



## Cr(III), Mn(III), Fe(III) and Co(III) Complexes of Schiff Bases Derived from 5-(Phenyl / Substituted Phenyl) -2-Hydrazino-1,3,4-Thiadiazole and Indoline-2,3-Dione

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ABSTRACT

A series of trivalent chromium, manganese, iron and cobalt complexes with Schiff bases (LH<sub>2</sub>), derived from 5-phenyl-2-hydrazino-1,3,4-thiadiazole and indoline-2,3-dione, of the type [M(L)<sub>2</sub>X(H<sub>2</sub>O)] [M = Cr, Mn, Fe, Co; X = Cl (for Cr and Fe) or CH<sub>3</sub>COO (for Mn and Co) have been synthesized in ethanol. The complexes were characterized by analyses, electrical conductance, magnetic moment and spectral (U.V-Vis, IR, and <sup>1</sup>H NMR) data. The presence of coordinated water molecule in these complexes has been inferred from TG studies. Tentative structures of the complexes have been proposed. The antifungal activity of the ligands and complexes were evaluated against *Aspergillus niger*, *Colletotrichum falcatum* and *Curvularia pallescens*. The complexes are found to be more potent against all species of fungi as compared to free ligands. The activity has been compared with the structural features of compounds.

## KEYWORDS

Schiff bases, chromium, manganese, iron, cobalt, UV-Vis., IR, antifungal activity.

## INTRODUCTION

1, 3, 4-Thiadiazole derivatives are important class of biological active compounds showing anti-inflammatory[1-3], antimicrobial and antitumor properties[4]. 2-Amino / substituted-amino-1, 3, 4-thiadiazoles and their Schiff bases have received significant importance because of their diverse biochemical properties[5-7]. One aspect of the use of coordination compounds of transition metals is their application as biologically active substance[8]. The attention of investigators has focused increasingly on bio-coordination compounds which can be used as biologically active preparations for medicine and agriculture. Thiadiazole ring is reported[9-11] to display fungicidal property by virtue of N=C-S- linkage, which is a possible toxophore in many pesticides, 2,5-disubstituted 1,3,4-thiadiazole moieties have been found to possess herbicidal, radioprotective, diuretic and bacteriostatic properties, Acetamide derivatives of 2-(benzoyl aminomethyl)-1,3,4-thiadiazole have been found to possess antiarrhythmic, antimetastatic, psychoneurosis, schistosomocidal, fungicidal, herbicidal and pesticidal activities. Cefozopram is one of the most commercially available antibiotic which contains 1,2,4-thiadiazole ring. Schiff bases derived from 1,3,4-thiadiazole have been synthesized and extensively studied because they have some typical properties such as manifestations of original structures, thermal stability, significant biological properties, high synthesis flexibility and therapeutic utility[12]. However, coordination behavior of such type of ligands towards trivalent first row transition metal ions is still unexplored. The present paper describes the synthesis, characterization and antifungal activities of chromium(III), manganese(III), iron(III) and cobalt (III) complexes with Schiff bases derived from 5-(phenyl / substituted phenyl)-2-hydrazino-1,3,4-thiadiazole and indoline-2,3-dione.

## MATERIALS AND METHODS

All the chemicals used were of A.R. grade. Ethanol and other solvents were distilled before use. Metal chlorides or acetates were procured from Sigma-Aldrich. The ligands and manganese(III) acetate were prepared as reported in the literature [13, 14].

## Preparation of the complexes

## Preparation of chromium(III), and iron(III) complexes with Schiff base derived from 5-(phenyl) -2-hydrazino-1,3,4-thiadiazole and indoline-2,3-dione (SIPTH)

To a magnetically stirred, methanolic solution (30 cm<sup>3</sup>) of CrCl<sub>3</sub>·6H<sub>2</sub>O (0.01 mol) or FeCl<sub>3</sub>·6H<sub>2</sub>O (0.01 mol) was added dropwise a solution of SIPTH (0.02 mol) containing sodium hydroxide (0.02 mol) in ethanol (20 cm<sup>3</sup>) over a period of 20 minutes. The solution was refluxed for ca. 10-18 h. The green / brown product was precipitated out which was filtered off, washed with ethanol (2 × 5 cm<sup>3</sup>), and finally with diethyl ether and dried *in vacuo*. The product was identified to be [M(SIPT)<sub>2</sub>X(H<sub>2</sub>O)] (M = Cr, Fe; X = Cl) Yield 58-68%.

