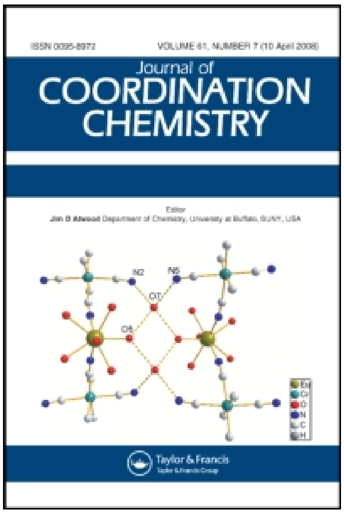

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SYNTHESIS AND CHARACTERIZATION OF MANGANESE(III) HYDROXYL-CONTAINING SCHIFF-BASE COMPLEXES: [Mn(III)(Hvanpa)$_2$(NCS)] AND [Mn(III)(Hvanpa)$_2$]Cl · H_2O (H_2vanpa = 1-(3-METHOXYSALICYLALDENEAMINO)-3-HYDROXYPROPANE)

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SYNTHESIS AND CHARACTERIZATION OF MANGANESE(III) HYDROXYL-CONTAINING SCHIFF-BASE COMPLEXES: [Mn(III)(Hvanpa)$_2$(NCS)] AND [Mn(III)(Hvanpa)$_2$]Cl · H$_2$O (H$_2$vanpa = 1-(3-METHOXYSALICYLALDENEAMINO)-3-HYDROXYPROPANE)

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The manganese complexes, [Mn(III)(Hvanpa)$_2$(NCS)] (1) and [Mn(III)(Hvanpa)$_2$]Cl · H$_2$O (2), have been prepared and the crystal structure of complex 2 determined using X-ray crystallography. The monomeric complex has a six-coordinate octahedral geometry. The complex crystallizes in the triclinic space group P-1 with $a = 11.446(5)$ Å, $b = 12.782(6)$ Å, $c = 9.023(3)$ Å, $\alpha = 93.92(3)°$, $\beta = 97.05(3)°$, $\gamma = 65.42(2)°$, $V = 1169.0(9)$ Å^3 and $Z = 2$. The Mn–O and Mn–N distances in the equatorial plane are in agreement with those found for other manganese (III) Schiff-base complexes. In the axial direction, the Mn–O distances of 2.256(3) and 2.236(3) Å, respectively, are about 0.4 Å longer than those in the equatorial plane due to Jahn–Teller distortion at the d^4 manganese(III) center. In the crystal, each chloride ion is linked through hydrogen bonding with two hydrogen atoms from the coordinated hydroxyl groups at the apical site. The lattice water molecules also interact with the phenolic oxygen atoms through hydrogen bonding.

Keywords: Manganese(III); Schiff base; hydrogen bonding; crystal structure; Jahn–Teller distortion

