

New Heterobimetallic Ion-pair Complexes of Ni(II) with Mn(II), Co(II) and Zn(II)

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Abstract: Some heterobimetallic ion-pair complexes of Ni(II) with Mn(II), Co(II) and Zn(II) using 1,10-phenanthroline (phen) and 1-tert-butylimidazole-2-thione ($\text{tm}^{\text{t-Bu}}$) ligands were prepared by co-crystallization of Ni(II)-phen cationic complex and $\text{Cl}^- / \text{tm}^{\text{t-Bu}}$ containing anionic complex in acetonitrile / methanol solvent. The $[\text{Ni}(\text{phen})_3][\text{MnCl}_4]$ (**1**) contains two molecule of acetonitrile and $[\text{Ni}(\text{phen})_3]^{2+}$ is hydrogen bonded with $[\text{MnCl}_4]^{2-}$. $[\text{Ni}(\text{phen})_3]_2[\text{Co}(\text{tm}^{\text{t-Bu}})\text{Cl}_3]$ (**2**) contains two molecule of acetonitrile and $[\text{Ni}(\text{phen})_3]^{2+}$ is hydrogen bonded with two molecule of $[\text{Co}(\text{tm}^{\text{t-Bu}})\text{Cl}_3]^{1-}$. The $[\text{Ni}(\text{phen})_2(\text{tm}^{\text{t-Bu}}\text{Cl})][\text{Zn}(\text{tm}^{\text{t-Bu}})\text{Cl}_3]$ (**4**) has both acetonitrile and methanol as solvent of crystallization and $[\text{Ni}(\text{phen})_2(\text{tm}^{\text{t-Bu}}\text{Cl})]^+$ is hydrogen bonded with $[\text{Zn}(\text{tm}^{\text{t-Bu}})\text{Cl}_3]^{1-}$ anion. All of these complexes have been characterized by magnetic measurement, thermal analysis and single crystal X-ray diffraction technique. The presence of different non-covalent interactions including π - π stacking in these complexes resulted the formation of three-dimensional supramolecular architecture. These complexes show no magnetic interaction as the distances between the metal ions present there in is too large.

Key Words: 1, 10-phenanthroline, cationic-anionic complexes, thioimidazole, crystal structure, magnetic properties.

INTRODUCTION

Molecular assemblies consisting of cationic and anionic units are of special interest for crystal engineering of molecular networks [1, 2]. The desired supramolecular architectures can be designed by using different types of intermolecular interactions [3, 4], such as co-ordination and hydrogen bonds, ionic and van der Waals interactions. The designed supramolecules may have interesting functional properties such as redox behaviour of separated metal ions and serve as redox chemosensors; they may also be useful materials for molecular electronics and molecular magnetisms [4].

2-Thioimidazole (N,N,S donors) and its alkyl derivatives have antithyroid activity and platelet inhibitory effects. These compounds also have immuno-modulating and / or cytokine-release-inhibiting action and are suitable for treating disorders associated with a disturbed immune system [5, 6]. Some metal complexes with 2-thioimidazole have been in literature [7] but its ion-pair complexes are very scarce excepting for the one reported by our group [8]. However many ion-pair compounds with different type of ligands have been reported [9-12]. 1,10-Phenanthroline (phen) is a well known neutral bidentate ligand and many six-coordinate metal-phen complexes containing only two, rather than three phen ligands were reported in the literature [13-17]. The ion-pair complexes having 1,10-phenanthroline and its different derivative as one component and different anionic molecules as other components are well studied [18-29]. The present

work reports the studies on hydrogen-bonded cationic-anionic assemblies based on nickel phenanthroline as cationic component and other anionic units like $[\text{MnCl}_4]^{2-}$, $[\text{Co}(\text{tm}^{\text{t-Bu}})\text{Cl}_3]^{1-}$ and $[\text{Zn}(\text{tm}^{\text{t-Bu}})\text{Cl}_3]^{1-}$.

EXPERIMENTAL

Materials and General Method

All solvents used were purified by the literature methods [30]. The reagents of the highest grade commercially available were used without further purification. All reactions were carried out in air atmosphere. 1,10-phenanthroline was purchased from Aldrich. $[\text{Ni}(\text{phen})_3]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ [31] and N-tert-butyl-thioimidazole ($\text{tm}^{\text{t-Bu}}$) [32] were synthesized by literature methods. Carbon, hydrogen, nitrogen and sulphur were analyzed with a Vario EL III elemental analyzer after carefully drying the samples under vacuum for several hrs. The UV-Vis spectra were recorded on Perkin-Elmer Lambda 35 UV/Vis spectrophotometer. IR spectra were obtained on a Thermo Nicolet Nexus FT-IR spectrometer in KBr. The magnetic susceptibility measurements at variable temperature (2 - 300 K) were performed on Quantum Design SQUID (MPMS) magnetometer. Thermo-gravimetric analyses (TGA) were carried out in air atmosphere (200 ml / min.) with heating rate of 10 °C / min in temperature range 25 - 700 °C using a Perkin Elmer (Pyris Diamond) thermal analyzer.

Synthesis

Synthesis of Complex 1

A solution of $[\text{Ni}(\text{phen})_3]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ (0.71 g, 1.0 mmol) in 10 mL methanol was added dropwise to a methanolic solution (5 mL) of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (0.19 g, 1.0 mmol). The

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resultant mixture was stirred for 30 min. The clear solution was filtered and evaporated to dryness under vacuum. The solid compound was dissolved in acetonitrile and pink colored single crystals suitable for X-ray data collection were obtained by slow evaporation at room temperature. (Yield: ~71%). Elemental analysis (%) Calcd. for $C_{36}H_{24}Cl_4MnN_8Ni$, $M = 824.07$: C, 54.27; H, 3.01; N, 14.07. Found (%): C, 54.34; H, 3.07; N, 14.11. IR (KBr pellet, cm^{-1}): $\nu(C=N)$ 1623. UV-Vis (CH_3CN , λ_{max} , nm, $\epsilon/M^{-1}cm^{-1}$): 242 (882), 516 (272).

