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Coordination assembly of *p*-substituted aryl azo imidazole complexes: Influences of electron donating substitution and counter ions

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ABSTRACT

The formation of a series of Cu(II), Zn(II) and Cd(II) complexes using the *p*-substituted aryl azo system has been reported. Presence of electron donating –Me, –OMe groups impart some unusual coordination behaviors in Cu(II) complexes. Varying coordination mode and electron density in the ligand results in the formation of an unusual Cu–S bond in complex **1** and an unusual equatorial coordination of H₂O in Cu(II) complex **2** with a square-pyramidal geometry.

The hydrogen bonding site along with the metal coordination site in the ligand results in the formation of higher dimensional self-assembled supramolecular architectures. Compatibility of the hard-soft nature of the metal ion and symbiosis effect of the ligand with metal is responsible for the formation of long range higher dimensional networks in the solid-state, which were confirmed by single crystal X-ray structure analysis. Furthermore, various physicochemical studies, *viz.* thermal behaviors, absorption spectra, electrochemistry and EPR studies, have been conducted to rationalize the structures in the solution phase.

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1. Introduction

Construction of metal-organic coordination frameworks via metal coordination-directed self-assembly processes has proven to be a fertile research field [1,2]. Metallosupramolecular chemistry, which involves the interplay between organic and metallic tectons, can be used to design network materials with predefined dimensional (1D, 2D or 3D) structural motifs [3-6]. The major approaches to such materials that have been employed are non-covalent interactions such as hydrogen-bonding, metal-ion coordination, electrostatic and hydrophobic forces [7,8]. Formation of such supramolecular metal-organic coordination structures [9] has attracted much attention in recent years due to their applications in diverse areas such as catalysis, optoelectronics, supramolecular storage of molecules, molecular recognition and magnetism. This approach allows the use of metal ion-ligand combinations as the metal complex as a whole behaves as a supramolecular synthon generating higher dimensional architectures.

Nitrogen containing heteroaromatic systems have been among the most researched kinds of organic compounds, primarily because of their importance [10] in pharmaceutical and chemical

industries. In fact, a large majority of these compounds are medicinally important, [11,12] and their motifs are found in many natural products. There has been a long-standing interest [13-16] in the coordination chemistry of 2-(aryl azo) imidazole ligands due to many reasons. The trans-isomer of this ligand forms stable complexes with several d-block elements. Our interest lies in the design of azo compounds containing a heterocyclic system. The presence of the -N=N- group can lead to the stabilization of low valent metal oxidation states due to its π acidity and presence of low lying azo-centered π^* -molecular orbitals [17,18]. The azo function is photochromic, [19,20] redox active [21,22] pH responsive [23,24] and its complexes act as a molecular switch [25,26]. Our recent work has involved incorporating some electron donating group in aryl azo systems and comparative studies upon the coordinations which form extended H-bonding network structures. Herein we have explored the coordination assembly of Cu(II), Zn(II) and Cd(II) metal complexes with two different *p*-substituted aryl azo imidazole ligands (Scheme 1). The complexes are $[Cu(II)(L_1)_2-$ (NCS)(SCN)] **1**, $[Cu(II)(L_2)(H_2O)(NO_3)_2]$ **2**, $[Zn(II)(L_1)_2(NCS)_2]$ **3**, $[Zn(II)(L_2)(NCS)_2(H_2O)]H_2O$ **4**, $[Cd(II)(L_1)_2Cl_2]$ **5** and $[Cd(II)(L_2)_2]$ $(NO_3)_2$ 6. We have compared the formation of coordination assemblies by considering the stereo-electronic effect of the substitutent on the phenyl ring in the aniline-imidazole dyes (Scheme 1). We also studied their comparative absorption spectral behaviours, electrochemical analysis, EPR and thermal properties.





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Scheme 1. The influence of electron donating substituents and counter ions for the self assembly of metal complexes assisted by the aryl azo system.

2. Experimental

2.1. Chemicals and reagents

All reagents were obtained from commercial sources and were used as received. Solvents were distilled freshly following standard procedures. Acetonitrile (MeCN) was dried by distillation from anhydrous CaH₂ and stored over 4 Å molecular sieves for electrochemical analysis.

2.2. Physical measurements

The IR spectra were recorded on a Perkin–Elmer-Spectrum One FT-IR spectrometer with KBr disks in the range 4000–400 cm⁻¹. The absorption spectra were recorded on a Perkin–Elmer Lamb-

Table 1

Crystal data and structure refinement for complexes 1-6.

da-25 UV-Vis spectrometer at 298 K. NMR spectra was recorded on a Varian FT-400 MHz instrument. The chemical shifts were recorded in parts per million (ppm) using tetramethylsilane (TMS) as a reference. Elemental analyses were carried out on a Perkin-Elmer 2400 automatic carbon, hydrogen and nitrogen analyzer. The solid-state magnetic susceptibility of the complexes at room temperature were recorded using a Sherwood Scientific balance MSB-1. Solution electrical conductivity measurements were made with a Systronics Conductivity meter 306. The thermo gravimetric analyses (TGA) of the compounds were performed using an SDTA 851 e TGA thermal analyzer (Mettler Toledo) with a heating rate of 2 °C per min in a N₂ atmosphere. Powder X-ray diffraction data were recorded with a Seifert powder X-ray diffractometer (XRD 3003T) with a Cu K α source (λ = 1.54 Å) on a glass surface of an air-dried sample. Cyclic voltammetric measurements were carried out using a CH Instruments make CHI660C electrochemistry system. The cell contained a glassy carbon working electrode, a Pt wire auxiliary electrode and a saturated calomel electrode (SCE) as the reference electrode. A salt bridge (containing supporting electrolyte, tetra-nbutylammonium perchlorate (TBAP) dissolved in dry MeCN) was used to connect the SCE with the electrochemistry solution [27]. All experiments were carried out under a dinitrogen atmosphere at RT and were uncorrected for junction potentials. Under our experimental conditions, the $E_{1/2}$ value (in volts) for the couple Fc⁺/Fc was 0.45 in MeCN vs. SCE. X-Band EPR spectra were recorded with a Jeol JES-FA series spectrometer fitted with a quartz dewar for measurements at liquid nitrogen temperature. The spectra were calibrated with an internal manganese marker.