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INTRODUCTION

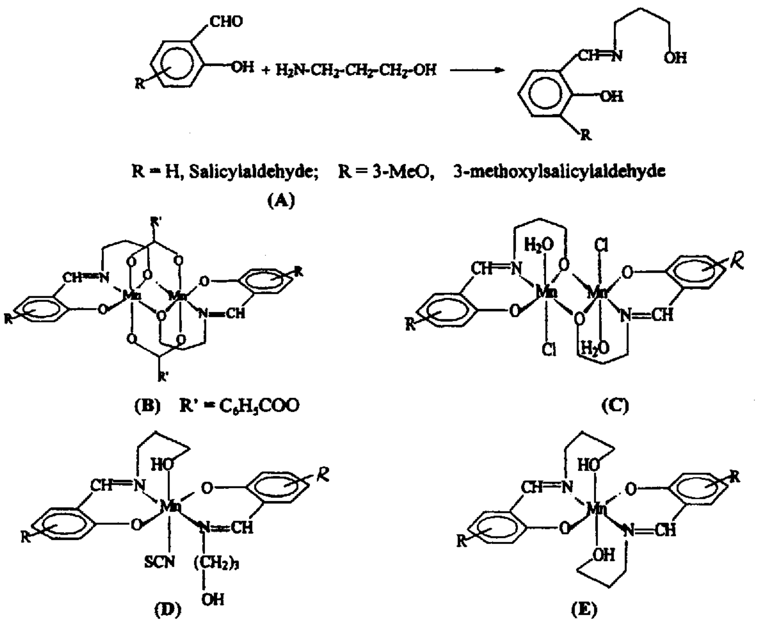
Manganese plays an important role in several biological redox-active systems, *e.g.* manganese superoxide dismutase,[1] manganese catalase,[2] manganese peroxidase,[3] manganese ribonucleotide reductase,[4] and the oxygen-evolving complex (OEC).[5,6] It is known that there are four manganese atoms per OEC,[7] but the exact arrangement of these four atoms has not been clearly determined. EXAFS analysis of OEC indicates the presence of one, two, or more short Mn ··· Mn distances.[8] Such close contact suggests a strong interaction between the manganese atoms involved in this substructure. In order to understand the interaction between manganese atoms, it is important to study model complexes with a wide range of ligand environments. Recently, di-μ-oxo bridged binuclear manganese(III) complexes were found to be a model of the photosystem-II in green plant photosynthesis, where manganese functions as a redox catalyst for the oxidation of water to molecular oxygen. Schiff-base ligands offer synthetic access to a variety of ligand environments with biologically relevant donors.[9] We have previously reported the synthesis of unsymmetrical Schiff-base ligands from the reactions of 3-hydroxypropaneamine with salicylaldehyde or 3-methoxy salicylaldehyde (Scheme 1A) and subsequently the manganese(III) complexes (Scheme 1B and C).[10,11] In this paper, we report two monomeric six-coordinate manganese(III) complexes, [Mn(III)(Hvanpa)$_2$(NCS)] and [Mn(III)(Hvanpa)$_2$]Cl · H_2O (Scheme 1D and E).

EXPERIMENTAL

Physical Measurements

Analyses for C, H and N were carried out with a Perkin Elmer Analyzer Model 240. IR spectra were recorded on a Perkin Elmer Paragon 1000 spectrophotometer with KBr discs. Magnetic moments for the complexes were performed on a Fudan University FD-MT-A Faraday balance. X-ray crystal structure determination was carried out on a Rigaku AFC7R diffractometer.

***Synthesis of Complex* 1** A deep green solution of the complex was generated by the addition of $Mn(ClO_4)_2 \cdot 6H_2O$ (3.60 g, 10 mmol) to a solution of 3-methoxy salicylaldehyde (1.56 g, 10 mmol) and 3-amino-1-propanol (0.75 g, 10 mmol). The mixture was stirred at room temperature for 4 h followed by the addition of an aqueous solution of NH_4SCN (0.93 g, 10 mmol) with stirring during which time, 1 mL of triethylamine was added.



SCHEME 1

Green prismatic crystals were obtained after the solution was filtered and left to stand for a week. Overall yield: 75%. *Anal. Calcd.* for $MnC_{23}H_{28}O_6N_3S$ (mol. wt. 529.42): C, 52.18; H, 5.33; N, 7.94; Mn, 10.38. Found: C, 51.95; H, 5.43; N, 8.05; Mn, 10.24%.

***Synthesis of Complex* 2** A red-brown solution of the title complex was generated by the addition of $MnCl_2 \cdot 4H_2O$ (2.00 g, 10 mmol) to a solution of 3-methoxy salicylaldehyde (1.56 g, 10 mmol) and 3-amino-1-propanol (0.75 g, 10 mmol). The mixture was stirred at room temperature for 4 h during which time 1 mL of triethylamine was added. Green prismatic crystals were obtained after the solution was left to stand for a week. Overall yield: 86%. *Anal. Calcd.* for $MnC_{22}H_{30}O_7N_2Cl$ (mol. wt. 524.88): C, 50.34; H, 5.76; N, 5.34; Mn, 10.47. Found: C, 50.30; H, 5.85; N, 5.15; Mn, 10.38%.