Synthesis of Complex 2

A solution of $[Ni(phen)_3]Cl_2 \cdot 2H_2O$ (0.71 g, 1.0 mmol) in 10 mL methanol was added dropwise to a solution of $Co(tm^t-Bu)Cl_3$ obtained by the reaction of $CoCl_2 \cdot 6H_2O$ (0.24 g, 1.0 mmol) and *N-tert-butyl-2-thioimidazole* (0.16 g, 1.0 mmol) in 5 mL of methanol (40 min. reaction time). The resultant mixture was further stirred for 30 min. and filtered through celite. The solvent was evaporated to dryness and the compound was dissolved in acetonitrile for crystallization. The green colored crystals suitable for X-ray data collection were obtained by slow evaporation at room temperature. (Yield: ~68%). Elemental analysis (%) Calcd. for $C_{50}H_{48}Cl_6Co_2N_{10}NiS_2$, $M = 1242.39$: C, 48.30; H, 3.86; N, 11.27; S, 5.15. Found (%): C, 48.24; H, 3.81; N, 11.21; S, 5.12. IR (KBr pellet, cm^{-1}): $\nu(N-H)$ 3416, $\nu(C-H)$ 3044, $\nu(C=N)$ 1627. UV-Vis (CH_3CN , λ_{max} , nm, $\epsilon/M^{-1}cm^{-1}$): 245 (876), 522 (264).

Synthesis of Complex 3

A methanolic solution (15 mL) of $NiCl_2 \cdot 6H_2O$ (0.24 g, 1.0 mmol), 1,10-phenanthroline (0.39 g, 2.0 mmol) and *N-tert-butyl-2-thioimidazole* (0.16 g, 1.0 mmol) were stirred for one hr. The reaction mixture was filtered over celite and evaporated to dryness under vacuum. (Yield: ~72%). Elemental analysis (%) Calcd. for $C_{31}H_{28}Cl_2N_6NiS$, $M = 646.26$: C, 57.67; H, 4.34; N, 13.02; S, 4.96. Found (%): C, 57.73; H, 4.39; N, 13.11; S, 5.05. IR (KBr pellet, cm^{-1}): $\nu(N-H)$ 3409, $\nu(C-H)$ 3053, $\nu(C=N)$ 1618. UV-Vis (CH_3CN , λ_{max} , nm, $\epsilon/M^{-1}cm^{-1}$): 245 (943), 531 (276).

Synthesis of 4

The solution of $[Ni(phen)_2(tm^t-Bu)Cl]Cl$ (**3**) (0.32 g, 0.5 mmol) in 10 mL methanol was added dropwise to a methanolic solution (5 mL) of $Zn(tm^t-Bu)Cl_3$ obtained from the reaction of $ZnCl_2$ (0.06 g, 0.5 mmol) and *N-tert-butyl-2-thioimidazole* (0.08 g, 0.5 mmol). The resultant solution was further stirred for 30 min. The green color solution was filtered and evaporated to dryness. The solid compound was dissolved in mixture of acetonitrile and methanol and light green colored crystals suitable for X-ray data collection were obtained by slow evaporation at room temperature. (Yield: ~64%). Elemental analysis (%) Calcd. for $C_{38}H_{48}Cl_4N_8NiS_2Zn$, $M = 946.87$: C, 48.61; H, 5.11; N, 11.94; S, 3.41%. Found (%): C, 48.55; H, 5.18; N, 11.88; S, 3.48. IR (KBr pellet, cm^{-1}): $\nu(N-H)$ 3402, $\nu(C-H)$ 3053, $\nu(C=N)$ 1621. UV-Vis (CH_3CN , λ_{max} , nm, $\epsilon/M^{-1}cm^{-1}$): 241 (832), 526 (282).

X-Ray Crystallographic Studies of Complexes 1, 2 and 4

The X-ray data collection and processing of complexes **1**, **2** and **4** were performed on Bruker Kappa Apex-II CCD diffractometer using graphite monochromated Mo-K α radiation ($\lambda = 0.71070 \text{ \AA}$) at 100 K. Crystal structures were solved by direct methods. Structure solution, refinement and data output were carried out with the SHELXTL program [33, 34]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometrically calculated positions and refined using a riding model. Images were created with the DIAMOND program [35]. Crystallographic data and experimental details for structural analyses are listed in Table 1 and H-bond distances are listed in Table 2. CCDC No. (660432 - 660434) contains the supplementary crystallographic data for complex **1**, **2**, **4**. This material can be obtained free of charge via <http://www.ccdc.cam.ac.uk/deposit>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Table 1. Crystal Data and Structure Refinement Details for **1.2CH₃CN**, **2.2CH₃CN**, **4.2CH₃CN.CH₃OH** Complexes

	1.2CH₃CN	2.2CH₃CN	4.2CH₃CN.CH₃OH
Empirical Formula	$C_{40}H_{30}N_8Cl_4MnNi$	$C_{54}H_{54}N_{12}S_2Cl_6Co_2Ni$	$C_{43}H_{40}N_{10}OS_2Cl_4NiZn$
Formula weight	878.15	1324.48	1042.87
Temperature (K)	100(2)	100(2)	100(2)
Wavelength (\AA)	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	C2/c	P2 ₁ /n
Unit Cell dimension (\AA)			
<i>a</i>	9.872(2)	23.030(3)	13.1861(2)
<i>b</i>	12.406(2)	15.383(2)	22.2517(4)
<i>c</i>	16.986(3)	19.866(4)	17.0737(3)
α	80.298(8)	90.00	90.00
β	85.098(8)	123.469(5)	110.5130(10)

Table 1. contd....

	1.2CH ₃ CN	2.2CH ₃ CN	4.2CH ₃ CN.CH ₃ OH
γ	85.648(8)	90.00	90.00
Volume (Å ³)	2039.1(6)	5870.9(15)	4692(14)
Z	2	4	4
D _{calc} (mg/m ³)	1.430	1.498	1.476
μ (mm ⁻¹)	1.073	1.268	1.275
Crystal size (mm)	0.24 × 0.21 × 0.19	0.26 × 0.23 × 0.22	0.25 × 0.23 × 0.20
F (000)	894	2712	2136
Range of h, k, l	-9/13, -17/17, -23/23	-35/31, -24/24, -31/31	-16/16, -27/27, -21/21
θ Range for data collection (°)	1.22-29.79	1.70- 33.68	1.57-26.26
Reflections collected/uni- que	11411/6798	1 1691/6864	9439/6697
Max. & min. Transmiss- ion	0.814 & 0.771	0.755 & 0.724	0.775 & 0.734
Data/restraints/parameters	11411/0/489	11691/0/356	9439/3/525
R(int)	0.0562	0.0317	0.0570
Goodness-of-fit on F ²	0.984	0.824	0.917
R ₁ ^a & wR ₂ ^b [I > 2 σ (I)]	R1 = 0.0588 wR2 = 0.1590	R1 = 0.0363 wR2 = 0.1064	R1 = 0.0465 wR2 = 0.1320
R ₁ ^a & wR ₂ ^b (all data)	R1 = 0.1078 wR2 = 0.1886	R1 = 0.0774 wR2 = 0.1361	R1 = 0.0738 wR2 = 0.1545
Largest diff. peak & hole (e Å ⁻³)	1.13 & -0.68	0.41 & -0.33	0.96 & -0.62

aR1 = $\sum(|F_o| - |F_c|)/\sum|F_o|$; bwR2 = $[\sum w(|F_o|^2 - |F_c|^2)^2/\sum w(F_o^2)^2]^{1/2}$, where F_o = observed and F_c = calculated structure factors, respectively.

