

Studies on some lutidinium tetrahalo cuprates(II)

D. SATYANARAYANA and B. K. MOHAPATRA

*Department of Chemistry, Ravenshaw College, Cuttack-3 (Orissa),
India*

Received 31 July 1973

Accepted for publication 29 April 1974

Copper(II) complexes having the formula CuL_2X_2 were allowed to react with chlorine and bromine and several crystalline complexes of the type $[\text{LH}]_2[\text{CuX}_4]$ (where L is 3,5-lutidine, 3,4-lutidine, 2,4-lutidine, and 2,6-lutidine and X is Cl^- or Br^-) and $[\text{LH}]_2[\text{CuX}_2\text{Y}_2]$ (where X is Cl^- , Y is Br^-) were isolated. All these complexes were characterized on the basis of their analyses, conductance, magnetic susceptibility, infrared, and electronic spectral data.

Halogenation reactions of several transition metal complexes of the type ML_2X_2 , where M is a bivalent metal like zinc, nickel, manganese, and cobalt, L is a nitrogen donor ligand and X is Cl^- or Br^- , were reported earlier [1–7]. Several tetra-, penta-, and hexa-coordinated anionic complexes were reported for bivalent nickel and zinc. Some interesting results [7] were obtained while undertaking the halogenation of copper(II) complexes. It was therefore thought worthwhile to extend the investigation to the case of copper(II) complexes of lutidines. A number of electrolytic complexes having the formula $[\text{LH}]_2[\text{CuX}_4]$ and $[\text{LH}]_2[\text{CuX}_2\text{Y}_2]$, where L is 3,5-, 3,4-, 2,4-, and 2,6-lutidine, X is Cl^- or Br^- , and Y is Br^- are reported in this communication.

Experimental

All the chemicals were of A.R. grade. CuL_2X_2 complexes were prepared by previously reported methods [8, 9].

Chlorination

To an ethanolic suspension of CuL_2Br_2 complexes pure and dry chlorine gas was passed slowly till a clear solution was obtained by exothermic reaction. The solution was cooled overnight when yellow crystalline compounds separated. Chlorination of CuL_2Br_2 complexes resulted in a complete replacement of bromine atoms by chlorine.

Bromination

To an ethanolic suspension of CuL_2Cl_2 and CuL_2Br_2 liquid bromine was added dropwise and the mixture was shaken till a clear solution was obtained by exothermic reaction. On cooling overnight, dark violet crystalline compounds separated. The compounds were suction filtered, washed with ethanol and ether, and dried *in vacuo*. Halogenation reaction did not succeed in CHCl_3 or CCl_4 media probably because of the absence of a solvolytic mechanism.

Table 1

Analysis, melting point, conductance, and magnetic susceptibility data of crystalline copper(II) complexes

Compound	Calculated/found			Colour	M.p. [°C]	Con- ductance [mhos]	μ_{eff} [B.M.]
	% Cu	% Cl	% Br				
[3,5-lutH] ₂ [CuCl ₄]	15.07	33.67	—	Yellow	150	241	1.93
[3,5-lutH] ₂ [CuCl ₂ Br ₂]	14.85	33.45	—	Dark violet	128	258	1.78
	12.45	13.91	31.30				
[3,5-lutH] ₂ [CuBr ₄]	12.14	13.85	30.98	Dark violet	145	260	1.81
	10.60	—	53.32				
[3,4-lutH] ₂ [CuCl ₄]	10.26	—	53.05	Yellow	176	271	1.95
	15.07	33.67	—				
[3,4-lutH] ₂ [CuCl ₂ Br ₂]	14.92	33.54	—	Dark violet	185	253	1.84
	12.45	13.91	31.30				
[3,4-lutH] ₂ [CuBr ₄]	12.61	13.76	31.15	Dark violet	148	264	1.79
	10.60	—	53.32				
[2,4-lutH] ₂ [CuCl ₄]	10.45	—	53.22	Yellow	161	252	1.91
	15.07	33.67	—				
[2,4-lutH] ₂ [CuCl ₂ Br ₂]	15.15	33.28	—	Dark violet	154	249	1.86
	12.45	13.91	31.30				
[2,4-lutH] ₂ [CuBr ₄]	12.30	13.79	31.08	Dark violet	172	245	1.83
	10.60	—	53.32				
[2,6-lutH] ₂ [CuCl ₄]	10.35	—	52.95	Yellow	182	263	1.98
	15.07	33.67	—				
[2,6-lutH] ₂ [CuCl ₂ Br ₂]	14.76	33.48	—	Dark violet	154	257	1.86
	12.45	13.91	31.30				
[2,6-lutH] ₂ [CuBr ₄]	12.22	13.67	31.18	Dark violet	168	254	1.82
	10.60	—	53.32				
	10.29	—	52.96				

lut = dimethyl pyridine.