2.3. X-ray crystallography

The intensity data were collected using a Bruker SMART APEX-II CCD diffractometer, equipped with fine focus 1.75 kW sealed tube Mo K α radiation (λ = 0.71073 Å) at 278(3) K, with increasing ω

	Complex 1	Complex 2	Complex 3	Complex 4	Complex 5	Complex 6
CCDC no.	653805	739712	739711	739713	653804	739716
Empirical formula	$C_{22}H_{20}CuN_{10}S_2$	C10H12CuN6O8	$C_{22}H_{20}N_{10}S_2Zn$	C ₁₂ H ₁₄ N ₆ O ₃ S ₂ Zn	C ₂₀ H ₂₂ CdCl ₂ N ₈	C20H20CdN10O8
Formula weight	552.17	407.81	554.01	419.82	557.77	640.87
T (K)	298(2)	298(2)	298(2)	298(2)	298(2)	298(2)
Radiation	Μο Κα	Μο Κα	Μο Κα	Μο Κα	Μο Κα	Μο Κα
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	Pca2 ₁	$P2_1/c$	$P2_1/n$	$P2_1/c$	C2/c	C2/c
a (Å)	11.8175(3)	9.7920(1)	11.0016(2)	10.2949(2)	11.7834(14)	15.4614(3)
b (Å)	12.7372(3)	6.9041(1)	15.0798(2)	13.2491(2)	12.9682(15)	10.9049(3)
c (Å)	17.0007(4)	23.3863(3)	15.5549(2)	13.1432(2)	15.504(2)	16.3198(4)
α (°)	90.00	90	90	90	90	90
β(°)	90.00	97.985(1)	92.6070(10)	91.698(1)	101.697(8)	116.295(3)
γ (°)	90.00	90	90	90	90	90
$V(Å^3)$	2558.98(11)	1565.70(3)	2577.92(7)	1791.92(5)	2320.0(5)	2466.88(12)
Ζ	4	4	4	4	4	4
μ	1.044	1.455	1.146	1.631	1.196	0.953
F(0 0 0)	1156	694	1136	692	1120	1288
hkl ranges	$-15 \le h \le 12$	$-13 \le h \le 13$	$-14 \le h \le 13$	$-13 \le h \le 13$	$-15 \le h \le 15$	$-20 \le h \le 20$
	$-16 \le k \le 16$	$-8 \le k \le 9$	$-19 \le k \le 19$	$-14 \le k \le 17$	$-17 \le k \le 16$	$-14 \le k \le 14$
	$-22 \le l \le 19$	$-31 \le l \le 30$	$-20 \le l \le 20$	$-17 \leq l \leq 17$	$-19 \le l \le 20$	$-16 \le l \le 21$
Reflections	5984/3858	3817/3290	6300/4541	4448/3670	2887/2695	3045/2628
$T_{\rm max}/T_{\rm min}$	0.786/0.711	0.812/0.735	0.874/0.829	0.629/0.521	0.861/0.789	0.761/0.687
Data/parameters	5984/1/318	3817/0/275	6300/0/397	4448/0/274	2887/0/141	3045/0/179
Maximum/minimum residual (e ų)	0.492/-0.320	0.297/-0.264	0.510/-0.477	0.619/-0.432	0.320/-0.366	0.379/-0.224
Goodness-of-fit (GOF) (S)	0.843	1.055	1.010	0.979	1.067	1.018
R _{int}	0.0304	0.0181	0.0230	0.0160	0.0359	0.0243
Final R indices	$R_1 = 0.0429$	$R_1 = 0.0260$	$R_1 = 0.0332$	$R_1 = 0.0295$	$R_1 = 0.0230$	$R_1 = 0.0242$
$[I > 2\sigma(I)]$	$wR_2 = 0.1171$	$wR_2 = 0.0712$	$wR_2 = 0.0720$	$wR_2 = 0.0630$	$wR_2 = 0.0615$	$wR_2 = 0.0583$
R indices (all data)	$R_1 = 0.843$	$R_1 = 0.0320$	$R_1 = 0.0563$	$R_1 = 0.0390$	$R_1 = 0.0253$	$R_1 = 0.0311$
	$wR_2 = 0.1432$	$wR_2 = 0.0744$	$wR_2 = 0.0808$	$wR_2 = 0.0674$	$wR_2 = 0.0629$	$wR_2 = 0.0615$

(width of 0.3° per frame) at a scan speed of 3 s/frame. SMART software was used for data acquisition. Data integration and reduction were undertaken with SAINT and XPREP [28] software. Multi-scan empirical absorption corrections were applied to the data using the program SADABS [29]. The structures were solved by direct methods using SHELXS-97 and refined with full-matrix least squares on F^2 using SHELXL-97 [30]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located from the difference Fourier maps and refined. Structural illustrations have been drawn with ORTEP-3 for Windows [31]. Selected crystallographic data are summarized in Table 1.

2.4. Synthesis of the ligands

The *p*-substituted aryl azo imidazole ligands (L_1 and L_2) were synthesized following the literature method [32,33].

2.5. Synthesis of complexes 1-6

2.5.1. Synthesis of $[Cu(L_1)_2(NCS)(SCN)]$ (1)

To a magnetically stirred solution of L₁ (0.372 g, 2 mmol) in CH₃OH (20 mL), was added solid CuCl₂ (0.171 g, 1 mmol) in portions. Then an aqueous solution of NH₄SCN (0.152, 2 mmol) was added to this mixture. The greenish-yellow precipitate that formed was filtered, washed with ether, and dried under vacuum. Yield: 0.524 g (95%). Single-crystals suitable for X-ray diffraction were obtained by slow evaporation of an EtOH:water (1:1) mixture of the compound at RT. *Anal.* Calc. (%) for C₂₂H₂₀N₁₀S₂Cu: C, 47.91; H, 3.66; N, 25.41. Found: C, 47.98; H, 3.60; N, 25.50%. IR (KBr disk) (cm⁻¹); vNCS), 2090 (s); vSCN), 2070 (s); v(C=N), 1595 (m); v(N=N), 1401 (m); v(C=S), 772 (m).