Table 2. Selected Bond Lengths (Å) and Angles (°) for Complex 1, 2 and 4

1			
Bond Distances			
Ni(1)-N(1)	2.089(3)	Ni(1)-N(2)	2.106(3)
Ni(1)-N(3)	2.107(3)	Ni(1)-N(4)	2.089(3)
Ni(1)-N(5)	2.086(3)	Ni(1)-N(6)	2.103(3)
Mn(2)-Cl(1)	2.3701(12)	Mn(2)-Cl(2)	2.3799(14)
Mn(2)-Cl(3)	2.3894(13)	Mn(2)-Cl(4)	2.3566(13)
Bond Angles			
N(1)-Ni(1)-N(2)	79.51(12)	N(1)-Ni(1)-N(3)	92.43(12)
N(1)-Ni(1)-N(4)	168.80(11)	N(1)-Ni(1)-N(5)	94.62(11)
N(1)-Ni(1)-N(6)	94.64(12)	N(2)-Ni(1)-N(3)	93.68(13)
N(2)-Ni(1)-N(4)	92.96(11)	N(2)-Ni(1)-N(5)	168.95(12)
N(2)-Ni(1)-N(6)	90.80(13)	N(3)-Ni(1)-N(4)	79.71(11)
N(3)-Ni(1)-N(5)	95.94(11)	N(3)-Ni(1)-N(6)	172.23(11)
N(4)-Ni(1)-N(5)	94.11(11)	N(4)-Ni(1)-N(6)	93.73(11)
N(5)-Ni(1)-N(6)	80.27(11)	Cl(1)-Mn(2)-Cl(2)	111.41(5)
Cl(1)-Mn(2)-Cl(3)	109.16(6)	Cl(1)-Mn(2)-Cl(4)	106.09(5)
Cl(2)-Mn(2)-Cl(3)	107.28(6)	Cl(2)-Mn(2)-Cl(4)	115.15(5)
Cl(3)-Mn(2) Cl(4)	107.61(5)		

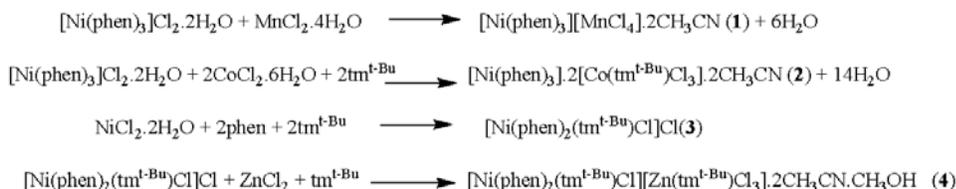
Table 2. contd....

2			
Bond Distances			
Ni(1)-N(1)	2.1044(15)	Ni(1)-N(2)	2.0785(15)
Ni(1)-N(3)	2.0936(14)	Co(1)-S(1)	2.3462(6)
Co(1)-Cl(1)	2.2700(6)	Co(1)-Cl(2)	2.2836(7)
Co(1)-Cl(3)	2.2638(6)		
Bond Angles			
N(1)-Ni(1)-N(2)	79.75(6)	N(1)-Ni(1)-N(2')	96.39(6)
N(1)-Ni(1)-N(3)	93.31(6)	N(1)-Ni(1)-N(3')	90.98(6)
N(1)-Ni(1)-N(1')	174.42(9)	N(1')-Ni(1)-N(2)	96.39(6)
N(1')-Ni(1)-N(2')	79.75(6)	N(1')-Ni(1)-N(3)	90.98(6)
N(1')-Ni(1)-N(3')	93.31(6)	N(2)-Ni(1)-N(2')	93.49(8)
N(2)-Ni(1)-N(3)	170.39(6)	N(2)-Ni(1)-N(3')	93.88(6)
N(2')-Ni(1)-N(3)	93.89(6)	N(2')-Ni(1)-N(3')	170.39(6)
N(3')-Ni(1)-N(3)	79.49(8)	S(1)-Co(1)-Cl(1)	96.43(2)
S(1)-Co(1)-Cl(2)	107.11(2)	S(1)-Co(1)-Cl(3)	120.95(2)
Cl(1)-Co(1)-Cl(2)	123.83(3)	Cl(1)-Co(1)-Cl(3)	106.66(2)
Cl(2)-Co(1)-Cl(3)	103.35(3)		
4			
Bond Distances			
Ni(1)-N(1)	2.084(3)	Ni(1)-N(2)	2.085(3)
Ni(1)-N(3)	2.117(3)	Ni(1)-N(4)	2.094(3)
Ni(1)-S(1)	2.5601(10)	Ni(1)-Cl(4)	2.4206(10)
Zn(1)-Cl(1)	2.2783(12)	Zn(1)-Cl(2)	2.2615(11)
Zn(1)-Cl(3)	2.2462(12)		
Bond Angles			
N(1)-Ni(1)-N(2)	80.02(12)	N(1)-Ni(1)-N(3)	92.99(12)
N(1)-Ni(1)-N(4)	171.50(13)	N(1)-Ni(1)-S(1)	93.58(9)
N(1)-Ni(1)-Cl(4)	92.99(9)	N(2)-Ni(1)-N(3)	89.86(12)
N(2)-Ni(1)-N(4)	96.12(12)	N(2)-Ni(1)-S(1)	80.12(8)
N(2)-Ni(1)-Cl(4)	173.02(9)	N(3)-Ni(1)-N(4)	79.37(13)
N(3)-Ni(1)-S(1)	166.89(9)	N(3)-Ni(1)-Cl(4)	90.42(9)
N(4)-Ni(1)-S(1)	93.21(9)	N(4)-Ni(1)-Cl(4)	90.79(9)
S(1)-Ni(1)-Cl(4)	100.55(4)	S(2)-Zn(1)-Cl(1)	110.36(4)
S(2)-Zn(1)-Cl(2)	110.18(4)	S(2)-Zn(1)-Cl(3)	104.26(4)
Cl(1)-Zn(1)-Cl(2)	109.23(5)	Cl(1)-Zn(1)-Cl(3)	112.05(5)
Cl(2)-Zn(1)-Cl(3)	110.68(5)		

RESULTS AND DISCUSSION

General Characterizations

The compounds **1**, **2** and **4** have been prepared according to the equation given below.



