

Synthesis and characterization of ionic heterobimetallic complexes of Ni(II), Cu(II), Zn(II) and Cd(II) ions containing nitrogen and sulphur donors

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A number of new ionic heterobimetallic complexes of copper(II), nickel(II), zinc(II) and cadmium(II) ions of the compositions, $[Cu(N-N)_2][M(S-S)_2]$ [$N-N$ = ethylenediamine (en), trimethylenediamine (tn); M = Ni(II), Zn(II) or Cd(II); $S-S$ = 1,1-dicyanoethylene-2,2-dithiolate, $(CN)_2C=CS_2^{2-}$, (i-MNT²⁻)] have been synthesized by the reaction of nitrogen coordinated metal cations and sulphur coordinated metal anions in aqueous/ aqueous-acetone medium and characterized. Complexed metal cations and complexed metal anions required for the synthesis have been prepared *in situ* by the known literature procedures. The molar conductance data reveal that the complexes have 1:1 electrolytic nature in DMSO solution. Magnetic and electronic spectral studies suggest four-coordinated metal ions in these complexes. Infrared spectral studies suggest bidentate chelating behaviour of ethylenediamine, trimethylenediamine and 1,1-dicyanoethylene-2,2-dithiolate ion in their complexes.

The coordination chemistry of transition as well as non-transition metal dithiolates has been an area of interest for several years^{1,2}. Recently, the role of dithioligands have been explored in the design of many electrically conducting molecular solids³⁻⁶. The interest in this area stems from various reasons such as stabilization of transition metal ions in its unusual oxidation states, facile redox behaviour, stabilization of square planar geometry around transition metal ions, interesting spectral and magnetic properties. In addition, dithiolates have a number of industrial and biological applications^{2,7}.

Among 1,1-dithioligands, 1,1-dicyanoethylene-2,2-dithiolate ion shows exciting coordination properties by virtue of its chelating and bridging behaviour. The chelating and bridging nature of i-MNT²⁻ ion has been found in its binary, ternary and heterobimetallic complexes^{2,8,9}. Our earlier communication¹⁰ includes the studies on reaction of ethylenediamine with $K_2Zn(i-MNT)_2$ and $K_2Cd(i-MNT)_2$ which yielded mixed ligand as well as ionic complexes. McCleverty *et al.*² have obtained and characterized a series of

mixed 1,1- and 1,2-dithio complexes of cobalt and iron. But, there is no report on the reaction products of aliphatic diamine coordinated copper(II) cations with sulphur coordinated nickel(II), zinc(II) or cadmium(II) anions.

In view of the above, we represent our result of investigations on the ionic heterobimetallic complexes involving complexed cations and complexed anion in this note.

Experimental

All chemicals were GR (Merck) or equivalent grades and were used without further purification. $K_2i-MNT.H_2O$ was prepared by literature procedure¹¹.

Synthesis of complexes

Complexes $Cu(en)_2(NO_3)_2.2H_2O$, $Cu(tn)_2(NO_3)_2.2H_2O$ and $K_2M(i-MNT)_2$ [M = Ni(II), Zn(II) or Cd(II)] required for the synthesis of complexes have been prepared by known literature procedures^{10,12,13}.

$[Cu(N-N)_2][M(i-MNT)_2]$ [$N-N$ = en, tn; M = Ni(II), Zn(II) or Cd(II)]

The complexes were precipitated by the reaction of equimolar aqueous/ aqueous-acetone solutions of $Cu(N-N)_2(NO_3)_2.2H_2O$ and $K_2M(i-MNT)_2$.

All synthesized complexes were filtered through suction, washed with water, alcohol, ether and dried *in vacuo* over $CaCl_2$. All the complexes were analysed for their metal and sulphur contents following standard literature procedures¹² after destroying organic matters. Sulphur was determined as $BaSO_4$. Carbon, hydrogen and nitrogen were determined microanalytically. The molar conductance values of the complexes in DMSO at $10^{-3}M$ concentration were measured with a WTW conductivity meter. Infrared spectra were recorded in nujol ($4000-200\text{ cm}^{-1}$) and KBr pellets ($4000-400\text{ cm}^{-1}$) on a Perkin-Elmer Infrared spectrophotometer.