X-ray Crystallography A red-brown prismatic crystal of complex **2** was mounted on a glass fiber. All measurements were made on a Rigaku AFC7R diffractometer with graphite monochromated Mo-Kα radiation and a 12 kW rotating anode generator. Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement using the setting angles of 21 carefully centered reflections in the range of $18.50° < 2\theta < 23.85°$

TABLE I Crystal data and structure refinement

Compound	$[Mn(III)(Hvanpa)_2]Cl \cdot H_2O$
Color/shape	Red brown/prismatic
Empirical formula	$C_{22}H_{30}O_7N_2ClMn$
Formula weight	524.88
Temperature	293 K
Crystal system	Triclinic
Space group	P-1
No. of reflections used for unit cell determination (2θ range)	21 (13.4°–21.6°)
a (Å)	11.446(5)
b (Å)	12.782(6)
c (Å)	9.023(3)
α (°)	93.92(3)
β (°)	97.05(3)
γ (°)	65.42(3)
Volume (Å^3)	1191.1(8)
Z	2
$D_{calcd.}$ (g/cm^3)	1.463
μ (Mo-Kα) (cm^{-1})	7.11
$F(000)$	548
Diffractometer	Rigaku AFC7R
Radiation	Mo-Kα ($\lambda = 0.71069$ Å) Graphite monochromated
Scan type	$\omega - 2\theta$
Scan width	$(1.21 + 0.30 \tan \theta)°$
$2\theta_{max}$	49.9°
No. of reflections measured	Total: 3660; unique: 3431 ($R_{int} = 0.036$)
Correction	Lp
Structure solution	Direct methods (SHELXS86)[18]
Refinement	Full-matrix least-squares
No. of observations ($I > 2.00\sigma(I)$)	2546
No. of variables	299
Reflection/parameters ratio	8.52
Residuals: R; Rw	0.041; 0.051
S	1.65
Max. peak in final diff. map	0.31 e Å^{-3}

Hydrogen atoms were refined isotropically. A summary of data collection and structure refinement is given in Table I, the final atomic positional parameters, selected bond lengths and bond angles are given in Tables II and III, respectively.

RESULTS AND DISCUSSION

Synthesis

In general, manganese(II) complexes with Schiff-bases are air-sensitive and easily oxidized to manganese(III) complexes by molecular oxygen. Our synthetic procedure is somewhat different from that reported by Pecoraro *et al.*[12]

TABLE II Atomic parameters and equivalent isotropic thermal parameters

Atom	*x*	*y*	*z*	*Beq* (Å^2)
Mn	0.02313(6)	−0.21962(5)	−0.26965(7)	2.02(1)
Cl	0.0776(1)	−0.3398(1)	0.2237(1)	3.81(3)
O1	0.1882(2)	−0.3184(2)	−0.3168(3)	2.39(6)
O2	0.4407(3)	−0.3911(3)	−0.3065(4)	4.26(8)
O3	−0.1441(2)	−0.1213(2)	−0.2234(3)	2.31(6)
O4	−0.3906(3)	−0.0565(3)	−0.2332(4)	4.26(8)
O5	−0.0644(3)	−0.2207(2)	−0.5075(3)	2.79(7)
O6	0.1060(3)	−0.2153(2)	−0.0328(3)	2.80(7)
O7	0.2141(4)	0.1792(3)	−0.0662(4)	5.6(1)
N1	−0.0169(3)	−0.3562(3)	−0.2481(4)	2.51(8)
N2	0.0591(3)	−0.0782(3)	−0.2848(3)	2.11(7)
C1	0.2604(4)	−0.4186(3)	−0.2513(4)	2.4(1)
C2	0.3963(4)	−0.4606(4)	−0.2450(5)	2.9(1)
C3	0.4736(4)	−0.5644(4)	−0.1802(5)	3.8(1)
C4	0.4212(5)	−0.6300(4)	−0.1200(6)	4.1(1)
C5	0.2900(5)	−0.5928(4)	−0.1266(5)	3.6(1)
C6	0.2084(4)	−0.4854(3)	−0.1896(5)	2.5(1)
C7	0.0716(4)	−0.4549(3)	−0.2076(5)	2.7(1)
C8	−0.1490(4)	−0.3482(4)	−0.2957(5)	2.9(1)
C9	−0.1731(4)	−0.3452(4)	−0.4661(5)	3.4(1)
C10	−0.1830(4)	−0.2370(4)	−0.5370(5)	3.0(1)
C11	0.5771(5)	−0.4333(6)	−0.3052(7)	6.4(2)
C12	−0.2169(4)	−0.0217(3)	−0.2886(4)	2.30(9)
C13	−0.3523(4)	0.0168(4)	−0.2954(5)	3.1(1)
C14	−0.4332(4)	0.1216(4)	−0.3572(5)	3.8(1)
C15	−0.3821(5)	0.1899(4)	−0.4146(5)	3.9(1)
C16	−0.2511(4)	0.1564(4)	−0.4061(5)	3.0(1)
C17	−0.1672(4)	0.0488(3)	−0.3445(4)	2.31(9)
C18	−0.0315(4)	0.0216(3)	−0.3201(4)	2.5(1)
C19	0.1904(4)	−0.0855(4)	−0.2332(5)	2.8(1)
C20	0.2136(4)	−0.0921(4)	−0.0647(5)	2.8(1)
C21	0.2272(4)	−0.2038(4)	−0.0019(5)	2.7(1)
C22	−0.5256(5)	−0.0209(5)	−0.2242(7)	6.0(2)

