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Synthesis, Characterization, and Conducting Properties of Heterobimetallic Salts of Cyanoiminomethanedithiolate Ligand[1]

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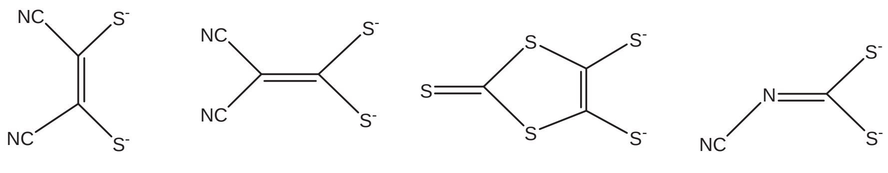
Heterobimetallic ion-pair complexes of the type $[M(bpy)_3][M'(cdc)_2]$ ($M = Fe^{2+}$, Co^{2+}, and Ni^{2+}; $M' = Ni^{2+}$ and Cu^{2+}; bpy = 2,2′-bipyridine, cdc^{2-} = cyanoiminomethanedithiolate ($C_2N_2S_2{}^{2-}$)) have been synthesized by reacting a solution of $K_2[M'(cdc)_2]$ with $[M(bpy)_3]X_2$ ($X = Cl^-$ and $SO_4{}^{2-}$) in equimolar ratio. These complexes have been characterized by elemental analysis, solution conductance, and magnetic susceptibility measurements, IR, ^1H and ^{13}C NMR, ESR, and UV–visible spectroscopies and pressed pellet conductivity technique. Three of these salts show behavior of semiconductors in the 295–443 K temperature range while the remaining are insulators. The lowering of the $\nu(C{\equiv}N)$ frequency in I_2-doped products of these complexes as compared to the parent complexes clearly reveals interaction of the $C{\equiv}N$ group of the ligand cdc^{2-} resulting in decrease in $\nu(C{\equiv}N)$ bond order and in turn partial reduction of I_2. The I_2-doped products of the majority of the complexes show enhanced room-temperature conductivity and exhibit semiconducting behavior.

Inorganic material chemistry dealing with sulfur rich complex based molecular electrical conductors, magnets, nonlinear optical materials, and photo-sensitizers has achieved significant advances in the recent years.[2–10] The description,[11,12] of $(TTF)[Ni(dmit)_2]_2$ (TTF = tetrathiafulvalene, $dmit^{2-}$ = 1,3-dithiol-2-thione-4,5-dithiolate) as the first superconductor revolutionized the designing and synthesis of a variety of monometallic charge-transfer salts of the ligand mnt^{2-} (maleonitriledithiolate) and other related 1,2-dithio ligands.[13] There is presently an upsurge of interest in heterobimetallic ion-pair and bridged complexes having two metals with diverse electronic configuration because of their importance in outer- and inner-sphere electron-transfer reactions, catalytic activities, molecular magnetism, and biological systems.[5,6,14–17] The properties of the resulting materials are predetermined by the nature of the molecular building unit as well as their packing in the lattice. When both complex cation and complex anion are magnetically different e.g. $[Fe(\eta^5\text{-}C_5Me_4SBu^t)_2][M'(mnt)_2]$ ($M' = Ni^{2+}$ and Pt^{2+}; Bu^t = tertiary butyl) interesting magnetic and conducting behavior are observed.[18–21] Several of these bimetallic salts have found useful applications particularly in the field of electrical conductivity and magnetism. In many cases, the ion-pair complexes contain two kinds of spin carriers due to the presence of either two different metal centers or different geometries associated with counter ions. Interactions in these bimetallic salts are considered to be ionic, because the metal ions present on the cationic centre attain their highest coordination number.

Transition-metal complexes with bifunctional unsaturated sulfur-containing ligands such as dinegative 1,2-dithio ligands, $dmit^{2-}$ and mnt^{2-} (Fig. 1) where the thio functions are at neighboring carbons and the dinegative 1,1-dithio ligands, e.g. 2,2-dicyanoethylene-1,1-dithiolate (i-mnt^{2-}) and cyanoiminomethanedithiolate (cdc^{2-}) where thio functions are on the same carbon atom differ significantly in chemistry and properties because (i) the former forms a less strained five-membered chelate ring while the latter a more strained four-membered chelate ring, (ii) the metal–ligand π bonding is more dominant in 1,2-dithio complexes resulting in higher S···S/M···S molecular stacking, one of the prerequisites for higher conductivity of molecular materials, and (iii) the uniqueness of the ligand cdc^{2-} like i-mnt^{2-} stems from its ability to exhibit a high degree of electron delocalization in the metal dithiolate ring and beyond the $M–S_2$ bonds. As a consequence, transition-metal dithio complexes exhibit electronic transitions at usually low energy and may be utilized in molecular conducting and magnetic materials exploration. Despite synthetic ability and chemical versatility, scant literature is available[22–28] on the monometallic and heterometallic complexes of ligand cdc^{2-}. Cationic metal polypyridine complexes such as $[M(bpy)_3]^{2+}$ ($M = Fe^{2+}$, Ru^{2+}, Os^{2+}, Co^{2+}, or Ni^{2+}) are of intense interest because of their facile redox



mnt^{2-} i-mnt^{2-} $dmit^{2-}$ cdc^{2-}

Fig. 1. Structure of the dithio ligands.

