Magnetic, Spectral, Thermal, and Electrical Properties of Coordination Polymers Derived from Terpolymers

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ABSTRACT

Coordination polymers of Cu(II), Ni(II), Co(II), Zn(II), Cr(III), Fe(III), oxovanadium (IV), and dioxouranium(VI) with salicylic acid (S)-thiourea (T)-trioxane (T) (STT) polymer were prepared. The analytical data agree with 1:1 metal-ligand stoichiometry. Elemental analyses, magnetic, spectral, and thermal properties, and electrical conductivities of STT and its chelates have been studied and probable structures are assigned to the coordination polymers. All the chelates are amorphous powders, insoluble in common organic solvents, and showing slight solubility in DMF.

INTRODUCTION

Coordination polymers having good thermal stability and catalytic activity have enhanced the development of polymeric materials either from polymeric or monomeric ligands. Salicylic acid has been used as a chelating agent for several transition metal ions [1, 2]. Transition metal complexes derived from polymers have occupied a central position in the development of coordination chemistry. This inspired

us to prepare a polymeric chelating ligand which would be able to form complexes with a variety of transition metals. This communication describes the preparation and characterization of the chelates prepared from salicylic acid-thiourea-trioxane (STT) polymer [3].

The stereochemistry of the polychelates has been studied from the diffuse reflectance spectra, infrared spectra, magnetic moment, and thermal analysis. The decomposition temperature of the polymeric chelates is in the order

STT > UO$_2$ > Ni > Zn, Fe > Cr, VO, Cu, Co
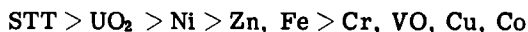
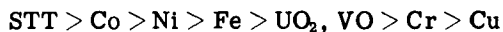while the thermal activation energy follows the order

STT > Co > Ni > Fe > UO$_2$, VO > Cr > Cu

and the activation energy obtained from semiconducting behavior is in the order

VO > Co > STT > Cr > Fe, Ni > Cu
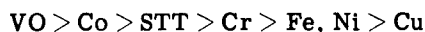
EXPERIMENTAL

Material

The STT polymer was prepared as described below. A mixture of salicylic acid and thiourea with trioxane in the ratio 1:1:2 was heated in the presence of 2 $\underline{M}$ HCl as catalyst in an oil bath at 130°C for 4 h [3]. The separated product was filtered off, washed with hot water, and dried. The purification was effected by dissolving the product in 5% NaOH solution and reprecipitating it by 1:1 HCl solution. The reaction taking place is

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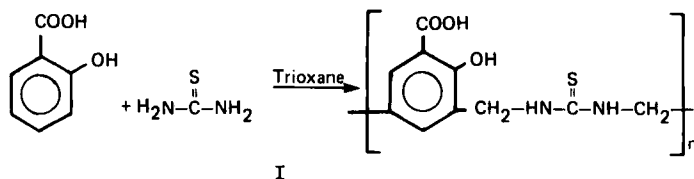
The coordination polymers were prepared by mixing a solution of STT in DMF. To the resulting colored solution a concentrated solution of sodium acetate, also in DMF, was added, whereby the product separated out. It was digested, filtered washed with DMF and hot

water, and dried in an oven at 60°C. In case of oxovanadium(IV) chelate, vanadyl sulfate was used. The polymeric ligand may act as a tetradentate ligand. The structure of the complexes are indicated later.

Measurements

The magnetic susceptibility was determined at room temperature by the Gouy method. Diffuse reflectance and IR spectra were recorded on a Beckman DU and a Carl Zeiss UR-10 spectrophotometer, respectively. The electrical resistivity of STT and its polychelates was measured over a wide range of temperatures in air by using a Million Megohmmeter Model RM 160 MK III A India on a Du Pont Thermal Analyzer 900.

RESULTS AND DISCUSSION

Elemental analysis (Table 1) showed that polychelates exhibit 1:1 metal-to-ligand stoichiometry. They have the general formula $[ML]_n$, where ML is a dimeric species as shown in Structure II.

The magnetic moment of copper polychelate is 1.92 BM which is very close to the spin only value of 1.73 BM (Table 3) expected for one unpaired electron, which offers the possibility of octahedral symmetry [4]. Ni(II) polychelate shows a magnetic moment of 2.58 BM which is in agreement to that of Ray et al. [5]. The lowering of the magnetic moment observed for the chelate indicates increased axial distortion or the polymeric nature of the complex leading to a distorted octahedral structure [5]. The low value for the Co(II) complex, 4.63 BM, reported here may be due to a polymeric octahedral structure [6].