2.5.2. Synthesis of $[Cu(L_2)(H_2O)(NO_3)_2]$ (2)

To a solution of L₂ (0.20 g, 1 mmol) in CH₃OH (3 mL), solid Cu(NO₃)₂ (0.23 g, 1 mmol) was added in portions, with constant stirring. The light green precipitate that formed immediately was collected by filtration, washed with ether (5 mL), and dried in vacuum. Yield: 0.37 g (90%). X-ray quality crystals having the composition [Cu(II)(L₂)(H₂O)(NO₃)₂] were grown by diffusion of an EtOH:water (1:1) solution of the complex. Desolvation of crystals occurred when they were kept without the mother liquor. *Anal.* Calc. (%) for C₁₀H₁₂N₆O₈Cu: C, 29.48; H, 2.97; N, 20.64. Found: C, 29.51; H, 2.95; N, 20.65%. IR (KBr disk) (cm⁻¹); v(N=O), 1497 (s); v(N=O), 1271 (m); v(ONO), 992; v(C=N), 1600 (m); v(N=N), 1406 (m).

2.5.3. Synthesis of $[Zn(L_1)_2(NCS)_2]$ (3)

To a magnetically stirred solution of L₁ (0.37 g, 2 mmol) in CH₃OH (20 mL), was added solid ZnCl₂ (0.13 g, 1 mmol) in portions. An aqueous solution of NH₄SCN (0.15, 2 mmol) was then added to this mixture. The yellowish-red precipitate that formed was filtered, washed with ether, and dried under vacuum. Yield: 0.47 g, 85% based on the ligand L₁. Slow evaporation of an EtOH:water (1:1) solution of the compound at RT produced single-crystals suitable for X-ray diffraction. *Anal.* Calc. (%) for C₂₂H₂₀N₁₀S₂Zn: C, 47.82; H, 3.65; N, 25.36. Found: C, 47.91; H, 3.58; N, 25.45%. IR (KBr disk) (cm⁻¹); ν (SCN), 2190 (s), 2140; ν (C=N), 1593 (m); ν (N=N), 1398 (m); ν (C=S), 685 (m).

2.5.4. Synthesis of $[Zn(L_2)(NCS)_2(H_2O)]H_2O(4)$

Complex **4** was synthesized using the same procedure as for complex **3**. Yield: 0.37 g, 90% based on the ligand L₂. *Anal.* Calc. (%) for $C_{12}H_{14}N_6O_3S_2Zn$: C, 34.45; H, 3.37; N, 20.10. Found: C, 34.55; H, 3.41; N, 20.02%. IR (KBr disk) (cm⁻¹); *v*(SCN), 2182 (s), 2130; *v*(C=N), 1598 (m); *v*(N=N), 1393 (m); *v*(C=S), 680 (m).

2.5.5. Synthesis of $[Cd(L_1)_2Cl_2]$ (5)

To a solution of L₁ (0.37 g, 2 mmol) in CH₃OH (20 mL), solid CdCl₂ (0.20 g, 1 mmol) was added in portions, with constant stirring. The light yellow precipitate that formed immediately was collected by filtration, washed with ether (20 mL), and dried in vacuum. Yield: 0.52 g, 90% based on the ligand L₁. Single-crystals suitable for X-ray diffraction were obtained from slow evaporation of an EtOH:water (1:1) solution of the compound. *Anal.* Calc. (%) for C₂₀H₂₂Cl₂N₈Cd: C, 43.01; H, 3.97; N, 20.07. Found: C, 43.11; H, 3.41; N, 20.01%. IR (KBr disk) (cm⁻¹); ν (C=N), 1606 (m); ν (N=N), 1407 (m).

2.5.6. Synthesis of $[Cd(L_2)_2(NO_3)_2]$ (6)

To a solution of L_2 (0.404 g, 2 mmol) in CH₃OH (20 mL), solid Cd(NO₃)₂ (0.30 g, 1 mmol) was added in portions, with constant stirring. The light yellow precipitate that formed immediately was collected by filtration, washed with ether (20 mL), and dried in vacuum. Yield: 0.52 g, 90% based on the ligand L₂. Single-crystals suitable for X-ray diffraction were obtained by slow evaporation of EtOH:water (1:1) solution of the compound. *Anal.* Calc. (%) for C₂₀H₂₀N₁₀O₈Cd: C, 37.38; H, 3.13; N, 21.80. Found: C, 37.42; H, 3.15; N, 21.88%. IR (KBr disk) (cm⁻¹); v(N=O), 1420 (s); v(N-O), 1275 (m); v(ONO), 980; v(C=N), 1604 (m); v(N=N), 1403 (m).

3. Results and discussion

3.1. Crystal structure studies

In our earlier report we have shown that 2-(phenylazo) imidazole can act as a borderline and/or soft donor ligand [34,35]. Here we also reported that the aryl azo imidazole system can form inter-molecular H-bonding in the solid-state, which in turn forms a 3D supramolecular network in the crystal of a different pattern. In the present studies, we have compared the solid-state structure of 2-(p-tolylazo) imidazole (L_1) with unsubstituted 2-(phenylazo) imidazole. In the solid-state, L1 contains two symmetrically independent molecules. Substitution in the para position with the electron donating group –CH₃ makes the ligand more planar than the unsubstituted one. The imidazole and phenyl rings are more planar and the azo group is virtually coplanar with these rings. The dihedral angle between the two least-squares planes is only 1.75°, compared to 2.1° in the unsubstituted ligand. The N=N bond length is 1.256(3) Å, which is similar to the previous one, but smaller than in similar systems [34,35]. The bond between the azo-N and the phenyl, as well as the imidazole ring, is longer than the unsubstituted system. However, the bond between the imidazole ring and azo-N is stronger than the phenyl ring and azo-N, showing a similar trend to known aryl azo systems [34,35]. However, the N=N distance is almost the same in both ligands (1.254 vs. 1.256 Å in L₁). The imidazole N-H forms inter-molecular strong hydrogen bonds with the imidazole N atom of the other asymmetric unit (N1...N6 = 2.845 Å and N2···N5 = 2.856 Å). It forms a 1D hydrogen bonded chain along the bc plane. The phenyl ring of the molecule is arranged in an alternative direction about the 1D-chain (Fig. 1). The solidstate packing shows the formation of alternate hydrophilic and hydrophobic layers, as depicted in Fig. 1. The stretching frequency of the endocyclic $v_{C=N}$ bond of L₁ appears at 1520 cm⁻¹ and is red shifted by 40–80 cm⁻¹ from that of the unsubstituted ligand. The $v_N = N$ mode in L₁ appears at 1230–1260 cm⁻¹ and is red shifted by 150–170 cm⁻¹ from that of unsubstituted ligand. The imidazole-N forms strong N-H···N hydrogen bonding in the free ligand. However, in the complexes this N is coordinated to the metal center. Hence, in the metal complexes N-H···N hydrogen bonding is absent. In the solid-state, the metal complexes of these azo ligands form different types of coordinative assemblies which are pat-



Fig. 1. Formation of a 1D hydrogen bonded chain in solid-state L₁.

terned by the counter anion and the metal coordination environment.

