn—O(6) | 96.0(3) | N(10)—Mn—N(1) | 73.8(3) |
| O(7)—Mn—O(6) | 85.9(3) | | |

[Mn(*phen*)($H_2O$)$_4$]$SO_4 \cdot 2H_2O$ (2)

| | | | |
|---|---|---|---|
| Mn—N(1) | 2.275(2) | O(7)—Mn—O(8) | 83.78(7) |
| Mn—N(10) | 2.251(2) | O(6)—Mn—N(10) | 161.58(8) |
| Mn—O(5) | 2.166(2) | O(5)—Mn—N(10) | 101.50(7) |
| Mn—O(6) | 2.159(2) | O(7)—Mn—N(10) | 86.85(7) |
| Mn—O(7) | 2.192(2) | O(8)—Mn—N(10) | 98.79(8) |
| Mn—O(8) | 2.209(2) | O(6)—Mn—N(1) | 91.36(8) |
| O(6)—Mn—O(5) | 87.60(7) | O(5)—Mn—N(1) | 87.08(7) |
| O(6)—Mn—O(7) | 86.81(7) | O(7)—Mn—N(1) | 103.45(8) |
| O(5)—Mn—O(7) | 168.19(7) | O(8)—Mn—N(1) | 168.76(8) |
| O(6)—Mn—O(8) | 97.69(8) | N(10)—Mn—N(1) | 73.36(8) |
| O(5)—Mn—O(8) | 86.66(7) | | |

Sulfate anions

| | (1) | (2) | | (1) | (2) |
|---|---|---|---|---|---|
| S—O(1) | 1.501(6) | 1.470(2) | O(3)—S—O(4) | 110.4(5) | 109.4(1) |
| S—O(2) | 1.459(7) | 1.470(2) | O(3)—S—O(2) | 109.3(5) | 109.3(1) |
| S—O(3) | 1.447(8) | 1.480(2) | O(4)—S—O(2) | 111.3(4) | 109.7(1) |
| S—O(4) | 1.456(8) | 1.469(2) | O(3)—S—O(1) | 110.1(4) | 109.3(1) |
| | | | O(4)—S—O(1) | 108.0(4) | 109.6(1) |
| | | | O(2)—S—O(1) | 107.8(4) | 109.4(1) |

ideal tetrahedral angle is ten times higher (± 1.3°) than in that corresponding to the sulfate anion in the compound **2** (± 0.15°). Geometrical features of the hydrogen bonds in both compounds are given in Table V.

In the molecular unit of the complex *fac*-[Mn(*phen*)(SO$_4$)(H$_2$O)$_3$], there is an intramolecular hydrogen bond O(6)—H···O(4) (see Fig. 1). The molecules are bidimensionally hydrogen-bonded as depicted in Figure 3A, the sheets being parallel to the *ab* plane. The phenanthroline moieties are roughly perpendicular to the 2-D network and alternatively arranged on both sides of the sheet; on each side of the sheet, the *phen* ligands are inclined to the *a* axis by 71.6° and superimposed, following the 1 0 0 direction, to each other at around 8 Å. The phenanthroline ligands coordinated on one side of the sheet with those coordinated in the other side define an acute dihedral angle of 36.8°. The sheets are packed with each other as shown in Figure 3B; each layer is inserted with neighbouring ones in such a way that each *phen* moiety is arranged in the middle of the square hole defined by each four phenanthroline ligands of the neighbouring sheet.

The hydrogen bonding pattern in the structure of compound **2** is similar to the above. There are bidimensional networks parallel to the *ab* plane (see Fig. 4A) with the 1,10-phenanthroline ligands also perpendicular to the