Fe(III) polychelate exhibits a magnetic moment of 5.03 BM which is lower than what is expected on the basis of the spin-only value for five unpaired electrons (6.0 BM). The lowering of the magnetic moment suggests the polymeric nature of the polychelate [7]. Cr(III) polychelate shows a magnetic moment of 3.74 BM which is close to the range (3.81 to 4.01 BM) required for high spin chromium complexes [8]. Such a lowering of the magnetic moment has been observed in binuclear complexes [9]. The magnetic moment of the oxovanadium-(IV) complex, 1.46 BM, is lower than the spin-only value (1.73 BM). This lowering of the moment may perhaps be attributed to the binuclear nature of the complex [10-12]. Dioxouranium(VI) and Zn(II) chelates are diamagnetic in nature, as expected.

The electronic spectra provide the most detailed information about the electronic structure. The diffuse reflectance spectra of the polymeric chelates have been studied between 7,692 and 27,780 cm^{-1}. The Cu(II) complex shows a broad band centered at 13,510 cm^{-1} which may

TABLE 1. Analytical Data and Other Physical Properties

Compound	Color	Elemental analysis[a]					MW of repeating unit (g/mol)	Decomposition temperature (°C)
		C (%)	H (%)	N (%)	S (%)	M (%)		
STT	Yellow	50.25 (50.42)	5.49 (4.2)	7.568 (11.77)	12.41 (13.44)	-	238	240
Cu STT H_2O	Light green	42.32 (37.79)	4.14 (3.14)	7.80 (8.81)	8.005 (9.54)	19.72 (20.01)	318	120
Ni STT H_3O	Pale yellow	39.26 (38.37)	3.87 (3.19)	7.89 (8.95)	6.85 (9.68)	19.48 (18.77)	313	160
Co STT H_2O	Light pink	40.16 (38.34)	3.59 (3.19)	8.155 (8.94)	8.92 (9.681)	16.93 (18.45)	313	100
Zn STT H_2O	Grey	45.53 (37.57)	4.43 (3.13)	8.27 (8.76)	9.21 (10.86)	14.32 (17.46)	319	140
Fe STT NO_3	Violet	37.1 (33.91)	3.89 (2.26)	10.03 (13.56)	7.97 (9.04)	17.99 (15.78)	354	140
Cr STT NO_3	Green	36.24 (34.28)	4.32 (2.28)	7.89 (12.1)	7.74 (9.87)	18.12 (15.84)	350	120
UO_2 STT	Rosy red	28.41 (19.79)	2.99 (2.31)	6.69 (4.61)	6.66 (8.4)	41.71 (39.36)	606	180
VO STT	Green	39.1 (39.61)	2.67 (2.04)	8.95 (9.24)	9.04 (11.13)	18.56 (16.81)	303	120

[a]Polymeric ligand prepared from salicylic acid, thiourea, and trioxane (STT) "a" values in parentheses are calculated.

be due to the overlapping of the three transitions (Table 2) expected for a distorted octahedral structure [4]. The Ni(II) chelate shows bends at 9,524, 15,380, and 24,390 cm^{-1} which are assigned as given in Table 2. This spectrum is similar to that expected for an octahedral or distorted octahedral spin-free nickel(II) complex [13, 14]. This structure is also further confirmed by the ratio of ν_2/ν_1 which

is 1.69, close to the value expected for the distorted octahedral structure [15]. The Racah parameter, B_{35}, is calculated using the relation [16]

$$B_{35} = \nu_2 + \nu_3 - \frac{3\nu_1}{15}$$

Transition energies ν_2 and ν_3 have been calculated [16] using the Racah parameter obtained from the above equation.

$$\nu_{1,3} = \frac{1}{2}(15B + 30Dq) \pm \frac{1}{2}[(15B - 10Dq)^2 + 12B \cdot 10Dq]^{1/2}$$

