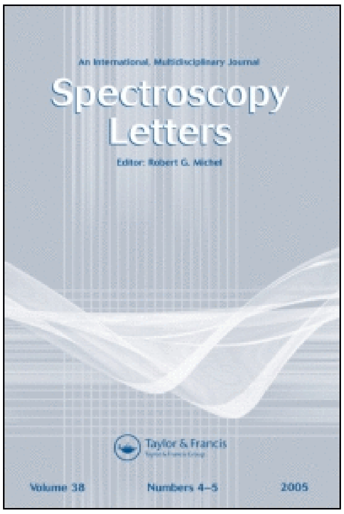

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

The Vibrational Spectra of Complexes with Planar Monothiooxamides. IV. The Copper(II) and Copper(I) Complexes of Neutral Monothiooxamides

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To cite this Article Manessi-Zoupa, E. , Perlepes, S. P. , Fabretti, A. C. and Desseyn, H. O.(1994) 'The Vibrational Spectra of Complexes with Planar Monothiooxamides. IV. The Copper(II) and Copper(I) Complexes of Neutral Monothiooxamides', Spectroscopy Letters, 27: 1, 119 — 138

To link to this Article: DOI: 10.1080/00387019408002512

URL: http://dx.doi.org/10.1080/00387019408002512

SPECTROSCOPY LETTERS, 27(1), 119-138 (1994)

THE VIBRATIONAL SPECTRA OF COMPLEXES WITH PLANAR MONOTHIOOXAMIDES - PART IV [1].
THE COPPER(II) AND COPPER(I) COMPLEXES OF NEUTRAL MONOTHIOOXAMIDES

Key Words: Monothiooxamides, Copper(II) complexes, Copper(I) complexes, Infrared spectra, Raman spectra

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ABSTRACT

The new complexes $CuX_2(LH_2)$, $CuX_2(SH_3)$ (X = Cl, Br), $CuX(LH_2)$, $CuX(SH_3)$ (X = Cl, Br, I), $CuX(H_4MTO)_2$ (X = Cl, Br), $CuI(H_4MTO)$ and $CuX(H_3MMTO)_2$ (X = Cl, Br, I), where LH_2 = N,N'-dimethylmonothiooxamide, SH_3 = $N_{(S)}$-methylmonothiooxamide, H_4MTO = monothiooxamide and H_3MMTO = $N_{(O)}$-methylmonothiooxamide, have been prepared. The complexes were characterized by elemental

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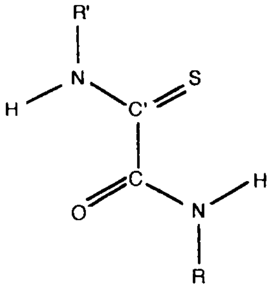
analyses, conductivity measurements,magnetic moments and spectroscopic (UV/VIS, FT-IR, Laser-Raman) studies. The vibrational analysis of the complexes has been given using NH/ND, CH_3/CD_3 and $^{63}Cu/^{65}Cu$ isotopic substitutions. The neutral monothiooxamides behave as monodentate ligands in the Cu(I) complexes coordinating through their thioamide sulfur atom. The ligands LH_2 and SH_3 act as bidentate chelating agents in the Cu(II) complexes with ligated atoms being the thioamide sulfur and the amide oxygen.

INTRODUCTION

The coordination chemistry of *monothiooxamides* and the vibrational spectroscopy of their metal complexes, have not yet been investigated, although monothiooxamide complexes could offer unique features in terms of structural, magnetic and spectroscopic properties. In Parts I [2] and II [3] of this series we reported on the vibrational spectra of transition metal complexes with singly and doubly *deprotonated* monothiooxamido ligands. In Part III [1] we started a systematic study of complexes with *neutral* monothiooxamides. Our study was initiated with Pd(II), a soft acid in terms of HSAB theory [4]. Monomeric 1:2 *trans* and 1:4 square planar complexes have been obtained, in which neutral monothiooxamides behave as monodentate ligands coordinating through their soft thioamide sulfur atom. We suspected, however, that this monodentate ligation mode is not the only coordinating behaviour of neutral monothiooxamides and that the amide group might also be involved in coordination to the metal ions through its hard oxygen atom in non alcalic media. Thus, we moved on to the logical second phase of the work with neutral monothiooxamides, the use of a metal ion which is a harder acid than Pd(II) in the HSAB classification. We selected Cu(II) for our studies. Another driving force behind our choice has been the well-known reducing ability of the thioamide group towards Cu(II) to give Cu(I) species [5] and, hence, the exciting possibility to prepare and study complexes of a given monothiooxamide ligand with both Cu(II) and Cu(I). We herein describe the results of our studies. The ligands used are shown in Fig. 1.



R = R' = H ; monothiooxamide (H_4MTO)
R = R' = CH_3 ; N,N'-dimethylmonothiooxamide (LH_2)
R' = H, R = CH_3 ; $N_{(O)}$-methylmonothiooxamide (H_3MMTO)
R' = CH_3, R = H ; $N_{(S)}$-methylmonothiooxamide (SH_3)

FIG. 1. The general formula of the monothiooxamides used in our studies and their abbreviations.