## Preparation of manganese(III), complex with Schiff base derived from 5-phenyl -2-hydrazino-1,3,4-thiadiazole and indoline-2,3-dione (SIPTH)

To a magnetically stirred, methanolic solution (30 cm<sup>3</sup>) of Mn(OAc)<sub>3</sub>·2H<sub>2</sub>O (0.01 mol) was added dropwise a solution of SIPTH (0.02 mol) containing sodium hydroxide (0.02 mol) in methanol (20 cm<sup>3</sup>) over a period of 30 minutes. The solution was refluxed for 16 h. The brownish product was filtered off, washed with methanol (2 × 5 cm<sup>3</sup>) and with diethyl ether and dried *in vacuo*. The product was identified to be [Mn(SIPT)<sub>2</sub>(OAc)(H<sub>2</sub>O)] Yield 58%.

## Preparation of cobalt(III) complex with Schiff base derived from 5-phenyl-2-hydrazino-1,3,4-thiadiazole and indoline-2,3-dione (SIPTH)

To a magnetically stirred, methanolic solution (30 cm<sup>3</sup>) of cobalt(II) acetate (0.01 mol) was added dropwise a solution of SIPTH (0.02 mol) containing sodium hydroxide (0.03 mol) in ethanol (20 cm<sup>3</sup>) over a period of 20 minutes. To this H<sub>2</sub>O<sub>2</sub> (30%, 6 cm<sup>3</sup>) was added slowly. The solution was refluxed for 15 h. The brown product was filtered off, washed with ethanol (2 × 5 cm<sup>3</sup>), and finally with diethyl ether and dried *in vacuo*. The product was identified to be [Co(SIPT)<sub>2</sub>(OAc)(H<sub>2</sub>O)] Yield 70%. The same synthetic procedure was adopted for the synthesis with other Schiff base ligands. The physical properties and analytical data of the complexes are given in table 1.

**Table 1 : Analytical data of chromium(III), manganese(III), iron(III) and cobalt(III) complexes with Schiff bases derived from 5-(phenyl / substituted phenyl) -2-hydrazino -1, 3, 4-thiadiazole and indoline-2,3-dione**

