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Manganese(II) complexes of 3,6,9-trioxaundecanedioic acid (3,6,9-tddaH$_2$): X-ray crystal structures of [Mn(3,6,9-tdda)(H$_2$O)$_2$]·2H$_2$O and {[Mn(3,6,9-tdda)(phen)$_2$·3H$_2$O]·EtOH}$_n$

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Abstract—3,6,9-trioxaundecanedioic acid (3,6,9-tddaH$_2$) reacts with Mn(CH$_3$CO$_2$)$_2$·4H$_2$O in ethanol to give [Mn(3,6,9-tdda)]·H$_2$O (**1**). Recrystallization of **1** from methanol gives crystals of [Mn(3,6,9-tdda)(H$_2$O)$_2$]·2H$_2$O (**2**). Complex **1** reacts with an ethanolic solution of 1,10-phenanthroline (phen) to give {[Mn(3,6,9-tdda)(phen)$_2$]·3H$_2$O·EtOH}$_n$ (**3**). All of the complexes are extremely water soluble. Complexes **2** and **3** were structurally characterised. The manganese(II) ion in **2** is seven coordinate, with an approximately pentagonal bipyramidal O$_7$ coordination sphere. The axial donors are water molecules and the pentagonal plane is occupied by the diacid, acting as a pentadentate ligand through the three ethereal oxygens and one oxygen atom from each of the carboxylate functions. In complex **3** the manganese(II) ion is six-coordinate, being bound to two bidentate phenanthroline ligands and to the carboxylate oxygen atoms from two symmetry related diacids which are coordinated in a *cis* fashion. The structure consists of polymeric chains, with diacid ligands bridging the manganese ions. There is π–π stacking of pairs of phenanthroline ligands on adjacent chains, running along both the z and y directions. © 1997 Elsevier Science Ltd

Keywords: 3,6,9-trioxaundecanedioic acid; manganese; phenanthroline; X-ray dicarboxylic acid; π–π stacking.

We have previously described the synthesis, X-ray crystal structures and catalase-type activity of a number of manganese(II) complexes containing aliphatic α,ω-dicarboxylic acid ligands [1–3]. In an effort to improve complex solubility, particularly in water, we have investigated the coordination of 3,6,9-trioxaundecanedioic acid HO$_2$CCH$_2$OCH$_2$CH$_2$OCH$_2$CH$_2$OCH$_2$CO$_2$H (3,6,9-tddaH$_2$) to manganese(II). This diacid ligand contains three ethereal oxygen atoms in its backbone and this should enhance the solubility of the resulting complexes in protic solvents. To our knowledge the only previous report of the coordination chemistry of 3,6,9-tddaH$_2$ was the measurement of the stability constants of the 1 : 1 complexes formed with alkaline earth metals [4]. The large stability constants found for complexes containing α,ω-dicarboxylic acids containing ether linkages, compared to those containing the corresponding saturated α,ω-dicarboxylic acids (equivalent chain length but without ether oxygens), indicated coordination of the ethereal oxygen atoms to the metal centres. Herein we outline the synthesis, X-ray crystal structures and physical properties of two manganese(II) complexes of 3,6,9-tddaH$_2$.

RESULTS AND DISCUSSION

3,6,9-tddaH$_2$ reacted with manganese(II) acetate tetrahydrate in ethanol to give a high yield of colour-