EXPERIMENTAL

All manipulations were performed under aerobic conditions. Details of the syntheses of monothiooxamides and their CD_3-forms can be found elsewhere [2,6]. Concentrated hydrochloric (37%), hydrobromic (48%) and hydroiodic (57%) acids were used to dissolve copper(II) salts. For the preparation of ^{63}Cu(II) and ^{65}Cu(II) isotopic complexes stock solutions of their salts in HX (X = Cl, Br, I) were used, prepared from ^{63}Cu (99.7%) and ^{65}Cu (99.2%) both purchased from Rohstoff-Einfuhr GmbH. Metal and halide analyses were performed by conventional titrimetric and gravimetric methods. Physicochemical measurements and spectroscopic techniques were carried out by published methods [2,7,8].

The complexes $CuX_2(LH_2)$ and $CuX_2(SH_3)$ (X = Cl, Br) were all prepared almost similarly. A total amount of 2.0 mmol of $CuCl_2.2H_2O$ or $CuBr_2$ was dissolved in 2 ml of the corresponding concentrated HX (X = Cl, Br). To this solution was slowly added a solution of the appropriate monothioooxamide (2.0 mmol) in 10 ml of glacial CH_3COOH. Precipitates formed almost immediately and the reaction mixtures were kept stirring for about 5 min. All solids were collected by filtration, washed with CH_3COOH (4 ml), EtOH (2 x 5 ml) and Et_2O (4 x 15 ml), and dried *in vacuo* over P_4O_{10}. Yields were in the 40-60 % range.

For the preparation of $CuCl(LH_2)$ and $CuCl(SH_3)$, a solution of $CuCl_2.2H_2O$ (2.0 mmol) and L-ascorbic acid (4-5 mmol) in 37% hydrochloric acid (3 ml) was added with strirring to a solution of the appropriate ligand (6.0 mmol) in glacial CH_3COOH (12 ml). Upon addition of the $CuCl_2$-ascorbic acid solution a precipitate formed. Stirring was continued for 30 min. The precipitates were filtered off, washed with CH_3COOH (2 x 3 ml), EtOH (2 x 10 ml), Et_2O (3 x 15 ml) and dried *in vacuo* over P_4O_{10}. The preparative method for $CuX(LH_2)$ and $CuX(SH_3)$ (X = Br, I) involved the direct reaction of a stirred solution of $CuBr_2$ (2.0 mmol) or CuI (2.0 mmol) in 3 ml of the corresponding concentrated HX with a solution of the appropriate ligand (6.0 mmol) in 15 ml of glacial CH_3COOH (15 ml). In the case of the bromo complexes a noticeable colour change from green to orange occurred gradually. The reactions proceeded smoothly and precipitates formed after *ca.* 5 min. Stirring was continued for 1 h. The solids were filtered off, washed with CH_3COOH (5 ml), EtOH (2 x 5ml) and copious amounts of Et_2O, and dried *in vacuo* over silica gel. Yields for the $CuX(LH_2)$ and $CuX(SH_3)$ complexes were *ca.* 80%.

For the preparation of $CuX(H_4MTO)_2$ (X = Cl, Br), $CuI(H_4MTO)$ and $CuX(H_3MMTO)_2$ (X = Cl, Br, I), a solution of 2.0 mmol of $CuCl_2.2H_2O$, $CuBr_2$ or CuI in 2.5 ml of the corresponding concentrated HX was added dropwise to a stirred solution of the appropriate free ligand (6.0 mmol) in 12 ml of glacial CH_3COOH. Noticeable colour changes occurred in the cases of chloro and bromo complexes. The resulting solutions were stirred at room temperature for 15 min. Solid products were deposited during this time, which were collected by filtration, washed with cold EtOH and Et_2O, and dried *in vacuo* over P_4O_{10}. Yields were in the 55-65% range for the 1:2 complexes and *ca.* 90% for $CuI(H_4MTO)$.

The deuterated compounds were prepared exactly as described for the normal complexes using $CuCl_2.2D_2O$, $CuBr_2$, CuI, normal ligands and deuterated solvents (CH_3COOD, DCl, DBr, DI). The precipitates were washed only with CH_3COOD and CD_3OD; no EtOH or Et_2O were used.

The CD_3-complexes were prepared exactly as the normal complexes using the CD_3-forms of LH_2, H_3MMTO and SH_3. The ^{63}Cu and ^{65}Cu isotopic complexes were prepared at small synthetic scales using the same methods as for their corresponding non-isotopic compounds.

RESULTS AND DISCUSSION

Preparation and Physical Properties of the Complexes

The Cu(II) and Cu(I) complexes are listed in Table 1 with their analytical data, colours and molar conductivity values. The following points are of synthetic interest.

First, the compounds described in the experimental section appear to be the only compounds that could be isolated in the solvent systems used, irrespective of the employed reaction conditions. The stoichiometry of the complexes and the metal geometry *(vide infra)* result from a delicate balance of several factors, among which metal oxidation state, anionic ligand polarizability, lattice energy, primary or secondary nature of the thioamide group and chelating capability of the monothiooxamide ligands play the predominant role.

Second, like the Pd(II) complexes [1], the formation of Cu(II) and Cu(I) complexes with *neutral* monothiooxamides is feasible only in strongly acidic media (HX-CH_3COOH), which prevent formation of complexes with the monoanionic form of the ligands [2,3].