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behavior and electronic absorption properties.[9] In addition to intermolecular stacking, partial oxidation–reduction of the compounds caused by I_2-doping or electrochemical methods is one of the important factors for the enhancement in the conductivity of the compounds. From our inspection of the existing literature in this field and complete absence of studies on the heterometallic ion-pair complexes involving the (S, S) binucleating ligand cdc^{2-} and (N–N) bidentate ligand bpy as well as in the quest for new conducting and magnetic materials we herein report the synthesis, characterization, and properties of a new series of heterobimetallic ion-pair complexes of the type $[M(bpy)_3][M'(cdc)_2]$ ($M = Ni^{2+}$, Co^{2+}, and Fe^{2+}; $M' = Ni^{2+}$ and Cu^{2+}) and their I_2-doped products.

Experimental

Materials and Methods. All manipulations and procedures were carried out in open air at room temperature. The starting chemicals cyanamide, 2,2′-bipyridine (bpy), and KOH were purchased from Sigma Aldrich Chemical Company and all other reagent grade chemicals were available from commercial sources and used as received. The potassium salt of the ligand cyanoiminomethanedithiolate (K_2cdc) was prepared according to known procedure[29] by the reaction of cyanamide, potassium hydroxide, and carbon disulfide in dry ethanol and characterized by elemental analysis, IR and ^{13}C NMR spectra. Solvents were distilled and where necessary dried before use. After decomposing the organic part of the complexes with conc. HNO_3/aqua-regia, sulfur was determined as $BaSO_4$. C, H, and N analysis were performed on a Carlo Erba 1108 elemental analyzer. Melting points were determined in open capillaries and are uncorrected. Magnetic susceptibilities of the powdered samples were measured on a Cahn Faraday electro balance using $CoHg(SCN)_4$ as calibrant. The diamagnetic corrections were made using Pascal's constant. The solution conductivities of the complexes were measured in 10^{-3} M DMSO solution on an Elico CM 180 conductivity meter using a platinum electrode with cell constant of $0.50\,cm^{-1}$ and AC current. Infrared ($4000–400\,cm^{-1}$) spectra were recorded on a JASCO FTIR-5300 spectrophotometer. Electronic absorption spectra were recorded in DMSO solution on a Pharma Spec. UV-1700 and UNICAM UV2-100 UV–vis spectrophotometers. The room-temperature EPR spectra of the powdered samples were obtained on a Varian Model 109 CE-line X-band spectrometer. The microwave frequency was calibrated against tetracyanoethylene (TCNE), $g = 2.00277$. The ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded in DMSO-d_6 using tetramethylsilane (TMS) as internal standard on a JEOL AL 300 FT NMR spectrometer. Pressed pellet electrical conductivities of the complexes and their I_2-doped products were measured over a 295–383 K temperature range using conventional two probe technique on a Keithley 236 source measure unit. The pellets were made at a pressure of $2.0 \times 10^5\,kN\,m^{-2}$ and contacts of on the pellet surfaces were made using silver paint.

Preparation of the Ion-Pair Complexes. $[M(bpy)_3][M'(cdc)_2]$ ($M = Ni^{2+}$, Fe^{2+}, or Co^{2+}; $M' = Ni^{2+}$ or Cu^{2+}): The potassium salt of the anionic metal complex moiety $K_2[M'(cdc)_2]$ was prepared in situ according to literature procedure[23,24] by gradual addition of a 30 mL solution of $NiCl_2 \cdot 6H_2O$ (0.238 g, 1 mmol) in EtOH–H_2O (50:50, v/v) to a 5 mL solution of K_2cdc (0.4 g, 2 mmol) in the same solvent mixture with vigorous stirring. The green precipitate, presumably of Ni(cdc), initially appeared is immediately dissolved producing a dark green solution of $K_2[Ni(cdc)_2]$. This was additionally stirred for 30 min. The wine red solution of $K_2[Cu(cdc)_2]$ was prepared in exactly analogous manner by reacting $Cu(NO_3)_2 \cdot 3H_2O$ (0.241 g, 1 mmol) and K_2cdc (0.4 g, 2 mmol) in EtOH–H_2O (80:20, v/v). Here also, the reddish brown precipitate of Cu(cdc) formed is instantly dissolved generating a wine-red solution of $K_2[Cu(cdc)_2]$.