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less product [Mn(3,6,9-tdda)]·H_2O (**1**). Recrystallization of **1** from methanol gave crystals of formula [Mn(3,6,9-tdda)$(H_2O)_2$]·$2H_2O$ (**2**). Complex **1** reacts with an ethanolic solution of 1,10-phenanthroline (phen) to give {[Mn(3,6,9-tdda)$(\text{phen})_2$]·$3H_2O$·EtOH}$_n$ (**3**) in good yield. Complexes **2** and **3** were structurally characterised and selected molecular dimensions for both structures are given in Table 1. The manganese(II) ion in **2** is seven coordinate (Fig. 1), with an approximately pentagonal bipyramidal O_7 coordination sphere. The axial donors are water molecules and the pentagonal plane is occupied by the diacid, acting as a pentadentate ligand through the three ethereal oxygens and one oxygen atom from each of the carboxylate functions. The diacid ligand forms a girdle around the metal comprising four five-membered chelate rings. The Mn—O distances vary from 2.141(1) Å for Mn—O(2)(water) to 2.440(1) Å for Mn—O(4)(ether), and as might be expected, the longest bonds are those to the ether donors. The mean Mn—O(ether) bond distance in **2** (2.331 Å) is slightly shorter than that in the manganese(II) complex [Mn(bdoa)$(H_2O)_3$] (bdoaH_2 = benzene-1,2-dioxyacetic acid $HO_2CCH_2O(C_6H_4)OCH_2CO_2H$) (2.413 Å) [5]. The pentagonal distortion from the ideal bond angle of 72° in **2** is not very great, the 'open' O(1)—Mn—O(7) angle (84.9°) being much the largest and the five diacid donors are close to coplanar. The two coordinated water molecules form hydrogen-bonds with two further non-coordinated water molecules which are also hydrogen-bonded to each other and to the carbonyl oxygen atoms of the diacid on adjacent molecules (Table 2). The resulting network of hydrogen bonds between asymmetric units can be seen in the packing diagram (Fig. 2).

In complex **3** (Fig. 3) the manganese(II) ion is six-coordinate, being bound to two bidentate phenanthroline ligands and to the carboxylate oxygen atoms from two symmetry related diacids which are coordinated in a *cis* fashion. The coordination sphere about the metal is quite irregular due to the acute binding angle of the phenanthroline ligands (71 and 72°). The structure consists of polymeric chains, with diacid ligands bridging the manganese ions (Fig. 4). There is π–π stacking of pairs of phenanthroline ligands on adjacent chains, running along both the z and y directions (Figs 4 and 5). The interplanar distance between the rings is *ca* 3.4 Å. There are two water and one ethanol solvate molecules in each asymmetric unit. These, together with the non-coordinated carbonyl oxygen atoms of the diacid, are all involved in hydrogen-bonding (Table 2).

Table 1. Selected bond lengths (Å) and angles (°) for **2** and **3**

Complex **2**			
Mn(1)—O(2W)	2.1406(11)	Mn(1)—O(1)	2.1460(11)
Mn(1)—O(7)	2.2168(11)	Mn(1)—O(1W)	2.2282(11)
Mn(1)—O(5)	2.2443(11)	Mn(1)—O(3)	2.3093(11)
Mn(1)—O(4)	2.4398(12)		
O(2W)—Mn(1)—O(1)	94.37(4)	O(2W)—Mn(1)—O(7)	87.78(4)
O(1)—Mn(1)—O(7)	84.94(4)	O(2W)—Mn(1)—O(1W)	174.09(4)
O(1)—Mn(1)—O(1W)	88.33(4)	O(7)—Mn(1)—O(1W)	97.71(4)
O(2W)—Mn(1)—O(5)	88.89(4)	O(1)—Mn(1)—O(5)	154.95(4)
O(7)—Mn(1)—O(5)	70.35(4)	O(1W)—Mn(1)—O(5)	90.89(4)
O(2W)—Mn(1)—O(3)	86.09(4)	O(1)—Mn(1)—O(3)	71.11(4)
O(7)—Mn(1)—O(3)	154.70(4)	O(1W)—Mn(1)—O(3)	89.81(4)
O(5)—Mn(1)—O(3)	133.94(4)	O(2W)—Mn(1)—O(4)	91.94(4)
O(1)—Mn(1)—O(4)	137.21(4)	O(7)—Mn(1)—O(4)	137.63(4)
O(1W)—Mn(1)—O(4)	82.53(4)	O(5)—Mn(1)—O(4)	67.28(4)
O(3)—Mn(1)—O(4)	67.17(4)		
Complex **3**			
Mn—O(1)	2.0966(12)	Mn—O(6)#1	2.1103(12)
Mn—N(2A)	2.2794(14)	Mn—N(2B)	2.2807(14)
Mn—N(1B)	2.321(2)	Mn—N(1A)	2.3700(14)
O(1)—Mn—O(6)#1	96.59(5)	O(1)—Mn—N(2A)	85.42(5)
O(6)#1—Mn—N(2A)	112.86(5)	O(1)—Mn—N(2B)	116.68(5)
O(6)#1—Mn—N(2B)	87.12(5)	N(2A)—Mn—N(2B)	149.10(5)
O(1)—Mn—N(1B)	93.35(5)	O(6)#1—Mn—N(1B)	159.18(5)
N(2A)—Mn—N(1B)	86.09(5)	N(2B)—Mn—N(1B)	72.07(5)
O(1)—Mn—N(1A)	156.66(5)	O(6)#1—Mn—N(1A)	91.14(5)
N(2A)—Mn—N(1A)	71.29(5)	N(2B)—Mn—N(1A)	85.60(5)
N(1B)—Mn—N(1A)	86.83(5)		

