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Benzothiazole-2-thiolato-Bridged Heterometallic Complexes and Their I_2-Doped Products: Preparation, Characterization, and Conducting Properties

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A series of new heterometallic complexes of the type $[MM'(bzta)_4]$ [$M = Co^{2+}$, Pd^{2+}, or $2Cu^{+}$; $M' = Ni^{2+}$; $M = Fe^{3+}$ or Co^{3+}; $M' = Cu^{+}$; $bzta^{-}$ = benzothiazole-2-thiolate ($C_6H_4NSCS^{-}$)] and their I_2-doped products have been synthesized. These have been characterized by elemental analyses, magnetic susceptibility measurement, IR and UV–visible spectroscopies, and solid-state electrical conductivity techniques. A significant observation is the ligand benzothiazole-2-thiolate mediated reduction of Cu^{2+} to Cu^{+} and subsequent oxidation of Co^{2+}/Fe^{2+} to Co^{3+}/Fe^{3+} in aqueous medium for some of the bimetallic complexes. Room-temperature solid-state electrical conductivities, σ_{rt}, $\approx 10^{-12}\,S\,m^{-1}$ and the increase in conductivity with increase in temperature in the 300–420 K range with activation energies, $E_a = 0.20$–0.68 eV show semiconducting properties of $[CoNi(bzta)_4]$, $[NiPd(bzta)_4]$, and $[FeCu(bzta)_4]$. The σ_{rt} of I_2-doped products of the complexes are increased 10–10^2 fold and show the behavior of semiconductors over the given temperature range.

Coordination polymers involving heterometals with different electronic properties and ambidentate (N, S) ligands have attracted considerable attention not only because of their structural diversities but also for their interesting electrical and magnetic properties.[1–6] There are numerous studies[7–9] on monometallic complexes of benzothiazole-2-thiolate ($bzta^{-}$). A detailed account of the chemistry of this ligand has been reviewed by Raper.[7] This ligand has potential as a rubber vulcanization accelerator.[8] The literature[5,10–14] contains limited examples of the heterobimetallic complexes of the ligand $bzta^{-}$, which show diversified coordination patterns with transition-metal ions (Figure 1).

Keeping in mind the interesting molecular conducting and magnetic[15,16] properties of the monometallic and heterobimetallic complexes of sulfur and nitrogen-containing ligands such as thiocyanate (SCN^{-})[17,18] and 1,1- as well as 1,2-dithio ligands,[19–21] herein we report the synthesis, characterization, and electrical properties of the heterobimetallic complexes formed with the ligand benzothiazole-2-thiolate and the metal ions Co^{2+}, Ni^{2+}, Pd^{2+}, Fe^{3+}, Co^{3+}, and Cu^{+}. An important aspect of undertaking the present work is that the ligand $bzta^{-}$ having an additional sulfur atom in the heterocyclic ring which is normally not associated in bonding with the metal ions may induce substantial S···S intermolecular stacking, an important prerequisite for the higher conductivities of the complexes.

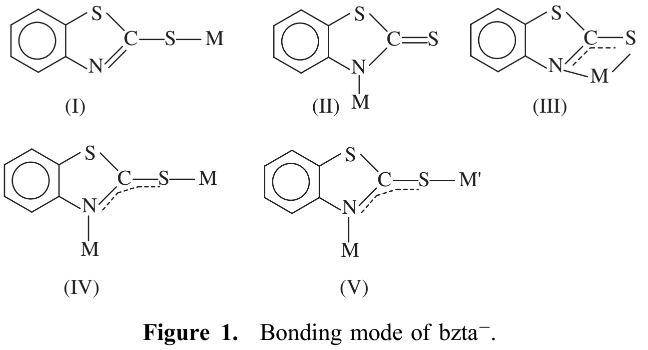

Figure 1. Bonding mode of $bzta^{-}$.