The cationic complexes $[M(bpy)_3]X_2$ ($X = Cl^-$ and $SO_4{}^{2-}$) required for the synthesis of the mixed-metallic ion-pair complexes were prepared in solution by reaction of a 5 mL EtOH–H_2O (50:50, v/v) solution of $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ (0.392 g, 1 mmol), $CoCl_2 \cdot 6H_2O$ (0.239 g, 1 mmol) or $NiCl_2 \cdot 6H_2O$ (0.238 g, 1 mmol), and 10 mL ethanolic solution of bpy (0.469 g, 3 mmol) which in turn were allowed to react with a freshly prepared 35 mL solution of $K_2[M'(cdc)_2]$ ($M' = Ni^{2+}$ and Cu^{2+}) as described above. The reaction mixture was stirred for 15 min. The colored heterobimetallic salts formed as microcrystalline solid were filtered off, washed with ethanol followed by diethyl ether successively and dried in vacuum over $CaCl_2$. The relevant analytical and physicochemical data are included in Table 1.

I_2-Doping of the Complexes. The I_2-doped products of the ion-pair complexes were obtained via vapor diffusion method by keeping 1 g of I_2 and 200 mg of the ground complex separately on a watch glass in a closed desiccator for 6–7 days. The I_2-doped powder products thus formed were dried in vacuum.

Results and Discussion

Ion-pair heterobimetallic complexes $[M(bpy)_3][M'(cdc)_2]$ were isolated in high yield by mixing stoichiometric quantities of $K_2[M'(cdc)_2]$ and $[M(bpy)_3]X_2$ in an EtOH–H_2O mixture according to the following metathesis reactions:

$$MX_2 + 3bpy \rightarrow [M(bpy)_3]X_2, \tag{1}$$

$$M'X_2 + 2K_2cdc \rightarrow K_2[M'(cdc)_2] + 2KX, \tag{2}$$

$$K_2[M'(cdc)_2] + [M(bpy)_3]X_2 \rightarrow [M(bpy)_3][M'(cdc)_2] + 2KX. \tag{3}$$

$$(M = Fe^{2+}, Co^{2+}, \text{ and } Ni^{2+}; M' = Ni^{2+} \text{ and } Cu^{2+}; X = Cl^-, SO_4{}^{2-}, \text{ and } NO_3{}^-)$$

These air-stable solids decompose in the temperature range 115–250 °C. The compounds were characterized by micro analysis, solution conductance, magnetic susceptibility, IR, UV–vis, ^1H and ^{13}C NMR, and ESR spectral measurements and pressed pellet conductivity technique. The compounds are insoluble in water as well as common organic solvents such as ethanol, methanol, acetone, acetonitrile, benzene, and dichloromethane but are fairly soluble in DMSO and DMF. The solution conductivity Λ_M (10^{-3} M): 22–97 $\Omega^{-1}\,cm^2\,mol^{-1}$ in DMSO suggests their ionic nature.[30] In the majority of cases Λ_M values are lower for 1:1 electrolytes and show extensive ion-pairing because of the existence of highly charged species in a solvent like DMSO of relatively low dielectric constant and higher Lewis basicity as shown in the following equilibrium.

$$[M(bpy)_3][M'(cdc)_2] \rightleftharpoons [M(bpy)_3]^{2+} + [M'(cdc)_2]^{2-} \rightleftharpoons [M(bpy)_3]^{2+}[M'(cdc)_2]^{2-} \tag{4}$$

NMR Spectra. The ^1H NMR spectra of the diamagnetic salt $[Fe(bpy)_3][Ni(cdc)_2]$ and weakly paramagnetic $[Fe(bpy)_3][Cu(cdc)_2]$ in DMSO-d_6 solution consist of a sharp multiplet for the former and relatively broad signals[31] for the later in