Symmetry transformations used to generate equivalent atoms: #1 x, y+1, z

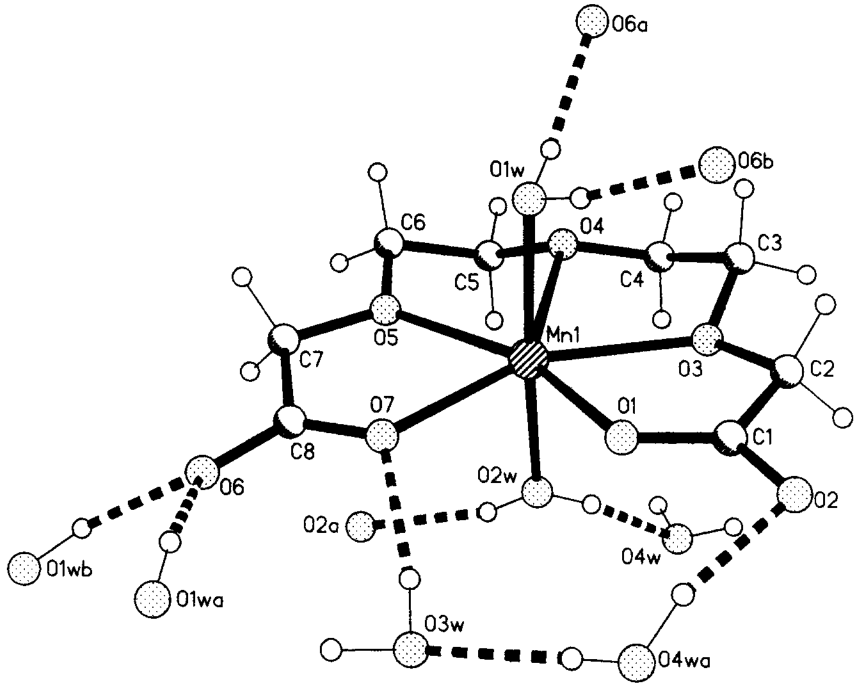

Fig. 1. Structure of complex **2** with hydrogen-bonding interactions.

