COORDINATION COMPOUNDS OF Cu(II) WITH THE NITROXYL RADICAL 2-ACETYL-2,5,5-TRIMETHYL-4-PHENYL-3-IMIDAZOLINE-3-OXIDE-1-OXYL THIOSEMICARBAZONE AND ITS 1-HYDROXY DERIVATIVE

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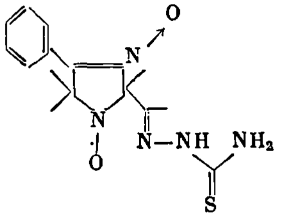
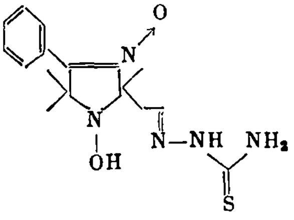
In the hitherto-known coordination compounds (CCs) with imidazolines containing the nitroxyl radical (NR), coordination of the ligand is brought about by the donor atoms of functional groups in the 3 and 4 positions of the heterocycle [1], the >N–O grouping not being involved in coordination [2]. Of special interest are CCs with a NR containing a donor functional group in the immediate vicinity of the radical center [3-6]. For this reason, the synthesis and physicochemical properties of CCs with 2-acetyl-2,5,5-trimethyl-4-phenyl-3-imidazoline-3-oxide-1-oxyl thiosemicarbazone (L^1H) have been studied. A feature of L^1H is the presence of a donor functional group in the 2 position of the heterocycle, rendering it possible for the metal ion to be coordinated at the thiosemicarbazone grouping and the >N–O fragment


(L^1H)


(L^2H)

The metal ion chosen was Cu(II), which has been used extensively for studies of CCs both with NRs and with thiosemicarbazones. In order to compare the structures and properties of the resulting CCs, in addition to the products of the reaction of Cu(II) salts with L^1H, CCs of Cu(II) with the diamagnetic L^2H were also examined.

EXPERIMENTAL

The reagents used in the preparation of the CCs were $CuCl_2\cdot 2H_2O$, $Cu(AcO)_2\cdot H_2O$, and KOH pure for analysis, ethanol rectified, chloroform "for narcosis," redistilled over P_4O_{10}, and redistilled methanol. The L^1H and L^2H were synthesized as described in [7]. L^1H was purified by chromatography on silica gel (L 40/100, eluent $CHCl_3$), and L^2H by recrystallization from ethanol. The compounds were characterized by their elemental analyses, and had the following properties: L^1H, mp 156-157°C, μ_{eff} 1.74 ± 0.03 B.m, $g = 2.0063$, $a_N = 13.7$ E, and L^2H, mp 206-207°C, diamagnetic. The IR spectra of L^1H and L^2H were in accordance with those given in [7].

The magnetic susceptibility of the solid samples was measured by Faraday's method. Diffractograms of the CCs were obtained on a DRON-UN-1 diffractometer using Cu K_α radiation. The EPR spectra of the compounds were obtained by E. G. Boguslavskii on an RE-1306 spectrometer. IR spectra (in KBr disks) were recorded on a Specord 75-IR spectrophotometer. Diffuse reflection spectra (DRS) of powders in the 400-1100 nm range were obtained using a Unicam SP-700A spectrophotometer, and electronic absorption spectra (EAS) on a Specord UV-VIS spectrophotometer. The electrical conductivity of solutions of the compounds was measured on an OK-102/1 conductivity meter.

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2,5,5-Trimethyl-4-phenyl-3-imidazoline-3-oxide-1-oxy-2-(1-thiosemicarbazonoethyl)dichlorocopper(II) [$CuCl_2(L^2H)$]. To a solution of 1 mmole of $CuCl_2 \cdot 2H_2O$ in 25 ml of methanol was added 1 mmole of L^2H or L^1H, and the mixture stirred for 0.5-1 h. The ligand dissolved, and the mixture became deep green in color. Methanol was distilled off until the volume reached 5-10 ml, and the bright-green solid which separated was filtered off, washed with cold methanol, and dried in vacuo over anhydrone (20 torr, 20°C). The other CCs were dried in the same way.

In the preparation of [$Cu(AcO)L^2 \cdot H_2O$] by the same method, the solvent was removed until the volume reached 2-3 ml. The CC was birch-green in color.