TABLE III Selected inter-atomic distances (Å) and bond angles (°)

Mn−O1	1.867(3)	Mn−O3	1.882(3)
Mn−O5	2.256(3)	Mn−O6	2.236(3)
Mn−N1	2.007(3)	Mn−N2	2.030(3)
Cl−H28	1.996(2)	Cl−H14*	1.985(3)
O(1)−Mn−O(3)	179.3(1)	O(1)−Mn−O(5)	92.6(1)
O(1)−Mn−O(6)	88.6(1)	O(1)−Mn−N(1)	89.7(1)
O(1)−Mn−N(2)	92.2(1)	O(3)−Mn−O(5)	87.0(1)
O(3)−Mn−O(6)	91.8(1)	O(3)−Mn−N(1)	89.7(1)
O(3)−Mn−N(2)	88.3(1)	O(5)−Mn−O(6)	178.8(1)
O(5)−Mn−N(1)	84.4(1)	O(5)−Mn−N(2)	96.8(1)
O(6)−Mn−N(1)	95.9(1)	O(6)−Mn−N(2)	82.9(1)
N(1)−Mn−N(2)	177.7(1)	Mn−O(1)−C(1)	124.4(2)
Mn−O(3)−C(12)	124.6(2)	Mn−O(5)−C(10)	119.5(2)
Mn−O(6)−C(21)	119.4(2)	Mn−N(1)−C(7)	122.0(3)
Mn−N(1)−C(8)	119.6(2)	Mn−N(2)−C(18)	122.4(3)
Mn−N(2)−C(19)	118.6(2)		

*Symmetry code: *x*, *y*, 1 + *z*.

First, we used the equimolar reactants of manganese salts $Mn(ClO_4)_2 \cdot 6H_2O$ or $MnCl_2 \cdot 4H_2O$ with Schiff-base ligand 1-(3-methoxysalicylaldeneamino)-3-hydroxypropane to react in ethanolic solution. Another difference is that we added the organic base, triethylamine, to the reaction mixture without reflux. Both of the procedures are remarkably different from that reported by Okawa *et al.*[13]

Crystal Structure

The molecular structure is shown in Figure 1. The crystal structure consists of discrete mononuclear $[Mn(III)(Hvanpa)_2]^+$ cations. The manganese atoms are six-coordinate. Several groups have shown the utility of using hydroxyl Schiff base ligands to form dimeric and trimeric manganese(III) or mixed valence manganese complexes. Kida *et al.*[14] reported the first binuclear manganese(III) complex containing di-μ_2-alkoxo oxygen atoms and two bridged bidentate acetato oxygen atoms. Pecoraro *et al.*[12] first reported an unsupported di-μ_2-alkoxo binuclear manganese(III) complex. Five-coordinate di-μ_2-alkoxo binuclear vanadium(IV) has recently appeared.[15] We have presented a chloride- and water-containing six-coordinate unsupported di-μ_2-alkoxo binuclear manganese(III) complex,[11] but sometimes, only monomeric complexes are formed.