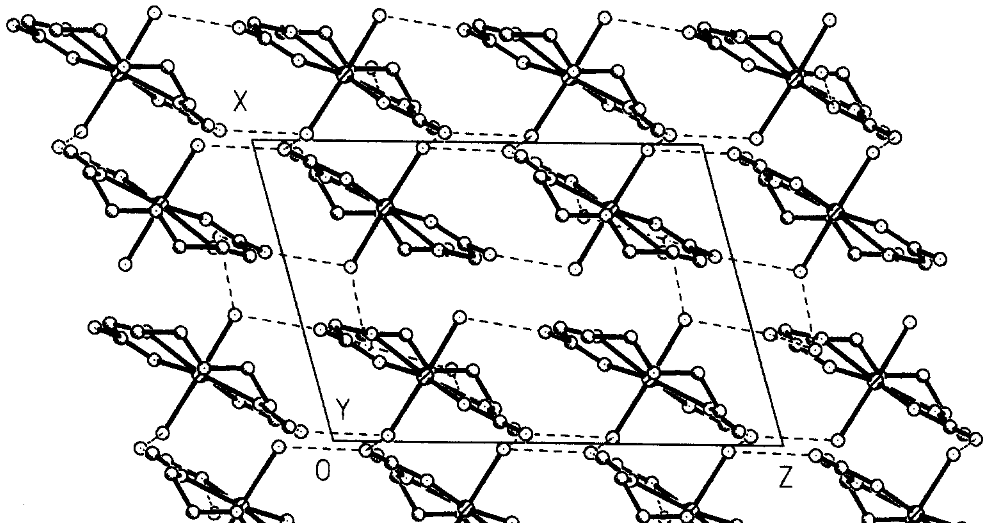

Fig. 2. Packing diagram for complex **2**.

The manganese(II) complexes **1**–**3** were very soluble in water, ethanol and methanol, and were insoluble in ethyl acetate and acetone. The molar conductivities of **1** and **3** in water ($\Lambda_M = 48$ and 116 S cm^2 mol^{-1}, respectively) indicates formation of the following ionic species in that solvent:

$$[\mathrm{Mn(3,6,9\text{-}tdda)}]\cdot \mathrm{H_2O}\ (\mathbf{1}) \overset{\mathrm{H_2O}}{\rightleftharpoons} [\mathrm{Mn(H_2O)}_x]^{2+} + \mathrm{3,6,9\text{-}tdda}^{2-}$$

$$\{[\mathrm{Mn(3,6,9\text{-}tdda)(phen)_2}]\cdot 3\mathrm{H_2O}\cdot \mathrm{EtOH}\}_n\ (\mathbf{3}) \overset{\mathrm{H_2O}}{\rightleftharpoons} [\mathrm{Mn(phen)_2(H_2O)}_y]^{2+} + \mathrm{3,6,9\text{-}tdda}^{2-}$$

The fact that the phenanthroline adduct **3** is more extensively dissociated in water is not totally surprising since the relatively stable $[\mathrm{Mn(phen)_2(H_2O)_2}]^{2+}$ ion has been observed as a discrete dication in the X-ray crystal structures of the ionic manganese(II) dicarboxylate salts $[\mathrm{Mn(phen)_2(H_2O)_2}][\mathrm{Mn}$