Hydroxido(2,5,5-trimethyl-4-phenyl-3-imidazoline-3-oxide-1-oxyl-2-(1-thiosemicarbazonatoethyl)copper(II) [$Cu(OH)L^1$]. To a suspension of freshly prepared copper(II) hydroxide in chloroform was added 1 mmole of L^1H or L^2H, and the mixture stirred for 1-2 h. During this time, the Cu(II) hydroxide partially dissolved, and the reaction mixture became deep violet in color. The solution was filtered, the solvent removed until the volume reached 5-10 ml, and hexane added until a solid separated. The deep violet solid was filtered off washed with hexane, and twice reprecipitated from chloroform with excess hexane. This CC was also obtained by treating [$CuCl_2(L^2H)$] with aqueous-alcoholic alkali.

Hydroxido(2,5,5-trimethyl-4-phenyl-3-imidazoline-3-oxide-1-oxy-trichloromethyl-2-(1-thiosemicarbazonatoethyl))copper(II) [$Cu(OH)L^3$]. A solution of 0.5 mmole of [$Cu(OH)L^1$] in 100 ml of chloroform was kept for 3 days at ∿20°C, and the solvent removed until the volume reached 15-20 ml. The green solid which separated was filtered off and washed with chloroform. The yield of [$Cu(OH)L^3$] was 30%, and of the other CCs, 60-70%. The elemental analyses and some properties of the compounds are shown in Tables 1 and 2. The compounds were stable in the solid state in air, the μ_{eff} values, IR spectra and DRS remaining unchanged over periods of several months. The complex [$CuCl_2(L^2H)$] was readily soluble in alcohols but sparingly soluble in water, [$Cu(OH)L^1$] was soluble in chloroform, and [$Cu(OH)L^3$] in chloroform and alcohols. The diffractometric data showed [$Cu(AcO)L^2 \cdot H_2O$] to be crystalline, the remaining CCs being x-ray amorphous.

DISCUSSION

Syntheses of CCs of Cu(II) with ligands containing the thiocarbonyl group are usually carried out in nonaqueous media in order to avoid possible difficulties arising as a result of redox reactions [8, 9]. In the present case, a convenient method for the preparation of the CC was by the reaction of methanolic solutions of Cu(II) salts with L^1H and L^2H. On reacting $CuCl_2 \cdot 2H_2O$ and $Cu(AcO)_2 \cdot H_2O$ with L^2H, compounds with the composition [$CuCl_2(L^2H)$] and [$Cu(AcO)L^2 \cdot H_2O$] respectively were isolated. This composition is characteristic of Cu(II) with a variety of thiosemicarbazones [9]. Also known are examples of the formation of intracomplex compounds when Cu(II) salts react with thiosemicarbazones in alcoholic media, including paramagnetic complexes [10]. The formation of bischelates of Cu(II) with L^1 and L^2 has not been reported. The μ_{eff} values of [$CuCl_2(L^2H)$] and [$Cu(AcO)L^2 \cdot H_2O$] correspond to the presence of a single unpaired electron (Table 2). The similar IR spectra of [$Cu(AcO)L^2 \cdot H_2O$] and [$Cu(OH)L^1$] differ from that of [$CuCl_2(L^2H)$] at 1300-1650 and 3000-3600 cm^{-1}. The greatest changes in the IR spectra of the CCs as compared with those of the free ligands are seen at 3100-3450 (νNH) and 1500-1650 cm^{-1} ($\nu C{=}N$). An unambiguous assignment of the $\nu C{=}N$ bands in the IR spectra of the CCs is complicated by the presence of several other C=N bonds, and furthermore δNH absorption also occurs in this region together with, in the case of [$Cu(AcO)L^2 \cdot H_2O$], stretching vibrations of the carboxyl group. However, the considerable differences in the absorption of the CCs at 1550-1650 cm^{-1} as compared with that of L^1H and L^2H are undoubtedly due to coordination of the copper atoms by the thiosemicarbazone grouping. The IR spectra of L^1H and L^2H show strong absorption at 840 cm^{-1}, principally due to $\nu C{=}S$, whereas there is no absorption of even medium intensity in this region in the spectra of any of the CCs, indicating that the sulfur atom of the thiosemicarbazone grouping is coordinated. In aqueous solution, [$CuCl_2(L^2H)$] is a 1:2 electrolyte (Table 1). The fact that the molecular electrical conductivity of methanolic solutions of [$CuCl_2(L^2H)$] is less than would be expected for a 1:2 electrolyte indicates that some of the anions are coordinated by copper atoms [11]. The following structure for [$CuCl_2(L^2H)$] is therefore proposed:

TABLE 1. Elemental Analyses and Properties of the Compounds Obtained

Compound	mp, °C	Found/Calculated %				ν, cm^{-1}*
		M	C	H	N	
$[CuCl_2(L^2H)]$ †	204–206	13,6/13,5	38,8/38,3	4,8/4,5	15,4/14,9	1118, 1167, 1563, 1632, 3260, 3396
$[Cu(AcO)L^2 \cdot H_2O]$	182–184	13,3/13,4	42,9/42,9	5,1/5,1	14,6/14,7	1172, 1350, 1480, 1600
$[Cu(OH)L^1]$	190–192	14,9/15,3	43,1/43,4	4,6/4,9	16,6/16,9	1167, 1353, 1490, 1593
$[Cu(OH)L^3]$ ‡	201–203	11,6/11,9	36,1/36,1	4,2/4,0	13.2/13.2	747, 1169, 1338, 1353, 1485, 1600, 1617

*Strongest absorption in the IR spectra.

†Found, Cl 14.8%, calculated 15.1%. The molecular electrical conductivity of solutions of $[CuCl_2(L^2H)]$ in water at 20°C 15 min after preparation (C, mole/liter) was 267 ($3.38 \cdot 10^{-3}$), 316 ($1.13 \cdot 10^{-3}$); in methanol, 80 ($2.5 \cdot 10^{-3}$).

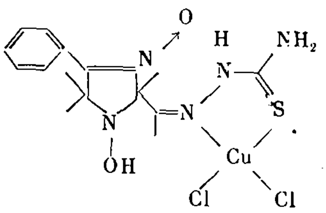
‡Found, Cl 20.8%, calculated 20.0%.

TABLE 2. Magnetic Moments and Electronic Spectral Data

Compound	μ_{eff}, m.B (T, °K)	Electronic spectra	
		absorption,* λ_{max}, nm (log $\bar{\varepsilon}$)	reflection, λ_{max}, nm
$[CuCl_2(L^2H)]$	1,82±0,06(294)	355(3.5), 700(2,3)	(340), 820
$[Cu(AcO)L^2 \cdot H_2O]$	1.82±0,05(295)	–	370, 640
$[Cu(OH)L^1]$	diamagnetene	† 382(3,5), 568(3,5)	380, 580
$[Cu(OH)L^3]$	1,99±0,03(292)	380(3,0), 609(2,3)	380, 615

*$[CuCl_2(L^2H)]$ solution in methanol; $[Cu(OH)L^1]$ and $[Cu(OH)L^3]$ in chloroform.

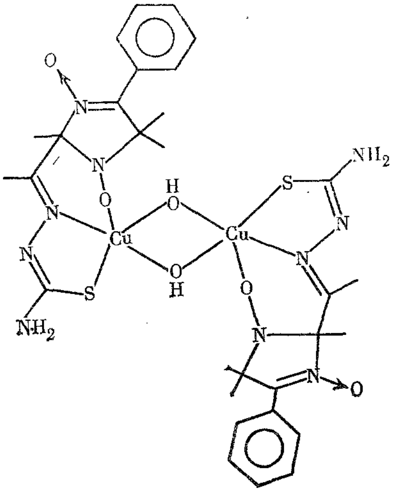
†Five minutes after preparing the solution.



It was not possible to measure the electrical conductivity of either methanolic or ethanolic solutions of $[Cu(AcO)L^2 \cdot H_2O]$ since in these solvents the CCs, as described below, are rapidly converted into $[Cu(OH)L^1]$.

When $CuCl_2 \cdot 2H_2O$ reacts with the NR L^1H in methanol, a CC is obtained which, from its spectral and analytical properties, is identical with the product of the reaction of $CuCl_2 \cdot 2H_2O$ with the diamagnetic L^2H, indicating that in the system $CuCl_2$–L^1H–MeOH the grouping $>N \to O$ is reduced to $>N{-}OH$. The formation of $[CuCl_2(L^2H)]$ during the reaction of $CuCl_2 \cdot 2H_2O$ with L^1H has also been observed in $CHCl_3$, CH_2Cl_2, and acetone. This reduction of the NR is undoubtedly due to the presence of Cu(II) in the reaction mixture. In the absence of Cu(II) salts, L^1H is quite stable in alcohols (methanol and ethanol), and can readily be recrystallized therefrom without loss of paramagnetism. Di(tert-butyl)nitroxyl is known to catalyze the oxidation of methanol in the presence of Cu(II) salts to give formaldehyde, being itself reduced to the hydroxylamine [12]. It is assumed that similar reactions occur in the system $CuCl_2$–L^1H–MeOH. A study of the oxidation products of acetone, $CHCl_3$, and CH_2Cl_2 will require a separate investigation.

