

## Mixed Chelate Complexes of Copper(II) with Ligands Containing Primary & Tertiary Nitrogen Donor Atoms

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Mixed chelate complexes of compositions,  $[Cu(bipy)(opd)]X_2$  and  $[Cu(bipy)(opd)Y_2]$  where bipy = 2,2'-bipyridine; opd = *o*-phenylenediamine;  $X = Cl^-$ ,  $Br^-$ ,  $NO_3^-$ ,  $ClO_4^-$  or  $BF_4^-$ ; and  $Y = NCS^-$  or  $N_3^-$  have been prepared and characterised through elemental analyses, molar conductance, magnetic susceptibility, infrared and electronic spectral data.

Mixed chelate complexes containing two different uninegative bidentate ligands have been studied earlier<sup>1-3</sup>. We now report the preparation and characterisation of mixed chelate complexes of copper(II) with two different neutral ligands containing primary and tertiary nitrogen donor atoms.

All the chemicals used were of AR grade.

### Preparation of $[Cu(bipy)(opd)]X_2$ ( $X = Cl^-, Br^-, NO_3^-$ & $ClO_4^-$ )

To an ethanolic solution of the metal salt, ethanolic solutions of 2,2'-bipyridine(bipy) and *o*-phenylenediamine(opd) were added (1:1:1 molar ratio) and contents stirred well. The precipitate formed was filtered; washed with ethanol followed by ether and dried *in vacuo*.

### Preparation of $[Cu(bipy)(opd)](BF_4)_2$ & $[Cu(bipy)(opd)Y_2]$ ( $Y = NCS^-$ or $N_3^-$ )

To a mixture containing ethanolic solutions of 2,2'-bipyridine and *o*-phenylenediamine, an ethanolic solution of cupric chloride was added (1:1:1 molar ratio). To this suspension an aqueous solution of  $NaBF_4/KCNS/NaN_3$  (in minimum volume of water) was added separately and contents stirred well. The precipitate was filtered, washed with ethanol followed by ether and dried *in vacuo*.

Copper and halogen were estimated by standard methods. Carbon and hydrogen were estimated using semi-micro methods. Infrared spectra were recorded in nujol mull in the range 5000-650  $cm^{-1}$  using Unicam SP-200 double beam spectrophotometer. IR spectra were recorded in the range 4000-200  $cm^{-1}$  in KBr using a Perkin-Elmer instrument. The electronic spectra were recorded using a Unicam SP-500 spectrophotometer. The magnetic susceptibilities were determined at room temperature using solid specimens by the Gouy method. Diamagnetic corrections were applied using Pascal's constants. The molar conductances of  $\sim 10^{-3} M$  solutions (acetone or DMSO) were measured using Systronic direct reading conductivity meter 303.

The analytical, molar conductance and magnetic susceptibility data are recorded in Table 1. The elemental analyses correspond to the stoichiometries of the compounds as indicated in Table 1. The compounds are soluble in acetone/dimethyl sulphoxide. The low molar conductance values for thiocyanato and azido complexes show them to be

Table 1—Characterisation Data of Mixed Chelates of Copper(II)

Compounds	Colour	$\Lambda_M$	$\mu_{eff}$ (B.M.)	Found (Calc.), %			
				Cu	C	H	Cl/Br
$[Cu(bipy)(opd)]Cl_2$	Light-green	198	1.83	15.71 (15.94)	47.00 (48.18)	3.70 (4.00)	17.62 (17.79)
$[Cu(bipy)(opd)]Br_2$	Light-green	205	1.83	12.98 (13.03)	37.54 (39.39)	2.87 (3.28)	32.10 (32.79)
$[Cu(bipy)(opd)](NO_3)_2$	Grey	200	1.81	14.12 (14.07)	44.70 (45.52)	3.00 (3.54)	—
$[Cu(bipy)(opd)](ClO_4)_2$	Grey	212	1.85	11.90 (12.06)	—	—	—
$[Cu(bipy)(opd)](BF_4)_2$	Dirty-green	200	1.86	12.45 (12.68)	—	—	—
$[Cu(bipy)(opd)(NCS)_2]$	Green	4.2	1.89	14.18 (14.32)	47.50 (48.69)	2.95 (3.60)	—
$[Cu(bipy)(opd)(N_3)_2]$	Yellowish-green	3.5	1.90	15.30 (15.43)	—	—	—

non-electrolytes. The molar conductance values for other complexes suggest them to be 1:2 electrolytes. The magnetic susceptibility measurements indicate that all the complexes are paramagnetic as expected for a  $3d^9$  ion containing one unpaired electron.

The modes of bonding of 2,2'-bipyridine and *o*-phenylenediamine in metal complexes are well known. Based on the shifting of the characteristic bands, it is concluded that these two ligands exhibit neutral bidentate behaviour in the complexes now reported.

