

Mn(III) tetradentate Schiff base complexes with pseudohalides: A brief introduction

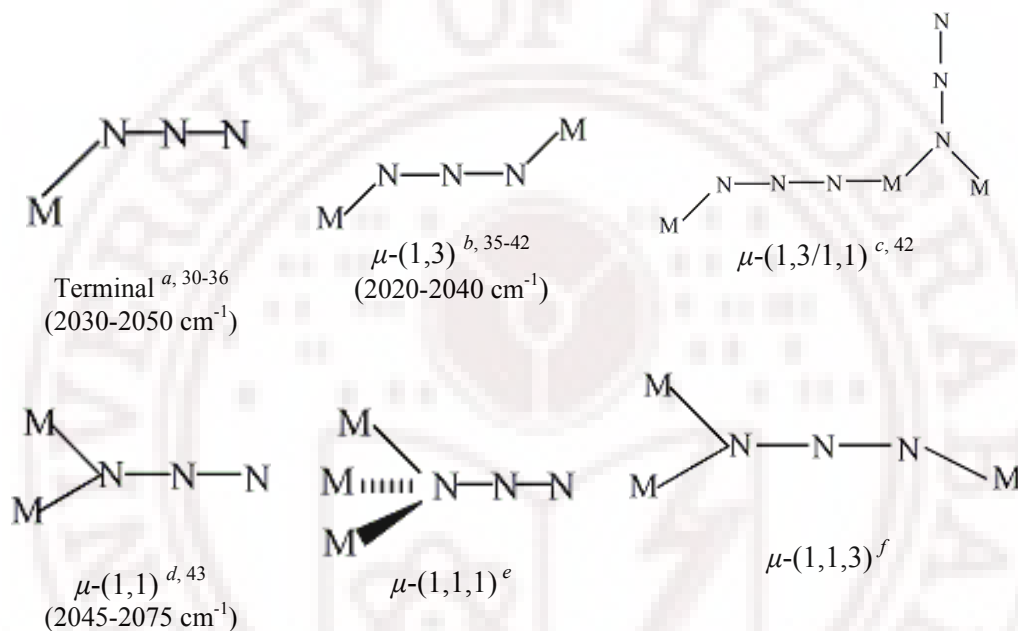
1.1. Introduction

Tetradentate Schiff base (SB) ligands form Mn(III) complexes of the type Mn(SB)X. The simplest SB ligand of this type is salen formed by condensing 1,2-diaminoethane with salicylaldehyde. Often the sixth coordination position is occupied by a solvent molecule (S), usually water. Numerous complexes of the type Mn(SB)Cl¹⁻¹⁵ and Mn(SB)(S)Cl¹⁶⁻²⁵ have been reported. The former include the widely used Jacobson catalyst, where SB is a chiral ligand leading to asymmetric epoxidation^{26,27} and aziridination^{28,29} of olefins. Besides the chloro complexes, analogous complexes where X is a pseudohalide ion are also known: N₃⁻,³⁰⁻⁴³ NCS⁻,^{15,32,44-51} NCO⁻,^{30,52-54} CN⁻.⁵⁵ Since the present thesis deals with pseudohalide complexes, a brief statement about the coordination modes of the pseudohalide ions is given in the next section.

1.2. Coordination modes of pseudohalide ions:^{56,57} Different observed coordination modes are depicted below. References are given only for Mn(III) complexes.

1.2.1. Coordination modes of azide (N₃⁻): The azide ion in ionic salts is linear and symmetric, having equal N-N distances (1.167 Å). But the covalently bonded azide has unequal bond distances (In M-N₁-N₂-N₃, N₁-N₂ distance is more than N₂-N₃). In