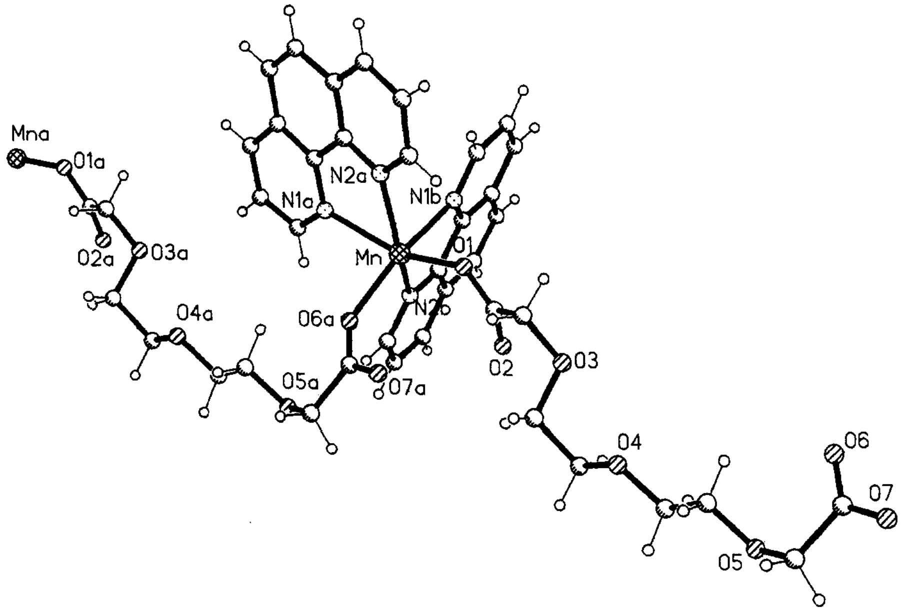

Fig. 3. Structure of repeat unit in the polymeric complex **3** (water and ethanol molecules omitted for clarity).

$(O_2C(CH_2)_5CO_2)$ $(phen)_2H_2O]$ $(O_2C(CH_2)_5(CO_2)\cdot 12.5H_2O$ [2] and $[Mn(phen)_2(H_2O)_2]O_2C(CH_2)_3CO_2\cdot 5H_2O$ [6]. Ethanolic solutions of **1** and **3** were found to be non-conducting.

EXPERIMENTAL

Chemicals were purchased from commercial sources and were used without further purification. Infrared spectra were recorded as KBr discs in the region 4000–400 cm^{-1} on a Nicolet Impact 400D FT-IR Spectrometer. Magnetic susceptibility measurements were made at room temperature using a Johnson Matthey Magnetic Susceptibility Balance, and conductivity measurements were made at 25°C with an AGB Scientific Ltd. model 10 conductivity meter. Elemental analysis were carried out by the Microanalytical Laboratory, University College Cork, Ireland.

Crystallography

Crystal data and details of the two structure determinations are listed in Table 3. Data for both crystals were collected at 153 K on a Siemens P4 diffractometer using graphite monochromated Mo-K_α radiation. The data were corrected for Lorentz and polarisation effects and empirical absorption corrections were applied. The structures were solved by direct methods [7] and all the data were used for refinement on F^2. Non-hydrogen atoms were assigned anisotropic atomic displacement parameters and hydrogen atoms bonded to carbon were inserted at calculated positions

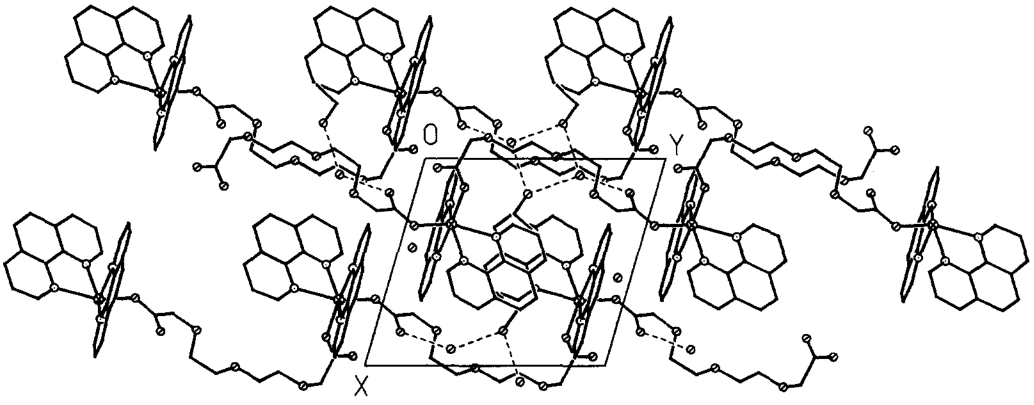

Fig. 4. Packing diagram illustrating polymeric chain structure of **3**.