The ionic nature of the anions ( $\text{NO}_3^-$ ,  $\text{ClO}_4^-$  &  $\text{BF}_4^-$ ) in these complexes, as revealed by conductance data, is also supported by the infrared spectral data. Ionic nitrate group has four fundamental vibrations<sup>4,5</sup>, three of which are IR active occurring at 1400, 830 and  $700\text{ cm}^{-1}$ . The bands observed for the nitrate complex are in accord with this observation. The ionic perchlorate group ( $T_d$  symmetry) exhibits<sup>6</sup> a very broad band at  $1170\text{--}1070\text{ cm}^{-1}$  and a strong band at  $\sim 1100\text{ cm}^{-1}$ ; in the present investigation, occurrence of these bands indicates ionic nature of perchlorate ion<sup>7</sup>. In the tetrafluoroborate compound, no splitting of  $\nu_3$  band is noticed and a broad band is observed at  $1080\text{--}1030\text{ cm}^{-1}$  indicating the ionic nature of tetrafluoroborate<sup>8,9</sup>. Thiocyanate group can be terminal N- or S-bonded or can function as a bridging group. Livingstone<sup>10</sup> has pointed out that the thiocyanate ion generally coordinates to class (a) metals through nitrogen and class (b) metals through sulphur. The changes in  $\nu(\text{C}-\text{N})$  and  $\nu(\text{C}-\text{S})$  consequent to different modes of bonding have been discussed earlier<sup>11-13</sup>. In the present compound,  $\nu(\text{C}-\text{N})$  and  $\nu(\text{C}-\text{S})$  bands appear at  $\sim 2060$  and  $805\text{ cm}^{-1}$  indicating the N-bonding of thiocyanate group to the metal ion. Ionic azide group  $\text{N}_3^-$ , which is symmetrical and centrosymmetric ( $D_{\infty h}$ ), exhibits IR active bands at 2041, 1344 and  $645\text{ cm}^{-1}$  respectively for asymmetric stretching, symmetric stretching and bending vibrations<sup>14-16</sup>. On coordination, the symmetry of the azide ion is destroyed and an asymmetric azide ( $C_{\infty v}$ ) shows a very strong stretching band just above  $2000\text{ cm}^{-1}$ , a relatively weak stretching above  $1300\text{ cm}^{-1}$  and another band<sup>17</sup> due to bending just above  $600\text{ cm}^{-1}$ . Similar bands are observed with the

present azido complex indicating its terminal coordination<sup>18,19</sup>.

The presence of a broad band around  $16000\text{ cm}^{-1}$ , as observed by earlier workers<sup>20</sup>, suggests square-planar structure for the tetracoordinated complexes of Cu(II). It has been suggested<sup>21</sup> that absorption in the vicinity of 700nm is indicative of a five- or six-coordinated copper(II) whilst four-coordinated copper(II) is characterised by absorption peaks at  $\sim 600\text{ nm}$ . The hexa-coordinated complexes reported here have absorption bands around 700nm and hence presumably have a distorted octahedral configuration. The occupation of the *trans*-axial positions when thiocyanate and azide are present resulting in a 6-coordinated compound indicates that the repulsion between the ligands and the lone electron of the metal ion is minimum. In all other cases, the axial positions are not occupied giving rise to 4-coordinated square-planar complexes.

## References

- 1 Purohit K M & Ramana Rao D V, *J Indian chem Soc*, **57** (1980) 363.
- 2 Purohit K M & Ramana Rao D V, *J Indian chem Soc*, **58** (1981) 78.
- 3 Purohit K M & Ramana Rao D V, *Indian J Chem*, **21A** (1982) 437.
- 4 Curtis N F & Curtis Y M, *Inorg Chem*, **4** (1965) 804.
- 5 Nakamoto K, *Infrared spectra of inorganic and coordination compounds*, (John Wiley & Sons, New York) 1963, 93.
- 6 Nakamoto K, *Infrared spectra of inorganic and coordination compounds*, (John Wiley & Sons, New York) 1969, 175.
- 7 Balundgi R H & Chakravorty A, *Inorg Chem*, **12** (1973) 981.
- 8 Greenwood N N, *J chem Soc*, (1959) 3811.
- 9 Proctor I M, Hathway B J & Nicholls P, *J chem Soc (A)*, (1968) 1678.
- 10 Livingstone S E, *Quart Rev*, **19** (1965) 386.
- 11 Mitchell P C & William R J P, *J chem Soc*, (1960) 1912.
- 12 Turco A & Pecile C, *Nature*, **191** (1961) 66.
- 13 Tramer A, *J chem Phys*, **59** (1962) 232.
- 14 Gray P & Waddington T C, *Trans Faraday Soc*, **53** (1957) 901.
- 15 Sartori G, Furlani C & Damiani A, *J inorg nucl Chem*, **8** (1958) 119.
- 16 Pepazian H A, *J chem Phys*, **34** (1961) 1614.
- 17 Agrell I, *Acta chem scand*, **24** (1970) 1247.
- 18 Thayer J S & West R, *Adv organometallic Chem*, **5** (1967) 169.
- 19 Dash K C & Ch Mohapatra K C, *J Indian chem Soc*, **56** (1979) 84.
- 20 Figgis B N, *Introduction to ligand fields*, (Interscience, New York) 1967, 316.
- 21 Waters J M & Waters T N, *J chem Soc*, (1959) 1200; (1964) 2489.