Third, chloro and bromo copper(II) complexes can be obtained only with ligands containing a *secondary* thioamide group (LH_2, SH_3). On the contrary, monothiooxamides with a *primary* thioamide group reduce Cu(II) spontaneously to give the Cu(I) complexes 11, 12, 14 and 15. These results are in accord with the well-known great reducing ability of the primary thioamide group towards Cu(II) [9]. The key point for the successful preparation of complexes 11, 12, 14 and 15 is the use of an excess of ligand; the minimum required ligand:Cu(II) molar ratio is 3:1. This very important experimental observation, which was also reported by Castan [5] and Devillanova's group [10] for heterocyclic thioamide ligands, has been explained by the fact that one extra thio-ligand molecule is required to reduce

TABLE 1

Colours, Analytical Results and Conduct. Data for the Prepared Complexes

Comp. number	Complex+	Colour	Elemental analyses (%)* Cu	Elemental analyses (%)* X	Λ_M++ (S cm^2 mol^{-1})
1	$CuCl_2(LH_2)$	green	23.9 (23.8)	27.0 (26.6)	31
2	$CuBr_2(LH_2)$	brown	17.4 (17.9)	45.3 (44.9)	12
3	$CuCl_2(SH_3)$	green	24.5 (25.2)	27.9 (28.1)	25
4	$CuBr_2(SH_3)$	brown	18.9 (18.6)	47.3 (46.8)	24
5	$CuCl(LH_2)$	yellow	27.8 (27.5)	15.0 (15.3)	8
6	$CuBr(LH_2)$	yellow	22.4 (23.0)	28.7 (29.0)	13
7	$CuI(LH_2)$	yellow	19.1 (19.7)	40.2 (39.3)	9
8	$CuCl(SH_3)$	yellow	29.3 (29.3)	16.8 (16.3)	10
9	$CuBr(SH_3)$	yellow-orange	23.7 (24.3)	30.6 (30.5)	11
10	$CuI(SH_3)$	yellow-orange	20.5 (20.6)	40.5 (41.1)	5
11	$CuCl(H_4MTO)_2$	yellow	19.9 (20.7)	10.9 (11.5)	13
12	$CuBr(H_4MTO)_2$	yellow-orange	18.3 (18.1)	22.3 (22.7)	5
13	$CuI(H_4MTO)$	orange	22.1 (21.6)	43.9 (43.1)	7
14	$CuCl(H_3MMTO)_2$	orange	18.4 (18.9)	10.8 (10.6)	8
15	$CuBr(H_3MMTO)_2$	orange	16.3 (16.7)	21.1 (21.0)	2
16	$CuI(H_3MMTO)_2$	orange	14.1 (14.9)	29.8 (29.7)	10

* Theoretical values are in parentheses.

\+ The anhydrous character of the complexes has also been confirmed by TG/DTG experiments.

++ Values of molar conductivity for *ca.* 10^{-3} M solutions in DMF at 25°C; the conductivities of some solutions change with time.

X = Cl, Br, I.

the metal, according to the following general reaction :

$$CuX_2 + nL \longrightarrow CuXL_{n-1} + HX + 0.5\,L'_2 \qquad (1)$$

were X is Cl, Br, n = 2, 3, ... and L' is a deprotonated form of the thio-ligand L. Why copper(I) iodide gives the 1:1 (and not the 1:2) complex with H_4MTO is difficult to rationalize; electronic factors may be involved.

Fourth, in extending the chemistry of copper complexes with neutral monothiooxamides, we considered it of interest to try to prepare chloro and bromo copper(I) complexes (in the iodo complexes copper always exists in the +1 oxidation state) with LH_2 and SH_3, *i.e.* the *secondary thioamide*-containing ligands. Chloro copper(I) complexes could be obtained using *L*-ascorbic acid as an external reductant, in accord with the well-established reducing behaviour of this reagent towards Cu(II) *in the presence of chloride ions* [11]. A final point of synthetic interest is the fact that the reaction between $CuBr_2$ and LH_2 or SH_3 is molar ratio-dependent. Using an 1:1 $CuBr_2$:ligand molar ratios, the bromo copper(II) complexes 2 and 4 were obtained. When the reaction was carried out in a 3:1 molar ratio (excess of ligand) using *a longer reaction time*, the bromo copper(I) complexes 6 and 9 were prepared, again emphasizing the need of excess of the thioamide ligand to accomplish metal reduction.

Compounds 1-4 and 11-16 are stable in air in the solid state. The primary thioamide function is capable of stabilizing Cu(I) in 11-16 with respect to oxidation. Compounds 5, 6, 8 and 9 are not particularly stable in air; they become pale green or greenish brown after several days. Complexes 5-10 and 13 are insoluble in H_2O and all common organic solvents, except DMF and DMSO; their insolubility is an indication that they are polymers. Complexes 1-4, 11, 12 and 14-16 are soluble in polar organic solvents, such as MeOH, MeCN, DMF and DMSO, but to varying extents. The Λ_M values of 2 and 5-16 in DMF are in accord with these complexes being formulated as non-electrolytes [12]. Complexes 1, 3 and 4 are partially ionized in DMF [12].