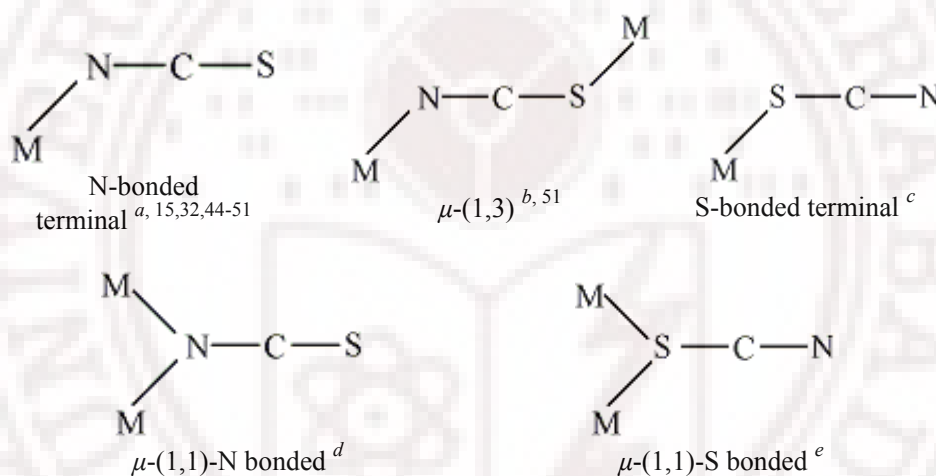
coordination complexes the azide ion has different kinds of binding modes like N-bonded terminal, μ -(1,3), μ -(1,3/1,1), μ -(1,1), μ -(1,1,1), μ -(1,1,3) as shown in Scheme 1.1. Depending upon the coordination mode of the azide ion, the IR spectra of the compounds are different.



Scheme 1.1. Different coordination modes of azide ion. References and IR frequencies ($\nu_{\text{a}}\text{N}_3^-$) are given for Mn(III)-azide complexes. CSD search results: ^a1455 for all transition metals, 15 Mn^{3+} . ^b415 for all transition metals, 9 Mn^{3+} . ^c35 for all transition metals, 1 Mn^{3+} . ^d525 for all transition metals, 1 Mn^{3+} . ^e26 for all transition metals. ^f18 for all transition metals.

1.2.2. Coordination modes of thiocyanate (NCS^-): Being an ambidentate ligand thiocyanate may coordinate the metal center through the nitrogen (M-NCS) or the sulfur (M-SCN) or both (M-NCS-M). The N-C and C-S bond distances of the thiocyanate ion are 1.149 Å and 1.689 Å, respectively. The coordination bond distance of N-bonded thiocyanate is less than S-bonded thiocyanate ion. The CN

stretching frequency of the N-bonded compound is nearly 2050 cm^{-1} , lower than that of S-bonded complex (nearly 2100 cm^{-1}). The bridging ion has frequencies in between the above values. The CS stretching vibrations are at $780\text{--}860\text{ cm}^{-1}$ for N-bonded and $690\text{--}720\text{ cm}^{-1}$ for S-bonded coordination complexes. The N-bonded complexes exhibit single sharp bending vibration at about 480 cm^{-1} , whereas the S-bonded complexes show several bands of low intensity near 420 cm^{-1} . Some important coordination modes of the thiocyanate ion are shown in Scheme 1.2.

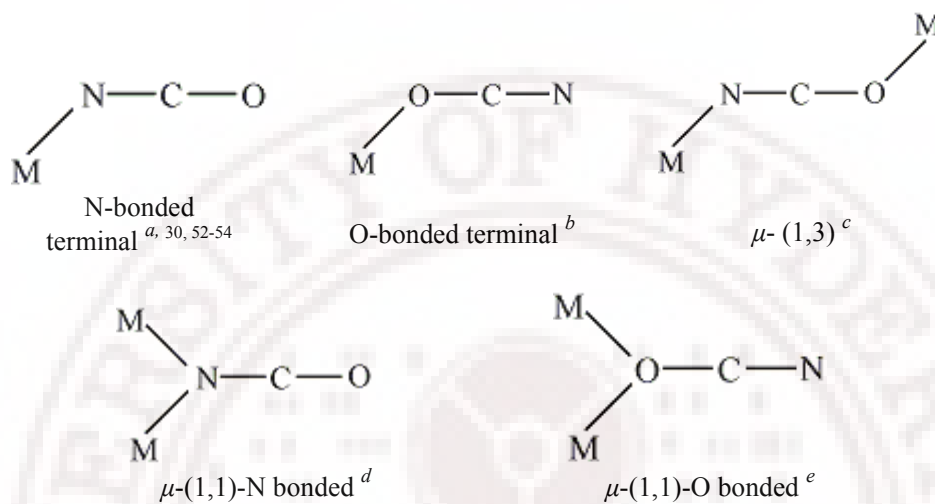


Scheme 1.2. Different coordination modes of thiocyanate ion. References are given for Mn(III)-thiocyanate complexes. ^a2801 for all transition metals, 28 Mn^{3+} . ^b191 for all transition metals, 1 Mn^{3+} . ^c2 for all transition metals. ^d42 for all transition metals. ^e21 for all transition metals.