Experimental

Materials and General Procedures. All experiments were carried out under open atmosphere without eliminating moisture and oxygen from the reaction chamber because the ligand Kbzta and the starting metal salts are stable in aqueous medium. All the reagents for the synthesis were commercially available and used without further purification. Potassium salt of the benzothiazole-2-thiolate (Kbzta) was prepared according to literature procedure[8] by reaction of benzothiazole-2-thiol (John Baker Inc., Colorado, USA) and KOH in ethanol and characterized by elemental analysis and IR spectroscopy. Elemental analysis (C, H, and N) was performed on a Carlo Erba 1108 element analyzer at CDRI, Lucknow. The compounds were decomposed by aqua-regia and the metals cobalt as anthranilate, nickel as dimethylglyoximate, copper as cuprous thiocyanate, and iron as oxinate were determined gravimetrically following standard procedures.[22] Sulfur was determined as $BaSO_4$. The experimental details dealing with the magnetic susceptibility and pressed pellet electrical conductivity measurements and recording of IR spectra (4000–400 cm^{-1}) as KBr disc were the same as described earlier.[4] The FAR-IR spectra were obtained with a Varian 3500 FTIR, the samples were ground and compacted as polyethylene discs. The electronic spectra of the complexes in Nujol mulls spread on a filter paper strip were recorded on a Shimadzu 1700 UV–visible spectrophotometer.

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Table 1. Analytical Data and General Properties of the Complexes

Compound (Empirical formula) $[MM'(bzta)_4]$[a)]	Color	Yield /%	Mp[b)] /°C	Found (Calcd, %)					
				C	H	N	S	M	M′
$[CoNi(bzta)_4]$	Bottle green	95	>300	42.54	1.96	6.92	32.49	6.94	7.09
$C_{28}H_{16}N_4S_8CoNi$				(42.98)	(2.06)	(7.16)	(32.77)	(7.53)	(7.50)
$[Cu_2Ni(bzta)_4]$	Light yellow	48	180–185	39.16	1.81	6.28	29.73	14.36	6.48
$C_{28}H_{16}N_4S_8Cu_2Ni$				(39.53)	(1.90)	(6.59)	(30.15)	(14.94)	(6.90)
$[PdNi(bzta)_4]$	Reddish brown	94	>300	40.13	1.86	6.55	30.41	—	6.84
$C_{28}H_{16}N_4S_8PdNi$				(40.52)	(1.94)	(6.75)	(30.90)		(7.07)
$[FeCu(bzta)_4]$	Brown	86	>300	42.5	1.8	6.7	31.6	6.8	7.7
$C_{28}H_{16}N_4S_8FeCu$				(42.88)	(2.06)	(7.14)	(32.70)	(7.12)	(8.10)
$[CoCu(bzta)_4]$	Light yellow	87	180–185	42.28	1.93	6.84	32.16	7.13	7.87
$C_{28}H_{16}N_4S_8CoCu$				(42.71)	(2.05)	(7.12)	(32.57)	(7.48)	(8.07)

Preparation of Heterobimetallic Complexes. $[MM'(bzta)_4]$ [$M = Co^{2+}$, Ni^{2+}, $2Cu^{+}$, Pd^{2+}, Fe^{3+}, and Co^{3+}; $M' = Ni^{2+}$ and Cu^{+}]: The heterobimetallic complexes were prepared according to the following general procedures by a one-pot reaction at room temperature. To a 25 mL of ethanol–water (90:10, v/v) stirred solution containing a mixture of two different metal salts i.e., $Co(NO_3)_2\cdot 6H_2O$ (0.29 g, 1.0 mmol) and $Ni(NO_3)_2\cdot 6H_2O$ (0.29 g, 1.0 mmol); $Cu(NO_3)_2\cdot 3H_2O$ (0.48 g, 2.0 mmol) and $Ni(NO_3)_2\cdot 6H_2O$ (0.29 g, 1.0 mmol); $Co(NO_3)_2\cdot 6H_2O$ (0.29 g, 1.0 mmol) and $Cu(NO_3)_2\cdot 3H_2O$ (0.24 g, 1.0 mmol); $(NH_4)_2Fe(SO_4)_2\cdot 6H_2O$ (0.39 g, 1.0 mmol) and $Cu(NO_3)_2\cdot 3H_2O$ (0.24 g, 1.0 mmol); or K_2PdCl_4 (0.33 g, 1.0 mmol) and $Ni(NO_3)_2\cdot 6H_2O$ (0.29 g, 1.0 mmol) was added gradually a 25 mL solution of Kbzta (0.82 g, 4.0 mmol) in the same solvent mixture. In each case, colored precipitate immediately formed and the mixture was left to stir for 4 days. The resulting precipitates were suction filtered and washed two times with 5 mL portions of ethanol–water mixture followed by two times with 2.5 mL portions of diethyl ether and dried in vacuo over $CaCl_2$. Analytical data and general properties of complexes are listed in Table 1.