TABLE V Hydrogen bonding details (D—H···A)

| *D* | *A* | *d*(*D*···*A*), Å | *d*(*H*···*A*), Å | ∠(*D*—*H*···*A*), ° |
|---|---|---|---|---|
| *fac*-[Mn(*phen*)(SO$_4$)(H$_2$O)$_3$] | | | | |
| O(5) | O(4)$^a$ | 2.787 | 2.043 | 150 |
| O(5) | O(2)$^b$ | 2.767 | 1.995 | 157 |
| O(6) | O(4) | 2.684 | 1.973 | 145 |
| O(7) | O(2)$^c$ | 2.750 | 1.951 | 161 |
| O(7) | O(3)$^b$ | 2.641 | 2.166 | 118 |
| [Mn(*phen*)(H$_2$O)$_4$] SO$_4$·2H$_2$O | | | | |
| O(5) | O(4) | 2.663 | 1.859 | 166 |
| O(5) | O(3)$^d$ | 2.768 | 2.086 | 141 |
| O(6) | O(3) | 2.791 | 2.033 | 154 |
| O(6) | O(1)$^e$ | 2.735 | 1.972 | 154 |
| O(7) | O(10)$^f$ | 2.672 | 1.889 | 159 |
| O(7) | O(8)$^g$ | 2.974 | 2.260 | 146 |
| O(8) | O(1)$^f$ | 2.682 | 1.970 | 145 |
| O(8) | O(2)$^d$ | 2.688 | 2.001 | 141 |
| O(9) | O(3)$^d$ | 2.858 | 2.016 | 156 |
| O(9) | O(2)$^b$ | 2.901 | 2.003 | 176 |
| O(10) | O(4) | 2.847 | 1.951 | 173 |
| O(10) | O(9) | 2.761 | 1.870 | 171 |

Symmetry codes: $^a\, -x,\ -1/2+y,\ 1/2-z$; $^b\, 1+x,\ y,\ z$; $^c\, -x,\ 1/2+y,\ 1/2-z$; $^d\, 1/2+x,\ 1/2-y,\ -z$; $^e\, -1/2+x,\ 1/2-y,\ -z$; $^f\, 1/2-x,\ 1/2+y,\ z$; $^g\, -x,\ 1-y,\ -z$.

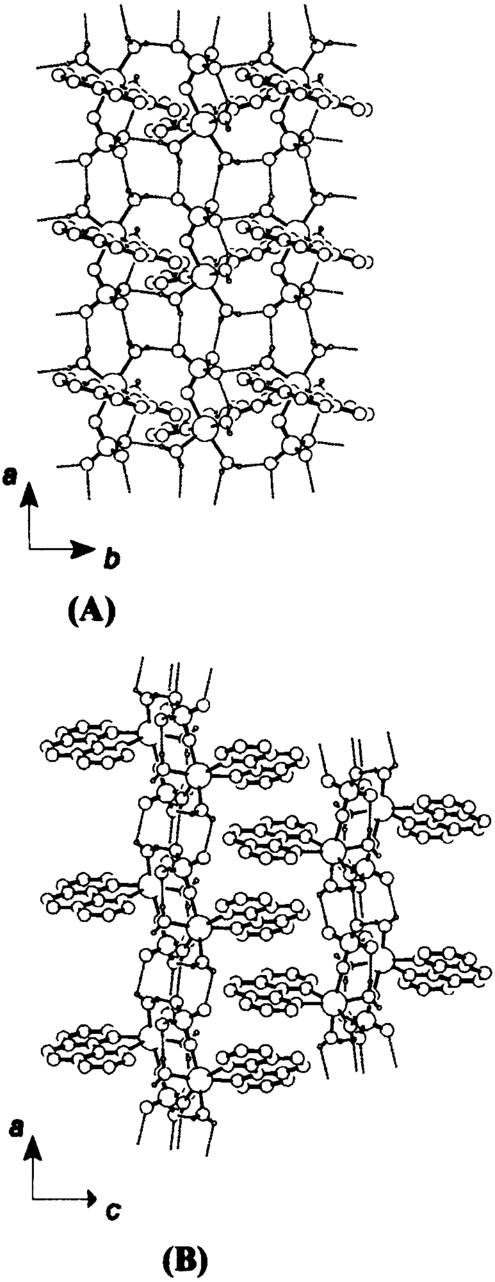

FIGURE 3 Hydrogen bonding in [Mn(*phen*)($SO_4$)($H_2O$)$_3$]: (A) view, from the 0 0 1 direction, of a 2-D network; (B) two neighbouring sheets, from the 0 1 0 direction (H-atoms from *phen* are omitted for clarity).