1.2.3. Coordination modes of cyanate (NCO^-): The linear cyanate ligand may coordinate the metal center through the nitrogen (M-NCO) or the oxygen (M-OCN) or both (M-NCO-M). The N-C and C-O bond distances of the cyanate ion are 1.17 \AA and 1.23 \AA , respectively. Majority of the reported complexes are N-bonded. The observed ranges for asymmetric stretching, symmetric stretching and bending

vibrations of the cyanate are 2050-2250, 1200-1400 and 420-480 cm^{-1} , respectively.

Expected coordination modes of the cyanate ion are shown in Scheme 1.3.



Scheme 1.3. Different coordination modes of cyanate ion. Reference is given for Mn(III)-cyanate complex. ^a260 for all transition metals, 4 Mn^{3+} . ^b16 for all transition metals. ^c12 for all transition metals. ^d51 for all transition metals. ^e1 for all transition metals.

1.3. Classification of the Mn(SB)X complexes:

1.3.1. Mononuclear complexes: these are divided into two types. (i) Five coordinated complexes^{1-15,44-47} in which the manganese ion has square pyramidal geometry. The tetradentate Schiff base ligand coordinates the Mn(III) atom in equatorial mode and the axial position is occupied by an anionic ligand. (ii) Six coordinated complexes^{16-25,32-35,42,48-51} have distorted octahedral geometry and the tetradentate ligand binds the Mn(III) atom in the equatorial mode and axial positions are occupied by anionic ligand and solvent molecule.

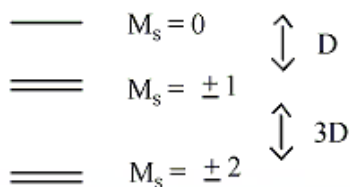
1.3.2. Dinuclear complexes: In these complexes the tetradentate Schiff base ligand can coordinate in two different modes. (i) Equatorial mode: In all phenoxo-bridged dimeric complexes³⁰, the tetradentate SB coordinates in the equatorial mode. (ii) *Cis*-octahedral mode: This mode, seen for example in $[\text{Fe}(\text{salpn})\text{N}_3]_2$,³⁸ wherein the azide ion acts as a bridging ligand is not known for Mn(III) complexes.

1.3.3. Polymers: Depending upon the crystallization conditions, the Mn(SB)X complexes may sometimes build *trans*- μ -(1,3)-bridged 1D-polymeric chains along the Jahn-Teller axis.^{35-42,51} In these complexes the tetradentate Schiff ligand coordinates in the equatorial mode, and the axial positions are occupied by X. A mixed *trans*- μ -(1,3/1,1)-azide bridged complex⁴² as well as a *trans*- μ -(1,1)-azide bridged polymer with an additional carboxylate ligand⁴³ has been reported. With the bidentate ligand acac, *trans*- μ -(1,3)-azide bridged polymeric chain is obtained in $\text{Mn}(\text{acac})_2\text{N}_3$.⁴¹

1.3.4. Weak interactions: Aggregation of mononuclear complexes into dimers and networks via H-bonding involving coordinated or lattice solvent molecules have been reported.³²

1.4. Magnetic Properties:⁵⁸

1.4.1. Mononuclear complexes: The low temperature magnetic moment in magnetically dilute Mn(III) compounds is influenced by zero field splitting. The splitting arises from a dipolar interaction of the form $S.D.S$ which lifts the 5-fold degeneracy in zero field as shown below.



The above scheme assumes axial symmetry so that the interaction can be written

has $D \{S_z^2 - \frac{1}{3}S(S+1)\}$, where $D = \frac{3}{2}D_{\parallel}$ and $D_{\perp} = -\frac{1}{2}D_{\parallel}$.

Further, the above ordering of levels assume a negative value of D , which is usually the case for octahedral Mn(III) complexes^{59a-c} wherein the axial component of the ligand is weaker than the equatorial component. The D parameter is generally small ($0-2 \text{ cm}^{-1}$) so that significant increase in magnetic moment is felt only below about 8K.