Table 2

Infrared and electronic spectra of copper(II) complexes [cm⁻¹]

Compound	$\delta(\text{N-H})$	$\bar{\nu}(\text{C-H})$	$\bar{\nu}(\text{N-H})$			$\lambda_{\text{max}} \epsilon$	
[3,5-lutH] ₂ [CuCl ₄]	1630	2980	3150,	3200,	3240	21 000 (1150),	13 200 (80)
[3,5-lutH] ₂ [CuCl ₂ Br ₂]	1625	2960	3160,	3210,	3250	17 000 (35) br	
[3,5-lutH] ₂ [CuBr ₄]	1620	2980	3150,	3210,	3260	17 200 (76) br	
[3,4-lutH] ₂ [CuCl ₄]	1625	2960	3160,	3220,	3310	20 800 (1200),	13 400 (98)
[3,4-lutH] ₂ [CuCl ₂ Br ₂]	1620	2975	3150,	3200,	3300	17 400 (41) br	
[3,4-lutH] ₂ [CuBr ₄]	1625	2960	3150,	3200,	3290	17 500 (60) br	
[2,4-lutH] ₂ [CuCl ₄]	1635	2990	3150,	3240,	3300	21 200 (1208),	1340 (115)
[2,4-lutH] ₂ [CuCl ₂ Br ₂]	1628	2985	3130,	3240,	3310	17 200 (25) br	
[2,4-lutH] ₂ [CuBr ₄]	1630	2980	3145,	3250,	3300	17 000 (48) br	
[2,6-lutH] ₂ [CuCl ₄]	1638	2980	3140,	3260,	3330	20 800 (1200),	13 000 (108)
[2,6-lutH] ₂ [CuCl ₂ Br ₂]	1635	2975	3150,	3260,	3310	17 200 (38) br	
[2,6-lutH] ₂ [CuBr ₄]	1630	2985	3145,	3250,	3320	17 000 (61) br	
	Far-infrared spectra [cm ⁻¹]			Diffuse reflectance spectra [nm]			
			M-Cl	M-Br			
[3,5-lutH] ₂ [CuCl ₄]			280 s,	240 s	—		
[3,5-lutH] ₂ [CuBr ₄]			—	240 s		[3,5-lutH] ₂ [CuCl ₄]	475, 740 > 1100
[3,5-lutH] ₂ [CuCl ₂ Br ₂]			325 s,	345 s	245 s		

br = broad.

Purity of the isolated compounds was established by estimating metal and halogen by standard methods. Conductance was measured in acetone medium (10^{-3} M soln.) using a Toshniwal conductivity bridge and a dip type cell. Magnetic susceptibility measurements were made over solid specimens at 25°C using Gouy method (CuSO_4 was used as calibrating material for calculating β of Gouy tube). The i.r. spectra were recorded on hexachlorbutadiene mulls using a Unicam SP-200 spectrophotometer. Far-infrared spectra were recorded by a Perkin-Elmer spectrophotometer. Electronic spectra in the visible range were recorded with 10^{-2} M acetone solutions using a Unicam SP-500 spectrophotometer. All the relevant analytical, conductance, and magnetic susceptibility data are recorded in Table 1. The infrared and electronic spectral data are given in Table 2.

Results and discussion

When chlorine gas was passed into the suspension of CuL_2X_2 complexes in ethanol, it could react in three ways: (i) Bivalent copper can be oxidized to the trivalent state, (ii) chlorine can get into the pyridine ring or (iii) chlorine can react with hydrogen of ethanol to form HCl which subsequently reacts with bonded ligand base forming quaternary halides. In the present case the oxidation has definitely not taken place as indicated from the magnetic susceptibility measurements. Neither the substitution in the pyridine ring has taken place. If it were so, the formula would have been $[\text{Cu}(\text{py} \cdot \text{Cl})_2\text{Cl}_2]$ and the analysis of the compound would have indicated the presence of only two halogen atoms since the ring halogen cannot be estimated by diluted HNO_3 treatment, but requires prior fusion. Further, such a compound would be a non-electrolyte.

The compounds now reported are yellow or dark violet crystalline solids and are fairly soluble in acetone in which medium they are 2 : 1 electrolytes, the molar conductance values (A_M) being near ~ 250 mhos (Table 1). The dark violet compounds give deep green solutions in acetone which undergo colour change on heating, on dilution, or on keeping for a day or two probably due to solvolysis. Infrared spectra (Table 2) indicate the presence of N—H stretching and bending frequencies in the ~ 3000 and $\sim 1600 \text{ cm}^{-1}$ region respectively; the interference of Nujol absorption in this region is avoided by using hexachlorbutadiene as the mulling agent. A number of four coordinated tetrahalo complexes of copper(II) have been reported [4, 5] in the literature. They were prepared by the reaction of copper halides and quaternary halides. The compounds now reported are new examples for this category. However, in the present work the method of preparation is different since the quaternary halide was obtained *in situ* from the bonded ligand base. *Mundie* and *Nuttal* [6] reported the synthesis of the $[\text{pyH}]_2[\text{MX}_4]$ type of complexes, where M is Zn(II), Ni(II), and Co(II), by the reaction of halogen with dipyridine metal halides, a method similar to the present one. They recorded the infrared spectra on Nujol mulls and reported the bands due to N—H stretching frequency. We could not resolve the spectra since the mulling agent Nujol also absorbs heavily in the same region. To avoid this interference, we recorded the spectra on hexachlorbutadiene mulls and could clearly resolve the bands due to N—H stretching frequency since the mulling agent does not absorb in this region. Further, the far-infrared spectra of three representative compounds were recorded (Table 2). The metal halogen stretching frequencies for the yellow complex indicate a tetrahedral [10] configuration whereas those for dark violet complexes indicate a square configuration.