Complex	Mol. formula	Colour	Yield (%)	Conductance	Analysis Found (Calcd) %			
					C	H	N	M
[Cr(SIPT) <sub>2</sub> Cl(H <sub>2</sub> O)]	[Cr (C <sub>32</sub> H <sub>22</sub> N <sub>10</sub> S <sub>2</sub> O <sub>3</sub> Cl)]	Green	58	8.2	51.3 (51.5)	2.9 (3.0)	18.6 (18.8)	6.8 (7.0)
[Cr(SIOCT) <sub>2</sub> Cl(H <sub>2</sub> O)]	[Cr (C <sub>32</sub> H <sub>20</sub> N <sub>10</sub> S <sub>2</sub> O <sub>3</sub> Cl <sub>3</sub> )]	Green	56	8.5	47.0 (47.1)	2.4 (2.5)	17.0 (17.2)	6.3 (6.4)
[Cr(SINT) <sub>2</sub> Cl(H <sub>2</sub> O)]	[Cr (C <sub>32</sub> H <sub>20</sub> N <sub>12</sub> S <sub>2</sub> O <sub>7</sub> Cl)]	Green	62	9.2	45.9 (46.0)	2.3 (2.4)	20.0 (20.1)	6.1 (6.2)
[Cr(SIMT) <sub>2</sub> Cl(H <sub>2</sub> O)]	[Cr (C <sub>34</sub> H <sub>26</sub> N <sub>10</sub> S <sub>2</sub> O <sub>3</sub> Cl)]	Green	58	9.0	52.5 (52.7)	3.3 (3.4)	18.0 (18.1)	6.5 (6.7)
[Mn(SIPT) <sub>2</sub> (OAc)(H <sub>2</sub> O)]	[Mn (C <sub>34</sub> H <sub>25</sub> N <sub>10</sub> S <sub>2</sub> O <sub>5</sub> )]	Light Brown	58	6.7	52.5 (52.8)	3.2 (3.3)	18.0 (18.1)	7.0 (7.1)
[Mn(SIOCT) <sub>2</sub> (OAc)(H <sub>2</sub> O)]	[Mn (C <sub>34</sub> H <sub>23</sub> N <sub>10</sub> S <sub>2</sub> O <sub>5</sub> Cl <sub>2</sub> )]	Light Brown	61	6.2	48.3 (48.5)	2.6 (2.8)	16.4 (16.6)	6.4 (6.5)
[Mn(SINT) <sub>2</sub> (OAc)(H <sub>2</sub> O)]	[Mn (C <sub>34</sub> H <sub>23</sub> N <sub>12</sub> S <sub>2</sub> O <sub>9</sub> )]	Light Brown	65	5.8	47.0 (47.3)	2.6 (2.7)	19.4 (19.5)	6.3 (6.4)
[Mn(SIMT) <sub>2</sub> (OAc)(H <sub>2</sub> O)]	[Mn (C <sub>36</sub> H <sub>29</sub> N <sub>10</sub> S <sub>2</sub> O <sub>5</sub> )]	Light Brown	65	5.2	53.8 (54.0)	3.5 (3.6)	17.4 (17.5)	6.8 (6.9)
[Fe(SIPT) <sub>2</sub> Cl(H <sub>2</sub> O)]	[Fe (C <sub>32</sub> H <sub>22</sub> N <sub>10</sub> S <sub>2</sub> O <sub>3</sub> Cl)]	Light Brown	68	7.5	51.0 (51.2)	2.9 (3.0)	18.3 (18.5)	7.2 (7.4)
[Fe(SIOCT) <sub>2</sub> Cl(H <sub>2</sub> O)]	[Fe (C <sub>32</sub> H <sub>20</sub> N <sub>10</sub> S <sub>2</sub> O <sub>3</sub> Cl <sub>3</sub> )]	Light Brown	59	7.8	46.9 (47.0)	2.4 (2.5)	17.0 (17.1)	6.6 (6.8)
[Fe(SINT) <sub>2</sub> Cl(H <sub>2</sub> O)]	[Fe (C <sub>32</sub> H <sub>20</sub> N <sub>12</sub> S <sub>2</sub> O <sub>7</sub> Cl)]	Brown	62	8.2	45.5 (45.7)	2.3 (2.4)	19.9 (20.0)	6.5 (6.6)
[Fe(SIMT) <sub>2</sub> Cl(H <sub>2</sub> O)]	[Fe (C <sub>34</sub> H <sub>26</sub> N <sub>10</sub> S <sub>2</sub> O <sub>3</sub> Cl)]	Brown	64	6.9	52.4 (52.5)	3.3 (3.4)	17.8 (18.0)	7.0 (7.2)
[Co(SIPT) <sub>2</sub> (OAc)(H <sub>2</sub> O)]	[Co (C <sub>34</sub> H <sub>25</sub> N <sub>10</sub> S <sub>2</sub> O <sub>5</sub> )]	Dark Brown	70	5.2	52.3 (52.6)	3.1 (3.2)	17.9 (18.0)	7.5 (7.6)
[Co(SIOCT) <sub>2</sub> (OAc)(H <sub>2</sub> O)]	[Co (C <sub>34</sub> H <sub>23</sub> N <sub>10</sub> S <sub>2</sub> O <sub>5</sub> Cl <sub>2</sub> )]	Dark Brown	70	4.8	48.0 (48.3)	2.5 (2.7)	16.3 (16.6)	6.8 (7.0)
[Co(SINT) <sub>2</sub> (OAc)(H <sub>2</sub> O)]	[Co (C <sub>34</sub> H <sub>23</sub> N <sub>12</sub> S <sub>2</sub> O <sub>9</sub> )]	Brown	55	6.1	47.0 (47.1)	2.6 (2.7)	19.3 (19.4)	6.7 (6.8)
[Co(SIMT) <sub>2</sub> (OAc)(H <sub>2</sub> O)]	[Co (C <sub>36</sub> H <sub>29</sub> N <sub>10</sub> S <sub>2</sub> O <sub>5</sub> )]	Dark Brown	70	5.6	53.5 (53.7)	3.5 (3.6)	17.2 (17.4)	7.1 (7.3)

