

Compounds of Cuprous Bromide with Substituted Anilines, Aminophenols, Aminobenzoic Acids, Substituted Pyridine and *p*-aminoacetanilide in Non-aqueous media

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The tendency of copper to form complexes varies from one valency state to another. Prasad and Sharma¹ have prepared complexes of cupric chloride with aminophenols. Binuclear copper (I) derivatives of pyrazine have been prepared by Lever, Lewis and Nyholm² in aqueous medium. Prasad and Trivedi^{3,4} have prepared the complexes of cuprous bromide with primary, secondary and tertiary amines and heterocyclic bases in non-aqueous media. The work has further been extended to the study of complexes of cuprous bromide with other organic ligands.

EXPERIMENTAL

All the chemicals used were either of E. Merck or B.D.H. extra-pure quality. Ethyl acetate was dried over fused calcium chloride and distilled before use.

All the reactions were carried out in glass-stoppered vessels under anhydrous conditions. The complexes were prepared by adding the solutions of organic compound in ethyl acetate to ethyl acetate solution of cuprous bromide when a precipitate was formed; in some cases, and in others it separated out on the addition of anhydrous ether or anhydrous benzene. The precipitate was allowed to settle, filtered through a dry filter paper, washed repeatedly with dry ethyl acetate till free of reactants, filter-pressed, dried in a vacuum desiccator over fused calcium chloride and analysed.

Copper was estimated as the α -benzoin oxime complex $\text{Cu}(\text{C}_{14}\text{H}_{11}\text{O}_2\text{N})$ and bromine as silver bromide by Piria and Schiff's method. In a few cases carbon and hydrogen were estimated by microanalytical methods and nitrogen by Duma's method.

General Properties.—All the compounds are coloured powders mostly insoluble in common organic solvents. The compounds are fairly stable in dry air. When heated some of the compounds melt with decomposition and the rest decompose without melting (cf. Table II).

Magnetic susceptibility of the complexes with *o*-aminobenzoic acid, *p*-aminophenol and *p*-aminoacetanilide were determined and it was found that all of them are diamagnetic.

1. S. Prasad and P. D. Sharma, *Jour. & Proc. Inst. Chemist.*, (India) 1958, 30, 254.
2. A. B. P. Lever, J. Lewis and R. S. Nyholm, *J. Chem. Soc.*, 1963, 3156-8.
3. Sarju Prasad and S. R. C. Trivedi, *J. Indian Chem. Soc.*, 1966, 43, 623-6.
4. Sarju Prasad and S. R. C. Trivedi, (communicated)

TABLE I

CuBr -aminophenol		CuBr -o-aminobenzoic acid		CuBr -p-aminoacetanilide	
Frequency cm^{-1}	Assignment	Frequency cm^{-1}	Assignment	Frequency cm^{-1}	Assignment
3352 s	OH and N-H stretch	3500 m	O-H stretch (due to hygroscopic nature)	3510 s	O-H stretch (due to hygroscopic nature)
2910 m	C-H stretch	3296 s		3415 s	N-H stretch
		3120 s	N-H stretch	1660 s	
1705 s	OH bend			1585 s	N-H bend
1632 s				1505 s	
1500 s	N-H bend	2909 m	C-H stretch	1425 s	
		1691 s	COOH stretch	1400 s	Ring vibrations
1416 s	Ring vibration			1365 s	
		1561 s	N-H bend		
1292 s		1500 m		1310 s	
	C-N stretch				
1233 s		1462 s, 1415 s, 1360m, 1280 w, 1200 w, 1154m, 1116 m, 1054 w	Ring vibration and C-N stretching	1235 s	
		960 w	—	1170 s	C-N stretch
		873 m		1035m	
				1010 w	
		820 m		840 s	
		761 s		805 m	C-H bend
		752 w	C-H bend	780 s	
		720 m		680 s	

s ... strong
m ... medium
w ... weak

Infra-red spectra of these complexes were recorded by Perkin-Elmer Infra-cord in KBr medium by disc rotation method. Since the spectra are of complex nature only a few stretching frequencies could be assigned. (cf. table I). with reasonable certainty.

DISCUSSION

From the analytical results, it is evident that the ratio of Cu:Br: organic compound was as 1: 1: 1 which is similar to the complex compounds with primary monoamines and secondary and tertiary amines^{5,6}. The hydroxyl, carboxyl, nitro and -NH groups do not coordinate in presence of a strong donor group like —NH_2 .

As the compounds are insoluble in all the common organic solvents, it has not been possible to characterise them.