Results and discussion

The analytical data and stoichiometries of the complexes reveal the formation of transition metal complexes involving Cu(II) and Ni(II), Zn(II) or Cd(II) ions of the composition $[Cu(N-N)_2][M(S-S)_2]$ [$N-N$ = ethylenediamine (en), trimethylenediamine (tn); M = Ni(II), Zn(II) or Cd(II); $S-S$ = 1,1-dicyano-

Table I—Characterization data of the complexes

Complex (Colour)	Dec. Temp., °C (% Yield)	Found (Calcd.), %						Λ_M ($\Omega^{-1} \text{cm}^2$ mol^{-1})	μ_{eff} (BM)
		Cu	Ni/Zn/Cd	S	N	C	H		
[Cu(en) ₂][Ni(i-MNT) ₂] Dirty yellow	210 (70)	11.80 (12.13)	10.92 (11.12)	24.01 (24.49)	21.21 (21.54)	27.32 (27.52)	2.98 (3.08)	65.20	1.70
[Cu(en) ₂][Zn(i-MNT) ₂] Dark brown	225 (65)	12.30 (11.98)	11.76 (12.32)	23.82 (24.18)	20.77 (21.27)	27.01 (27.18)	2.81 (3.04)	78.30	1.74
[Cu(en) ₂][Cd(i-MNT) ₂] Pinkish brown	201 (82)	11.41 (11.00)	19.75 (19.47)	21.93 (22.21)	18.99 (19.54)	24.50 (24.96)	2.61 (2.79)	70.10	1.73
[Cu(tn) ₂][Ni(i-MNT) ₂] Greenish yellow	240 (75)	11.23 (11.52)	10.21 (10.64)	23.01 (23.24)	20.14 (20.44)	30.18 (30.48)	3.05 (3.65)	66.42	1.72
[Cu(tn) ₂][Zn(i-MNT) ₂] Brown	215 (60)	11.78 (11.38)	10.62 (11.70)	22.34 (22.97)	19.87 (20.20)	29.87 (30.11)	3.12 (3.61)	75.20	1.94
[Cu(tn) ₂][Cd(i-MNT) ₂] Maroon	205 (72)	10.12 (10.49)	18.01 (18.56)	20.89 (21.18)	18.13 (18.63)	27.02 (27.77)	3.01 (3.33)	67.25	1.78

ethylene-2,2-dithiolate (i-MNT²⁻) and their compositions are presented in Table I. The complexes are insoluble in water and common organic solvents but soluble in DMSO and DMF. The electrical conductance values of the complexes in DMSO solution lie in the range 65.2-78.3 mho cm² mol⁻¹ are consistent with 1:1 electrolytic nature¹⁴. The complexes decompose in the temperature range 201-240°C.

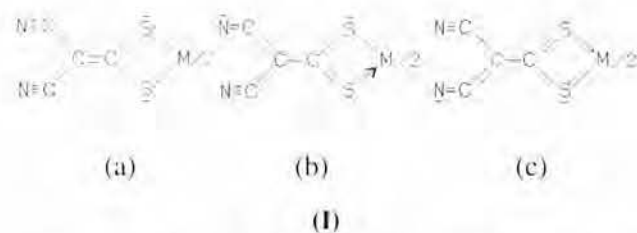
Magnetic moments of the complexes show the values in the range 1.70-1.94 B.M. corresponding to one unpaired electron.

All complexes except [Cu(tn)₂][Cd(i-MNT)₂] show three electronic absorption bands in the ranges 15625-18382, 21978-22727 and 25974-28571 cm⁻¹; [Cu(tn)₂][Cd(i-MNT)₂] shows only two absorption bands at 15625 and 25974 cm⁻¹.

The square planar Ni(II) complexes exhibit absorption in the visible region between 15000-25000 cm⁻¹ and in many cases a second more intense band between 23000 - 30000 cm⁻¹. These are referred to as ν_1 and ν_2 which have been assigned as $^1A_{1g} \rightarrow ^1B_{1g}$ and $^1A_{1g} \rightarrow ^1A_{2g}$ respectively. The [Cu(en)₂][Ni(i-MNT)₂] and [Cu(tn)₂][Ni(i-MNT)₂] exhibit two bands at 15625, 21978 and 15649, 22026 cm⁻¹ respectively which are within the range for square planar geometry around Ni(II)¹⁵ ion in the complexes. The possibility of tetrahedral or octahedral arrangement around Ni(II) in these complexes may be ruled out as no electronic absorption bands occur below 10000 cm⁻¹.