Where,

SIPTH = Schiff base derived from 5-(phenyl) -2-hydrazino -1, 3, 4-thiadiazole and indoline-2,3-dione

SIOCTH = Schiff base derived from 5-(o-chlorophenyl) -2-hydrazino -1, 3, 4-thiadiazole and indoline-2,3-dione

SINTH = Schiff base derived from 5-(p-nitrophenyl) -2-hydrazino -1, 3, 4-thiadiazole and indoline-2,3-dione

SIMTH = Schiff base derived from 5-(p-methoxyphenyl) -2-hydrazino -1, 3, 4-thiadiazole and indoline-2,3-dione

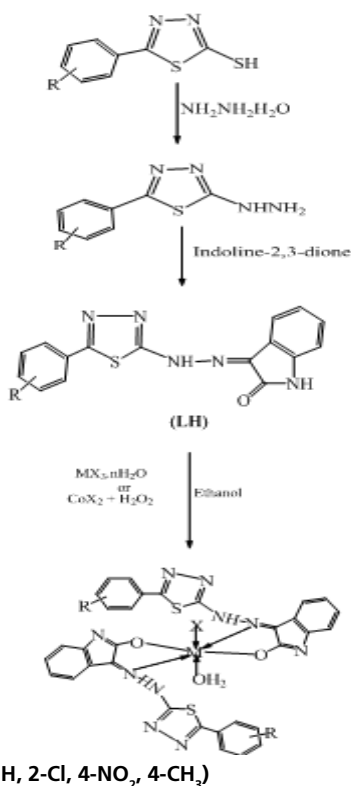
**Characterization of ligands and metal complexes :** The melting points of ligands and their metal complexes were determined by open capillary method and are uncorrected. C, H and N analyses were carried out at B.H.U., Varanasi. Metals were estimated gravimetrically. The IR spectra of the ligands and complexes were recorded in the range 4000-200 cm<sup>-1</sup> in potassium bromide medium on Matson 1000 model FTIR spectrophotometer and Beckman Acculab-9 spectrometer model 2000. The <sup>1</sup>H NMR spectra of ligands and few complexes were recorded in DMSO-d<sub>6</sub> on JEOL AI 300 spectrometer at the sweep width of 900 Hz and a sweep time of 300 sec. Chemical shifts are expressed relative to an internal reference TMS ( 1% by volume). Magnetic susceptibility measurements were made by the Faraday method using ferrous ammonium sulphate as calibrant.

For antifungal activity, all compounds were tested against all the test fungi by the food poison technique at three concentration ( 10, 100 and 1000 mg/L). For this, the desired amount of chemical was dissolved in 0.5 ml of acetone and mixed with the culture medium on the basis of the volume of the medium in each petri plate (about 100 mm diameter ). Oatmeal-agar medium were used for all the test fungi. In controls, the same amount of medium containing the requisite amount of solvent was poured in place of the test chemicals. A mycelia disk ( 5 mm diameter ) obtained from the periphery of 2-week-old cultures was taken and transferred to the center of each petriplate. Plated were incubated for 7 days at 28 ± 2°C. Each treatment was repeated three times, and the inhibition was recorded relative to percent mycelial inhibition calculated using the formula :  $dc-dt/dc \times 100$  where dc is the

average diameter of the mycelia I colony of the control and dt is the average diameter of the mycelia colony of the treatment