Often mononuclear complexes are not magnetically dilute in the solid state. This is due to presence of weak intermolecular interactions such as H-bonding and π -stacking. In such situations one or more exchange terms are superimposed on the zero field term in the spin Hamiltonian. It is not normally practical to include each exchange coupling individually since such an approach may lead to over parametrization. Instead, it may be possible to model the intermolecular interaction using the molecular field approximation,^{59d} which simply adds a single average term to the molecular susceptibility.

1.4.2. Dinuclear complexes: The spin Hamiltonian can be written as $\beta S_1 \cdot g_1 \cdot H + \beta S_2 \cdot g_2 \cdot H - 2JS_1 \cdot S_2 + S_1 \cdot D_1 \cdot S_1 + S_2 \cdot D_2 \cdot S_2 + S_1 \cdot D_{12} \cdot S_2 + d_{12} S_1 \times S_2$ (positive J implies ferromagnetic coupling such that for $S_1 = S_2 = 1/2$, the singlet-triplet gap = $2J$). Often simplifying assumptions are made in using this Hamiltonian.^{58b} If the exchange

parameter J is sufficiently large compared to zero field splitting it may be possible to use the dimer equation⁶⁰ to fit magnetic susceptibility data. However if J is not large enough zero field splitting can not be neglected and the susceptibility has to be calculated by including the population of energy levels at each temperature, the energy level being derived by diagonalisation of the full Hamiltonian matrix.⁶¹ In both approaches interdimer interactions may be included within the molecular field approximation.

Several phenoxo-bridged complexes have been characterized (Table 1.1). The exchange parameters are within the range -3.4 to 12.6 cm^{-1} . Some of the phenoxo-bridged complexes are ferromagnetic and have been investigated for their single molecule magnetism (SMM).^{30,64,69} SMM implies the following: (i) High spin ground state for the molecule and (ii) molecular compound after being magnetized by an applied field retains its magnetism even when the field is removed. This implies slow relaxation within a zero dimensional system (molecule). Usually this is observed only at very low temperature ($\leq 10\text{K}$). Relaxation is then studied by frequency dependent measurements in an AC susceptibility apparatus. In AC susceptibility measurements, magnetic susceptibility is measured at small ($\sim 1 \text{ Oe}$) oscillating magnetic field. A plot of both in-plane (χ') and out-of-plane (χ'') component of the susceptibility is plotted against temperature. An SMM compound shows a maximum in both plots. The maxima shift to higher temperature as the frequency is increased. The inverse of the frequency gives an estimate of the relaxation time (τ) at the temperature corresponding to the maximum in the χ'' versus T plot. A plot of $\ln \tau$ versus $1/T$ is generally straight line as a result of the Arrhenius law.

$$\tau = \tau_0 e^{\frac{T_0}{T}}$$

This measurement yields τ_0 and T_0 . These quantities can also be determined in presence of a static field. It should be mentioned that if there are more than one relaxation mechanisms, the Arrhenius plot may correspond to more than one straight line. In Mn(III) phenoxo-bridged dimers the negative D value of the dimer is believed to favor slow relaxation and the emergence of the SMM property.

Table 1.1. Selected bond distances (Å) and bond angles (°) and magnetic parameter of few phenoxo-bridged Mn(III) dimers. (F = ferro, AF = antiferromagnetic interaction, NI = non interaction and ND = no data in the literature)