I_2-Doping of the Complexes. I_2-doped products of the heterobimetallic complexes were isolated by placing 1 g of iodine and about 200 mg of each complex separately in Petri dishes in a closed desiccator. The I_2 vapor exposure was for 7 days. The dark brown I_2-doped products thus obtained were dried in vacuo. Elemental analyses of the I_2-doped products do not correspond to any definite stoichiometry of the complexes but are reproducible. The IR and UV–visible spectra of the I_2-doped products are similar to the parent mixed-ligand heterobimetallic complexes suggesting that the complexes are not decomposed on exposure to iodine vapors instead a few chemical reactions occurred rather than the absorption of iodine.

Results and Discussion

When a solution containing two different metal salts MX_2 and $M'X_2$ in equimolar ratio was treated with a solution of four molar equivalents of the ligand Kbzta in EtOH–H2O mixture, heterobimetallic complexes $[MM'(bzta)_4]$ were obtained in high yield according to the following equations:

$$C_6H_4NSCSH + KOH \rightarrow KC_6H_4NSCS\ (Kbzta) + H_2O \tag{1}$$

$$Co(NO_3)_2 + Ni(NO_3)_2 + 4Kbzta \rightarrow CoNi(bzta)_4 + 4KNO_3 \tag{2}$$

$$PdCl_2 + 2KCl \rightarrow K_2[PdCl_4] \tag{3}$$

$$K_2[PdCl_4] + Ni(NO_3)_2 + 4Kbzta \rightarrow PdNi(bzta)_4 + 4KCl + 2KNO_3 \tag{4}$$

$$2Cu(NO_3)_2 + Ni(NO_3)_2 + 6Kbzta \rightarrow Cu_2Ni(bzta)_4 + C_6H_4NSCS\text{–}SCSNH_4C_6 + 6KNO_3 \tag{5}$$

$$\begin{aligned} &Cu(NO_3)_2 + Co(NO_3)_2/(NH_4)_2Fe(SO_4)_2\cdot 6H_2O + 4Kbzta \\ &\quad \rightarrow (Co/Fe)Cu(bzta)_4 + 4KNO_3 \\ &\qquad /(2KNO_3 + K_2SO_4 + (NH_4)_2SO_4 + 6H_2O) \end{aligned} \tag{6}$$

The ligand-mediated redox-reactions presumably proceed[7,16] via oxidation of the ligand $bzta^-$ into [bis(benzothiazol-2-yl)disulfide] and its subsequent reduction into the original form according to the following scheme:

$$Cu^{2+} + C_6H_4NSCS^- \rightarrow Cu^+ + 1/2C_6H_4NSCS\text{–}SCSNH_4C_6 \tag{7}$$

$$Co^{2+}/Fe^{2+} + 1/2C_6H_4NSCS\text{–}SCSNH_4C_6 \rightarrow Co^{3+}/Fe^{3+} + C_6H_4NSCS^- \tag{8}$$

$$Co^{3+}/Fe^{3+} + Cu^+ + 3C_6H_4NSCS^- + C_6H_4NSCS^- \rightarrow (Co/Fe)Cu(C_6H_4NSCS)_4 \tag{9}$$

All the complexes are stable in air and decompose in the 180–300 °C temperature range. Elemental analyses for all the complexes are in good agreement with the calculated values of their assigned formulae. These are insoluble in water, ethanol, methanol, dichloromethane, benzene, DMSO, and DMF indicating their polymeric nature. Insolubility prevented their solution conductivity measurements, recording of UV spectra in solution and growing of single crystals for structural elucidation.

IR, Magnetic Moment, and Electronic Absorption Spectra. There is much evidence[7–9] that the resonance forms (Figure 2) play an important role in the structure and bonding of the benzothiazole-2-thiolate complexes. Based on single-crystal X-ray analysis and spectroscopic studies it is now well established that the thionate form with delocalized $N\overset{\cdots}{-}C\overset{\cdots}{-}S$ group is the major contributor to the overall structure of the heterobimetallic complexes and binds two different metals through its amido N atom and exocyclic S atom in a bridging fashion.[10,11]

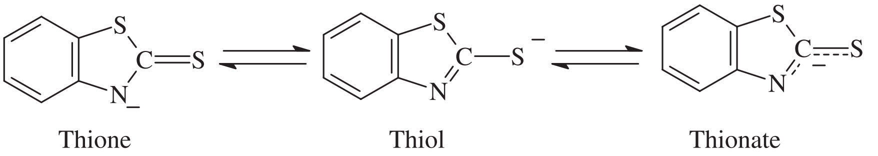


Figure 2. Resonance form of bzta$^-$.