Table 1. Analytical and Physical Data of the Complexes

Compound (Empirical formula)	Color	Yield /%	Dec. temp /°C	Found (Calcd.)/% C	H	N	S	Λ_M (DMSO) /Ω^{-1} cm^2 mol^{-1}	σ_{rt} /S cm^{-1}	E_a /eV	Color$^{a)}$	$\sigma_{rt}{}^{a)}$ /S cm^{-1}	$E_a{}^{a)}$ eV
[Ni(bpy)$_3$][Ni(cdc)$_2$] $Ni_2C_{34}N_{10}H_{24}S_4$	Dark brown	85	245–250	49.82 (50.00)	2.84 (2.96)	17.01 (17.16)	15.45 (15.67)	97	6.9×10^{-9}	0.41	Dark brown	1.1×10^{-7}	0.81
[Co(bpy)$_3$][Ni(cdc)$_2$] $CoNiC_{34}N_{10}H_{24}S_4$	Green	87	205–210	49.61 (49.89)	2.92 (2.96)	17.08 (17.11)	15.43 (15.67)	45	2.7×10^{-5}	0.44	Dark brown	4.0×10^{-8}	1.36
[Fe(bpy)$_3$][Ni(cdc)$_2$] $FeNiC_{34}N_{10}H_{24}S_4$	Maroon	83	225–230	50.72 (50.80)	2.88 (2.97)	17.10 (17.18)	15.62 (15.73)	69	9.9×10^{-9}	0.51	Dark$^{b)}$ brown	—	—
[Ni(bpy)$_3$][Cu(cdc)$_2$] $NiCuC_{34}N_{10}H_{24}S_4$	Brownish yellow	84	115–120	49.68 (49.70)	2.79 (2.95)	17.00 (17.06)	15.49 (15.58)	50	1.0×10^{-10}	—	Dark brown	1.0×10^{-7}	0.61
[Co(bpy)$_3$][Cu(cdc)$_2$] $CoCuC_{34}N_{10}H_{24}S_4$	Brown	83	135–140	49.55 (49.64)	2.80 (2.94)	17.00 (17.04)	15.56 (15.76)	22	8.5×10^{-9}	—	Dark brown	2.0×10^{-8}	1.12
[Fe(bpy)$_3$][Cu(cdc)$_2$] $FeCuC_{34}N_{10}H_{24}S_4$	Maroon	86	135–140	49.56 (49.79)	2.80 (2.95)	17.04 (17.08)	15.57 (15.63)	31	9.2×10^{-9}	—	Dark brown	9.8×10^{-8}	0.81

a) Iodine-doped complexes. b) Sticky product.

Table 2. Selected IR Bands (KBr, cm^{-1}) of the Complexes$^{a)}$

Compound	ν(C≡N)	ν(C≡N)$^{b)}$	ν(C=N)	bpy
K$_2$cdc	2151 s		1317 s	
[Ni(bpy)$_3$][Ni(cdc)$_2$]	2175 s	2102 s 2068 s	1450 s	645 w, 432 m
[Co(bpy)$_3$][Ni(cdc)$_2$]	2174 s	2066 s	1441 s	652 m, 444 m
[Fe(bpy)$_3$][Ni(cdc)$_2$]	2168 s	2112 m	1421 s	640 w, 435 w
[Ni(bpy)$_3$][Cu(cdc)$_2$]	2172 s	2202 m 2119 w	1396 s	643 w, 432 m
[Co(bpy)$_3$][Cu(cdc)$_2$]	2174 s	2091 m s 2068 m s	1443 s	650 m, 442 m
[Fe(bpy)$_3$][Cu(cdc)$_2$]	2170 s	2168 m	1421 s	640 w, 432 w

a) m = medium, s = strong, w = weak. b) Iodine-doped complexes.

Table 3. Magnetic Moment and Electronic Absorption Bands of the Complexes in DMSO (Solution)

Complex	μ_{eff}/μ_B	λ_{max}/nm
[Ni(bpy)$_3$][Ni(cdc)$_2$]	2.7	620, 470
[Co(bpy)$_3$][Ni(cdc)$_2$]	4.9	550–700, 470
[Fe(bpy)$_3$][Ni(cdc)$_2$]	dia	530, 500, 450
[Ni(bpy)$_3$][Cu(cdc)$_2$]	3.9	700, 450
[Co(bpy)$_3$][Cu(cdc)$_2$]	3.1	700, 450
[Fe(bpy)$_3$][Cu(cdc)$_2$]	0.8	730, 540, 500, 450

the δ 7.5–9.0 region for the aromatic protons of the ligand 2,2′-bipyridine. Their ^{13}C NMR spectra produced sharp signals at δ 124–158 characteristic of carbons of the ligand bpy in the cationic fragment [Fe(bpy)$_3$]$^{2+}$ and at δ 214 and δ 120 due to S$_2$C=N and N–C≡N moieties of the coordinated ligand cdc^{2-} in [M′(cdc)$_2$]$^{2-}$ (M′ = Ni^{2+} and Cu^{2+}). The position and features of the NMR resonances confirm the purity and composition of the complexes. The NMR studies clearly reveal that no ligand-exchange reaction occurs in solution.

IR Spectra. The IR spectra of the complexes (Table 2) show strong absorption bands near 2170 and 1375–1450 cm^{-1} characteristic[22–24] of the nitrile (C≡N) and imido (C=N)) stretching frequencies of the ligand cdc^{2-}. A perceptible increase in the ν(C≡N) and ν(C=N)) frequencies compared to the uncoordinated cdc^{2-} in K$_2$cdc is concomitant with the change in delocalization over the S$_2$C–N–C group suggesting an (S, S) chelating mode[22–24] of the ligand cdc^{2-} to the metal ions M′ in the complex bimetallic salts. Also, the bands near 640 and 435 cm^{-1} characteristic of out of plane and in plane ring deformation of the bpy indicate (N–N) bidentate coordination of this ligand to the metal ions M in the complexes.