	Mn-O	Mn-O*	O-Mn-O*	Mn-O-Mn*	Mn-Mn*	F/AF	Magnetic Properties				Ref.
							g	J/cm ⁻¹	D/cm ⁻¹	zJ/cm ⁻¹	
1	1.916(1)	2.513(1)	79.43	100.58(4)	3.428	F	2.022	0.42(2)	0.0006	0.002	This thesis
2	1.902(2)	2.588(2)	81.46	98.55	3.433	F	2.000	0.58(1)	-2.32	-0.06	
3	1.912(1)	2.493(1)	78.76	101.23	3.425	AF	1.997	-0.20(2)	-0.009	-0.05	
4	1.907(2)	2.411(2)	77.88	102.1(1)	3.374	AF	2.017	-0.7(1)	-0.6(1)	-0.02	
5	1.922(2)	2.492(2)	78.53	101.5(5)	3.437	F	2.01	0.88	-0.025	0.026	
a	1.901(5)	2.412(6)	79.42(2)	100.6(2)	3.334(3)	F	2.0000	6.30	-1.70		62
b	1.894(3)	2.411(3)		100.4	3.325	F	2.0150	3.70		0.41	63
c	1.911(2)	2.341(2)	80.42(7)	99.58(7)	3.258(5)	F	1.96	1.8	-4.5		64
d	1.909(2)	2.434(2)	78.42(1)	101.6(1)	3.381(1)	F	1.93	1.79	-2.53	-0.79	15
e	1.896(3)	2.662(3)	79.4(1)	100.6(1)	3.541(1)	F	1.96	1.20	-0.38		
f	1.872(2)	3.441(2)	83.76(8)	96.24(8)	4.092(8)	F	1.99	0.55	-1.25		
g	1.877(2)	3.758	83.43(1)	96.57	4.388(9)	F	2.03	0.12	-1.00		
h	1.892(5)	3.505(5)	85.8(2)	94.2(2)	4.102(2)	F	2.04	0.38	-1.87		
i	1.891(1)	2.813(5)	99.57(5)		3.641(5)	F	1.98	1.35	-1.9		30
j	1.863(4)	3.190(2)	98.4(2)		3.922(2)	F	1.98	0.6	-1.0		
k	1.898(1)	2.793(0)	97.82(0)		3.584	F	2.03	0.73	-0.3		
l	1.918(7)	2.728(2)	100.0(1)		3.597(3)	F	2.00	0.55	-4.1		
m	1.908	2.395(3)	99.85(1)		3.307(4)	AF	1.96	-0.45	-1.0		
n	1.93(6)	2.120(3)		99.93(7)	3.539(6)	F	2.01	0.42	0		36
o	1.88(1)	2.87(1)	83.22	96.76	3.611	F	1.99	1.32			31
p	1.912(4)	2.375(5)	78.2(2)	101.83	3.341(2)	AF	2.00	-0.55			

<i>q</i>	1.912(3)	2.305(2)	76.6(1)	103.4(1)	3.318(1)	AF		-1.68			65
<i>r</i>	1.906(6)	2.419(7)			3.350	AF					66
<i>s</i>	1.891(3)	2.490(3)	80.7(1)	99.3(1)	3.361	AF					67
<i>t</i>	1.880(6)	2.750(6)	81.3(2)	98.7(2)	3.558(3)	AF					68
<i>u</i>	1.923(3)	2.539		100.00	3.441(1)	NI					51
<i>v</i>	1.902(3)	2.557(3)	80.14(1)	99.86	3.438	-	-	-	-	-	46b