Magnetochemistry and Solid-State Electronic Spectra

Table 2 gives the room temperature magnetic moments and details of the diffuse reflectance electronic spectra for the Cu(II) complexes 1-4.

TABLE 2

Solid-State Effective Magnetic Moments and Electronic Spectral Data in the 29400-5000 cm^{-1} region for the Cu(II) Complexes

Complex	μ_{eff}*,+(BM)	Diffuse reflectance spectra++ (10^3 cm^{-1}) d-d	XMCT	σ(S)→Cu(II) CT
1	1.79	15.63	24.29 sh	27.40
2	1.89	14.13	22.47	26.81
3	1.82	15.80	24.62 sh	27.13
4	1.85	14.79	21.99	27.01

* Per metal ion.

\+ Measured at room temperature.

++The spectra also exhibit very weak bands at *ca.* 21 kK which could not be assigned; these bands may be due to Cu(d)→π^* (ligands) CT transitions.

XMCT = *halogen-to-metal charge transfer; CT = charge transfer; sh=* shoulder.

Assignments have been given by studying literature [13] for analogous Cu(II) complexes.

Complexes 5-16 were shown to be diamagnetic, confirming that they are Cu(I) species. The room temperature μ_{eff} values indicate that the Cu(II) compounds 1-4 are magnetically dilute. The d-d frequencies of these complexes (15.80-14.13 KK) are fairly typical of a tetragonal stereochemistry [13]. A structure with four strong planar bonds (one Cu–S, one Cu–O, two Cu–X) and two longer axial bonds, due to interaction with two other complex units, may be possible [13,14]. The electronic spectra of 1-4 are, in general, similar with those obtained for the 1:1 Cu(II) halo complexes with neutral dithiooxamides [14].

The Solid-State Vibrational Spectra of the Cu(II) and Cu(I) Complexes

The full vibrational analysis of the free ligands has been published [6, 29-31]. It was possible to obtain satisfactory Raman spectra only for the Cu(I) complexes 5-10. Tables 3 and 4 summarize the most characteristic and diagnostic fundamentals of the copper complexes of LH_2 and SH_3. The full solid-state vibrational analysis of 11-13 and 14-16 is given in Tables 5 and 6, respectively. Fig. 2 illustrates the mid-IR spectra of $CuX(SH_3)$ (X = Cl, Br, I).

The assignments have been given in comparison with the data obtained for the free ligands [6, 15-17] and for metal complexes containing amide [18,19] or thioamide [8,20-22] groups, and have been assisted by NH/ND, CH_3/CD_3, *simultaneous* NH/ND and CH_3/CD_3, and $^{63}Cu/^{65}Cu$ isotopic substitutions. Since all diagnostic vibrational frequencies and their assignments have been tabulated, the spectroscopic discussion is confined only to the most important features in relation to the coordination modes of LH_2, SH_3, H_3MMTO and H_4MTO, and to the structures of their Cu(II) and Cu(I) complexes.

Considering the amide function of the complexes, the spectra show the typical bands of neutral primary (3, 4, 8-13) and *trans*-secondary (1, 2, 5-7, 14-16) amide groups. The absence of large systematic shifts of the characteristic amide modes $\nu_{as}(NH_2)$, $\nu_s(NH_2)$, $\nu(NH)$, $\delta(NH_2)$, $\delta(NH)$, $\rho(NH_2)$, $\omega(NH_2)$, $\tau(NH_2)$, $\pi(NH)$, $\nu(CO)$ and $\nu(CN)$ in the spectra of the Cu(I) complexes 5-16, compared with the frequencies in the spectra of the corresponding free ligands, implies that there is no interaction between the primary and secondary amide groups and Cu(I). For example, the $\nu(CO)$ vibration appears in the 1680-1670 cm^{-1} region in the spectra of $CuX(LH_2)$ (see Table 3), practically at the same frequency for free LH_2 (1675 cm^{-1}) [15]. In the spectra of the Cu(II) complexes 1-4 the $\nu(CO)$ band shifts considerably to lower frequencies, while the $\nu(CN)$ band shifts to higher frequencies, compared with the positions of these modes in LH_2 and SH_3, and also in their Cu(I) complexes. These shifts indicate amide coordination to Cu(II) through oxygen [2,3].

Although the $\nu(C'S)$ vibration is not pure [16,22], the bands with high $\nu(C'S)$ character in the spectra of all the complexes seem to be situated at lower frequencies than for the free ligands, whereas the $\nu(C'N)$ vibration shows a significant frequency increase. These shifts are consistent with thioamide sulfur coordination [8,21,22]. On coordination *via* sulfur, the positively charged metal ions stabilize the negative charge on the sulfur atom.

