Polyhedron Vol. 5, No. 3, pp. 655–657, 1986
Printed in Great Britain

0277-5387/86 $3.00+.00

SYNTHESIS OF DISUBSTITUTED AMMONIUM TRICHLORODICUPRATE(I) FROM THE REACTION OF $CuCl_2 \cdot 2H_2O$ WITH *N,N′*-THIOBISAMINES

CARLOS DÍAZ

Universidad de Chile, Facultad de Ciencias, Departamento de Química, Casilla 653, Santiago, Chile

(*Received* 17 *January* 1985; *accepted* 26 *May* 1985)

Abstract—The reaction of $CuCl_2 \cdot 2H_2O$ with various *N,N′*-thiobisamines $S(NR_2)_2$, NR_2 = dimethylamine, diallylamine, dibenzylamine and piperidine in ethanol have been investigated. With *N,N′*-thiobisdimethylamine and *N,N′*-thiobisdiallylamine the compounds $[(CH_3)_2NH_2][Cu_2Cl_3]$ and $[CH_2{=}CH{-}CH_2)_2NH_2)][Cu_2Cl_3]$ have been obtained and characterized by elemental analysis and IR spectroscopy. From the reaction with other *N,N′*-thiobisamines, mixtures of other products were isolated.

Although *N,N′*-thiobisamines are apparently quite unreactive species, the first complexes with these compounds as ligands have been reported.[1] The redox activity of *N,N′*-thiobisamines was found in reactions with Cu(II) and Ag(I) ions.[2] From the reactions of *N,N′*-thiobismorpholine with $CuCl_2 \cdot 2H_2O$, the complex morpholinium trichlorodicuprate(I) was obtained.[2] In spite of the fact that the preparation of this compound has been previously described it has not been well characterized.[3] In order to find synthetic applications in the redox properties of *N,N′*-thiobisamines, the reactions of $CuCl_2 \cdot 2H_2O$ with *N,N′*-thiobisdimethylamine, *N,N′*-thiobisdiallylamine, *N,N′*-thiobisbenzylamine and *N,N′*-thiobispiperidine were studied and are described in this paper.

EXPERIMENTAL

N,N′-thiobisamines were prepared by the method reported earlier.[4] $CuCl_2 \cdot 2H_2O$ and ethanol (Merck) were used without further purification. All reaction were performed under an atmosphere of oxygen-free nitrogen in a Schlenk apparatus. IR spectra were obtained with a Perkin–Elmer 621 spectrophotometer using KBr pellets.

Reactions

General procedure. To a solution of copper(II) chloride (*ca* 9 mmol) in ethanol—previously deoxygenated with nitrogen—was added the equimolar amount of the respective *N,N′*-thiobisamine solution [2:1 stoichiometry, Cu(II):thiobisamine]. All reactions were performed with stirring and at room temperature. The white solid formed was filtered and then dried *in vacuo.* Analytical data for compounds are given in Table 1. The SO_2 evolved from the reactions was confirmed by the common chemical methods.[5] For the reaction of *N,N′*-thiobisdibenzylamine the products remained in solution, but a white solid was isolated by the addition of cyclohexane. With *N,N′*-thiobispiperidine a black solid only was obtained. Potentiometric titration (PHM-62 Potentiometer) of $CuCl_2 \cdot 6H_2O$ (4.05 mmol) in CH_3CN gave at the end-point 2.1 mmol of *N,N′*-thiobisdiallylamine.

RESULTS AND DISCUSSION

N,N′-thiobisdimethylamine and *N,N′*-thiobisdiallylamine react with $CuCl_2 \cdot 2H_2O$ in ethanol as solvent to give the complexes

$$[(CH_3)_2NH_2][Cu_2Cl_3]$$

and

$$[CH_2{=}CH{-}CH_2)_2NH_2][Cu_2Cl_3]$$

respectively. The stoichiometric compositions of these compounds were established by elemental analysis (see Table 1). The complexes are white crystalline solids which turned brown and afterwards green when exposed to the air. Moreover SO_2

Table 1. Analytical data for the trichlorodicuprate(I) compounds

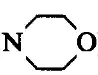
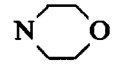
Compound	M.p. (°C)	Yield (%)	Analysis (%) [found (calc.)]				
			C	H	N	Cu	Cl
$[(CH_3)_2NH_2][Cu_2Cl_3]$	120–121	65	8.5	2.9	4.9	45.6	39.3
	(dec.)		(8.6)	(2.9)	(5.0)	(45.5)	(38.0)
$[(CH_2{=}CH{-}CH_2)_2NH_2][Cu_2Cl_3]$	105	41	21.4	3.6	3.2	38.8	31.2
	(dec.)		(21.7)	(3.6)	(4.2)	(38.3)	(32.1)
Mixture[a]						19.3	21.7
						(19.7)[b]	(21.8)[b]

[a] Mixture: 65% $[Cu_2Cl_3][H_2N(CH_2{-}C_6H_5)_2]$ and 35% $Cl[H_2N(CH_2{-}C_6H_5)_2]$.
[b] Calculated for the mixture.

evolved from the reaction was observed. Hence the reaction can be written as:

$$2CuCl_2 \cdot 6H_2O + S(NR_2)_2 \rightarrow [Cu_2Cl_3][H_2NR_2] + SO_2 + [R_2NH_2]Cl.$$

The stoichiometry of this reaction has been confirmed by potentiometric titration.