The Cu(II) complexes are also expected to show two bands in the region 14000-25000 cm⁻¹ which is an overlapping region with that of the Ni(II) complexes. The complexes [Cu(N-N)₂][M(i-MNT)₂] [N-N = en, tn; M = Zn(II) or Cd(II)] show bands in the region expected for square planar geometry¹⁶ while these bands in [Cu(en)₂][Ni(i-MNT)₂] and [Cu(tn)₂][Ni(i-MNT)₂] complexes are overlapping with that of Ni(II) square planar complexes. The magnetic moment values and electronic spectral bands suggest square planar arrangement around Ni(II) and Cu(II) ions and tetrahedral arrangement around Zn(II) and Cd(II) ions in these complexes.

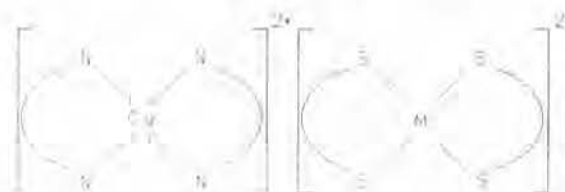
The infrared spectra of the complexes synthesized have been interpreted in the light of earlier investigations^{11,13,17-20} on transition metal dithiolates. The i-MNT²⁻ ligand ion may be described by resonating structures (I) in its complexes which undergoes particular vibrations and contributes certain peaks to IR spectra. The electron delocalisation in the chelated i-MNT²⁻ ring leads to the coupling of vibrational modes so that few bands in IR spectra represent pure vibrations. Accordingly, assignments have generally been given to those vibrations which make the most dominant contribution to each IR band. The IR spectra of complexes display characteristic stretching frequencies associated with C \equiv N, C=C, C-S and M-S from i-MNT²⁻ and N-H and M-N vibrations from diamine moieties.



The $\nu(\text{C}\equiv\text{N})$ vibrations appearing at 2195 cm^{-1} with a shoulder at 2200 cm^{-1} in $\text{K}_2\text{i-MNT}$ is observed in the range $2197\text{--}2213\text{ cm}^{-1}$ in these complexes. The $\nu(\text{C}=\text{C})$ absorption band at 1360 cm^{-1} in $\text{K}_2\text{i-MNT}$ is observed in the range $1373\text{--}1385\text{ cm}^{-1}$. The positive shifts observed in stretching frequencies of $\text{C}\equiv\text{N}$, $\text{C}=\text{C}$ suggest that resonance form (a) (I) is more dominant in these complexes of i-MNT^{2-} ligand ion. A band at 960 with a shoulder at 985 cm^{-1} on the higher frequency side is observed in the IR spectrum of $\text{K}_2\text{i-MNT}$ due to $=\text{CS}_2$ group. The corresponding band in the complexes is found in the range $924\text{--}957\text{ cm}^{-1}$. The $\nu(\text{C-S})$ occurring in the spectrum of $\text{K}_2\text{i-MNT}$ at 860 cm^{-1} appears in $864\text{--}895\text{ cm}^{-1}$ region in the complexes indicating symmetrical bonding of both sulphur atoms to metal ions. Similar bonding behaviour of i-MNT^{2-} ion is reported¹³ in $\text{K}_2[\text{Ni}(\text{i-MNT})_2]$ where a single band due to $\nu(\text{C-S})$ band is observed at 900 cm^{-1} .

The infrared spectra of the complexes contain bands characteristic of coordinated neutral nitrogen bases as reported earlier indicating bonding through the basic nitrogen atom(s)^{17,19}. The non-ligand bands observed in the regions $310\text{--}390$ and $220\text{--}320\text{ cm}^{-1}$ in the spectra of complexes are tentatively assigned to $\nu(\text{M-N})$ ¹⁸ and $\nu(\text{M-S})$ ²⁰ modes respectively.

Based on stoichiometries and spectrochemical studies described above, the tentatively proposed structures of the complexes are II.



[N-N = en, m; S-S = $(\text{CN})_2\text{C}=\text{CS}_2^{2-}$; M = Ni(II), Zn(II), Cd(II)]

(II)

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