The molecular structure of the complex $[Cu(II)(L_1)_2(NCS)(SCN)]$ (1) along with the numbering scheme is shown in Fig. 2a. It forms an axially elongated neutral monomeric square-pyramidal complex ($\tau = 0.05$) [36] with two ambident SCN⁻ ligands bonded to Cu(II). The anion SCN⁻ is bonded with Cu(II) in an equatorial position with the N donor (Cu-N = 1.998 Å) whereas in axial position it bonds with the S donor (Cu-S = 2.559 Å). Normally in biological systems, Cu(II)Pc (plastocyanin) contains Cu(II) bonded with the S atom of cystine thiolate or a neutral methodize thioether [37,38]. However, in non-biological systems complexes of Cu(II) with thiocyanate (SCN⁻) are not so favored energetically, and hence are less common in the literature. One of the ligands is bonded to the Cu(II) in a bidentate manner in the equatorial plane. The Cu(II) centre lies exactly on the equatorial plane formed by the four coordinating atoms. The bite angle of the ligand in the equatorial plane is much smaller (\sim 74°) than the other angles in the equatorial plane. In the solid-state it forms several C–H···N, C–H···S, C–H··· π weak interactions [39].

One of the imidazole N–H groups forms a N–H \cdots π interaction with the π -bond of the C=N group in the equatorial NCS ion. It forms a double-stranded 1D polymeric hydrogen bonded chain along the *b*-axis (Fig. 2b). All the metal ions are lined up along the *b*-axis. Analysis of the packing diagram of complex **1** reveals that in each complex only one of the two imidazole N-H groups forms a strong conventional hydrogen bond $(N-H \cdots N = 2.717 \text{ Å})$ with the thiocyanate N of a neighbouring molecule in the same layer. Moreover, there exist weak C–H···S and C–H··· π interactions between neighbouring molecules. The cumulative effects of these non-covalent interactions lead to the formation of a 1D helical architecture along the *b*-axis (Fig. 2c). Along these chains two Cu(II) atoms are separated by 9.423 Å and the repeating period in the helical column is about 11.817 Å. In this system an inner channel runs parallel to the helical axis. The IR spectrum of complex 1 exhibits a strong sharp stretch at 2090 and 2070 cm⁻¹, which corresponds to $v_{\rm C} =_{\rm N}$ of the SCN and NCS coordinating anions, respectively [38]. The medium intense peak at 772 cm⁻¹ corresponds to $v_{\rm C}$ =s stretching of the coordinated anion [39]. The magnetic moment, $\mu_{\rm eff}$, is \sim 1.78 BM at 300 K, as expected for an isolated S = 1/2 (d⁹) Cu(II) monomeric distorted square-pyramidal complex.



Fig. 2. (a) ORTEP plot of complex **1**. Thermal ellipsoids are set at the 50% probability level; (b) packing of complex **1** viewed along the *a*-axis and (c) view of inter-molecular N-H…N interactions between adjacent molecules that lead to the formation of a 1D helical chain in complex **1** along the *b*-axis.



Fig. 3. (a) ORTEP plot of complex 2. Thermal ellipsoids are set at the 50% probability level and (b) packing of complex 2 viewed along the c-axis.

In the absence of NH₄SCN, L₂ forms the neutral monomeric complex $[Cu(II)(L_2)(H_2O)(NO_3)_2]$ (2) when treated with $Cu(NO_3)_2$ (Fig. 3a). The Cu(II) centre has a distorted square-pyramidal coordination geometry (τ = 0.05). Both the nitrates are monodentate in nature. The Cu(II) atom lies exactly on the square plane. The azo-N forms the axial bond (Cu-N₄ = 2.3787). L₂ act as a bidentate chelating ligand. The equatorial bite angle is similar (\sim 75°) to that of the Cu(II) complex 1. The imidazole-N forms strong hydrogen bonds with the oxygen atoms of the nitrate [39]. Metal bound water forms strong O-H···O type hydrogen bonds with neighbouring oxygen atoms of the nitrate. The methoxy group is involved in a C–H···O type hydrogen bond. Additionally a π ··· π interaction plays a crucial role in forming a brick wall structure along the *ab* plane (Fig. 3b) in the solid-state. Complex 2 shows strong sharp peaks at 1497, 1271 and 992 cm⁻¹, which can be defined as the $v_{\rm N=0}$ stretching frequencies of the unidentate bonding of the nitrate anion [40]. The magnetic moment of the complex is \sim 1.89 BM, and this is due to the existence of the Cu(II) ion in the square-pyramidal environment [42,43].

In contrast to the Cu(II) complex **1** with the ligand L_1 , Zn(II) forms a completely different coordination geometry with the same ligand under the same reaction conditions. The Zn(II) complex **3** forms a mononuclear, neutral distorted tetrahedral complex (Fig. 4a), which is confirmed by the measurement of angles around the Zn(II) center. Moreover, the ambidentate thiocyanate ions bind to the Zn(II) center only through the N-atom, unlike in complex **1**. The difference in coordinating behavior of the thiocyanate ions in complexes **1** and **3** can be explained on the basis of the HSAB principle. Both ligands are unidentate and they are oriented in the *cis* orientation relative to the metal center. The ligands are oriented in opposite direction to each other. Careful analysis of the crystal packing diagram [39] reveals that both imidazole-NH units form N-H…S type hydrogen bonds with the neighboring same thiocyanate-S atom. However, the other thiocyanate-S atom is involved in

weak C–H···S type non-covalent interactions in the solid-state. The benzene ring of one ligand in the asymmetric unit forms π -stacking interactions (π ··· π , 3.667 Å) [39] with the nearest imidazole ring of the same ligand. The other ligand in the asymmetric unit does not form this type of interaction as it is oriented perpendicularly with the neighboring ligand. It forms a 2D honeycomb network structure along the *bc* plane in the crystal (Fig. 4b). The FT-IR spectrum of complex **3** exhibits strong stretches at 2190, 2140 and 685 cm⁻¹, which are in agreement with $v_{C=N}$ and $v_{C=S}$, respectively. [40,41] Under similar reaction conditions, but different crystallization conditions, L₂ forms a Zn(II) complex with a trigonal bipyramidal (TBP) geometry [44] ($\tau = 0.88$).