Although from physico-chemical studies, Wartenberg⁵ and Jellinek⁶ have given the

5. H. V. Wartenberg and O. Bosse, *Z. Electrochem.*, 1922, 26, 384.

6. K. Jellinek and A. Rudat, *Z. Physikal Chem.*, 1929, 143, 58.

TABLE II

S. No	Compound of CuBr ₂ with	Colour	M.P., °C	% Bromine		% Copper		% Nitrogen		% Carbon		% Hydrogen		Formula
				Found	Reqd.	Found	Reqd.	Found	Reqd.	Found	Reqd.	Found	Reqd.	
1.	o-Aminophenol	Black	226	31.63	32.01	25.16	24.88	—	—	28.50	23.22	2.77	2.70	CuBr. HN(C ₆ H ₄)OH
2.	m-Aminophenol	Black	320*	31.63	32.22	25.15	24.56	5.54	5.51	—	—	—	—	CuBr. NH ₂ C ₆ H ₄ OH
3.	p-Aminophenol	Black	285*	31.63	31.91	25.16	24.85	—	—	—	—	—	—	CuBr. NH ₂ C ₆ H ₄ OH
4.	o-Aminobenzoic acid	Blackish Green	260	28.47	27.60	22.64	21.20	4.99	4.93	—	—	—	—	CuBr. NH ₂ C ₆ H ₃ COOH
5.	m-Aminobenzoic acid	Dark Green	182	28.47	28.95	22.64	21.62	—	—	29.93	29.90	2.50	2.56	CuBr. NH ₂ C ₆ H ₃ COOH
6.	p-Aminobenzoic acid	Dark Green	158	28.47	28.10	22.64	21.48	4.99	4.95	—	—	—	—	CuBr. NH ₂ C ₆ H ₄ COOH
7.	o-Nitroaniline	Dark Green	118	28.37	29.00	22.56	22.00	9.94	9.97	—	—	—	—	CuBr. NH ₂ C ₆ H ₃ NO ₂
8.	m-Nitroaniline	Light Brown	115	28.37	29.12	22.56	21.98	9.94	9.99	—	—	—	—	CuBr. NH ₂ C ₆ H ₃ NO ₂
9.	p-Nitroaniline	Grey	111	28.37	28.80	22.56	21.86	—	—	25.57	25.50	2.13	2.21	CuBr. NH ₂ C ₆ H ₃ NO ₂
10.	Methyl-benzylaniline	Dark Blue	120	29.47	23.72	18.66	18.80	4.11	4.19	—	—	—	—	CuBr. C ₆ H ₄ N (CH ₃) (CH ₃ C ₆ H ₅)
11.	Ethyl-benzylaniline	Bluish Green	194*	22.54	22.62	17.93	17.64	3.95	3.91	—	—	—	—	CuBr. C ₆ H ₄ N (C ₂ H ₅) (CH ₃ C ₆ H ₅)
12.	2-Aminopyridine	Grey	132-35	33.62	34.12	26.74	26.23	11.79	11.68	—	—	—	—	CuBr. NH ₂ C ₅ H ₄ N
13.	2-Amino-6-methylpyridine	Greenish yellow	108	31.76	31.50	25.25	25.42	11.13	11.42	—	—	—	—	CuBr. C ₅ H ₃ N. CH ₃ NH ₂
14.	p-Aminoacetanilide	Violet	142*	27.20	27.94	21.64	21.01	9.54	9.50	—	—	—	—	CuBr. CH ₃ CONHC ₆ H ₄ NH ₂

*decomposition temperature.

molecular formula of cuprous bromide as Cu_2Br_2 , the complex may be simply represented as



Although their simple representation can be shown as above but in a crystalline form, there may be polymerization leading to Cu (I) attaining a tetrahedral coordination as in the case of $\text{Et}_3\text{AsCuX}^7$ and $\text{Ph}_3\text{P CuX}^8$ (where X is a halide) which are tetrametric.

A strong band near 3000 to 3460 shows that band order has shifted to a lower value and confirms the bond formation by nitrogen atom of the organic ligand. Rest of the bands and ring vibration, C-H bond etc., appear at more or less original positions showing thereby that there is no structural change in the benzene ring during coordination.

Grateful thanks of the authors are due to the authorities of the Banaras Hindu University for providing necessary facilities, Director, C.D.R.I., Lucknow and Prof. J. N. Chatterjee of Patna University for infra-red spectra and to Prof. S. P. Ghosh of Patna University for magnetic measurements. One of the authors (S.R.C.T.) is thankful to the Ministry of Education, Govt. of India, for the award of a research training scholarship.

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Received, June 9, 1967.

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