The compounds **1-4** gave satisfactory elemental analysis, stable at room temperature and decompose above 200 °C. The IR spectrum of **1-4** exhibited $\nu(\text{C}=\text{N})$ band (of phenanthroline) in the range of 1618-1627 cm^{-1} . The free thioimidazole ligand showed $\text{C}=\text{S}$ stretching band at 1117 cm^{-1} which were shifted to lower wave number upon complexation i.e., at 1092 cm^{-1} in **1**, 1089 cm^{-1} in **2** and 1084 cm^{-1} in **4** suggested the coordination of ligand through sulphur atom.

Crystal Structure of Complex 1

The complex **1** is ionic in nature, comprises of one complex cation $[\text{Ni}(\text{phen})_3]^{2+}$, one complex anion $[\text{MnCl}_4]^{2-}$ and two acetonitrile molecules in asymmetric unit. The molecular structure (Fig. (1)), demonstrated that the metal centre in $[\text{Ni}(\text{phen})_3]^{2+}$ is in octahedral environment, the equatorial plane of which is formed by the four nitrogen atoms and the axial positions are occupied by other two nitrogen atoms of phen with Ni-N bond distances range from 2.086(3) Å to 2.107(3) Å (Table 2). The dihedral angles between the planes of the neighboring phen rings are 83.86°, 83.83° and 85.43°. The cis-angles in the octahedron are slightly deviated from the value of 90° and trans angle in axial position are an average of 170° (Table 2).

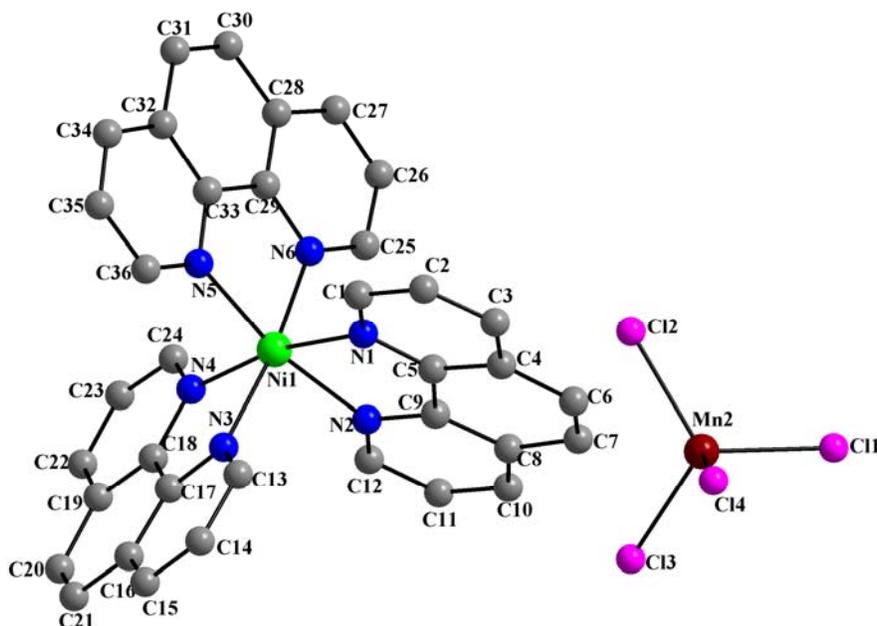


Fig. (1). Molecular structure view of complex $[\text{Ni}(\text{phen})_3][\text{MnCl}_4]$ **1**. Hydrogen atoms and solvent molecules have been omitted for clarity.

The $[\text{MnCl}_4]^{2-}$ anion shows average angle of 110.83°, slightly deviating from regular tetrahedral geometry. Manganese is coordinated by four chlorine atoms available in reaction mixture due to dissociation of $[\text{Ni}(\text{phen})_3]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ and form distorted tetrahedral geometry with different Mn-

Cl bond distances. These Mn-Cl bond distances are in the range of 2.356(13) to 2.389(13) Å and are in good agreement with the literature value [36]. There are no intramolecular interactions between the constituent atoms of the cation and anion but all the four chloride ions attached to the manganese centre are extensively involved in intermolecular hydrogen bonding with hydrogen atoms of phen moiety (Table 3). Due to the presence of several intermolecular interactions, the complex cation is linked to seven anionic complex (Fig. (2)) and complex anion is linked to seven cationic complex (Fig. (S1)) through hydrogen bonds (intermolecular $\text{C}-\text{H} \cdots \text{Cl}$ bonds are in the range of 2.732(12) to 2.937(9) Å). In crystal packing of complex **1**, the cationic-anionic layers are formed alternatively along the b-axis (Fig. (3)) and both layers are united by H-bonds. In **1**, all the rings of coordinated 1,10-phenanthroline ligands are planar. The distance between Ni(II) and Mn(II) centre is of 8.832 Å which is too large for any kind of interactions between two metal centers.

Crystal Structure of Complex 2

The single crystal X-ray studies of **2** revealed that the complex is centrosymmetric, ionic in nature and is composed of one complex cation $[\text{Ni}(\text{phen})_3]^{2+}$ and two complex anions