## RESULTS AND DISCUSSION

The reactions of chromium(III) chloride hexahydrate, manganese(III) acetate and iron(III) chloride hexahydrate with Schiff bases (LH) derived from 2-hydrazino-5-(phenyl / substituted phenyl)-1,3,4-thiadiazole and indoline-2,3-dione have been carried out in ethanol, which leads to the formation of complexes of type  $[M(L)_2X(H_2O)]$  ( $M = Cr(III)$  or  $Fe(III)$ ,  $X = Cl$ ;  $M = Mn(III)$ ,  $X = CH_3COO$ ), as shown in Scheme-I. Similarly cobalt(II) acetate reacts with these ligands in the presence of  $H_2O_2$  which leads to the formation of cobalt(III) complexes of type  $[Co(L)_2(CH_3COO)(H_2O)]$ .



### Scheme-I

The elemental analyses (Table 1) indicate 1:2 metal to ligand stoichiometry. The complexes are coloured solids; soluble in dimethylformamide, dimethylsulphoxide, nitrobenzene. The complexes decompose in the temperature range 170-275 °C. The electrical conductance measurements in dimethylformamide (Table 1) reveal that they are essentially non-electrolytes.

### Magnetic Moments

The magnetic moments of all the chromium(III), manganese(III), iron(III) and cobalt(III) complexes are obtained in order to have information of their probable geometry. The magnetic moments of chromium(III) complexes lie in the range 3.84-3.90 B.M., corresponding to three unpaired electrons[15]. The magnetic moments of manganese(III) complexes are at around 4.70-4.90 B.M. at room temperature which are consistent with the high-spin nature of these complexes[16,17]. The magnetic moments of iron(III) complexes lie around 4.85-4.90 B.M at room temperature[16]. The values are found to be close to spin-only value (5.92 B.M.). The cobalt(III) complexes are diamagnetic.

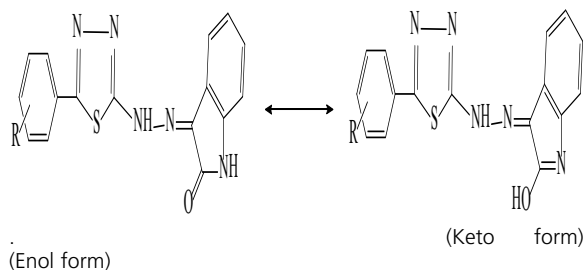
### Electronic Spectra

The electronic spectra of all complexes were recorded in DMSO. The electronic absorption spectra of chromium(III) complexes, show three absorption bands in the range 17,800-

18,500  $cm^{-1}$ , 20,000-22,520  $cm^{-1}$  and 25,990-27,100  $cm^{-1}$ . The lowest energy spin allowed transition is  $(v_1) {}^4A_{2g} \longrightarrow {}^3T_{2g}(F)$ . The other two bands are assigned to  ${}^4A_{2g} \longrightarrow {}^4T_{1g}$  and  ${}^4A_{2g} \longrightarrow {}^4T_{1g}(P)$  transitions respectively. The position of these bands confirm the octahedral geometry around the Cr(III) ion[18-21]. The electronic spectra of manganese(III) complexes show bands in the regions 14,200-14,350, 18,000-18,300 and 21,100-22,000  $cm^{-1}$  which are assigned to the transition  ${}^5B_g \longrightarrow {}^5A_{1g}$ ,  ${}^5B_{1g} \longrightarrow {}^5A_{2g}$ , and  ${}^5B_{1g} \longrightarrow {}^5E_{1g}$ [16,17]. The iron(III) complexes show a sharp band in the region 39,000-39,200  $cm^{-1}$  corresponding to charge transfer processes which are of high quantum energy. A broad band observed at ca. 26,400-27,100  $cm^{-1}$  is due to  $T_{2g} \longrightarrow \pi^*$  transitions. A shoulder and a band appearing at ca. 16,630-16,667 and 13,700-14,350  $cm^{-1}$  are considered to be due to  ${}^6A_{1g} \longrightarrow {}^4T_{2g}$  and  ${}^6A_{1g} \longrightarrow {}^4T_{1g}$  transitions respectively. These transitions favor an octahedral geometry for the Fe(III) complex[19-21]. The electronic spectra of cobalt(III) complexes show bands in the regions 16,110-16,400, 21,400-22,200 and 24,155-24,200  $cm^{-1}$ . These resemble those reported for other six-coordinated cobalt(III) complexes[25,26] and may be assigned to  ${}^1A_{1g} \longrightarrow {}^3T_{2g}$ ,  ${}^1A_{1g} \longrightarrow {}^1T_{1g}$  and  ${}^1A_{1g} \longrightarrow {}^1T_{2g}$  transitions, respectively. The appearance of three bands in cobalt(III) complexes indicates a low symmetry ligand field.