The I$_2$-doped products of these complexes give rise to ν(C≡N) bands (Table 2) at lower wavenumbers i.e. 2066–2119 cm^{-1}. This lowering in ν(C≡N) for all the complexes excepting [Fe(bpy)$_3$][Cu(cdc)$_2$] may be ascribed to considerable interaction between the C≡N group of the ligand cdc^{2-} and I$_2$, thereby decreasing C≡N bond order in turn causing partial reduction of the I$_2$ molecule.

Magnetic Moment. The effective magnetic moment values are listed in Table 3. [Fe(bpy)$_3$][Ni(cdc)$_2$] is diamagnetic suggesting low-spin octahedral geometry about iron(II) with intact [Fe(bpy)$_3$]$^{2+}$ and square-planar environment around nickel(II) in the [Ni(cdc)$_2$]$^{2-}$ fragment. In the case of the

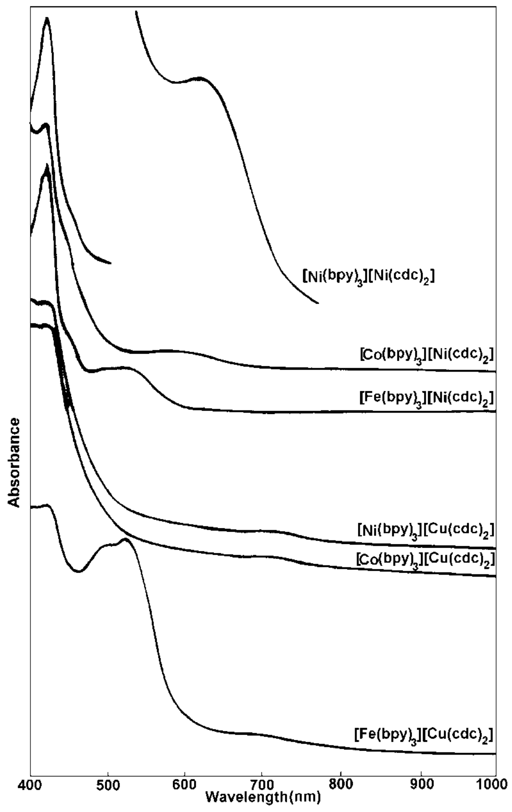


Fig. 2. The UV–vis absorption spectra of the complexes in DMSO (solution).

ion-pair complexes [M(bpy)$_3$][Cu(cdc)$_2$] (M = Fe^{2+}, Co^{2+}, or Ni^{2+}) the μ_{eff} values are lower than the sum of the magnetic moments contributed by Co^{2+} 3d^7, Ni^{2+} 3d^8, or Cu^{2+} 3d^9 paramagnetic centers showing some sort of antiferromagnetic interaction between (M–Cu or Cu–Cu) in these species. The room-temperature μ_{eff} values correspond to the spin only values for the isolated ion-pairs possessing high-spin octahedral geometry about Co^{2+} and low-spin square-planar coordination about Ni^{2+} in [Co(bpy)$_3$][Ni(cdc)$_2$] and [Ni(bpy)$_3$][Ni(cdc)$_2$] respectively.

UV–Vis Spectra. The electronic absorption bands of the complexes are summarized in Table 3 and displayed in Fig. 2. The DMSO solution electronic absorption spectra of [Fe(bpy)$_3$][Ni(cdc)$_2$] and [Fe(bpy)$_3$][Cu(cdc)$_2$] exhibit weak to intense bands near 450 nm ($\varepsilon \cong 9 \times 10^3\,\text{M}^{-1}\,\text{cm}^{-1}$), 500–540 nm ($8 \times 10^3\,\text{M}^{-1}\,\text{cm}^{-1}$), and 730 nm ($300\,\text{M}^{-1}\,\text{cm}^{-1}$) assignable to Ni^{2+} or Cu^{2+} $\leftarrow$ S(cdc^{2-}), iron(II) to bpy MLCT and d–d transitions respectively following square-planar geometry about nickel(II) and copper(II) and low-spin octahedral geometry about iron(II).[22,23,32] Absorption bands near 450–470 ($\varepsilon = 10^3\,\text{M}^{-1}\,\text{cm}^{-1}$) and 550–700 nm ($\varepsilon$ = 70–250 $\text{M}^{-1}\,\text{cm}^{-1}$) in the UV–vis spectra of [M(bpy)$_3$][M′(cdc)$_2$] (M = Co^{2+} and Ni^{2+}; M′ = Ni^{2+} and Cu^{2+}) correspond to M′ $\leftarrow$ S(cdc)$^{2-}$ and d–d transitions respectively showing presence of high-spin octahedral [M(bpy)$_3$]$^{2+}$ and square-planar [M′(cdc)$_2$]$^{2-}$ moieties in these bimetallic complexes. The features of the electronic absorption bands of the I$_2$-doped products of these salts are almost comparable to the parent complexes showing no significant charge transfer on metal centers occurring during the doping. In all the complexes the bands below 400 nm are attributed to intraligand charge-transfer transitions.