Table 3. Hydrogen-Bonding Geometry (Å, °) for Complexes 1, 2 and 4

D-H...A	d(D-H)	d(H...A)	d(D...A)	D-H...A
Complex 1				
C(6)-H(6)...Cl(2)	0.93	2.937(9)	3.825(13)	160
C(20)-H(20)...Cl(3)	0.93	2.902(10)	3.673(13)	141
C(27)-H(27)...Cl(1)	0.93	2.869(14)	3.733(17)	155
C(24)-H(24)...Cl(1)	0.93	2.860(14)	3.531(18)	130
C(1)-H(1)...Cl(1)	0.93	2.732(12)	3.472(15)	137
C(10)-H(10)...Cl(4)	0.93	2.743(9)	3.539(10)	144
C(21)-H(21)...Cl(4)	0.93	2.802(12)	3.678(15)	157
Complex 2				
C(13)-H(13)...Cl(1)	0.93	2.840(11)	3.626(12)	143
C(15)-H(15)...Cl(2)	0.93	2.874(6)	3.774(8)	163
C(24)-H(24)...Cl(2)	0.93	2.923(5)	3.559(3)	127
C(11)-H(11)...Cl(3)	0.93	2.687(8)	3.534(10)	152
C(1)-H(1)...Cl(3)	0.93	2.983(13)	3.772(16)	144
C(21)-H(21A)...Cl(3)	0.96	2.914(4)	3.616(6)	131
C(16)-H(16)...Cl(3)	0.93	2.707(2)	3.616(6)	131
N(5)-H(5)...Cl(2)	0.83	2.463(24)	3.232(10)	154
Complex 4				
C(11)-H(11)...Cl(1)	0.93	2.824(1)	3.711(5)	160
C(12)-H(12)...Cl(2)	0.93	2.723(2)	3.527(6)	145
C(3)-H(3)...Cl(2)	0.93	2.747(1)	3.656(6)	166
C(29)-H(29)...Cl(2)	0.93	2.733(1)	3.558(5)	148
C(26)-H(26)...Cl(4)	0.93	2.859(2)	3.735(5)	157
C(14)-H(14)...S(2)	0.93	2.970(1)	3.849(6)	158
N(6)-H(6)...Cl(1)	0.86	2.317(1)	3.148(4)	163
N(8)-H(7)...Cl(4)	0.86	2.286(1)	3.069(3)	151

[Co(tm^{t-Bu})(Cl)₃] along with two acetonitrile molecules as solvent of crystallization in one asymmetric unit (Fig. (4)). The anionic complex [Co(tm^{t-Bu})(Cl)₃]⁻ acts as monomer and mainly responsible for layered structure. The nickel centre in [Ni(phen)₃]²⁺ (Fig. (4)) is in an octahedral environment as in complex 1 with slight differences in dihedral angles between the planes of the neighboring phen rings (78.50°, 85.58° and 85.70°). The cis-angles in the octahedron (Table 2) are slightly deviated from the value of 90° and the average trans angle in axial position is 171.73°.

The equatorial plane of [Co(tm^{t-Bu})(Cl)₃]⁻ shows distortions with the average angles of 111.28° which is slightly less than the standard tetrahedral value. The cobalt ion is coordinated by three chlorine atoms and one sulphur atom of tm^{t-Bu} in a distorted tetrahedral geometry. The Co-Cl bond

distances are in the range of 2.263(6) to 2.283(7) Å which are larger than the reported distances in the literature [37-40]. The metal centre in this complex is 0.678 Å above from the equatorial plane and three chloride ions attached to the cobalt centre are extensively involved in intermolecular C-H...Cl hydrogen bonding. Due to the presence of several intermolecular non-covalent interactions between the chloride ions bonded to cobalt centre and hydrogen atoms present on phenanthroline moiety, the complex cation is linked to six complex anions, (Fig. (S2)), whereas the complex anion is linked to three complex cations and one complex anion, (Fig. (S3)) (Table 3). Besides these C-H...Cl intermolecular interactions, the complex anion also shows intramolecular N-H...Cl interaction (2.463(24) Å) between bonded chloride ion and hydrogen atom present on the nitrogen of thioimidazole ring

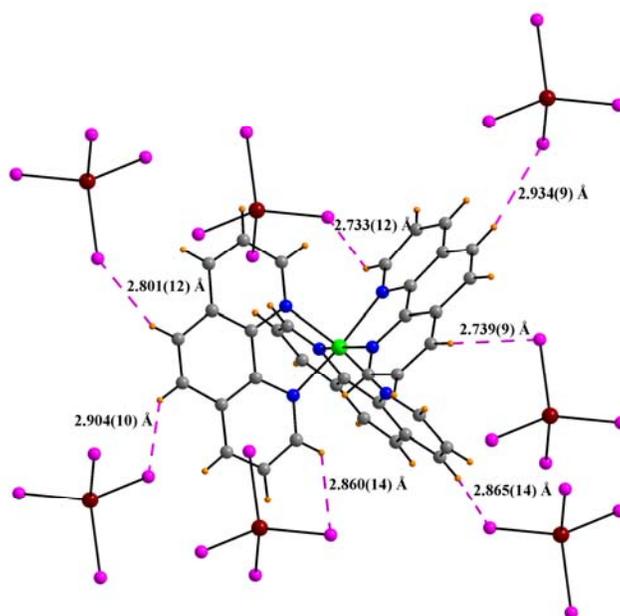


Fig. (2). View of intermolecular C-H...Cl interactions (pink dotted) shown by one cation molecule with anion molecules in complex 1.