The octahedral geometry is distorted. The equatorial approximate square plane involving the manganese atoms at its center is formed by two imino

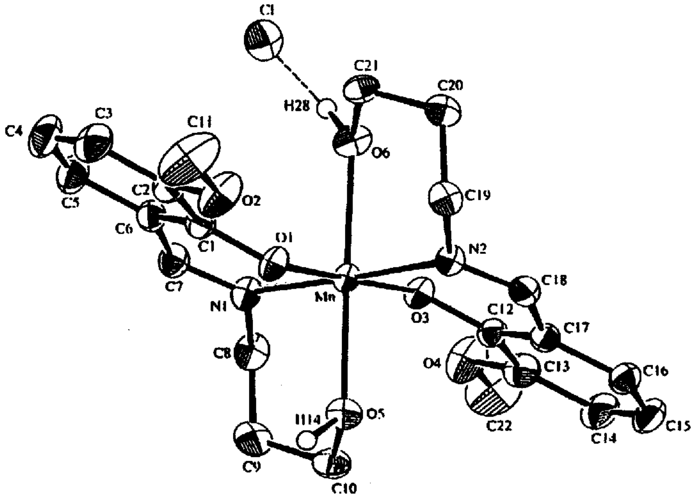


FIGURE 1 Crystal structure of $[Mn(III)(Hvanpa)_2]^+$ cation with thermal ellipsoids (50% probability level).

nitrogen atoms and two phenolic oxygen atoms of the Hvanpa$^-$ ligands. The Mn–O1 (1.867 Å), Mn–O3 (1.882 Å), Mn–N1 (2.007 Å) and Mn–N2 (2.030 Å) are normal for the in-plane bonds of manganese(III) complexes.[12,16] The bond angles around the manganese atoms vary from 83° to 97°. The axial Mn–O distances (2.256 and 2.236 Å) are considerably longer than the in-plane Mn–O distances. Thus the coordination geometry around the manganese atom significantly deviates from a regular octahedron and this tetragonal elongation is attributed to a Jahn–Teller distortion at the d^4 manganese center.

Each bond length in the Hvanpa$^-$ ligand has a normal value. The Hvanpa$^-$ moiety forms two six-membered chelate rings with the manganese atom. The N1–C7 and N2–C18 bond distances of 1.289 and 1.295 Å, respectively, suggest that they are double-bonded confirmed by the IR spectrum with a strong vibration band at 1615 cm^{-1}.

The distances of Cl ··· H28 and Cl ··· H14* (*, symmetry code: $x, y, 1+z$) are 1.996(2) and 1.985(3) Å respectively, indicating that the chloride ions are hydrogen-bonded with H28 and H14* from the hydroxyl groups of the Hvanpa$^-$ ligands and thus form a chain with the [Mn(Hvanpa)$_2$] cations (as shown in Figure 2). The lattice water molecules also interact with the phenolic oxygen atom O3 through hydrogen bonding (as shown in Figure 3). These hydrogen bonds make the complex stable for a prolonged time.

FT-IR Spectra and Magnetic Moments

FT-IR spectrum of mononuclear [Mn(Hvanpa)$_2$(NCS)] shows three bands at 3500(m), 3400(s) and 3250(m) cm^{-1}, which are attributed to the alcoholic

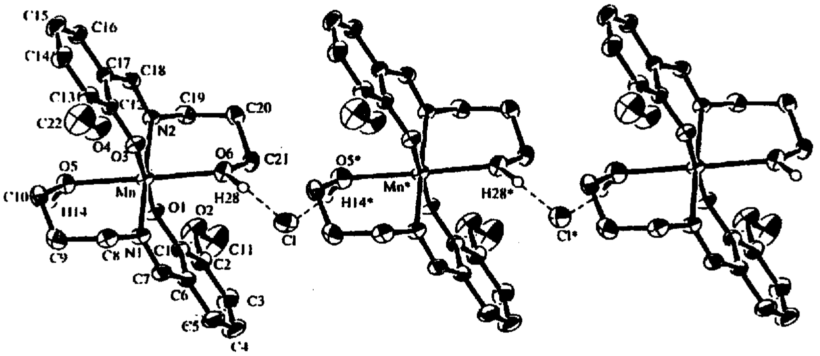


FIGURE 2 One-dimensional chain diagram which contains Cl ··· H hydrogen bonds.