In complex 4, the Zn(II) centre is surrounded by two thiocyanate linkages, one bidentate L₂ ligand and one water molecule (Fig. 5a). The Zn(II) atom lies exactly on the equatorial plane. The azo-N and the water molecule are in the axial positions. The ligand behaves as a bidentate ligand, in contrast to Zn(II) complex **3**. The molecular packing shows a 1D coordination polymer running along the *c*-axis [39]. The distances between the two nearest Zn(II) ions in the polymer chain is 6.673 Å. Ligands in adjacent 1D polymeric chains are directed in opposite directions. The closest inter chain distance is 3.698 Å. The water of crystallization forms one strong N-H···O hydrogen bond and three more weak hydrogen bonds [39]. It forms a 1D water chain along the *c*-axis (Fig. 5c). The metal bound water simultaneously forms weak hydrogen bonds with two adjacent S atoms of SCN ions, and acts as bridge. It forms a ten membered chair type hydrogen bonded ring (Fig. 5b). The IR spectrum of complex 4 exhibits strong sharp stretches at 2182 and 2130 cm⁻¹, which corresponds to the $v_{\rm C} = N$ bond, and one at 680 cm⁻¹ which corresponds to $v_{C=S}$ [40,41].

The ligand L_1 forms the neutral mononuclear complex **5** (Fig. 6a) with CdCl₂, where Cd(II) is surrounded by two unidentate L_1 ligands and two Cl⁻ ions in a distorted tetrahedral fashion. Both ligands are disposed in opposite directions with respect to the



Fig. 4. (a) ORTEP plot of complex 3. Thermal ellipsoids are set at the 50% probability level and (b) packing of complex 3 along the bc plane.



Fig. 5. (a) ORTEP plot of complex **4**. Thermal ellipsoids are set at the 50% probability level; (b) the water bridge ten membered chair type hydrogen bonded architecture in complex **4** and (c) the packing of complex **4** along the *b*-axis.

metal center. The imidazole-N–Cd–N-imidazole angle is 133.88°, which is much higher than a tetrahedral angle. The torsion angle between the two rings of the ligand is 4.86° *i.e.* the ligand is less planar than L₁ of the previous complex. Each imidazole N–H forms a relatively strong hydrogen bond with the neighbouring coordinated chloride ion. This has a significant role in the formation of a 3D network of rhombohedra, where each of them share a corner with the adjacent one [39]. The *para*-substituted methyl groups form weaker C–H··· π interactions. These interactions help to form a 1D chain along the *c*-axis [39]. Complex **5** forms a flower mosaic architecture (Fig. 6b) in the solid-state.

Ligand L_2 also forms the neutral mononuclear complex **6** (Fig. 7a) with Cd(NO₃)₂. The structure shows that the Cd(II) ions adopt a distorted octahedral geometry. The metal center is surrounded by two unidentate ligands and two bidentate chelating nitrate groups. Both the ligands are on the same side of the metal ion. The imidazole N atoms form stronger bonds than the oxygen atoms of the nitrate groups [45]. Each imidazole N–H forms a relatively strong hydrogen bond with the O-atom of a neighboring coordinated NO₃⁻⁻ ion. The C–H moiety adjacent to the imidazole nitrogen forms a C–H···O type hydrogen bond with the O-atom of a neighboring coordinated NO₃⁻⁻ ion. This combination of interactions re-



Fig. 6. (a) ORTEP plot of complex 5. Thermal ellipsoids are set at the 50% probability level and (b) packing of complex 5 along the *a*-axis.



Fig. 7. (a) ORTEP plot of complex 6. Thermal ellipsoids are set at the 50% probability level and (b) packing of complex 6 along the c-axis.

sults in the formation of a diamond shape higher dimensional coordination assembly [39]. The packing diagram reveals that the self-assembly of complex **6** forms a flower mosaic architecture along the *c*-axis (Fig. 7b). The FT-IR spectrum of the cadmium nitrate complex exhibits strong stretches at 1420, 1275 and 980 cm⁻¹ which are in agreement with coordinated O–NO₂ moieties [40,41].

3.2. Absorption spectral studies

The electronic absorption spectrum of aniline-imidazole [46] dye shows an intense broad absorption band in the visible region at ca. 362 nm in MeOH. The *para*-substituted ligands L_{1-2} show a bathochromic shift with respect to the unsubstituted ligand (Fig. 8a). The maximum red-shift is found in case of L_2 (-OMe substituted) and the minimum effect is observed for L_1 (-Me substituted). The amount of shift is attributed to the electronic effect of the substituted group. These absorption bands, between 362 and 385 nm, correspond to intra-ligand $n \rightarrow \pi$ as well as $\pi \rightarrow \pi$ electronic transitions [47]. In addition, L_2 shows a weak shoulder at 421 nm. In the Cu(II) complexes of L_1 and L_2 , the absorption bands in the visible region are shifted to higher wavelengths relative to the free ligands. In complex **1**, the observed $\Delta\lambda_{max}$, $n \rightarrow \pi$ is ~14 nm, whereas in the case of com-

plex **2** the observed $\Delta \lambda_{max}$, $n \rightarrow \pi$ is ~30 nm and $\Delta \lambda_{max}$, $\pi \rightarrow \pi$ is \sim 26 nm. Additionally, in the Cu(II) complex, a third band is observed in the visible region, at \sim 434 nm for complex 1 and at \sim 443 nm for complex **2**. This higher wavelength band originates from the forbidden d-d transition of the metal center, which is generally weak in nature⁻ [47]. In the presence of Cu(II), Zn(II) and Cd(II) metal ions, a bathochromic shift is observed due to MLCT transitions (Fig. 8b). However, the ligands, as well as the complexes, do not exhibit any significant solvatochromism. Similar results have been found for other ligands. In both the Cu(II) complexes, a weak spectral band is observed at ~550-660 nm $(\varepsilon = 825 - 85 \text{ M}^{-1} \text{ cm}^{-1})$, which is generally attributed to d_{xz} , $d_{yz} \rightarrow d_{x2-y2}$ transitions. This band probably appears due to the typical penta-coordinated square-pyramid geometry of the Cu(II) complexes [48]. Overall the features are from the effect of the electron releasing substituents which increase the electron density of the ligand system, and as a result sharp changes are observed in the absorption behavior.