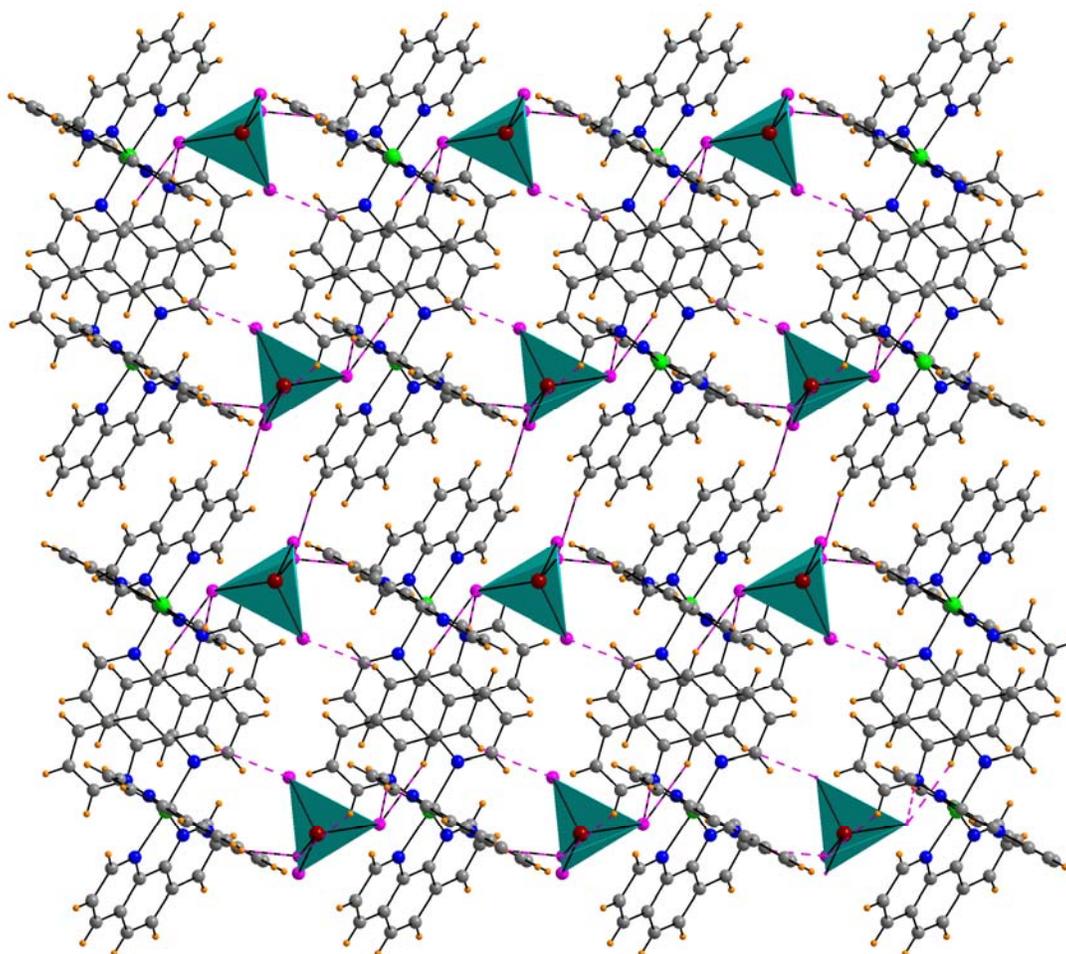


Fig. (3). View of three-dimensional arrangement in complex 1 due to C-H...Cl interactions.

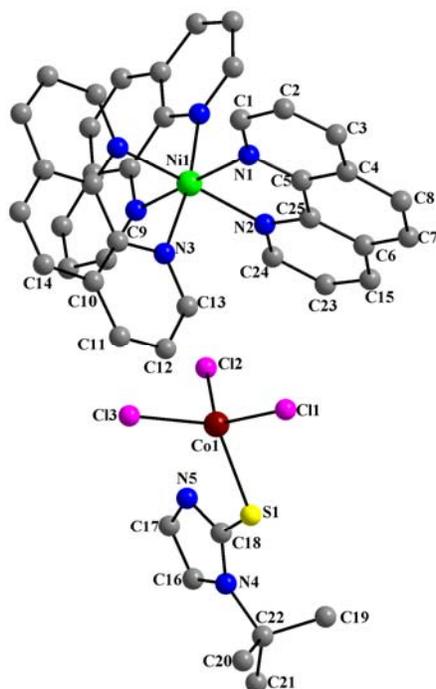


Fig. (4). Molecular structure view of complex $[\text{Ni}(\text{phen})_3][\text{Co}(\text{tm}^{\text{t-Bu}})\text{Cl}_3]_2$ **2**. Hydrogen atoms and solvent molecules have been omitted for clarity.

and π - π stacking (3.528 Å) between two thioimidazole rings of the complex anion (Fig. (S3)). It is important to mention here that out of three bonded chloride ions, only one (Cl2) is involved in both intramolecular as well as in intermolecular interactions, (Fig. (S3)), whereas the other two chloride ions are involved only in intermolecular hydrogen bond forma-

tion. The two cationic layers are united with anionic layers by hydrogen bonds, (Fig. (5)). Weak C-H \cdots Cl hydrogen bond and π - π stacking play prominent roles in the stabilization of the layered-structure. It is also significant that there is no π - π stacking between the phenanthroline moiety present in the lattice.

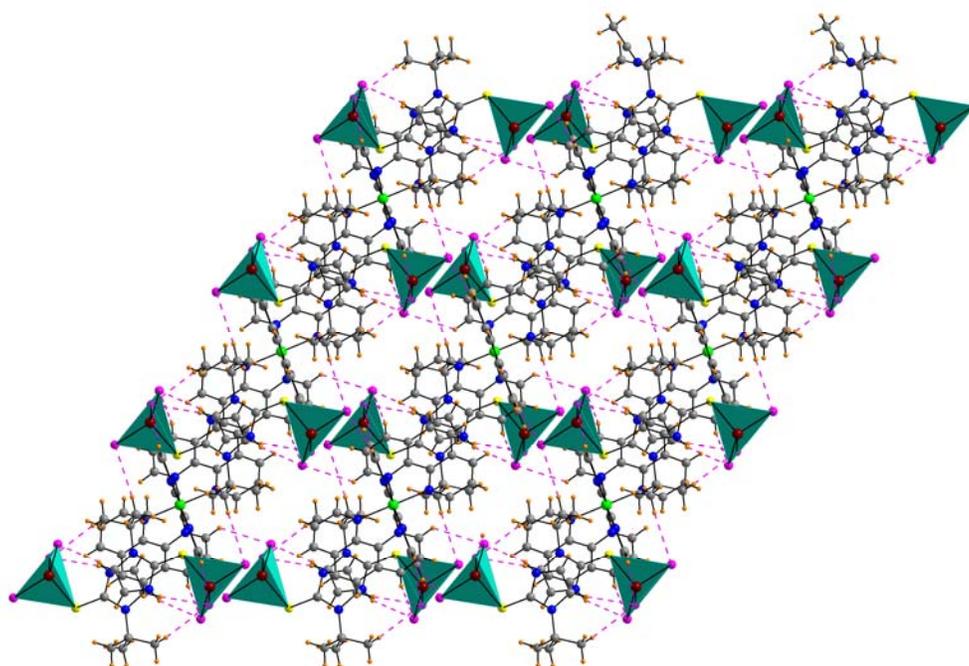


Fig. (5). View of three-dimensional arrangement in complex **2** due to non-covalent interactions.