In nickel(II) polychelate having octahedral symmetry, the value of ν_1 corresponds to 10Dq, which has been calculated using the equation [16]

$$\nu_1 = 10Dq = \frac{1}{3}(\nu_2 + \nu_3) - 5B$$

The ν_1 transition splits into two bands which are assigned to the transition arising from the splitting of the $^3T_{2g}(F)$. The ν_2 transition is also found to split into two bands arising from the splitting of $^3T_{1g}(F)$ [15]:

$$^3A_{2g}(F) \longrightarrow {}^3T_{2g}(F) = \nu_1 \Big\langle \begin{array}{l} 8{,}756 \ cm^{-1} \\ 10{,}290 \ cm^{-1} \end{array}$$

$$^3A_{2g}(F) \longrightarrow {}^3T_{1g}(F) = \nu_2 \Big\langle \begin{array}{l} 14{,}270 \ cm^{-1} \\ 16{,}490 \ cm^{-1} \end{array}$$
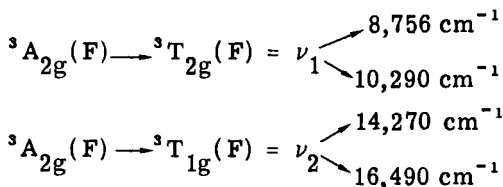
Various spectral parameters were calculated by known methods [15, 17]:

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TABLE 2. Electronic Spectral Data of STT Polychelates

| Compound | Energies (cm^{-1}) | | Assignment |
	Observed	Calculated	
Cu STT H_2O			$^2B_{1g} \rightarrow {}^2B_{2g}$
	13,510	-	$^2B_{1g} \rightarrow {}^2E_g$
			$^2B_{1g} \rightarrow {}^2A_{1g}$
Ni STT H_2O	9,524	9,526	$^3A_{2g} \rightarrow {}^3T_{2g}(G)$
	15,380	15,292	$^3A_{2g} \rightarrow {}^3T_{1g}(F)$
	24,390	24,478	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$
Co STT H_2O	9,009	9,008	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$
	-	19,148	$^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$
	19,230	19,228	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$
Fe STT NO_3	11,810	-	$^6A_{1g} \rightarrow {}^4T_{1g}$
	17,860	-	$^6A_{1g} \rightarrow {}^4T_{1g}$
	21,740	-	$^4T_{1g} \rightarrow {}^4E_g$
Cr STT NO_3	11,110	-	$^4A_{2g} \rightarrow {}^2E_g$
	17,390	-	$^4A_{2g} \rightarrow {}^4T_{2g}$
	23,530	-	$^4A_{2g} \rightarrow {}^4T_{1g}$
VO STT	11,430	-	$^2B_2 \rightarrow {}^2e$
	15,380	-	$^2B_2 \rightarrow {}^2B_1$
	25,000	-	$^2B_2 \rightarrow {}^2A_1$

$$\nu_2/\nu_1 = 1.69 \qquad D_t = 175.31 \ cm^{-1}$$

$$Dq = 722.2 \ cm^{-1}, \qquad Dq_{av} = 722.2 \ cm^{-1}$$
$$DS = 1215.1 \ cm^{-1}$$

$$D_{35} = 833.33, \qquad \beta_{35} = 0.905$$

$$LFSE = 32.667 \ kcal/mol$$

In cobalt(II) polychelate the transitions observed at 9,009 and 19,230 cm^{-1} may be assigned to distorted octahedral geometry (Table 2) [18, 19]. The Racah parameter is calculated using the known relation [16]

$$\nu_2 = \frac{1}{2}[30Dq - 15B] + \frac{1}{2}[(10Dq + 15B)^2 - 12B \cdot 10Dq]^{1/2}$$

$$\nu_3 = [(10Dq + 15B)^2 - 12B \cdot 10Dq]^{1/2}$$

using observed ν_1 and ν_3. ν_2 at 19,148 cm^{-1} was calculated. The transition energies ν_1 and ν_3 have been calculated using calculated ν_2 [16], and the values of B_{35}, β_{35}, and LFSE are as given below:

$$B_{35} = 757, \qquad \beta_{35} = 0.675$$

$$LFSE = 17.388 \ kcal/mol$$

Iron(III) chelate shows bands at 14,810, 17,860 and 21,740 cm^{-1} which may be assigned to the transition given in Table 2 for the octahedral structure [20]. In chronium(III) polychelate the transitions observed at 11,110, 17,390 and 23,530 cm^{-1} may best be assigned to octahedral geometry [21]. The lowest energy transition is a spin-forbidden one due to $^4A_{2g}(F) \rightarrow {}^2E_g$, the lowest energy spin allowed band is $^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ (17,390 cm^{-1}), and the other band is due to the transition $^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ (Table 2).