3.3. EPR spectra analysis

The EPR spectra were recorded for both the Cu(II) complexes. The X-band EPR spectrum of complex **1** in MeOH glass (77 K) is displayed in Fig. 9a. The spectrum is typical for a monomeric Cu(II)



Fig. 8. (a) Absorption spectra of L₁ and L₂ in MeOH and (b) absorption spectra of L₂ in the presence of Cu(II), Zn(II) and Cd(II) metal ions.



Fig. 9. X-band EPR spectra measured in methanol at 77 K of (a) complex $\mathbf{1}$ and (b) complex $\mathbf{2}$.

complex in a distorted square-pyramidal geometry with (g_{\perp} = 2.06, $g_{11} = 2.33$, $A_{11} = 175$ G) with a $dx^2 - y^2$ ground state. Thus, the stronger effect of the axial S donor as compared with a N donor is indicative of a slightly stronger perturbation to the Cu(II) centre [49,50]. This may be attributed to a marked deviation of the axial Cu-S bond from the unique axis of the tetragonal square basal plane, as has been demonstrated for a violet thiocyanate S-Cu(II) complex with a distorted square-pyramidal structure. Also in the solid-state, complex **1** exhibits a broad EPR signal around g = 2with no visible hyperfine interactions at 300 K. In contrast, for complex 2 we have shown that the monomeric Cu(II) is surrounded by three O-donors and one N-donor in the basal plane and a weak azo-N donor is in the axial position. The EPR spectrum of complex 2 in methanol glass at 77 K resembles the monomeric Cu(II) EPR spectrum (g_{\perp} = 2.05, g_{11} = 2.20, A_{11} = 182.3 G) in solution (Fig. 9b) [51].

3.4. Electrochemistry

The electrochemical properties of the Cu(II) complexes were examined by cyclic voltammetry at a platinum working electrode in acetonitrile (0.1 M TBAP) and the potentials are reported with reference to SCE (at 50 mV s⁻¹ scan rate). The voltammograms display a metal based redox couple on the positive side and a ligand based redox couple on the negative side, with respect to the SCE (Fig. 10). The oxidation peak of the ligand L₁ shows one (Table 2) oxidation response at a negative potential which may be attributed to the redox couple irreversible peak ($E_{pa} = -0.133$ V) (Fig. 10a) [52,53]. In the complex one quasi-reversible couple peak is observed, which may be due to azo bond oxidation ($E_{pa} = -0.604$ V,

 $E_{\rm pc} = -0.695$ V, $\Delta E_{\rm p} = 91$ mV and $E_{1/2} = -0.65$ V) (Fig. 10b). The voltammogram of the Cu(II) complex **1** shows only a single reduction peak of Cu(II)/Cu(I) at 0.508 V ($E_{\rm pc}$) during the anodic potential scan, and just after the reduction peak a cathodic peak is observed at 0.414 V ($E_{\rm pa}$) (Fig. 10c). The separation between the anodic and cathodic peak potentials ($\Delta E_{\rm p}$) of 94 mV indicates a quasi-reversible redox process assignable to the Cu(II)/Cu(I) couple and $E_{1/2}$ is equal to 0.46 V.

It is believed that this response arises from oxidation of the azoimine function. The role of the azoimine function in bringing about the high Cu(II)/Cu(I) potential is well established [54,55]. Substitution of the *para*-H with electron donating –Me/–OMe groups increases the overall electron density in the ligand frame, which in turn increases the oxidation potential of the ligand compared to the unsubstituted one [34,35]. In the case of L₂, the oxidation peak remains similar without any significant change ($E_{pa} = -0.156$ V). In the complex **2**, however, one quasi-reversible couple peak is observed which may be due to azo bond oxidation ($E_{pa} = -0.613$ V, $E_{pc} = -0.705$ V, $\Delta E_p = 91$ mV and $E_{1/2} = -0.65$ V) and the Cu(II) complex **2** shows the quasi-reversible CV response ($E_{pa} = 0.441$ V, $E_{pc} = 0.534$ V, $\Delta E_p = (92$ mV and $E_{1/2} = 0.66$ V) corresponding to the Cu(II)/Cu(I) redox process [39].

3.5. Thermal studies

The interaction between the complexes and the solvent molecules in the solid-state can be commented on with the help of thermo gravimetric analysis. The onset temperature of weight loss and decomposition temperature were 160 and 200 °C for L₂, 220 and 250 °C for L₁, respectively (Fig. 11a). The metal complexes of these azo dyes were thermally more stable than the azo-dyes alone, which is reflected in their higher thermal stability. All the complexes containing solvent molecules in their crystal structure (*viz.* complexes **2** and **4**) decomposed thermally in a number of steps. However, the other complexes showed either a single step or a continuous weight loss in between 50 and 600 °C [39]. The robustness of the solid-state framework is reflected in the TGA [56–59]. Complex **2** shows a thermal release of metal bound water at ~150 °C (130–165 °C; $\Delta m = 4.42\%$ Calc. 4.18% found), followed by

Table 2		
Cuclic voltammetry data of I	and I	and with the

Cyclic voltammetry data of L_1 and L_2 and with their corresponding $\mbox{Cu}(II)$ salts.

Entry	$E_{\rm pc}$ (V)	$E_{\rm pa}\left({\sf V}\right)$	$\Delta E_{\rm p}~({\rm mV})$	$E_{1/2}(V)$
L ₁	-	-0.133	-	-
L ₂	-	-0.156	-	-
L_1 -Cu(II) complex	0.414	0.508	94	0.46
	-0.695	-0.604	91	0.65
L ₂ -Cu(II) complex	0.441	0.534	93	0.537
	-0.705	-0.613	92	0.660



Fig. 10. (a) Cyclic voltammogram of L₁ in MeCN; (b) reduction of the Cu(II)/Cu(I) couple in complex 1; (c) oxidation of the azo system in complex 1.