Crystal Structure of Complex 4

The complex **4** crystallizes in monoclinic system with space group $P2_1/n$. The molecular structure of complex **4** is given in Fig. (6). It is also ionic in nature and comprises of one complex cation $[\text{Ni}(\text{phen})_2(\text{tm}^{\text{-Bu}})\text{Cl}]^+$ and one complex anion $[\text{Zn}(\text{tm}^{\text{-Bu}})\text{Cl}_3]^-$ along with two acetonitrile and one methanol molecule as solvent of crystallization in the asymmetric unit (solvent molecules exhibit thermal disorder and we are unable to add hydrogen atoms on solvent molecules). The Ni(II) in $[\text{Ni}(\text{phen})_2(\text{tm}^{\text{-Bu}})\text{Cl}]^+$ (Fig. (6)) is in octahedral environment where the equatorial plane is formed by the three nitrogen atoms of two phenanthroline units and one sulphur atom from $\text{tm}^{\text{-Bu}}$. The axial positions are occupied by another nitrogen atom of phen and a chloride atom with an angle of $173.02(9)^\circ$. The Ni-N bond distances are in the range of 2.084(3)-2.117(3) Å whereas the Ni-S bond distance is 2.560(10) Å which is well within the reported range in literature [8]. The Ni-Cl bond distance in **4** is 2.420(10) Å and the dihedral angle between the planes of the neighboring phen rings is 88.92° . The cis angles in the octahedron (Table 2) are slightly deviated from the value of 90° and trans angle in axial position is $173.02(9)^\circ$.

The $[\text{Zn}(\text{tm}^{\text{-Bu}})\text{Cl}_3]^-$ shows distortions deviating slightly from the regular tetrahedral geometry. Zn(II) is coordinated by three chlorine atoms and one sulphur atom of $\text{tm}^{\text{-Bu}}$ leaving overall one negative charge on the complex. The Zn-Cl bond distances are in the range of 2.246(12) to 2.278(12) Å which is very close to Zn-Cl bond distance in other complexes [41]. The complex anion also exhibited intermolecular C-H...S bonding (2.970(1) Å) and intramolecular N-H...Cl bonding (2.317(1) Å) due to the interaction between coordinated sulphur atom and hydrogen atom of phenanthroline moiety and between bonded chloride ions and hydrogen atom of thioimidazole molecule respectively. The chloride ions present on both Ni(II) and Zn(II) ions are extensively involved in intermolecular hydrogen bonding (C-H...Cl) during complex cation to cation and cation to anion interactions. Due to the presence of such type of non-covalent interactions in unit cell, each complex cation is linked to two complex cations and two complex anions as demonstrated in Fig.

(S4). The cationic unit also shows one intramolecular N-H...Cl interaction (2.286(1) Å) between the bonded chloride ion on nickel centre and hydrogen atom present on thioimidazole moiety but this interaction does not take part in crystal packing. In complex **4**, the one anionic unit has the capability to interact with three complex cations and one complex anion through C-H...Cl hydrogen bonding interaction, (Fig. (S5)), and both cation and anion serve as receptor as well as acceptor for each other. The presence of various non-covalent interactions resulted in three dimensional packing view Fig. (7) for complex **4**.

Magnetic Properties

In electromagnetism the magnetic susceptibility is the degree of magnetization of a material in response to an applied magnetic field. The variable temperature magnetic susceptibility were recorded on a polycrystalline sample for complexes between 300 and 2 K temperature range at a field of 1kOe. The temperature dependence of the product of magnetic susceptibility and temperature ($\chi_M T$) for complex **1** is shown in Fig. (8). The room temperature value is 7.93 emu mol⁻¹K and is quite well with that expected for the sum of the $\chi_M T$ of Ni(II) ion ($S = 1$, $g = 2$) and Mn(II) ion ($S = 5/2$, $g = 2$) in high spin state as they were magnetically isolated due to large separation of 8.832 Å. This distance is too large for any kind of magnetic interaction. Below 30 K, $\chi_M T$ value slightly decreases which may be due to zero-field splitting and / or intermolecular magnetic coupling. The value of the $\chi_M T$ product is 9.14 emu mol⁻¹K for **2** (Fig. (S6)) and 2.63 emu mol⁻¹K for **4** (Fig. (S7)) (Table 4). The metal-metal separation in **2** and **4** are 5.873 Å and 8.488 Å respectively. The $\chi_M T$ product of 9.14 emu mol⁻¹K for **2** can be explain due the presence of one complex cation and two complex anion where all the metal centers {i.e. one Ni(II) ($S = 1$) and two Co(II) ($S = 3$)} are in high-spin states. This value agrees with the theoretical value (8.99 emu mol⁻¹K) for sum of the spin state of metal ions present in this complex. In complex **4**, the diamagnetic zinc is present in anionic component and the experimental $\chi_M T$ value corresponds to Ni(II) with $S = 1$ only. Normally molecular assemblies consisting of cationic

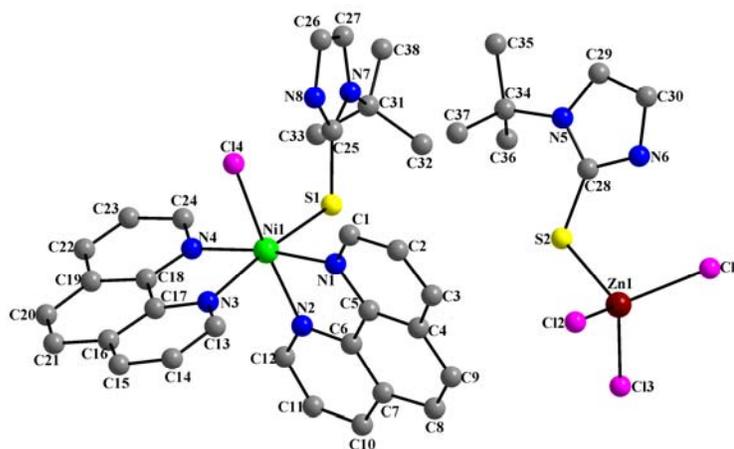


Fig. (6). Molecular structure view of complex $[\text{Ni}(\text{phen})_2(\text{tm}^{\text{-Bu}})\text{Cl}] [\text{Zn}(\text{tm}^{\text{-Bu}})\text{Cl}_3]$ **4**. Hydrogen atoms and solvent molecules have been omitted for clarity.