Oxovanadium(IV) chelate exhibits three transitions at 11,430, 15,380 and 25,000 cm^{-1}. These bands are not well resolved and appear as weak bands except the band at 25,000 cm^{-1}. However, the positions of these bands are inconsistent with distorted octahedral oxovanadium(IV) complexes [22].
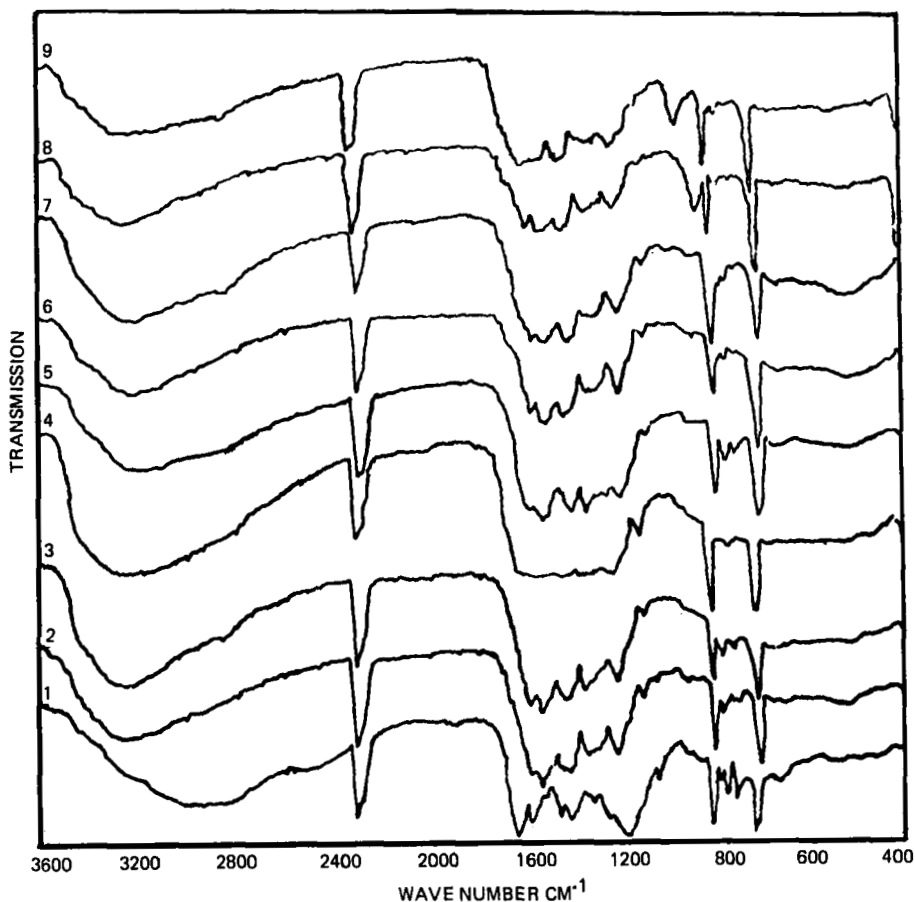
FIG. 1.   Infrared absorption spectra of (1) STT, (2) Cu-STT $\cdot$ H$_2$O,
(3) Ni-STT $\cdot$ H$_2$O, (4) Co-STT $\cdot$ H$_2$O, (5) Zn-STT $\cdot$ H$_2$O, (6) Fe-STT $\cdot$ NO$_3$,
(7) Cr-STT $\cdot$ NO$_3$, (8) UO$_2$-STT, and (9) VO-STT.

The infrared spectra of STT and its metal chelates are given in Fig.
1.   The IR spectra of all polychelates are similar to that of ligand but
are found to be comparable with each other, which suggests some dif-
ference from the polymeric ligand.   The bands in the regions 2800-
3300, 1400-1500, 1200-1350, and 750-800 cm^{-1} suggest the presence
of methylene bridges in the STT polymer [23].   The IR spectra of the
ligand show strong absorptions between 2800-3300 cm^{-1} (also attributed
to −CH$_2$− bridges) and a medium intensity band at 2650 cm^{-1} which may
be attributed to ν(−OH) with hydrogen bonding.   This band is also found
in the spectra of metal chelates, indicating coordination of the −OH group

[24]. Moreover, spectra show –NH stretching vibrations in the region 3200-3400 cm^{-1}. The sharp strong band at 1616 cm^{-1} in the STT due to C=N stretch shifts to lower frequencies at ~1600 cm^{-1} in the coordination polymers, showing coordination through nitrogen atom of