Fig. 11. (a) TGA analysis of ligands L1 and L2, (b) TGA analysis of complex 2 and 4.



Scheme 2. Scheme of diverse coordination modes with different metal ions in aryl azo systems.

complete decomposition in the temperature range 190–340 °C [37], whereas complex **4** shows successive thermal release of water of crystallization and metal bound water followed by complete decomposition of the complex (Fig. 11b). The TGA of complex **4** in N₂ atmosphere shows the release of one crystal water molecule (100–125 °C; $\Delta m = 4.30\%$ Calc. 4.48% found) and one metal bound water molecule at a relatively higher temperature range (190–220 °C; $\Delta m = 4.50\%$ Calc. 4.76% found) and complete decomposition is achieved at ~310 °C, which is in good agreement with the X-ray crystal structure.

4. Conclusions

This work describes the structural similarities and dissimilarities of Cu(II), Zn(II) and Cd(II) metal complexes with some electron rich *p*-substituted (-Me, -OMe) 2-phenylazo imidazole ligands, where counter ions also play a vital role in the higher dimensional structures obtained. Though the -*p*- substitutions are away from the coordination site, they still have a strong influence in the self-assembly processes of the metal complexes in the solid-state. The counter anions and metal ions tune the coordination environment of the complexes. A change in the coordination sphere has been reflected in their crystal structures and other physico-chemical properties. We have seen that the Cu(II), Zn(II) and Cd(II) salts show mononuclear (1:2) complexes in unsubstituted as well as -*p*-Me substituted systems. On the other hand, addition of the Cd(II)

salt resulted in the formation of a mononuclear (1:2) complex whereas the Cu(II) and Zn(II) salts formed mononuclear (1:1) complexes in the *-p*-OMe substituted system (Scheme 2).

The Cu(II) ion shows a marked preference for the N end of the ambidentate thiocyanate ligand. However, CSD search shows that only \sim 6–7% of mononuclear Cu(II) complexes containing the SCN⁻ anion have the Cu(II) center bonded through the S end. In the complex **1** we have both types of bonding at the same time. This can be rationalized by Pearson's hard–soft acid–base principle which requires matching hardness of two species for effective bonding. Bonding of SCN⁻ through the S end to Cu(II) is not favoured energetically. However, in complex **1**, an inter-molecular H-bond between the N atom of the thiocyanate and the N–H proton of the adjacent ligand (L₁) favoured this type of bonding.

The NO_3^- ligand shows both monodentate (complex **2**) and bidentate bridging (complex **6**) coordination modes. The single crystal of the different complexes also shows the formation of multifaceted networks in the resulting complexes. Solvent induced changes in the solid-state structures have also been observed in complexes **2** and **4**. Both the Cu(II) complexes **1** and **2** have similar geometries, but different coordination environments. In complex **1** two ligands are attached to the metal center, while in **2** only one ligand is coordinated to Cu(II). More than 75% of the coordination sphere of **1** is hydrophobic while in **2** less than 25% of the surface is hydrophobic. This is clearly reflected in their solid-state packing.

The presence of an electron donating group in the ligand increases the electron density in the ring which in turn reduces the N=N bond strength in comparison to the unsubstituted ligand. The C-H bonds attached to the OMe group are more polarized in L_2 than L_1 where they are attached to a -Me group. Moreover, the presence of electronegative O atoms in the neighboring position in the solid-state helps to form C-H···O type hydrogen bonds in complex **2**. On the other hand, the C-H bonds of the *para* -Me group form weak C-H··· π type interactions with the imidazole ring in the solid-state.

The presence of metal coordinated as well as crystal water molecules in complex **4**, compared to the another Zn(II) complex **3**, resulted in the formation of a greater number of strong and weak hydrogen bonds in the solid-state. Coordination of the azo-N decreases the electron density from N=N, which in turn decreases the azo bond strength. This also affects the ligand planarity, which controls the solid-state packing. The N=N bond is more elongated in complex **4** than in the similar complex **3**. This is due to the bidented behavior of the ligand in complex **4**.

The results of this study not only illustrates the coordination mode of ligands but also shows the nature of the neutral ligands, playing an important role in the construction of a variety of coordination networks. Thermal studies show that most of the metal-azo dyes have good thermal stability up to 300 °C, which is an important criterion to be a recording material for DVD-R. We are currently extending this result by preparing new imidazole containing aryl azo ligands of this type with different substituted organic functional groups and their new transition metal complexes.

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Appendix A. Supplementary data

CCDC 653805, 739711, 739712, 739712, 653804, 739716 contain the supplementary crystallographic data for **1–6**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, 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. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2010.03.022.

References

- [1] G.R. Desiraju, Crystal Design: Structure and Function, Wiley, Chichester, 2003.
- [2] J.M. Lehn, Supramolecular Chemistry: Concepts and Perspectives, VCH Publishers, New York, 1995.
- [3] R. Murugavel, A. Choudhury, M.G. Walawalkar, R. Pothiraja, C.N.R. Rao, Chem. Rev. 108 (2008) 3549.
- [4] G.-Z. Reyes, H. Herbert, J. Am. Chem. Soc. 127 (2005) 3120.
- [5] K.M. Fromm, Coord. Chem. Rev. 252 (2008) 856.
- [6] A.Y. Robin, K.M. Fromm, Coord. Chem. Rev. 250 (2006) 2127.
- [7] D. Tareste, F. Pincet, M. Brellier, C. Mioskowski, E. Perez, J. Am. Chem. Soc. 127 (2005) 3879.
- [8] M.A. Mateos-Timoneda, J.M.C.A. Kerckhoffs, C.-C. Mercedes, D.N. Reinhoudt, Angew. Chem., Int. Ed. Engl. 44 (2005) 3248.