Magnetic measurements indicated the complexes to be paramagnetic in the presence of one unpaired electron (μ_{eff} values ranging between 1.78 to 1.98 B.M.) as expected

for a copper(II) ion with d^9 configuration. Moments of complexes containing $[\text{CuCl}_4]^{2-}$ ions are more than 1.9 B.M. typical of Cu(II) ion in a tetrahedral environment. For truly tetrahedral compounds the moment is about 2.2 B.M., but the moments in the present case are lower. This might be because of quenching of some orbital contribution to the moment due to distortion from regular tetrahedral symmetry.

On the basis of the electronic spectra (Table 2) the complexes can be classified into two categories. The first category of compounds containing $[\text{CuCl}_2\text{Br}_2]^{2-}$ and $[\text{CuBr}_4]^{2-}$ ions show a single band in the $17\,000\text{ cm}^{-1}$ region presumably indicative of a square configuration [11–14]. The second category of complexes containing $[\text{CuCl}_4]^{2-}$ ions exhibit a broad band in the $13\,200\text{--}13\,400\text{ cm}^{-1}$ region. From the spectra and crystal structure determination both planar and distorted tetrahedral stereochemistry have been suggested [5, 14–16] for a compound containing $[\text{CuCl}_4]^{2-}$ ions. A truly tetrahedral compound should exhibit [11] one broad band below $10\,000\text{ cm}^{-1}$. But Sacconi and Ciampolini [18] obtained bands at 8500, 13 600, and $21\,000\text{ cm}^{-1}$ in the electronic spectra of a salicylaleneaminato copper(II) complex and suggested that flattening of tetrahedron results in the splitting of both the ground and the excited levels. In the spectra of chloro complexes now reported, we could not record the band below $10\,000\text{ cm}^{-1}$ due to the limitation of the instrument used, but we obtained two other bands near the same regions reported by Sacconi et al. Further in the reflectance spectra of the compound $[\text{3,5-lutH}]_2[\text{CuCl}_4]$ bands were observed at 475, 740, and $> 1100\text{ nm}$ indicative of tetrahedral or pseudo-tetrahedral environment around the metal ion. Thus it is expected that the tetrachloro complexes reported now have pseudo-tetrahedral configuration. This is also in conformity with the more recent observation [19] that tetraalkylammoniumtetrachloro cuprates contain discrete distorted tetrahedral CuCl_4^{2-} ions.

References

1. Mohapatra, B. K. and Ramana Rao, D. V., *J. Inst. Chem. (India)* **42**, 199 (1970).
2. Mishra, M. K. and Ramana Rao, D. V., *J. Organometal. Chem.* **22**, 227 (1970).
3. Das, A. K. and Ramana Rao, D. V., *Z. Anorg. Allg. Chem.* **379**, 213 (1970).
4. Gill, N. S. and Taylor, F. B., *Inorg. Syn.* **9**, 136 (1967).
5. Furlani, C. and Morpurgo, G., *Theor. Chim. Acta* **1**, 102 (1963).
6. Mundie, J. H. and Nuttal, R. H., *J. Inorg. Nucl. Chem.* **31**, 479 (1969).
7. Mohapatra, B. K. and Ramana Rao, D. V., *J. Indian Chem. Soc.* **49**, 1066 (1972).
8. Allana, J. R., Brown, D. H., Nuttal, R. H., and Sharp, D. W. A., *J. Chem. Soc. (London)* **A1966**, 1031.
9. Mohapatra, B. K. and Ramana Rao, D. V., *Indian J. Chem.* **8**, 564 (1970).
10. Adams, D. M. and Lock, P. J., *J. Chem. Soc. (London)* **A1967**, 620.
11. Goodgame, D. M. L. and Cotton, F. A., *J. Chem. Soc. (London)* **A1961**, 2298.
12. Baldwin, D. A., Lever, A. B. P., and Parish, R. V., *Inorg. Chem.* **8**, 107 (1969).
13. Jørgensen, C. K., *Absorption Spectra and Chemical Bonding*. Pergamon Press, London, 1962.
14. Lever, A. B. P., *Inorganic Electronic Spectroscopy*. Elsevier, Amsterdam, 1968.
15. Morosin, B. and Lingafelter, E. C., *J. Phys. Chem.* **65**, 150 (1961).
16. Willet, R. D., *J. Chem. Phys.* **41**, 2243 (1964).
17. Ferguson, J., *J. Chem. Phys.* **40**, 3406 (1964).
18. Sacconi, L. and Ciampolini, M., *J. Chem. Soc. (A)* **1964**, 276.
19. Bonamico, M. and Dessy, G., *Acta Crystallogr.* **A21**, 136 (1966).