### Infrared Spectra

The IR spectra provide valuable information regarding the nature of functional group attached to the metal atom. Schiff bases shows a medium intensity band ca. 3250-3180  $cm^{-1}$  due to  $\nu(N-H)$  which remains almost at the same position in the complexes indicating the non-involvement of (N-H) group in the bond formation[27]. The ligands show strong intensity band at ca. 1620-1590  $cm^{-1}$  assignable to  $\nu(C=N)$  which shift to lower frequency (ca. 20-15  $cm^{-1}$ ) in the complexes. This shift indicates the coordination of azomethine nitrogen to metal ion[28]. Schiff bases exist in both keto and enol tautomeric forms suggested by a broad band (solution spectra) at ca. 2610  $cm^{-1}$  due to intramolecular hydrogen bonded -OH group. This band disappears in the metal complexes and a new band is observed at ca. 485-465  $cm^{-1}$  (M-O) (enolic) indicating the coordination of enolic oxygen to metal ion through deprotonation[29]. The  $\nu(C-S-C)$  vibration appears as a strong band at ca. 1125  $cm^{-1}$  in the free ligand[28]. The position of which remains the same in the complexes indicating non-coordination through thiadiazole ring sulphur to metal ion. The complexes exhibits bands around ca. 435-415  $cm^{-1}$  which are assignable[29] to  $\nu(M-N)$  vibration.



The presence of coordinated water molecules in these complexes is indicated [30,31] by a medium band at ca. 3380  $cm^{-1}$ .

### <sup>1</sup>H NMR spectra

The proton magnetic resonance spectra of cobalt(III) complexes have been recorded in DMSO- $d_6$ . The intensities of all the resonance lines were determined by planimetric integration. The following conclusion can be derived on comparing the spectra of ligands with their corresponding cobalt(III) complexes.

Schiff bases exhibit signals at ca. 12.10 and 5.50 ppm due to hydrazino NH proton and indoline-2,3-dione NH proton, respectively. In cobalt(III) complexes, indoline-2,3-dione NH sig-

nal disappear.

Multiplet is observed at 7.00-8.80 ppm due to aromatic ring protons in Schiff bases and their corresponding complexes.

The signal due to protons of water in the complexes appears at 5.5 ppm.

The complexes exhibit a signal at ca. 2.16-2.45 ppm due to methyl protons.

Thus, IR and <sup>1</sup>H NMR spectra reveal that the Schiff bases of type (LH) behave as monobasic, bidentate chelating agents having coordination sites at oxygen atom of isatin ring (through deprotonation) and azomethine nitrogen atom.

#### APPLICATIONS

All the ligands and their corresponding complexes were

screened in-vitro for their antifungal activity against *Aspergillus niger*, *Colletotrichum falcatum* and *Curvularia pallescens*. The results of antifungal screening are present in Table 2. The activity was compared with those of the standard drug fluconazole. Metal complexes are found to be more active than their corresponding ligands. In other words, chelation increases the fungicidal activity. For any particular species of fungus, manganese(III) derivatives show better activity than cobalt(III) derivatives. Chromium(III) complexes show least activity as compared to manganese(III) iron(III) and cobalt(III) derivatives. The activity of the ligands is affected by the nature of the substituents, this in relation to the lipophilicity of the ligands and their membrane permeability, a key factor in determining their entry inside the cell. The presence of -Cl or -OCH<sub>3</sub> group at the phenyl rings of the ligands increases the activity of the derivatives. The activity decreases on dilution.