TABLE 3

Most Characteristic Fundamentals for the Cu(II) and Cu(I) Complexes of LH_2

$CuCl_2(LH_2)$	$CuBr_2(LH_2)$	$CuCl(LH_2)$		$CuBr(LH_2)$		$CuI(LH_2)$		
		IR	Raman	IR	Raman	IR	Raman	Assignments*
3247 vsb	3251 vsb	3305 sb		3296 sb		3293 sb		$\nu(NH)_{amide}$
3142 m	3135 m	3189 vs		3194 vsb		3188 sb		$\nu(NH)_{thio}$
1640 vs	1645 vs	1680 vs	1679 (1)	1679 vs		1670 vs		Amide I [$\nu(CO)$]
1579 s	1577 s	1560 vs	1557 (2)	1564 vs	1569 (1)	1548 vs	1552 (5)	Amide II [$\nu(CN)+\delta(NH)_{amide}$]
1552 s	1547 vs	1538 s	1525 (1)	1537 s	1530 sh	1516 s	1525 sh	$\nu(C'N)$
1328 ms	1325 m	1371 s	1375 (1)	1370 s		1360 m	1361 (1)	$\delta(NH)_{thio}$
		1253 m	1251 (5)	1255 m	1252 (1)	1245 m	1246 (9)	Amide III [$\nu(CN)+\delta(NH)_{amide}$]
1176 m	1175 m							Amide III [$\nu(CN)$ + $\delta(NH)_{amide}$],$\nu(NR)$
1086 m	1085 s	1080 w		1082 m	1082 (3)	1080 m	1080 (4)	$\rho(CH_3)$, $\nu(CC')$
1025 ms	1023 s	1054 s	1046 (5)	1051 s		1051 s	1051 (9)	$\rho(CH_3)$, $\nu(CC')$
964 ms	962 s	966 w	961 (4)	966 m	963 (1)	968 w	996 (5)	$\nu(CC')$
817 s	814 vs	825 m		824 m				$\nu(C'S)$
769 m	767 m	794 m	801 (5)	792 m	808 (10)	796 m	803 (3)	$\nu(C'S)$, $\delta(NCO)$
648 s	640 s	748 mb		744 mb		751 mb		$\pi(NH)_{amide}$
673 s	661 sh	661 m		645 m				$\pi(NH)_{thio}$

$CuCl_2(LH_2)$		$CuBr_2(LH_2)$		$CuCl(LH_2)$ IR		$CuCl(LH_2)$ Raman	$CuBr(LH_2)$ IR		$CuBr(LH_2)$ Raman	$CuI(LH_2)$ IR	$CuI(LH_2)$ Raman	Assignments*
^{63}Cu	^{65}Cu	^{63}Cu	^{65}Cu	^{63}Cu	^{65}Cu		^{63}Cu	^{65}Cu				
332.4 m	331.0 m	319.7 m	318.0 m	353.3 m	352.6 m	347 (2)	340.6 s	339.9 s		324 m		$\nu(CuS)$
301.5 s	300.1 s	230.0 s	228.8 s	219.4 m	218.6 m	224 (1)	153.1 s	152.8 s	148 (3)	110 m	107 (1)	$\nu(CuX)$
265.2 m	264.2 m	244.0 s	242.5 s									$\nu(CuO)$

*Assignments have been assisted by NH/ND, CH_3/CD_3, and *simultaneous* CH_3/CD_3 and NH/ND isotopic substitutions.

b = broad ; m = medium ; s = strong ; sh = shoulder ; v = very ; w = weak.

TABLE 4

Most Characteristic Fundamentals for the Cu(II) and Cu(I) Complexes of SH_3

$CuCl_2(SH_3)$		$CuBr_2(SH_3)$		$CuCl(SH_3)$		$CuBr(SH_3)$		$CuI(SH_3)$		
				IR	Raman	IR	Raman	IR	Raman	Assignments*
3338 sb		3342 sb		3430 vs		3431 vs		3430 vs		$\nu_{as}(NH_2)$
3205 s		3199 s		3315 s		3317 s		3318 s		$\nu_s(NH_2)$
3166 mb		3153 mb		3191 vs		3193 vs		3199 vs		$\nu(NH)$
1678 vs		1666 vs		1708 vs		1704 vs		1699 vs		$\nu(CO)$
1594 w		1586 sh								$\delta(NH_2)$
1572 vs		1563 vs					1564 (3)		1563 (4)	$\nu(C'N)$
				1569 vs	1570 (3)	1568 vs	1572 (3)	1566 vs	1569 (4)	$\nu(C'N)$, $\delta(NH_2)$
1434 m		1439 m		1429 m	1426 (1)	1419 mb	1410 (1)	1418 w	1425 (2)	$\nu(CN)$
1385 s		1406 m								$\delta(NH)$, $\delta(CH_3)$
				1374 s	1371 (4)	1372 vs	1370 (4)	1370 s	1368 (4)	$\delta(NH)$
1111 s		1101 s		1088 m		1083 m		1078 m		$\rho(NH_2)$
1056 s		1051 s		1046 m	1050 (3)	1040 m	1044 (3)	1035 m	1040 (2)	$\rho(CH_3)$, $\nu(CC')$
1001 s		999 m		1002 m	996 (10)	999 m	993 (10)	996 m	989 (10)	$\nu(CC')$, $\rho(CH_3)$
715 s		710 s		753 s		755 s		757 s		$\omega(NH_2)$
664 vsb		650 sb		695 sb	702 (5)	693 ms	700 (5)	691 m	698 (4)	$\pi(NH)$, $\delta(NCO)$
588 s		582 s		606 m	597 (6)	603 m	595 (5)	601 m	591 (5)	$\tau(NH_2)$, $\pi(NCO)$
^{63}Cu	^{65}Cu	^{63}Cu	^{65}Cu							
350.8 w	349.9 w	347.0 m	345.9 m	325 m	317 (1)	321 m	314 (2)	309 m	311 (3)	$\nu(CuS)$, $\pi(NR')$
300.5 s	296.8 s	234.0 m	232.5 m	234 m	228 (5)	187 m		97 m		$\nu(CuX)$
258.7 w	257.8 w	255.0 s	253.0 s							$\nu(CuO)$

*Assignments have been assisted by NH/ND, CH_3/CD_3, and *simultaneous* CH_3/CD_3 and NH/ND isotopic substitutions.