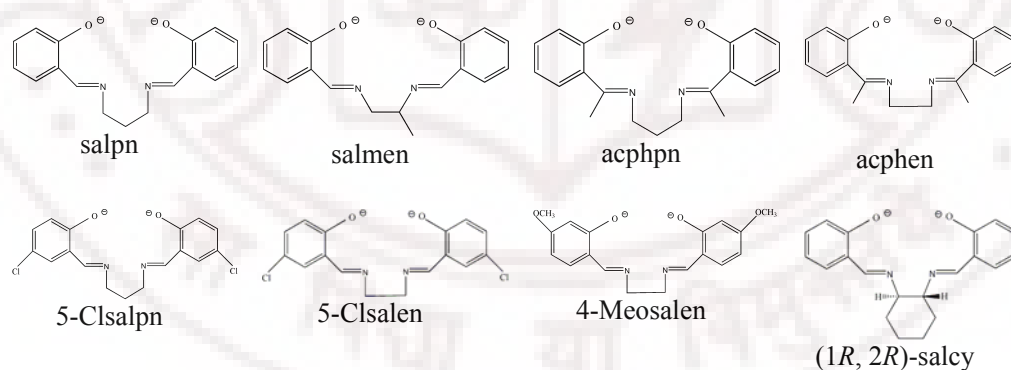
1. [Mn(salpn)NCO]₂. 2. [Mn(salmen)N₃]₂. 3. [Mn(acphpn)N₃]₂. 4. [Mn(acphen)NCS]₂. 5. [Mn(5-Clsalpn)N₃]₂. ^a[Mn(salen)(H₂O)]₂(ClO₄)₂. ^b[Mn(L)(H₂O)]₂(ClO₄)₂[L = *N,N'*-bis(2-hydroxyacetophenylidene)-1,2-diaminopropane]. ^c[Mn(salpn)H₂O]₂. ^d[Mn(saltmen)(H₂O)]ClO₄. ^e[Mn(naphtmen)(H₂O)]ClO₄. ^f[Mn(saltmen)(NCS)]. ^g[Mn(naphtmen)(NCS)]. ^h[Mn(naphtmen)(Cl)]. ⁱ[Mn(saltmen)(O₂CCH₃)₂·2CH₃CO₂H]. ^j[Mn(saltmen)(N₃)]₂. ^k[Mn(salen)(NCO)]₂. ^l[Mn(3,5-Brsalen)(3,5-Brsalicylaldehyde)]₂. ^m[Mn(5-Brsalen)(CH₃OH)]₂(ClO₄)₂. ⁿ[Mn(5-Clsalen)N₃]₂. ^o[Mn₂(L²)₂(N₃)₂], [L² = bis(*o*-hydroxyacetophenone)-ethylenediimine]. ^p[Mn₂(L¹)₂(N₃)₂], [L¹ = *N,N'*-(1,1-dimethylethylene)-bis-(salicylaldimine)]. ^q[Mn(L)(H₂O)]₂(ClO₄)₂ [L = *N*-(acetylacetylidene)-*N'*-(α -methylsalicylidene)-ethylenediamine]. ^r[Mn₂(bsalen)₂(H₂O)]₂(ClO₄)₂ [bsalen = *N,N'*-ethylenebis(5-bromosalicylideneiminato) dianion]. ^s[Mn(salen)(H₂O)]₂(ClO₄)₂·H₂O. ^t[Mn((salen)(NCS))]. ^u[Mn(salpn)NCS]₂. ^v[Mn((salen)(Him)]₂(ClO₄)₂·2MeOH. ^w[Mn(saltmen)(H₂O)](TCNQ). ^x[Mn₂(5-Clsaltmen)₂(H₂O)]₂(ClO₄)₂. ^y[Mn₂(5-Clsaltmen)₂(5-Clsal)]₂(ClO₄)₂. ^z[Mn(L²)(TCEA)][L²=*N,N'*-(1,1,2,2-tetramethylethylene)bis(3-hydroxy-4-naphthylideneiminato) (TCEA = tricyanoethenolate). ^v[Mn(salen)NCS]₂.

1.4.3. Extended systems: Magnetic characterization of linear chain compounds have been reported for azide and thiocyanate complexes.^{35-39,41a,43,51} These chains are built from 1,3-pseudohalide bridges. The interaction is antiferromagnetic with J in the range, -3.0 to -6.5 cm⁻¹. Spin canting leading to weak ferromagnetism has been observed.^{35,36,51} While mononuclear as well as dinuclear complexes often assemble into higher dimensional structures via intermolecular interactions, a systematic study of the effect of these interaction on magnetic property has not yet been made.

1.5. Electronic spectra of Mn(III) compounds: For d^4 ion in octahedral symmetry, a single d-d band is expected. However low symmetry distortions lead to splitting of this band giving rise to 3 bands in the high energy end of visible region extending into UV. Charge transfer and intra ligand absorption bands are superimposed on the d-d bands. When chiral Schiff base ligands are used, it is possible to observe circular dichroism (CD) for the absorption bands.⁷⁰ This may help in the assignment, because circular dichroism arising from the chiral center in the ligand is expected to be more pronounced for intra ligand and charge transfer bands than d-d bands.

1.6. Scope of the present work:

(i) Preparation of several Mn(SB)X, where SB is tetradentate Schiff base ligand including chiral ligands and X is a pseudohalide ion. The ligand systems used are given in Scheme 1.4.



Scheme 1.4.

Nomenclature of the Schiff bases are given in the list of abbreviation.

(ii) Structural characterization of the above complexes and observation of polymorphs wherever possible. Polymorphs may arise due to different mode of aggregation of Mn(SB)X: dimerisation through phenoxo-bridge; 1,3-bridged chain; 1,1-bridged chain.

(iii) Characterization of intermolecular interaction which may have important bearing on magnetic properties.

(iv) Measurements of the magnetic data wherever possible with collaboration with other groups. Measurements include variable temperature magnetic susceptibility at static and oscillating fields in order to characterize SMM systems.

(v) Analysis and interpretation of magnetic data and attempts at magneto-structural correlation.

1.7. References

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