Table 2. Magnetic Moment, Electronic Absorption Bands, Electrical Conductivities, and FAR-IR Bands of the Complexes

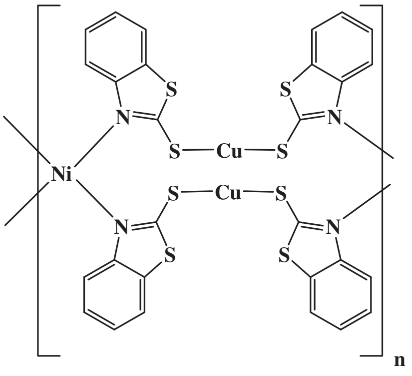
Compound	μ_{eff} /μB	$\lambda_{\max}$/nm (Nujol mull)	σ_{rt} /S cm^{-1}	E_a /eV	$\sigma_{\mathrm{rt}}$$^{a)}$ /S cm^{-1}	$E_a$$^{a)}$ /eV	ν(M–N)	ν(M′–S)	δ(N–M–N)/ δ(S–M′–S)
[CoNi(bzta)$_4$]	2.23	450, 620, 740	4.7×10^{-12}	0.20	0.17×10^{-8}	0.18	329	310	170 mb 197 mb
[Cu$_2$Ni(bzta)$_4$]	Dia	350, 500, 750	8.2×10^{-12}	—	1.43×10^{-10}	0.52	360	277	215/167 m
[PdNi(bzta)$_4$]	Dia	350, 400, 560,	4.0×10^{-11}	0.22	0.85×10^{-8}	0.4	345 wb	270 m	172 mb
								250 w	225 w
[FeCu(bzta)$_4$]	4.71	400–850	3.0×10^{-12}	0.68	0.16×10^{-9}	0.63	362/340 w	277 s	233/215
[CoCu(bzta)$_4$]	Dia	420, 600, 720	2.7×10^{-12}	—	4.8×10^{-12}	0.39	380	285 w	216 mb
								260 w	162 mb

a) I_2-doped.

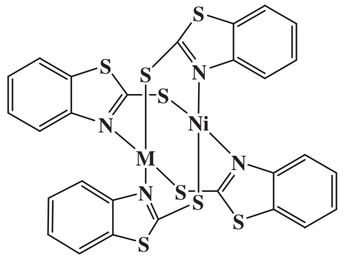
The IR spectra of the complexes have several common features and could be assigned in the light of previous reports.[7–10] The two prominent features of the spectra are (i) the stretching frequencies in the 1377–1410 and 1079–1087 cm^{-1} range mainly from the C=N and C=S bonds are not pure in nature instead result from the skeletal vibration of the delocalized N$\cdots$C$\cdots$S unit of the ligand bzta$^-$ and (ii) the C=N and C=S bonds within the N$\cdots$C$\cdots$S delocalized unit of the free ligand are only slightly perturbed upon coordination showing bonding through both amido N and exocylic S atoms of the ligands in the heterobimetallic complexes. In the I_2-doped compounds the IR frequencies are slightly changed as compared to the parent compounds which may be attributed to some sort of reactions between I_2 molecules and the compounds causing partial oxidation–reduction of the metals.

To gain further insight into the metal–ligand bonding behavior the FAR-IR spectra (400–100 cm^{-1}) of the complexes have been recorded (Table 2). The weak and medium intensity absorptions in the 360–380 and 329–345 cm^{-1} region have been assigned to ν(M$^+$–N) and ν(M$^{2+/3+}$–N) modes.[23,24] The bands located in the 270–280 cm^{-1} region are assigned to ν(M′–S) vibration in these complexes. As expected the stretching frequencies decrease as the oxidation state of the metal M increases from Cu$^+$ to Co^{2+}/Ni^{2+} to Co^{3+}/Fe^{3+} in accordance with the reduced mass effect. In all the complexes the bands in the 162–233 cm^{-1} have been assigned to δ(S–M–S)/δ(S–M′–S) and δ(N–M–N)/δ(N–M′–N) modes.