TABLE 5

The Infrared Vibrational Analysis (4000-100 cm^{-1}) of the Complexes $CuX(H_4MTO)_2$ (X = Cl, Br) and $CuI(H_4MTO)$

$CuCl(H_4MTO)_2$		$CuBr(H_4MTO)_2$	$CuI(H_4MTO)$	Assignments*
Normal	Deuterated			
3390 s		3375 vs	3378 s	$\nu_{as}(NH_2)$amide
3341 m		3341 vs	3355 sh	$\nu(NH_2)$
3317 s		3320 s		$\nu_{as}(NH_2)$thio
3223 s		3217 s	3227 s	$\nu_s(NH_2)$amide
3156 s		3162 s	3153 m	$\nu_s(NH_2)$thio
	2540 m			$\nu_{as}(ND_2)$amide
	2498 s			$\nu_{as}(ND_2)$thio
	2458 m			$\nu_s(ND_2)$amide
	2387 m			$\nu(ND_2)$
	2332 m			$\nu_s(ND_2)$thio
1700 m		1705 sh	1709 vs	$\nu(CO)$
1691 s	1690 s	1691 vs		$\nu(CO)$
1612 vs		1608 vs	1594 vs	$\delta(NH_2)$amide
1596 vs		1592 vs	1578 vs	$\delta(NH_2)$thio
1443 m	1507 vs	1441 s	1432 s	$\nu(C'N)$
1401 m	1415 m	1395 s	1378 m	$\nu(CN)$
	1385 s			$\nu(CN)$
	1312 s			$\delta(ND)$thio
	1274 s			$\delta(ND)$thio
1244 m		1239 s	1220 m	$\rho(NH_2)$thio
	1198 m			$\delta(ND_2)$amide
1102 m		1079 m	1092 m	$\rho(NH_2)$amide
	1007 m			$\rho(ND_2)$thio
933 m		926 s		$\nu(CC')$

TABLE 5 *(Contd.)*

$CuCl(H_4MTO)_2$		$CuBr(H_4MTO)_2$	$CuI(H_4MTO)$	Assignments*
Normal	Deuterated			
923 w		910 s		$\nu(CC')$
	918 m			$\rho(ND_2)_{amide}$, $\nu(CC')$
911 m		905 s		$\nu(CC')$
901 m			901 ms	$\nu(CC')$, $\nu(C'S)$
795 m	775 s	793 m	776 m	$\nu(C'S)$
738 mb		740 sb	739 mb	$\omega(NH_2)_{amide}$, $\nu(C'S)$
	690 m			$\delta(NCO)$
676 mb		670 sb	666 sh	$\omega(NH_2)_{thio}$, $\delta(NCO)$
			623 sb	$\delta(NCO)$, $\delta(NC'S)$
	605 m			$\omega(ND_2)_{amide}$, $\delta(NC'S)$
	586 mb			$\omega(ND_2)_{thio}$, $\delta(NC'S)$
563 mb		563 mb	558 mb	$\tau(NH_2)_{thio}$, $\delta(NC'S)$, $\tau(NH_2)_{amide}$
	516 mb			$\tau(ND_2)_{thio}$, $\pi(NCO)$
	485 mb			$\tau(ND_2)_{amide}$, $\pi(NC'S)$
	463 mb			$\pi(NC'S)$
430 w		431 w		$\rho(NCO)$, $\rho(NC'S)$
323 s	314 s	323 s	335 s	$\nu(CuS)$
250 w	247 w	170 m		$\nu(CuX)$
197 m	207 m	131 m	105 m	$\nu(CuX)$

* Overtones and combination bands have been omitted.

TABLE 6

The Infrared Vibrational Analysis (4000-100 cm^{-1}) of the Complexes $CuX(H_3MMTO)_2$ (X = Cl, Br, I)