Table 2. Hydrogen-bonding distances (Å) for **2** and **3**

Complex **2**	
O(4w)—O(3w)*	2.833 (0.002)
O(4w)—O(2)*	2.787 (0.002)
O(3w)—O(7)	2.803 (0.002)
O(6)—O(1w)†	2.723 (0.002)
O(6)—O(1w)#	2.796 (0.001)
O(2w)—O(2)#	2.683 (0.001)
O(2w)—O(4w)	2.686 (0.002)
Symmetry transformations	* $1-x, y-0.5, 0.5-z$ † $-x, 0.5+y, 0.5-z$ # $x, 0.5-y, 0.5+x$

Least-square plane (x, y, z in crystal coordinates) and deviations from them (* indicates atom used to define plane)

$6.704(0.002)x+1.416(0.003)y+6.881(0.003)z = 3.343(0.001)$

* −0.145 (0.001) O(1)
* 0.164 (0.001) O(3)
* −0.107 (0.001) O(4)
* 0.011 (0.001) O(5)
* 0.077 (0.001) O(6)
−0.007 (0.000) Mn

Rms deviation of fitted atoms = 0.114

Complex **3**	
O(2w)—O(7)*	2.780 (0.002)
O(2w)—O(7)†	2.781 (0.002)
O(2w)—O(3w)#	2.753 (0.002)
O(1w)—O(2)	2.810 (0.002)
O(1w)—O(30)‡	2.831 (0.002)
O(1w)—O(30)¶	2.712 (0.002)
O(1)—N(2a)	2.971 (0.002)
Symmetry equivalents	* $1+x, 2+y, z$ † $1-x, -y, 2-z$ # $x, 1+y, z$ ‡ $x, y-1, z$ ¶ $-x, -y, 1-z$

with anisotropic temperature factors riding on those of their carrier atoms. Hydrogen atoms bonded to oxygen were located from difference maps and not further refined. All programs used in the structure refinements were contained in the SHELXL-93 package [8].

$[Mn(3,6,9\text{-}tdda)] \cdot H_2O$ (**1**)

To a solution of 3,6,9-trioxaundecanedioic acid (5.45 g, 24.53 mmol) in ethanol 50 cm^3) was added a solution of $Mn(CH_3CO_2)_2 \cdot 4H_2O$ (5.0 g, 20.4 mmol) in ethanol (250 cm^3). The resulting colourless solution was refluxed for 1 h during which time the colourless product precipitated. The hot suspension was filtered and the solid was washed with two small portions of chilled ethanol and then dried *in vacuo*; yield: 5.14 g (86%). Found: C, 32.2; H, 4.6. Calc.: C, 32.8; H, 4.8%; $\mu_{eff} = 5.4$ B.M.; IR: 3280, 2930, 1585, 1430, 1330, 1250, 1130, 1090, 1055, 965, 920, 840, 720, 475 cm^{-1}; $\Lambda_M(H_2O) = 48$ S cm^2 mol^{-1}. The complex was soluble in water, ethanol and methanol, and insoluble in chloroform, ethyl acetate and acetone. Recrystallization of **1** from methanol gave crystals of formula $[Mn(3,6,9\text{-tdda})(H_2O)_2] \cdot 2H_2O$ (**2**) which were suitable for X-ray analysis.

$\{[Mn(3,6,9\text{-}tdda)(phen)_2] \cdot 3H_2O \cdot EtOH\}_n$ (**3**)

To a solution of 1,10-phenanthroline monohydrate (1.5 g, 7.57 mmol) in ethanol (100 cm^3) was added **1** (0.651 g, 2.22 mmol). The resulting yellow solution was left to stand at room temperature for *ca* 3 days and during this time the product formed as yellow crystals. The solid was filtered off, washed with two small portions of cold ethanol and then dried *in vacuo*. Concentration of the reaction filtrate by rotary evaporation, followed by addition of ethyl acetate, yielded more of the yellow product; yield: 1.135 g (62%).