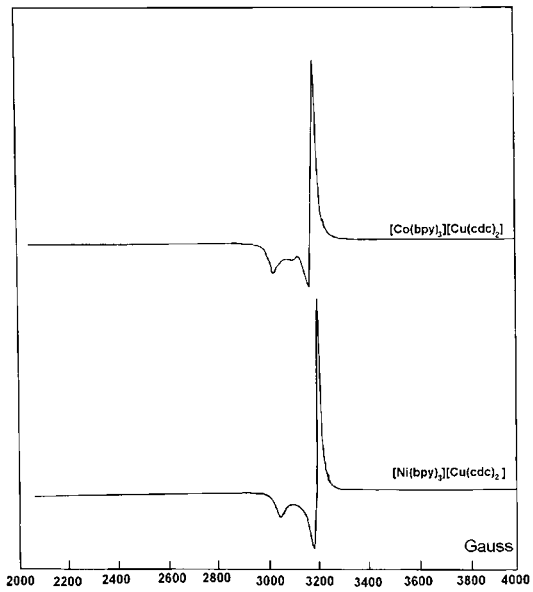
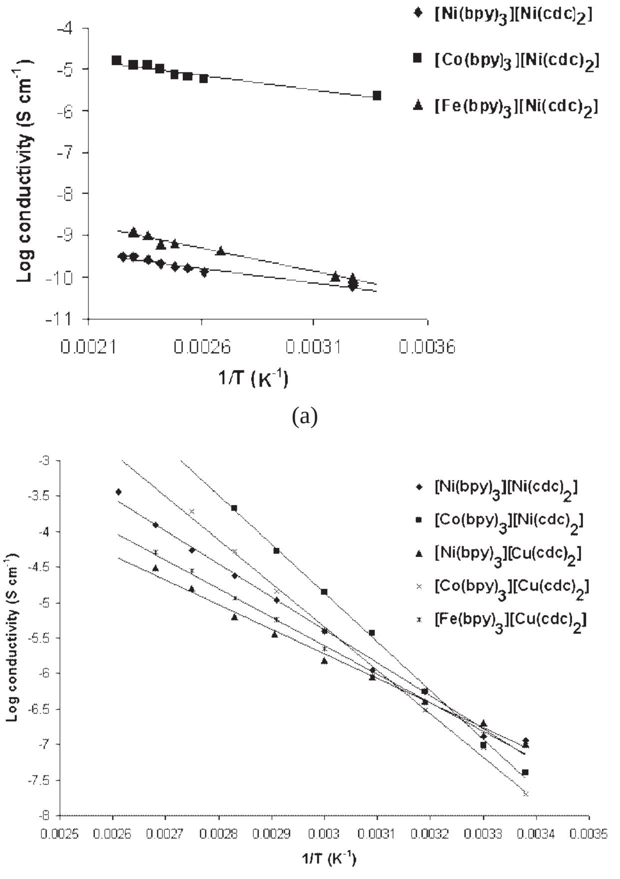


Fig. 3. The X-band ESR spectra of the complexes.

ESR Spectra. Powder X-band ESR spectra Fig. 3 of the [Co(bpy)$_3$][Cu(cdc)$_2$] and [Ni(bpy)$_3$][Cu(cdc)$_2$] are similar and do not show well-resolved parallel and perpendicular features. However, the derived g values $g_{\parallel} = 2.13$, $g_{\perp} = 2.024$, $g_{\text{av}} = 2.06$ with the trend $g_{\parallel} > g_{\perp} > g_{\text{e}} = 2.0023$ show that the unpaired electron resides in the $\text{d}_{x^2-y^2}$ orbital of the Cu^{2+} in these ion-pair complexes. The spectra and the values are close to the reported Cu^{2+} dithiolates possessing distorted square-planar geometry about Cu^{2+}.[33,34] The bimetallic salt [Fe(bpy)$_3$][Cu(cdc)$_2$] is weakly paramagnetic ($\mu_{\text{eff}} = 0.79$ μ_{B}) and yields a poor quality spectrum showing no typical feature of strong Cu–Cu antiferromagnetic coupling because the half field signal characteristic of dimeric structure is not located in the $\Delta M_{\text{S}} = \pm 2$ region.