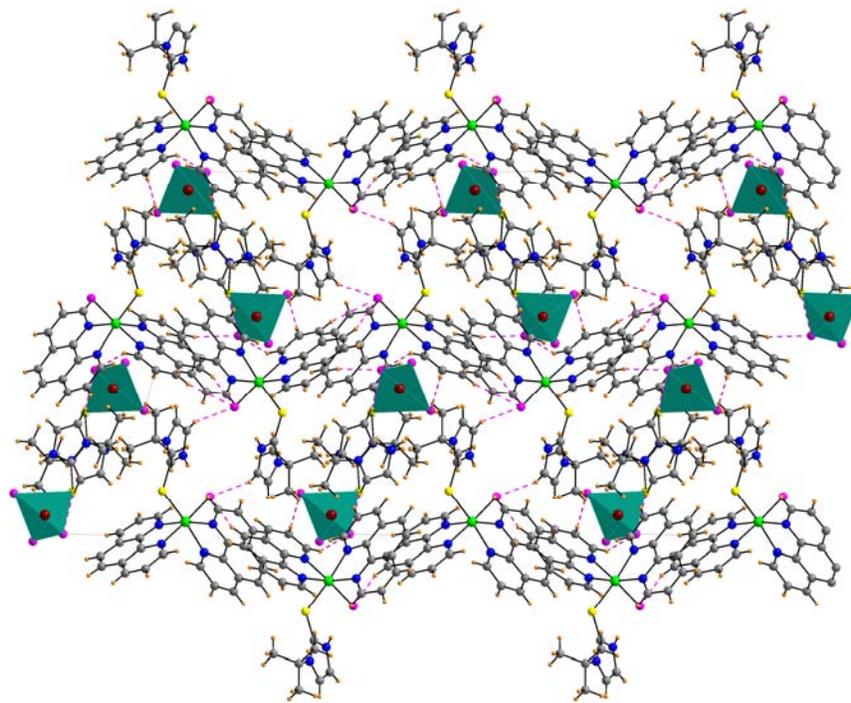


Fig. (7). View of three-dimensional arrangement in complex **4** due to non-covalent interactions.

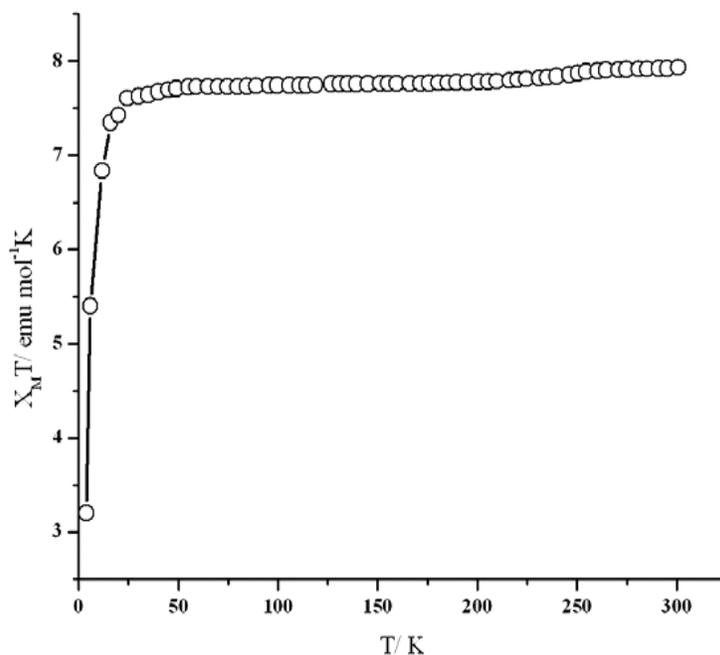


Fig. (8). Temperature dependence of the $\chi_M T$ product for complex **1**.

and anionic molecules show interesting magnetic behavior [19-21, 42, 43]. However in magnetic measurements of these complexes, we did not observe any interaction between metal ions because of the large separation between them but results show that these complexes are magnetically non-active.

Thermal Analysis

Thermo-gravimetric analyses (TGA) were carried out in air atmosphere in temperature range 25-700 °C for complexes **1**, **2** and **4** with the heating rate of 10.0 °C min⁻¹ (Fig. (S8-S10)). The TGA curve of complex **1** shows two well

Table 4. $\chi_M T$ Products for Complexes 1, 2 and 4

Complex	Metals Spin State	$\chi_M T$ / Emu Mol ⁻¹ K (Theoretical)	$\chi_M T$ / Emu Mol ⁻¹ K (Experimental)
1	Ni (S = 1) and Mn (S = 5/2)	7.81	7.93
2	Ni (S = 1) and Co (S = 3/2)	8.99	9.14
4	Ni (S = 1) and Zn (S = 0)	2.45	2.63

separated stages. The first weight loss of 9.85 % occurs in the temperature range of 100-200 °C, corresponds to the loss of acetonitrile molecules (calculated value 9.33 %). Subsequent to this, distinct weight loss stage of 59.41 % in the temperature range 200-460 °C, can be attributed to the loss of three phen molecules against calculated value 61.52 %. The TGA curve of complex 2 shows three well-separated weight loss stages. The first weight loss of 6.46 % occurs in the temperature range of 100-200 °C, which corresponds to the loss of acetonitrile molecules (calculated value 6.19 %). Second weight loss of 25.26 % was observed at the temperature range 200-240 °C was due to loss of two 1-tert-butylimidazole-2-thione molecules (calculated value 23.56 %). In the third stage, 42.05 % weight loss in the temperature range 240-435 °C corresponds to the loss of two phen molecules (calculated value 40.78 %). Similar to complex 2, the 4 also exhibits three well-separated weight loss stages in the temperature range of 100-200, 200-250 and 250-415 °C as given in its TGA curve, corresponding to the losses of solvent molecules, 1-tert-butylimidazole-2-thione molecule and phen molecule respectively. Later, it can be assumed that in all these complexes, both metal ions form oxides as their TGA curves become constant at around 700 °C. This study reflected that the thermal stability of 1, 2 and 4 are same because all these complexes involve same extent of inter- as well as intramolecular interaction as demonstrated in their three dimensional packing view.

CONCLUSION

In conclusion, we have reported some ion-pair complexes where the metal-metal separation is too large for exhibiting magnetic interaction. The three dimensional packing view of these complexes demonstrated the presence of C-H \cdots Cl and C-H \cdots S hydrogen bonding interactions between cationic complexes like [Ni(phen)₃]²⁺, [Ni(phen)₂(tm^{t-Bu})Cl]⁺ (that has H-donor sites) and the anionic complexes like [MnCl₄]²⁻, [Co(tm^{t-Bu})Cl₃]⁻ and [Zn(tm^{t-Bu})Cl₃]⁻ (which have Cl⁻ and sulphur a hydrogen bond acceptor sites). Thus we have explored the utility of [Ni(phen)₃]²⁺ as anion receptor like [MnCl₄]²⁻ and other thioimidazole complex anion.

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SUPPLEMENTARY MATERIAL

Supplementary material is available on the publishers Web site along with the published article.

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