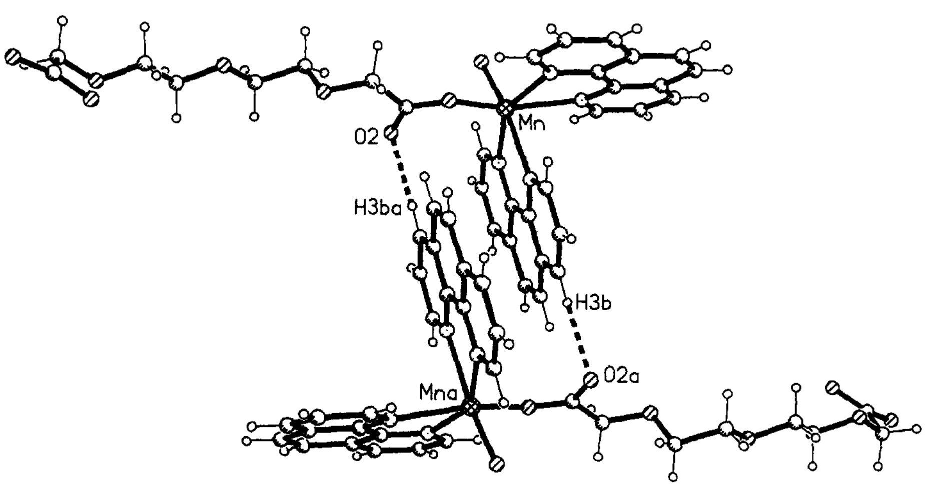

Fig. 5. π–π Stacking in 3.

Table 3. Summary of crystal data, data collection, structure solution and refinement details

	$[Mn(3,6,9\text{-tdda})(H_2O)_2]\cdot 2H_2O$ (**2**)	$\{[Mn(3,6,9\text{-tdda})(phen)_2]\cdot 3H_2O\cdot EtOH\}_n$ (**3**)
Empirical formula	$C_8H_{20}MnO_{11}$	$C_{34}H_{40}MnN_4O_{11}$
Formula weight	347.18	735.64
Crystal description	Colourless block	Yellow block
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
a (Å)	9.612(1)	10.669(1)
b (Å)	10.845(1)	12.523(1)
c (Å)	14.016(2)	13.955(1)
α (°)	90	108.81(1)
β (°)	105.61(1)	90.55(1)
γ (°)	90	105.21(1)
V (Å^3)	1407.2(3)	1694.0(2)
Z	4	2
Density (calculated, Mg/m^3)	1.639	1.442
μ (mm^{-1})	0.99	0.46
F(000)	724	770
Crystal size (mm)	0.25 × 0.20 × 0.25	0.76 × 0.55 × 0.52
θ range for data collection (°)	2.0 to 25.0	2.0 to 25.0
Index ranges	$-9 < h < 11$ $-8 < k < 12$ $-16 < l < 16$	$-4 < h < 12$ $-13 < k < 13$ $-16 < l < 16$
Reflections collected	3295	6876
Independent reflections	2482	5844
Max. and min. transmission	0.775 and 0.865	0.827 and 0.895
Data/restraints/parameters	2482/0/182	5843/0/451
Goodness-of-fit on F^2 (all data)	1.072	1.070
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0228$ $wR2 = 0.601$	$R1 = 0.0307$ $wR2 = 0.0772$
R indices (all data)	$R1 = 0.0246$ $wR2 = 0.0613$	$R1 = 0.0362$ $wR2 = 0.0811$
Largest peak and hole (eÅ^{-3})	0.23 and −0.35	0.25 and −0.58

Found: C, 52.7; H, 5.2; N, 7.4. Calc.: C, 55.5; H, 5.5; N, 7.6%; $\mu_{eff} = 6.0$ B.M.; IR: 3410, 2915, 1625, 1585, 1515, 1425, 1325, 1120, 1075, 845, 730, 635 cm^{-1}; $\Lambda_M(H_2O) = 116$ S cm^2 mol^{-1}. The complex was soluble in water, ethanol and methanol, and insoluble in ethyl acetate and acetone.

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