$CuCl(H_3MMTO)_2$	$CuBr(H_3MMTO)_2$	$CuI(H_3MMTO)_2$	Assignments$^{*,+}$
3320 sb	3327 sb	3363 mb	$\nu_{as}(NH_2)$
		3331 m	$\nu_{as}(NH_2)$
		3308 s	$\nu(NH_2)$
3200 m	3196 m	3233 m	$\nu_s(NH_2)$
3141 m	3132 m	3173 m	$\nu(NH)$
1689 vs	1690 vs	1686 s	Amide I [$\nu(CO)$]
1625 w	1622 m	1609 m	$\delta(NH_2)$
1589 vs	1587 vs	1583 vs	$\delta(NH_2)$
1529 sb	1528 vsb	1526 m	$\nu(C'N)$,Amide II [$\nu(CN) + \delta(NH)$]
1438 m	1438 w	1429 m	$\delta(CH_3)$
1410 s	1410 s	1408 m	$\delta(CH_3)$
1283 m	1281 w		$\rho(NH_2)$
	1248 w		$\rho(NH_2)$
1225 s	1222 s	1221 m	Amide III [$\delta(NH) + \nu(CN)$]
1160 m	1161 m	1162 w	$\nu(NR)$
1052 m	1050 m	1059 m	$\rho(CH_3)$, $\nu(CC')$
928 s	925 s	933 m	$\nu(CC')$
		924 m	$\nu(CC')$
808 s	808 m	807 m	$\nu(C'S)$, $\nu(CC')$
799 m	794 m		$\nu(C'S)$, $\delta(NCO)$
784 mb	783 m		$\nu(C'S)$, $\delta(NCO)$
		747 m	$\delta(NCO)$
727 m	717 w	693 m	$\omega(NH_2)$
670 sh	677 sb	662 mb	$\pi(NH)$
652 sb	657 sb		$\pi(NH)$
568 s	567 s	604 m	$\tau(NH_2)$, $\delta(NC'S)$, $\pi(NCO)$
452 w	448 w	437 w	$\pi(NC'S)$
		393 m	$\rho(NCO)$

TABLE 6 *(Contd.)*

$CuCl(H_3MMTO)_2$	$CuBr(H_3MMTO)_2$	$CuI(H_3MMTO)_2$	Assignments*,+
386 s	390 s	384 m	ρ(NCO), ρ(NC'S)
337 s	334 m	330 mb	ν(CuS)
257 mb	183 m	108 m	ν(CuX)
244 w	147 w	104 m	ν(CuX)
194 m	191 mb	172 m	rv, lm

* Overtones, combination bands, the ν(CH_3) modes in the 3050-2850 cm^{-1} region and very weak bands in the low-frequency region have been omitted.

+ Assignments for all three complexes have been assisted by NH/ND, CH_3/CD_3, and *simultaneous* CH_3/CD_3 and isotopic substitutions.

rv = ring vibration ; lm = latice mode.

The thioamide function now occurs in its polar resonance form and, thus, the double bond character of the C'N bond increases, while the double bond character of the C'S bond decreases. The different magnitude of the ν(C'N) shift reflects the different polarization ability of Cu(II) and Cu(I). The greater the charge of the metal, the higher will be the frequency position of the C'N stretching vibration. Consideration of the spectra of the LH_2 and SH_3 complexes (only for these two ligands complexes of both Cu(II) and Cu(I) are available) shows that this trend is clear only for the complexes of LH_2; this is probably due to the fact that in the Cu(I) complexes of SH_3 (8-10), the ν(C'N) vibration overlaps with $\delta(NH_2)_{amide}$. For a given ligand, the ν(C'N) vibration in the Cu(I) complexes is found at higher wavenumbers according to the sequence iodo complex < bromo complex < chloro complex, implying a stronger Cu^I–S bond in the same sequence; this is also confirmed by the ν(Cu^IS) frequencies *(vide infra)*.

The study of the NH_2 and NH modes reveals that intermolecular hydrogen bonds of the N–H···X type exist in the Cu(II) complexes 1-4. According to the positions of the NH_2 and NH stretching and deformation bands, for a given ligand, the hydrogen bonding strength in the Cu(II)

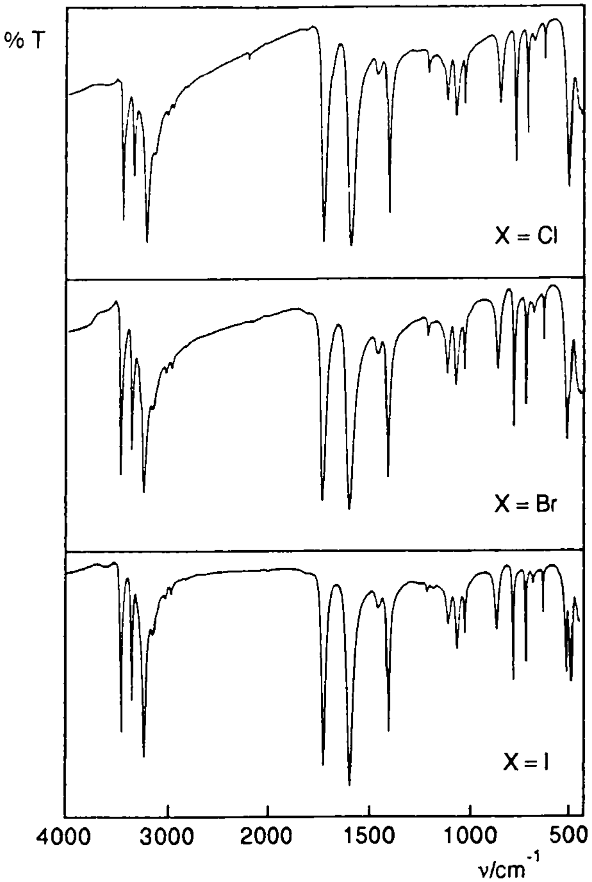


FIG.2. The FT-IR spectra of the complexes CuX(SH3) in the 4000-500 cm^{-1} region.

complexes increases on passing from the bromo to the chloro complexes, as expected [21,22]. The relative strength of the intermolecular hydrogen bonds in the Cu(II) compounds is demonstrated in the frequency of the pure ν(C'N) vibration, which is situated at a higher frequency in 1 than in 2, and in 3 than in 4. The higher frequency for the chloro complexes is in accord with a larger contribution of the polar resonance form to the structure of the thioamide function, due to stronger hydrogen bonding.