**Table 2: Fungicidal screening data of Cr(III), Mn(III), Fe(III) and Co(III) complexes of Schiff bases derived from 5-(phenyl / substituted phenyl)-2-hydrazino-1,3,4-thiadiazole and indoline-2,3-dione**

S.No	Compound	Fungicidal Inhibition (%)						Compound dose (ppm)		
		Aspergillus niger			Colletotrichum falcatum			Curvularia pallescens		
		10	100	1000	10	100	1000	10	100	1000
1	SIPTH	17.0	21.8	24.5	18.0	22.0	25.0	17.0	21.9	24.0
2	SIOCTH	25.0	29.0	32.0	26.0	30.5	33.8	25.5	29.2	32.2
3	SINTH	18.0	22.8	28.4	18.4	25.4	28.9	18.2	22.9	30.0
4	SIMTH	24.0	26.2	29.2	24.8	27.0	30.4	23.8	26.0	30.6
5	[Cr(SIPT) <sub>2</sub> Cl(H <sub>2</sub> O)]	40.1	50.9	59.4	38.6	50.4	60.4	41.3	48.8	50.4
6	[Cr(SIOCT) <sub>2</sub> Cl(H <sub>2</sub> O)]	42.4	56.4	64.2	46.4	54.2	63.2	45.9	55.1	65.4
7	[Cr(SINT) <sub>2</sub> Cl(H <sub>2</sub> O)]	40.4	52.1	60.1	42.4	53.4	61.4	43.5	54.5	62.3
8	[Cr(SIMT) <sub>2</sub> Cl(H <sub>2</sub> O)]	41.3	54.3	59.9	39.4	56.2	57.4	42.4	55.5	58.6
9	[Mn(SIPT) <sub>2</sub> (OAc)(H <sub>2</sub> O)]	56.5	68.4	72.5	50.2	65.5	71.5	50.5	56.8	65.5
10	[Mn(SIOCT) <sub>2</sub> (OAc)(H <sub>2</sub> O)]	62.5	70.9	78.8	59.4	70.2	77.5	59.2	69.8	76.5
11	[Mn(SINT) <sub>2</sub> (OAc)(H <sub>2</sub> O)]	54.2	69.7	75.5	54.5	65.9	75.4	56.4	64.3	73.2
12	[Mn(SIMT) <sub>2</sub> (OAc)(H <sub>2</sub> O)]	60.5	69.9	76.4	56.5	66.8	74.4	54.3	66.5	74.5
13	[Fe(SIPT) <sub>2</sub> Cl(H <sub>2</sub> O)]	50.4	65.2	70.0	48.9	61.0	70.2	48.7	50.9	60.4
14	[Fe(SIOCT) <sub>2</sub> Cl(H <sub>2</sub> O)]	55.4	69.4	80.4	53.4	69.4	78.4	53.9	65.4	76.5
15	[Fe(SINT) <sub>2</sub> Cl(H <sub>2</sub> O)]	48.4	63.4	74.2	46.5	56.4	73.4	47.4	50.4	73.2
16	[Fe(SIMT) <sub>2</sub> Cl(H <sub>2</sub> O)]	52.4	65.4	76.4	50.4	59.5	75.4	51.4	56.5	74.5
17	[Co(SIPT) <sub>2</sub> (OAc)(H <sub>2</sub> O)]	46.1	60.4	69.4	44.2	59.5	69.4	44.2	49.8	59.4
18	[Co(SIOCT) <sub>2</sub> (OAc)(H <sub>2</sub> O)]	50.4	67.2	72.4	56.4	66.4	73.4	52.9	57.4	64.5
19	[Co(SINT) <sub>2</sub> (OAc)(H <sub>2</sub> O)]	47.4	64.3	73.5	52.4	64.2	70.4	50.4	53.4	61.4
20	[Co(SIMT) <sub>2</sub> (OAc)(H <sub>2</sub> O)]	49.5	63.4	70.4	53.8	64.8	71.2	51.4	55.4	63.4

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