The magnetic moment values and Nujol mull electronic absorption spectra of the complexes are included in Table 2. The $\mu_{\mathrm{eff}} = 2.23$ μB is indicative of low-spin square-planar environment[25] about cobalt(II) and nickel(II) in the bimetallic complex [CoNi(bzta)$_4$] because for the reported monometallic complex [Co(bzta)$_2$], the effective magnetic moment is in the range of tetrahedral Co$^{\mathrm{II}}$ complexes while [Ni(bzta)$_2$] is diamagnetic square-planar.[5,7] Both the diamagnetic square-planar nickel(II) and low-spin square-planar cobalt(II) complexes are expected to exhibit several transitions in the visible region. The UV–visible spectrum of this complex shows three absorption bands at 450, 620, and 740 nm which may arise from MLCT and d–d transitions for the square-planar coordination about both nickel(II)[26] and cobalt(II).[27] The most interesting observation is that the ligand bzta$^-$ is stabilizing low-spin square-planar environment about both cobalt(II) and nickel(II) in a single entity. This is in sharp contrast to the magnetic and electronic properties of the [CoZn(bzta)$_4$] and [CoHg(bzta)$_4$][5] where both metal centers prefer tetrahedral coordination. A majority of the six coordinate cobalt(III) complexes are low spin and diamagnetic. [CoCu(bzta)$_4$] is diamagnetic which shows the presence of Cu$^+$ and Co^{3+} centers in this complex. Its electronic absorption spectrum displays medium absorption bands at 420, 600, and 720 nm. Since all ligands are similar, there is no change in the ligand field strength. The low-energy bands may be ascribed to the distorted octahedral geometry about cobalt(III) and the higher-energy band at 420 nm to the copper(I) → S(ligand) charge-transfer transition.[28] The distortion in geometry may be attributed to crowding of bzta$^-$ ligands about cobalt(III) in this complex. Diamagnetism together with the electronic absorption bands at 350, 400, 460, 500, and 660 nm show square-planar coordination geometry about nickel(II) and palladium(II) in [Cu$_2$Ni(bzta)$_4$] and [PdNi(bzta)$_4$].[26] The absorption band at 400 nm is ascribed to copper(I) → S(ligand) charge-transfer transition.[29] The $\mu_{\mathrm{eff}} = 4.71$ μB for [FeCu(bzta)$_4$] is in between the spin only value for $S = 3/2$ and $S = 5/2$ (Fe^{3+}, 3d^5) suggesting coupling between spin and orbital angular momentum for the d electrons. Departures from the spin only magnetic moment are expected for 3d^5 complexes. All transitions in the high-spin iron(III), complexes are spin forbidden which results in generally weak bands. Somewhat larger band intensity of this acentric complex may be the result of larger metal–ligand bond covalency. UV–visible spectrum of this complex shows two absorptions at 440 and 850 nm assignable to spin forbidden transition following high spin distorted octahedral coordination[26,29] about iron(III). Very low intensity d–d absorptions are often obscured by the strong ligand to metal charge-transfer bands because of the high oxidizing power of iron(III) complexes.



$[Cu_2Ni(bzta)_4]$

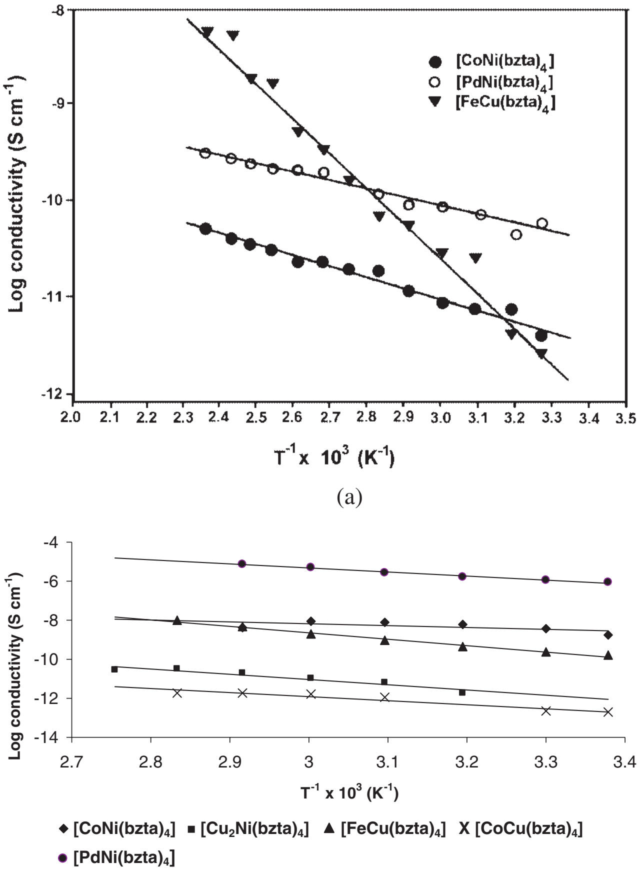


$[MNi(bzta)_4]$ $[M = Co^{2+}, Pd^{2+}]$

Figure 3. Proposed polynuclear and dinuclear structure for the heterobimetallic complexes.