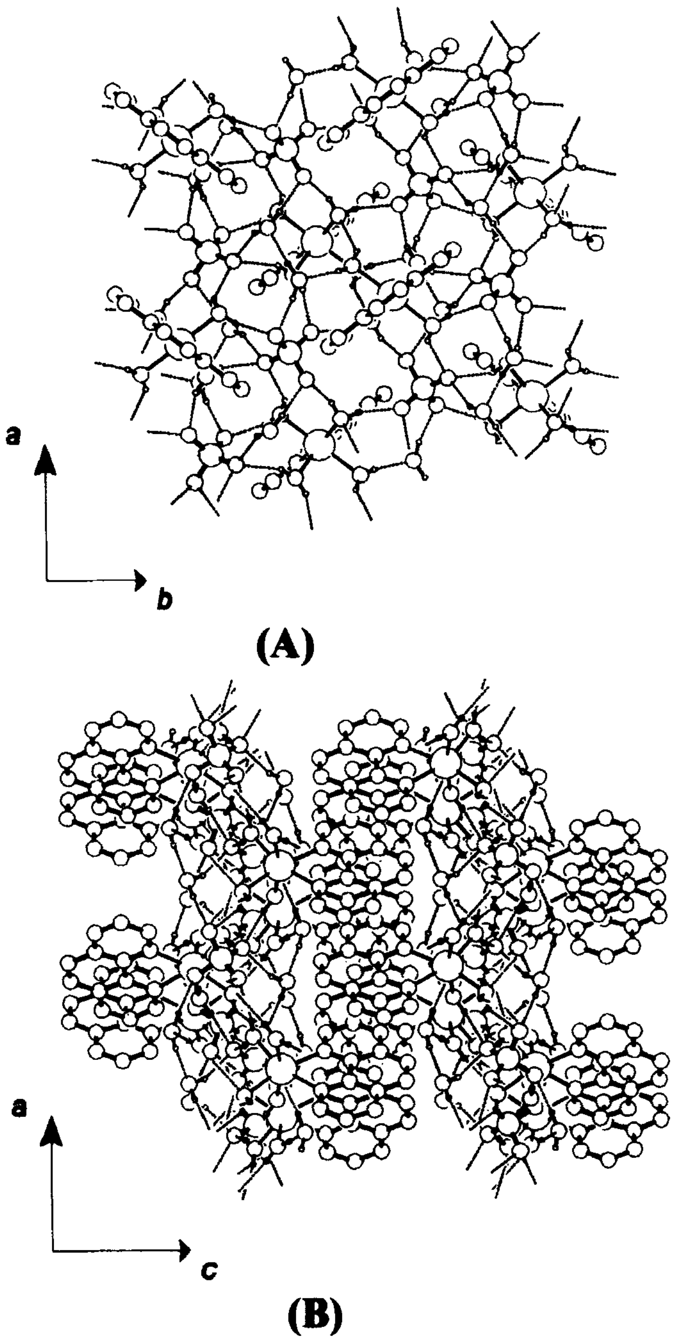

FIGURE 4 H-bond interactions in [Mn(*phen*)($H_2O$)$_4$]$SO_4 \cdot 2H_2O$: (A) a portion of the 2-D network; (B) view, from the *b* axis, of two neighbouring sheets showing the alternate arrangement of layers of polar and non-polar moieties (H-atoms from *phen* are omitted for clarity).

sheets, but in this case, on each side of the layer there are two differently oriented *phen* ligands which are inclined to each other at 104.6°. As is depicted in Figure 4B, the existence of two different orientations in the *phen* ligands gives rise to more complicated insertion of these molecules from different layers but, essentially, the sheets are piled up in the same way as in the structure of **1**. There are polar layers made by the extensively hydrogen bonded species (the aqua ions, sulfate anions, and water molecules) which are alternated with apolar layers formed by the 1,10-phenanthroline ligands in some $\pi-\pi$ stacking interactions. Interplanar distances are at around 4 Å. In both cases, the examination of the structure with PLATON [13] showed that there were no solvent-accessible voids in the crystal lattices.

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## *Supplementary Material*

The CIF files and lists of calculated and observed structure factors (pp. 53) are available from the authors upon request.

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