$\underset{|}{SH}$

–N=C– [20]. The strong band at 856 cm^{-1} in STT (Table 3) may be very safely assigned to C=S stretch [9]. The weak band observed at 2424 cm^{-1} is due to the presence of a small thioenolic form even in the free STT [24]. However, this ν(SH) band disappears in complexes, showing that the M–S band is formed due to deprotonation of the –SH group. Besides, a strong and sharp band is observed at 760 cm^{-1} in the ligand and has been attributed to the coupled bands of ν(C–S) and ν(C–N) [25]. This band on coordination with metal complexes shifts to a lower frequency region and appears at ~735 cm^{-1}, clearly implying the coordination of sulfur and nitrogen atoms. Therefore, it is obvious that thioenolization is more favored during complex formation. A medium band due to ν(C=O) of the carboxyl group observed at 1656 cm^{-1} in STT shifts to lower frequency in all the chelates, indicating coordination through the carboxyl (COO$^-$) group [26]. The sharp, intense band observed at 1270 cm^{-1} in the ligand may be due to the phenolic C–O stretching vibration [27]. Additional bands which appear in the case of Fe(III) and Cr(III) chelates at 1500, 1310, 1025, and 940 cm^{-1} can be attributed to the coordinated NO$_3^-$ group [28]. In oxovanadium(IV) and dioxouranium(VI) complexes, sharp bands at 964 and 920 cm^{-1}, respectively, are assigned to the ν(V=O) and ν(U=O) modes [29, 30]. Cu(II), Ni(II), Zn(II), and Co(II) polychelates exhibit weak bands at ~775 and ~1590 cm^{-1} which are attributed to coordinated water [31]. Considering the position of the potential donor atoms and from the infrared spectral studies and elemental analyses, the dimeric S bridged Structure II has been suggested for all metal chelates.
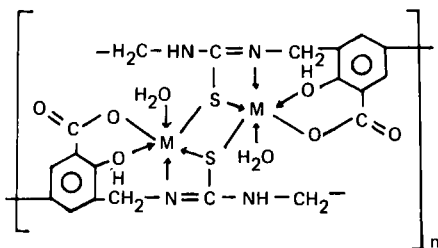
II

Table 4 shows the loss of weight at different temperatures of STT and its polychelates, calculated from the respective TGA curves. Thermal analysis also confirms the presence of water molecules in all the complexes excluding oxovanadium(IV), chromium (III), iron(III), and dioxouranium(VI) coordination polymers. Voges [32] has reported

ABLE 3. Magnetic Moments and Infrared Spectral Data (cm^{-1}) of STT and Its Polychelate

μ_{eff} (BM)	IR sp bands					
	C–S (cm^{-1})	$-CH_2-$ (cm^{-1})	$-OH$ (H bonded) (cm^{-1})	C=N (cm^{-1})	C=S (cm^{-1})	$-OH$ stretching (cm^{-1})
-	-	2800-3300	2650	1616	856	2800-3200
1.92	1020	2850-3300	2650	1600	816	3200-3400
2.58	1012	2900-3300	2645	1606	808	3200-3350
4.63	1016	2800-3000	2650	1605	810	3200-3300
Diamagnetic	1012	3000-3200	2600	1595	810	3250
5.03	1020	3100-3300	2650	1600	832	3200-3300
3.74	1024	3100-3300	2650	1604	816	3200-3300
Diamagnetic	1010	3050-3300	2660	1600	816	3200-3400
1.46		3100-3300	2680	1590	808	3200

TABLE 4. Results of Thermogravimetric Analysis

Compound	Temperature (°C) Weight loss (%)							E (kcal/mol)	n (order of reaction) Temperature (°C)	
	100	200	300	400	500	600	700		n = 1	n = 2
STT	2	5	21	37	52	80	84	14.416	500-700	220-500
Cu STT H_2O	3	11	29	45	59.5	79.5	81	4.318	220-620	60-220
Ni STT H_2O	4.5	13	23.5	51	65.5	84	88.5	9.212	300-560	40-160
Co STT H_2O	4.5	12	22.5	52.5	75	89.5	89.5	10.59	280-620	60-180
Zn STT H_2O	3.0	7.5	26.5	46.5	57	82	84.5	5.96	240-640	60-220
Fe STT NO_3	3.0	8.0	25.0	42.0	60.0	80.0	87.5	6.77	220-540	40-140
Cr STT NO_3	2.0	8.5	15.0	32.5	49.5	63.5	65.0	5.54	280-560	40-280
UO_2 STT	1.5	5.0	12.5	33.5	44.5	59.0	64.5	5.98	280-600	40-280
VO STT	3.5	11.5	26.0	47.0	68.5	85.5	87.0	5.98	280-560	40-220