Based on foregoing physicochemical studies the ionic structure for the complexes having octahedrally coordinated complex cation [M(bpy)$_3$]$^{2+}$ (M = Ni^{2+}, Co^{2+}, and Fe^{2+}) and square-planar complex anion [M′(cdc)$_2$]$^{2-}$ (M′ = Ni^{2+} and Cu^{2+}) in Fig. 1 have been postulated.

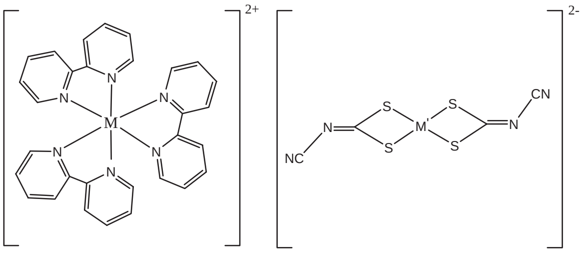
Electrical Conductivity. The temperature dependence of the pressed pellet electrical conductivities of the powdered complexes and their I$_2$-doped products are shown in Figs. 4a and 4b. All compounds exhibit electrical conductivity $\approx 10^{-10}$–$10^{-5}\,\text{S cm}^{-1}$ at room temperature. The ion-pair complexes [M(bpy)$_3$][Ni(cdc)$_2$] (M = Fe^{2+}, Ni^{2+}, and Co^{2+}) exhibit semiconducting behavior over a 295–443 K temperature range (with E_{a} = 0.41–0.51 eV) as their conductivities increase with the increase in temperature. Exceptionally, somewhat higher conductivity $\sigma_{\text{rt}} \approx 10^{-5}\,\text{S cm}^{-1}$ of [Co(bpy)$_3$][Ni(cdc)$_2$] may be ascribed to the participation of an unpaired electron on the Co^{2+} centre in the conductivity mechanism. However, analogous [M(bpy)$_3$][Cu(cdc)$_2$] complexes are insulators in the considered temperature range. Interestingly the I$_2$-doped products of all the complexes except that of [Co(bpy)$_3$][Ni(cdc)$_2$] for which σ_{rt} is decreased i.e. $10^{-7}\,\text{S cm}^{-1}$, show enhanced conductivity at room temperature i.e. 10^{-8}–



(a)

(b)

Fig. 4. Temperature dependence of electrical conductivities: (a) the complexes, (b) I_2-doped complexes.



$[M(bpy)_3]^{2+}[M'(cdc)_2]^{2-}$
($M = Fe^{2+}, Ni^{2+}, Co^{2+}$; $M' = Ni^{2+}, Cu^{2+}$; bpy = 2,2'-bipyridine; cdc^{2-} = cyanoiminomethanedithiolate)

Fig. 5. Suggested structure of the ion-pair complexes.

$10^{-7}\,S\,cm^{-1}$ and show behavior of semiconductors in the above temperature range. This indicates that a solid-state reaction occurred between the complex and I_2 with partial charge transfer resulting in reduction of I_2 during doping rather than its absorption. In general the lower conductivities of these salts may be attributed to weaker S···S/M···S interaction due to the presence of larger cations $[M(bpy)_3]^{2+}$.

Conclusion

In conclusion the important findings of this study may be summarized.

(i) Ligand-exchange reactions do not occur between the cationic and anionic centers of the intact heterobimetallic ion-pair complexes $[M(bpy)_3][M'(cdc)_2]$ (Fig. 5) during their preparation and solution properties (electronic and NMR) measurements.

(ii) Three of the compounds $[M(bpy)_3][Ni(cdc)_2]$ ($M = Ni^{2+}$, Co^{2+}, and Fe^{2+}) show the behavior of semiconductors while $[M(bpy)_3][Cu(cdc)_2]$ ($M = Ni^{2+}$, Co^{2+}, and Fe^{2+}) are insulators. All of the I_2-doped products exhibit behavior of semiconductors. Conductivities of the I_2-doped products $[M(bpy)_3][M'(cdc)_2]$ are remarkably increased showing partial charge-transfer interaction between I_2 and the C≡N group of the ligand cdc^{2-} resulting in partial reduction of I_2, and rules out the possibility of absorption of I_2.

(iii) Considerable antiferromagnetic interaction between Cu–Cu/M–Cu centers occurs in $[M(bpy)_3][Cu(cdc)_2]$ ($M = Fe^{2+}$, Co^{2+}, and Ni^{2+}).

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References

1 Presented at the 43rd Annual Convention of Chemists, December 23–27, **2006**, Dr. B A M University, Aurangabad, India.

2 A. Kobayashi, E. Fujiwara, H. Kobayashi, *Chem. Rev.* **2004**, *104*, 5243.

3 P. Cassoux, L. Valade, H. Kobayashi, A. Kobayashi, R. A. Clark, A. E. Underhill, *Coord. Chem. Rev.* **1991**, *110*, 115.