- [9] S.R. Batten, S.M. Neville, D.R. Turner, Coordination Polymers: Design, Analysis and Application, Royal Society of Chemistry, 2008.
- [10] M.S. Butler, J. Nat. Prod. 67 (2004) 2141.
- [11] G. Bischoff, S. Hoffmann, R. Martínez, L. Chacón-García, Curr. Med. Chem. 9 (2002) 321.
- [12] R. Martínez, L. Chacon-Garcia, Curr. Med. Chem. 12 (2005) 127.
- [13] R.A. Krause, K. Krause, Inorg. Chem. 19 (1980) 2600.
- [14] M. Panda, C. Das, G.H. Lee, S.M. Peng, S. Goswami, J. Chem. Soc., Dalton Trans. (2004) 2655.
- [15] K.K. Sarker, D. Sardar, K. Suwa, J. Otsuki, C. Sinha, Inorg. Chem. 46 (2007) 8291.
- [16] P. Pratihar, T.K. Mondal, A.K. Patra, C. Sinha, Inorg. Chem. 48 (2009) 2760.
- [17] M. Kurihara, A. Hirooka, S. Kume, M. Sugimoto, H. Nishihara, J. Am. Chem. Soc.
- 124 (2002) 8800. [18] K. Yamaguchi, S. Kume, K. Namiki, M. Murata, N. Tamai, H. Nishihara, Inorg. Chem. 44 (2005) 9056.
- [19] H. Rau, H.I. Durr, H. Bouas-Laurent, Photochromism: Molecules and Systems, Elsevier, Amsterdam, 1990.
- [20] (a) N. Tamai, H. Miyasaka, Chem. Rev. 100 (2000) 1875;
- (b) S. Yagai, T. Karatsu, A. Kitamura, Chem.-Eur. J. 11 (2005) 4054.
- [21] V. Glezer, in: S. Patai (Ed.), The Chemistry of the Hydrazo, Azo and Azoxy Groups, Wiley and Sons, New York, 1997, p. 729.
- [22] N. Paul, S. Samanta, S. Goswami, Inorg. Chem. doi:10.1021/ic9016195.
- [23] N. DiCesare, J.R. Lakowicz, J. Phys. Chem. A 105 (2001) 6834.
- [24] W. Wu, T. Zhou, M. Aiello, S. Zhou, Chem. Mater. 21 (2009) 4905.
- [25] C. Renner, L. Moroder, Chem. Biol. Chem. 7 (2006) 868.
- [26] J. Otsuki, T. Akasaka, K. Araki, Coord. Chem. Rev. 252 (2008) 32.
- [27] D.T. Sawyer, J.L. Roberts Jr., Experimental Electrochemistry for Chemists, Wiley, New York, 1974. p. 347.
- [28] SMART, SAINT and XPREP, Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA, 1995.
- [29] G.M. Sheldrick, SADABS: Software for Empirical Absorption Correction, University of Gottingen, Institute fur Anorganische Chemieder Universitat, Tammanstrasse 4, D-3400 Gottingen, Germany, 1999–2003.
- [30] G.M. Sheldrick, SHELXS-97, University of Gottingen, Germany, 1997.
- [31] L.J. Farrugia, J. Appl. Crystallogr. 30 (1997) 565.
- [32] P. Chattopadhyay, B.K. Dolui, C. Sinha, Indian J. Chem. Sect. A 36 (1997) 429.
- [33] H.K. Fun, K. Chinnakali, X.F. Chen, X.H. Zhu, X.Z. You, Acta Crystallogr., Sect. C 55 (1999) IUC9900025.
- [34] A. Pramanik, G. Das, Cryst. Growth Des. 8 (2008) 3107.
- [35] A. Pramanik, S. Majumdar, G. Das, Cryst. Eng. Commun. 12 (2010) 250.
- [36] A.W. Addision, T.N. Rao, J. Reedijk, J. van Rijn, G.C. Verschoor, J. Chem. Soc.,
- Dalton Trans. (1984) 1349. [37] B.K. Santra, P.A.N. Reddy, M. Nethaji, A.R. Chakravarty, Inorg. Chem. 41 (2002) 1328.
- [38] S. Sen, S. Mitra, D.L. Hughes, G. Rosair, C. Desplanches, Polyhedron 26 (2007) 1740.
- [39] See supporting information.
- [40] R.T. Conley, Infrared Spectroscopy, Allyn & Bacon, Boston, 1966.
- [41] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, fifth ed., John Wiley & Sons, Inc., New York, 1997.
- [42] A. Earnshaw, Introduction to Magnetochemistry, Academic Press, London, 1968.
- [43] B.N. Figgis, J. Lewis, Prog. Inorg. Chem. 6 (1964) 37.
- [44] P. Bhattacharyya, J. Parr, A.M.Z. Slawin, J. Chem. Soc., Dalton Trans. (1998) 3263.
- [45] D. Das, B.G. Chand, J. Dinda, C. Sinha, Polyhedron 26 (2007) 555.
- [46] R. Gup, E. Giziroglu, B. Kırkan, Dyes Pigments 73 (2007) 40.
- [47] D. Das, B.G. Chand, K.K. Sarker, J. Dinda, C. Sinha, Polyhedron 25 (2006) 2333.
- [48] G.A. McLachlan, G.D. Fallon, R.E. Martin, L. Spiccia, Inorg. Chem. 34 (1995) 254.
- [49] U. Sakaguchi, A.W. Addison, J. Chem. Soc., Dalton Trans. (1979) 600.
- [50] P. Bhunia, D. Banerjee, P. Datta, P. Raghavaiah, A.M.Z. Slawin, J.D. Woollins, J. Ribas, C. Sinha, Eur. J. Inorg. Chem. (2010) 311.
- [51] M.A. Ali, A.H. Mirza, R.J. Fereday, R.J. Butcher, J.M. Fuller, S.C. Drew, L.R. Gahan, G.R. Hanson, B. Moubaraki, K.S. Murray, Inorg. Chim. Acta 358 (2005) 3937.
- [52] S. Pal, T.K. Mishra, P. Chattopadhyay, C. Sinha, Proc. Indian Acad. Sci. 111 (1999) 687.
- [53] T.K. Misra, D. Das, C. Sinha, Polyhedron 16 (1997) 4163.
- [54] D. Datta, A. Chakravorty, Inorg. Chem. 22 (1983) 1085.
- [55] G. Wilkinson, Comprehensive Coordination Chemistry, vol. 5, Pergamon Press, Oxford, 1987.
- [56] A. Pramanik, S. Abbina, G. Das, Polyhedron 26 (2007) 5225.
- [57] H. Thakuria, B.M. Borah, G. Das, Eur. J. Inorg. Chem. 4 (2007) 524.
- [58] H. Thakuria, G. Das, Polyhedron 26 (2007) 149.
- [59] A. Pramanik, G. Das, J. Chem. Crystallogr. 39 (2009) 416.