that the thermal stability of polymer is higher than that of the poly-chelates because of hydrogen bonding. Our results also show that STT is more stable than the chelates, and the order of the stability has been found to be STT $>$ VO$_2$ $>$ Ni $>$ Zn, Fe $>$ Cr, Cu, Co, VO, which is comparable to the order of Ni $>$ Cu $>$ Co which has been observed by Goodwin and Bailar [33]. In general, the water of hydration may be considered as either the crystal or as coordination water. According to Nikolaev et al. [34], water eliminated below 150°C can be considered as the crystal water, and water eliminated above 150°C may be due to its coordination to the metal atom present in chelates. In the present study, in the case of dioxouranium(VI) complex, at $\sim$160°C the removal of water from the complex is complete. The water is probably crystal water. The removal of water above 150°C in the case of Cu(II), Ni(II), Co(II), and Zn(II) chelates indicates the presence of coordinated water molecules. The thermal activation energy has been calculated using the Broido method [35], and the values are summarized in Table 3.

Semiconducting behavior was systematically developed by Brattain et al. [36] Pekaln and Kotosonov have studied the electrical conductivity of phenol formaldehyde resin [37]. An industrially useful semiconducting material has been reported [38].

The conductivity measurements were made over a wide range of temperatures. The electrical conductivity (σ) varies exponentially with the absolute temperature according to the relationship

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{RT}\right)$$

where E is the activation energy of the semiconductor and σ_0 is a constant. At higher temperature the above equation seems to hold good, and a linear relationship has been observed when the logarithm of the conductivity is plotted against reciprocal of absolute temperature. The linear relationship has not been observed at lower temperatures. The values of σ and σ_0 at room temperature and in the temperature range 373 to 513 K and E_a are given in Table 5.

The electrical conductivity at room temperature is in the order Ni $>$ Fe $>$ Cu $>$ Co as shown in Table 5. The activation energy increases the order CO $>$ Co $>$ STT $>$ Cr $>$ Ni, Fe $>$ Zn $>$ Cu, which is in partial agreement with that order [39]. The results indicate that the electrical conductivity of metal chelates is slightly higher than that of the polymer STT, which may be due to the incorporation of metal ion in the STT which increases the ionization tendency [40].

TABLE 5. Semiconductor Data for STT and Its Polychelates

Compound	Electrical conductivity		Specific conductivity		E_a (eV)
	Ω^{-1} (cm^{-1})	(T)	Ω^{-1} (cm^{-1})	(T)	
STT	3.8×10^{-12}	(308)	5.75×10^{10}	(308)	1.36
	2.5×10^{-12}	(373)	5.62×10^{7}	(373)	
Cu STT H$_2$O	5.72×10^{-11}	(308)	6.309×10^{-3}	(308)	0.496
	2.64×10^{-11}	(423)	2.45×10^{-4}	(423)	
Ni STT H$_2$O	1.58×10^{-10}	(308)	2.51×10^{6}	(308)	0.993
	6.0×10^{-11}	(513)	3.55×10^{-1}	(513)	
Co STT H$_2$O	8.2×10^{-11}	(308)	2.08×10^{11}	(308)	1.37
	6.61×10^{-11}	(513)	1.95×10^{3}	(513)	
Zn STT H$_2$O	5.72×10^{-11}	(308)	1.48×10^{-1}	(308)	0.577
	0.77×10^{-10}	(443)	6.03×10^{1}	(443)	
Fe STT NO$_3$	1.53×10^{-11}	(308)	2.45×10^{5}	(308)	0.993
	6.2×10^{-11}	(463)	0.39×10^{1}	(463)	
Cr STT NO$_3$	2.5×10^{-11}	(308)	2.29×10^{3}	(308)	1.19
	0.14×10^{-11}	(453)	5.13×10^{-3}	(453)	
VO STT	1.92×10^{-12}	(308)	1.12×10^{17}	(308)	1.763
	8.2×10^{-12}	(403)	1.02×10^{11}	(403)	

ACKNOWLEDGMENTS

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