4 N. Robertson, L. Cronin, *Coord. Chem. Rev.* **2002**, *227*, 93.

5 E. Cerrada, M. S. Diaz, C. Diaz, M. Laguna, A. Sabater, *Synth. Met.* **2001**, *119*, 91.

6 P. I. Clemenson, *Coord. Chem. Rev.* **1990**, *106*, 171.

7 A. T. Coomber, D. Beljonne, R. H. Friend, J. L. Bredas, A. Charlton, N. Robertson, A. E. Underhill, M. Kurmoo, P. Day, *Nature (London)* **1996**, *380*, 144.

8 N. Singh, S. Gupta, *Polyhedron* **1999**, *18*, 1265.

9 V. Balzani, F. Scandola, *Supramolecular Photochemistry*, Ellis Howard, Chichester, U.K., **1991**; K. Kalyansundaram, *Photochemistry of Polypyridine and Porphyrin Complexes*, Academic Press, London, **1991**.

10 W. W. H. Wong, D. Curiel, S.-W. Lai, M. G. B. Drew, P. D. Beer, *Dalton Trans.* **2005**, 774.

11 L. Brossard, M. Ribaut, M. Bousseau, L. Valade, P. Cassoux, *C. R. Acad. Sci., Paris, Ser. 2* **1986**, *302*, 205.

12 M. Bousseau, L. Valade, J.-P. Legros, P. Cassoux, M. Garbauskas, L. V. Interrante, *J. Am. Chem. Soc.* **1986**, *108*, 1908.

13 S. Dorbes, L. Valade, J. A. Real, C. Faulmann, *Chem. Commun.* **2005**, *69*.

14 H. Taube, *Electron Transfer Reactions of Complex Ions in Solution*, Academic Press, New York, **1970**.

15 E. S. Gould, *Acc. Chem. Res.* **1985**, *18*, 22.

16 O. R. Evans, W. Lin, *Acc. Chem. Res.* **2002**, *35*, 511.

17 T. J. Mizoguchi, S. J. Lippard, *Inorg. Chem.* **1997**, *36*, 4526.

18 A. Togni, M. Hobi, G. Rihs, G. Rist, A. Albinati, P. Zanella, D. Zech, H. Keller, *Organometallics* **1994**, *13*, 1224.

19 M. Hobi, S. Zurcher, V. Gramlich, U. Burckhardt, C.

Mensing, M. Spahr, A. Togni, *Organometallics* **1996**, *15*, 5342.

20 M. Hobi, O. Ruppert, V. Gramlich, A. Togni, *Organometallics* **1997**, *16*, 1384.

21 S. Zurcher, V. Gramlich, D. V. Arx, A. Togni, *Inorg. Chem.* **1998**, *37*, 4015.

22 C. J. Burchell, S. M. Aucott, H. L. Milton, A. M. Z. Slawin, J. D. Woollins, *Dalton Trans.* **2004**, 369.

23 J. P. Fackler, Jr., D. Coucouvanis, *J. Am. Chem. Soc.* **1966**, *88*, 3913.

24 F. A. Cotton, J. A. McCleverty, *Inorg. Chem.* **1967**, *6*, 229.

25 R. S. Prasad, U. C. Agarwal, *Polyhedron* **1992**, *11*, 1117.

26 F. A. Cotton, C. B. Harris, *Inorg. Chem.* **1968**, *7*, 2140.

27 M. L. Caffery, D. Coucouvanis, *J. Inorg. Nucl. Chem.* **1975**, *37*, 2081.

28 N. Singh, A. Prasad, R. K. Sinha, *Inorg. Chem. Commun.* **2006**, *9*, 1058.

29 W. A. Thaler, J. R. McDivitt, *J. Org. Chem.* **1971**, *36*, 14.

30 W. J. Geary, *Coord. Chem. Rev.* **1971**, *7*, 81.

31 C. W. Liu, R. J. Staples, J. P. Fackler, *Coord. Chem. Rev.* **1998**, *174*, 147.

32 A. B. P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier, Amsterdam, **1984**, pp. 479–507.

33 a) G. A. McLachlan, G. D. Fallon, R. L. Martin, L. Spiccia, *Inorg. Chem.* **1995**, *34*, 254. b) H. J. Emeleus, A. G. Sharpe, in *Advances in Inorganic Chemistry and Radiochemistry*, ed. by B. A. Goodman, J. B. Raynor, Academic Press, New York., **1970**, Vol. 13.

34 *Comprehensive Coordination Chemistry*, ed. by B. J. Hathway, G. Wilkinson, R. D. Gillard, J. A. McCleverty, Pergamon Press, Oxford, England, **1987**, Vol. 5, p. 479.