BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 2396—2398 (1969)

Infrared Spectra of Bis(2,4-dichloro-6-ethoxymercapto-isocyano-*s*-triazino-*N*,*S*) Copper(II)

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(Received February 3, 1969)

In a previous paper, the infrared and Raman spectra of 2,4-dichloro-6-isocyanodichloro-*s*-triazine(tetrameric cyanogen chloride: DCT-$NCCl_2$) have been reported1). The present paper will deal with the preparation of the bis(2,4-dichloro-6-ethoxymercaptoisocyano-*s*-triazino-*N*,*S*) copper(II) complex, [Cu(DCT-$NCSOC_2H_5$)$_2$], and with the infrared spectra of the complex and 2,4-dichloro-6-ethoxythiocarbamido-*s*-triazine, DCT-$NHCSOC_2H_5$, which is a derivative of DCT-$NCCl_2$ and the parent molecule of the ligand of the complex, in order to assign the observed spectra.

Experimental

2,4-Dichloro-6-ethoxythiocarbamido-*s*-triazine: DCT-$NHCSOC_2H_5$. This was prepared by the method described previously2) and was identified analytically.

By the addition of sodium hydroxide to an aqueous solution of cupric nitrate (0.02 mol), its pH was adjusted to 7.4; it was kept at about 0°C. A solution of DCT-$NHCSOC_2H_5$ (0.02 mol) in chloroform was stirred drop by drop into the aqueous solution of cupric nitrate. The stirring continued for about five hours. The reaction mixture was then placed in a separatory funnel in order to separate the chloroform portion from the aqueous one. By evaporating the chloroform portion under reduced pressure, the red-brown colored crystal was precipitated and dried *in vacuo*. Recrystallization from carbon tetrachloride gave bis(2,4-dichloro-6-ethoxymercaptoisocyano-*s*-triazino-*N*,*S*) copper(II).

Found: Cu, 10.01; C, 25.34; N, 19.56; H, 1.90%. Calcd for $CuC_{12}N_8O_2S_2H_{10}Cl_4$: Cu, 11.19; C, 25.39; N, 19.74; H, 1.90%.

The infrared spectra were recorded by a Nujol or hexachloro-1,3-butadiene mull from 4000 to 250 cm^{-1} with Hitachi-Perkin-Elmer 125 and Hitachi EPI-L spectrometers. The frequencies of the observed bands may be expected to be accurate to ± 2 cm^{-1}; they may tentatively be assigned as is shown in Table 1.

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1) K. Kawai, Y. Kodama and F. Mizukami, *Spectrochim. Acta*, **24A**, 1013 (1968).

2) Y. Kodama and S. Shinohara, *Yuki Gosei Kagaku Kyokai-shi (J. Soc. Org. Synth. Chem. Japan)*, **22**, 669 (1964).

TABLE 1. THE ASSIGNMENT OF THE INFRARED SPECTRA OF 2,4-DICHLORO-6-ETHOXYTHIOCARBOAMIDO-*s*-TRIAZINE AND BIS(2,4-DICHLORO-6-ETHOXYMERCAPTOISOCYANO-*s*-TRIAZINO-*N*,*S*) COPPER(II) (cm^{-1})