Assignments of far-IR and low-frequency Raman bands in Tables 3-6 have been carefully given by studying (i) the frequencies of the internal modes of the free ligands,(ii) bands principally dependent on X (X = Cl, Br, I) for a given ligand, (iii) variation in band position with NH/ND, CH_3/CD_3 and $^{63}Cu/^{65}Cu$ substitutions, and (iv) extensive literature reports [2, 3, 8, 10, 18, 19, 21, 23-26].

The frequencies of ν(CuS) and ν(CuO) in the Cu(II) complexes of SH_3 (3, 4) show that the Cu–S and Cu–O bond strengths are comparable between these complexes. In the Cu(II) complexes of LH_2 (1, 2), the rather great variation of ν(CuS) and ν(CuO) was unexpected. The positions of these two bands in all four complexes indicate a strong Cu–S bond and a rather weak Cu–O bond. The ν(Cu^IS) band in 5-16 is situated above 300 cm^{-1} indicating strong Cu^I–S bonds; it is well known [4] that copper(I), being a typical soft acid, forms strong interactions with soft ligands, *e.g.* sulfur. According to HSAB principles [4] the Cu^I–X bond strength increases according to the series Cl<Br<I. Therefore, for a given ligand, the electron density and the strength of the Cu^I–S bond, and also the ν(Cu^I–S) frequency increase in the opposite series, *i.e.*, I<Br<Cl. This trend is not observed between $CuBr(H_4MTO)_2$ and $CuI(H_4MTO)$, due to the coordination number change from 4 in the 1:2 bromo complex to 3 in the 1:1 iodo compound (see concluding comments). Bands at *ca.* 300 cm^{-1} in the far-IR spectra of $CuCl_2(LH_2)$ and $CuCl_2(SH_3)$, and at *ca.* 230 cm^{-1} in the far-IR spectra of the analogous bromo complexes, are consistent with terminal ν(CuX) (X = Cl, Br) [21,26]. The low frequencies of the ν(Cu^IX) modes in the spectra of the Cu(I) complexes 5-16 are clearly indicative of the existence of bridging copper(I)-halogen bonds in 3- or 4-coordinate environments [24]. The presence of two IR-active ν(Cu^IX) vibrations in the spectra of $CuX(H_4MTO)_2$ (X = Cl, Br) and $CuX(H_3MMTO)_2$ (X = Cl, Br, I) is a strong evidence of a dinuclear halogen-bridged structure of C_{2h} symmetry [26].

CONCLUDING COMMENTS

In summary, the results of this study show that the neutral monothiooxamides LH_2 and SH_3 behave as chelating S,O-ligands in the tetragonal Cu(II) complexes 1-4. According to the $CuX_2(AH_2)$ complexes

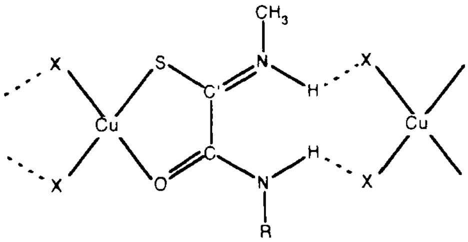


FIG. 3. The proposed structure of the complexes $CuX_2(LH_2)$ and $CuX_2(SH_3)$ (X = Cl, Br).

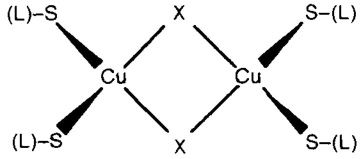


FIG. 4. The proposed dinuclear structure of the complexes $CuX(H_4MTO)_2$ (X = Cl, Br) and $CuX(H_3MMTO)_2$ (X = Cl, Br, I). (L)- denotes the remaining non-coordinated part of the neutral monothiooxamide ligand.

(AH_2 = various neutral dithiooxamides) [21], the present complexes may have a distorted C_{2v} (or C_2) structure (Fig. 3) ; weak axial associations, however, can not be ruled out. In the Cu(I) complexes the neutral monothiooxamides behave as monodentate ligands coordinating through their thioamide sulfur atom. All data for the 1:1 Cu(I) complexes (5-10, 13) suggest polymeric 3-coordinate structures with Cu^ISX_2 coordination spheres, formed by monodentate monothiooxamides and bridging halo ligands. Although it is difficult to decide on dimeric or polymeric structures, the solubility properties and the data from the vibrational study suggest rather a dimeric 4-coordinate structure for 11, 12 and 14-16 (Fig. 4).

The interesting chemical point of this work is the capability of neutral monothiooxamides to behave as O,S-chelating ligands towards relatively hard metal ions, like Cu(II). These ligands clearly exhibit a monodentate behaviour in their complexes with soft metal ions, like Cu(I) and Pd(II) [1].

From the vibrational spectroscopy point of view, the interest of this work arises from the fact that the nature of the fundamentals of metal complexes with neutral ligands having both amide and thioamide groups coordinated has been discussed for the first time.

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Date Received: May 14, 1993
Date Accepted: September 10, 1993