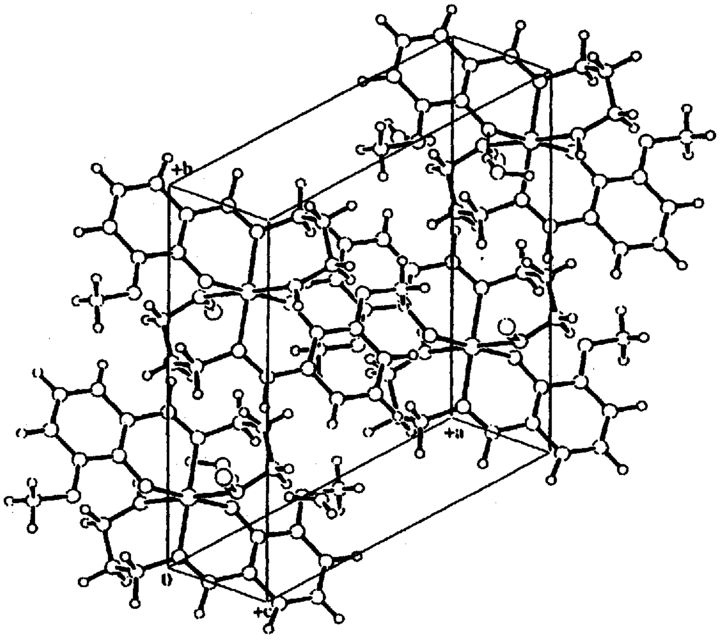


FIGURE 3 Crystal package down the *c* axis.

OH groups of the Hvanpa$^-$ ligands (as shown in Figure 4, upper). It is likely that one Hvanpa$^-$ acts as a bidentate ligand and the other as a tridentate ligand as is shown in Scheme 1D. The C–N and C–S stretching bands of NCS$^-$ ion were observed at 2070 and 810 cm^{-1}, respectively, indicating coordination of the NCS$^-$ ion to the metal through the nitrogen atom.[17] Thus, the infrared spectrum and the composition of the mononuclear complex indicate that it possesses a six-coordinate structure.

The infrared spectrum of complex **2** shows three absorption peaks at 3550(m), 3450(m) and 3300(m) cm^{-1}, which are assigned to the O–H stretching bands of the coordinated OH groups. The broad absorption peak of the lattice water molecules is covered by the moderately stronger alcoholic OH-stretching bands (as shown in Figure 4, lower).

The strong bands at 1618 and 1615 cm^{-1} for [Mn(Hvanpa)$_2$(NCS)] and [Mn(Hvanpa)$_2$]Cl, respectively, are attributed to ν(C=N) vibration.

The magnetic moments for [Mn(Hvanpa)$_2$(NCS)] and [Mn(Hvanpa)$_2$]Cl are 4.88 and 4.85 BM, respectively, which are in agreement with a high-spin d^4 system with no magnetic interactions between the manganese centers.

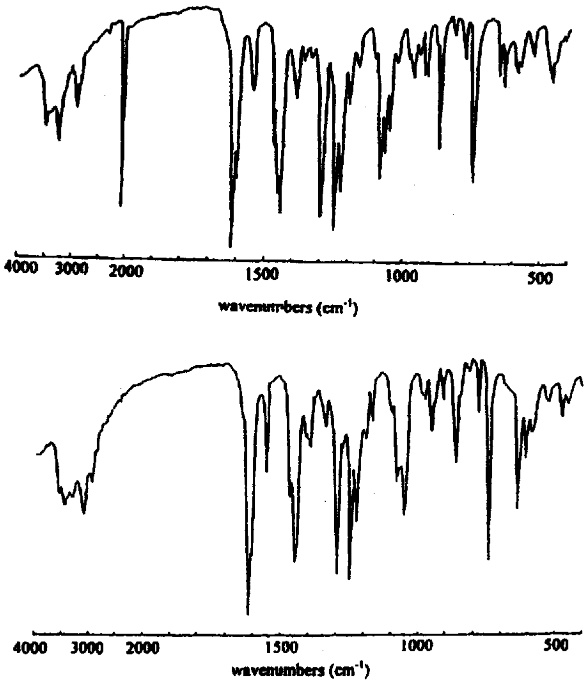


FIGURE 4 IR spectra for the complexes (upper, [Mn(III)(Hvanpa)$_2$(NCS); lower, [Mn(III)(Hvanpa)$_2$Cl · H_2O).

Acknowledgments

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