DCT-$NHCSOC_2H_5$	[Cu(DCT-$NCSOC_2H_5)_2$]	Assignment
3430 w		ν(N-H)
3138 m	3205 w	ν(C-H)
3065 m		
2990 w	2985 m	
2935 w	2825 m	
	1703 w	1241+465=1706
1646 vw		1001+646=1647
1575 s		δ(N-H)
1526 vs		ν(C=N) triazine ring
1503 vs	1488 vs, b	
1470 w		1036+435=1471
1440 w		797+646=1443
1403 s		ν(C=S)
1386 s	1389 s	δ(CH_3)
	1355 m	ν(C=N)as. chelate ring
1311 w, sh		855+460=1315
1295 vs		ν(C-N)as.
	1291 s	ν(C=N)s. chelate ring
1280 w		646+635=1281
1249 vs	1241 vs	ν(C=N) triazine ring
1218 vs	1216 vs	
1159 vs	1159 m	ν(C-O)as.
	1112 m	ν(C=S)
1100 m		ν(C-N)s.
1036 m	1032 m	ν(C-O)s. or CH_3 rocking
1001 m	1000 m	triazine ring breathing
965 w	968 w	ν(C-C)
911 vw		
899 vw		
894 vw, sh		460+435=895
855 s	851 s	ν(C-Cl)
	805 w	
797 s	794 s	triazine ring out-of-plane
783 m	762 m	
688 m		
646 w	677 m	
635 m	624 m	
	596 w, sh	
	546 w	
	538 w	
472 w		
460 w	465 w	
435 w		
	419 w	ν(Cu-N)
273 vw	311 vw	

vs=very strong, s=strong, m=medium, w=weak, vw=very weak, sh=shoulder, b=broad, s.=symmetric and as.=asymmetric.

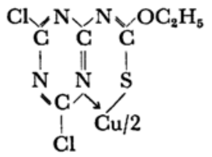
The NMR spectra were also recorded, using a Japan Electron Optics C-60H spectrometer at the frequency of 60 Mcps in deuterium-chloroform, with tetramethylsilane as an internal standard; this examination revealed the signals of two groups, a quartet at τ 5.38 and a triplet at τ 8.60, in the complex, and the signals of three groups, a singlet at τ 1.18, a quartet at τ 5.45, and a triplet at τ 8.55, in DCT-$NHCSOC_2H_5$.

Results and Discussion

The absence of the band assigned to the N-H stretching vibration in the infrared spectra of the complex is confirmed by its NMR spectra, in which only the signals due to the presence of a typical ethyl group have been observed.

A very strong and broad band at 1488 cm^{-1} assigned to the triazine ring-stretching vibration of the complex may be the overlap of two or more bands; the frequency has shifted toward frequencies lower than the 1526 and 1503 cm^{-1} of DCT-$NHCSOC_2H_5$ or those assigned to the ring-stretching vibration in several triazine derivatives.[1,3-5] This frequency shift suggests that there may be small differences in the nature of the bonds in the triazine ring and a decrease in the C=N stretching force constant of the ring as a result of the formation of the complex with the chelate ring.

The great difference between the infrared spectra of DCT-$NHCSOC_2H_5$ and those of the complex may arise from the C=S and C=N stretching frequencies in the chelate ring. By comparing the spectra of the two compounds, the strong band at 1403 cm^{-1} and the two bands at 1100 and 1295 cm^{-1} of DCT-$NHCSOC_2H_5$ may be assigned to the C=S stretching vibration and the symmetric and asymmetric C–N stretching vibrations of the $-\underset{\|}{C}(\text{ring})-\overset{|}{N}-\underset{\|}{C}-$ group respectively; the C=S stretching frequency of the complex shifts lower by means of the coordination of the sulfur atom, that is, by the contribution of $C-S^{-}\rightarrow Cu$. On the other hand, the C=N stretching frequencies in the chelate ring shift higher because of the increase in the double-bond character. On the basis of the above facts and the assignment of other bands, the three bands at 1112, 1291, and 1355 cm^{-1} of



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3) J. C. Lorquet, *Bull. Soc. Royale Science Liege*, **29**, 298 (1960).

4) J. E. Griffithe and D. E. Irish, *Can. J. Chem.*, **42**, 690 (1964).

5) T. S. Hermann, *Spectrochim. Acta*, **21**, 663 (1965).

the complex may be assigned to C=S stretching, symmetric C=N stretching, and asymmetric C=N stretching vibrations of the chelate ring respectively. Although some of the observed bands, including most of those in the lower frequency region, have not been assigned, the infrared spectra suggest that the complex is the chelate compound shown in Scheme I.

The authors are greateful to the members of the laboratory of Microanalysis, Faculty of Pharmacology of this University, for their microanalyses.