The IR spectra of the complexes show, in the range 1550–1576 cm^{-1}, the $\delta(NH_2)^+$ modes characteristic of $[R_2NH_2]X$ salts.[6–8] In Table 2 are summarized the IR frequencies for the complexes. The data for $[Cu_2Cl_3][H_2$$]$ are also included. The N—H stretching frequencies values are different from other $[NR_2H_2^+][X^-]$ compounds[6–8] which can be attributed to a distinct degree of hydrogen bonding between the anion and the cation. In the spectra it was also possible to assign some characteristic modes for the $N(CH_3)_2$, $N(CH_2{-}CH{=}CH_2)_2$ and  groups. This was performed according to vibrational studies reported for compounds containing these groups.[9–13] Further, the rocking mode of the NH_2 group assigned in the range 780–805 cm^{-1} is in reasonable agreement with assignments for other $[R_2NH_2]X$ salts.[6–8]

From the reaction of $CuCl_2 \cdot 2H_2O$ with *N,N′*-thiobisdibenzylamine a white solid was isolated whose elemental analysis suggested a mixture of

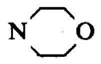
$$[(C_6H_5{-}CH_2)_2NH_2][CuCl_3]\ (65\%)$$

and

$$[(C_6H_5{-}CH_2)_2NH_2]Cl\ (35\%).$$

The IR spectra of this solid are also consistent with

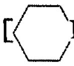
Table 2. IR spectra of the $[Cu_2Cl_3][H_2NR_2]$ complexes[a,b]

$N(CH_3)_2$		$N(CH_2{-}CH{=}CH_2)_2$			
3190 s	$\nu(NH_2)^+$ asym	3090 m	$\nu(NH_2)^+$ asym	3190 m	$\nu(NH_2)^+$ asym
3105 s	$\nu(NH_2)^+$ sym	3060 m	$\nu(NH_2)^+$ sym	3060 m	$\nu(NH_2)^+$ sym
1575 m	$\delta(NH_2)^+$	1550 m	$\delta(NH_2)^+$	1576 s	$\delta(NH_2)^+$
1460 m	$\delta(CH_3)$	1433 s	$\delta({=}CH_2)$ p	1440 s	$\delta(CH_2)$
1442 s		1415 vs		1210 w	$\rho(CH_2)$ twist
1428 w		986 m	$\nu(CN)$	1178 s	
1400 w	$\rho(CH_2)$ rock	960 s	$\delta({=}CH_2)$ op	1095 vs	$\nu(C{-}O{-}C)$ asym
1382 vs		930 vs		1039 m	
1006 s	$\nu(CN)$ asym	780	$\rho(NH_2)$ rock	876 s	$\nu(C{-}O{-}C)$ sym
878 w	$\nu(CN)$ sym			872 s	$\rho(NH_2)^+$ rock
810 m	$\rho(NH_2)^+$ rock			865	$\rho(CH_2)$ rock

[a] Principal characteristic bands only.
[b] Frequencies in cm^{-1}. Solid samples (KBr pellets). Abbreviations: vs, very strong; s, strong; m, medium; w, weak; p, plane; op, out-of-plane.

this. Attempts to isolate the pure

$$[(C_6H_5\text{—}CH_2)_2NH_2][Cu_2Cl_3]$$

complex, have failed. On the other hand, from the reaction of $CuCl_2 \cdot 2H_2O$ with *N*,*N'*-thiobispiperidine only a black solid was isolated and the analogous [$NH_2][Cu_2Cl_3]$ complex was not obtained.

Although chlorocuprates(I) are well-known compounds, only a few of those with composition $M[Cu_2Cl_3]$ have been reported, e.g. the solids

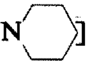
$$Cs[Cu_2Cl_3],^{14}\ [(CH_3)_3NH][Cu_2Cl_3]$$

and

$$[C_7H_{13}NH][Cu_2Cl_3],^{15}$$

and the fused salts at room temperature,

$$[Et_3PH][Cu_2Cl_3],\ [Et_3NH][Cu_2Cl_3],$$
$$[Bu_3NH][Cu_2Cl_3]$$

and [EtHN$][Cu_2Cl_3]^{15}$. However other halogenometallates with similar compositions have been reported, e.g. $[C_6H_5N_2][Cu_2Br_3]^{16}$ and $Cs[Ag_2I_3]$.[14] These compounds are usually prepared by direct reaction of copper(I) chloride with the metal halide or the respective trialkylphosphonium or ammonium chloride under strictly anhydrous and deoxygenated conditions. In the preparation of ammonium trichlorodicuprate(I) from *N*,*N'*-thiobisamines, the SO_2 reductive atmosphere precludes the oxidation of the Cu(I) salts.

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