In the light of above studies and based on the known structures,[10,11] the polynuclear structure for $[Cu_2Ni(bzta)_4]$ and the dinuclear structures with strong π–π stacking[30,31] for $[MNi(bzta)_4]$ ($M = Co^{2+}$ and Pd^{2+}) have been postulated (Figure 3).

Electrical Conductivity. The temperature dependence of the compressed pellet electrical conductivities of the powder samples was measured in the 300–420 K temperature range by employing a conventional two probe technique[32] on a Keithley 236 source measure unit. The contact on pellet surfaces and electrodes was made using silver paste. Metal chalcogen rich complexes exhibit higher electrical conductivities because of the dominant S···S/M···S intermolecular stacking and extended delocalized networks as well as partial oxidation–reduction of the complexes. The oxidized species exhibit appreciably increased electrical conductivities which are due to the formation of electron conduction pathways through more extended S···S molecular contacts caused by the ligand centered oxidation. For the higher conductivities, planar molecules are preferred over the linear/tetrahedral or octahedral species because of the greater tendency of the former to form columnar-stacked structures which increased the overlap of sulfur orbitals between the sheets introduce an extra dimension in the conductivity of the compounds. All complexes exhibit room temperature conductivity, σ_{rt} (303 K) $\approx 10^{-12}$ S cm^{-1}. Interestingly, $[CoNi(bzta)_4]$, $[PdNi(bzta)_4]$, and $[FeCu(bzta)_4]$ show the behavior of semiconductors as their conductivity increases progressively with increasing temperature. The plots (Figure 4a) of log σ vs. T^{-1} are nearly linear and comparable for $[CoNi(bzta)_4]$ and $[NiPd(bzta)_4]$ where both metal centers possess square-planar geometry. The activation energies of the order $\approx$0.20 eV obtained from the slopes indicate small band gaps for these compounds. A remarkable increase in the conductivity i.e., 3 orders of magnitude at higher temperature for $[FeCu(bzta)_4]$ may be ascribed to its having different packing/stacking arrangement of the molecules where charge carriers have increasing difficulties at lower temperature to cross the nonconducting barriers. The thermal energy activates the charge-carriers and increases their mobilities. Somewhat higher activation energy $\approx$0.68 eV with larger slope for this complex may be attributed to the preferred octahedral and linear environment about iron(III) and copper(I) respectively which may not facilitate higher conductivity because of the weaker tendency to form columnar stacked structures. On repeating the measurements their conductivities fall almost in the same range concomitant with the temperature dependence of conductivity. $[Cu_2Ni(bzta)_4]$ and $[CoCu(bzta)_4]$ are insulators in the considered temperature range. In general weakly conducting properties of these complexes may be attributed to noninvolvement of endocyclic sulfur atoms of the ligand bzta$^-$ in the interlayer S···S/M···S contact formation. In the case of paramagnetic complexes $[CoNi(bzta)_4]$ and $[FeCu(bzta)_4]$ the unpaired electrons seem not to exhibit an important role in the conduction mechanism. The σ_{rt} of the I_2-doped products are greatly enhanced in the order of $\approx$3 magnitudes (Figure 4b). The increase in the conductivity may be due to some solid-state



(a)

(b)

Figure 4. Temperature-dependent electrical conductivities of (a) the heterobimetallic complexes and (b) the I_2-doped heterobimetallic complexes.

reaction between I_2 molecules and the compounds. All of the I_2-doped products exhibit semiconducting behavior in the considered temperature range.

Conclusion

The ligand benzothiazole-2-thiolate (N,S-exocyclic)-bridged heterometallic complexes [MM′(bzta)$_4$] have been synthesized and their electrical, magnetic, and spectral properties studied. The ligand induced redox-reactions frequently occur thereby stabilizing especially +1 oxidation states of copper and +3 of iron and cobalt in the bimetallic complexes. [PdNi(bzta)$_4$], [CoNi(bzta)$_4$], and [FeCu(bzta)$_4$] exhibit semiconducting behavior.

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