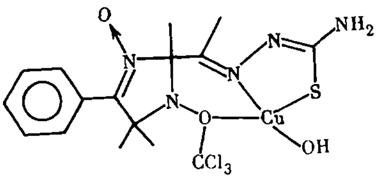
Reaction of freshly prepared Cu(II) hydroxide with a solution of L^1H in $CHCl_3$ or methanol gives the CC $[Cu(OH)L^1]$. The EPR spectra of the powdered CC and its solution in chloroform show low-intensity signals for Cu(II) and a triplet for the NR which cannot be attributed to the bulk of the compound. Measurement of the magnetic susceptibility of powdered $Cu(OH)L^1$ showed (Table 1) that the compound is diamagnetic. This is difficult to explain in terms of a redox reaction between Cu(II) and the $>\!N\overset{\cdot}{-}O$ group. The electronic spectra of CCs of Cu(I) with ligands possessing donor atoms similar to LH [13], differ considerably from the EAS of $[Cu(OH)L^1]$. The assumption that Cu(II) is oxidized to Cu(III) with the formation of the $>\!N-O^-$ anion is not in accordance with the formation, described below, of $[Cu(OH)L^1]$ when either L^1H or L^2H is used as the ligand. The most likely reason for the diamagnetism of $[Cu(OH)L^1]$ is, in our view, strong antiferromagnetic interaction between the unpaired electrons of Cu(II) and the NR arising as a result of coordination of the $>\!N\overset{\cdot}{-}O$ group by the Cu(II) ion. Support for this view is provided by the increase in the intensities of the signals for the NR and Cu(II) ions when pyridine is added to a chloroform solution of $[Cu(OH)L^1]$, thus displacing the $>\!N\overset{\cdot}{-}O$ group from the coordination sphere. This increase in the intensity of the EPR signal is independent of the concentration of dissolved oxygen, since the increase in the intensity of the signal is the same for solutions of $[Cu(OH)L^1]$ which had been flushed out with argon for a considerable length of time and for solutions which had not been flushed out. The appearance of a charge-transfer band at 568 nm (Table 2) in the EAS of $[Cu(OH)L^1]$ solutions may also be attributed to coordination of the $>\!N\overset{\cdot}{-}O$ group by the Cu(II) ion. It is at this stage difficult to decide whether the antiferromagnetic effect is mediated by coordination of the $>\!N\overset{\cdot}{-}O$ by one or more than one Cu(II) atoms. Ebullioscopic measurement of the molecular mass of samples of $[Cu(OH)L^1]$ in chloroform, in which the CC is quite soluble, gives values close to those calculated for $[Cu(OH)L^1]_2$: found, 830, 850; calculated 828. This finding should, however, be treated with caution since $[Cu(OH)L^1]$ is unstable in chloroform, especially on heating. The following version of the structure of $[Cu(OH)L^1]_2$ is proposed:



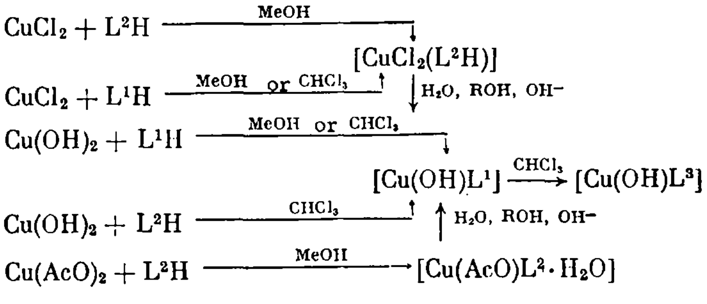
The decrease with time in the intensity of the EAS bands in solutions of $[Cu(OH)L^1]$ in chloroform indicates that the CC undergoes conversion. Keeping the solution for 5-6 h at $\sim$20°C results in a decrease in the intensity of the band with λ_{max} 568 by approximately an order of magnitude, while λ_{max} is slowly displaced to longer wavelengths. After 1 day, the color of the solution changes from deep violet to bright green, and absorption with λ_{max} 609 nm is seen in the visible region of the EAS. The absorption maxima in the EAS of freshly prepared chloroform solutions of $[Cu(OH)L^1]$ and the DRS of this CC are similar, showing that the immediate environment of the central atom remains unchanged with respect to its structure and symmetry on dissolution. In the solid state $[Cu(OH)L^1]$, as mentioned above, is quite stable.

Periodic recording of the EAS of solutions of $[Cu(OH)L^1]$ over the range 333-714 nm shows a family of optical density curves with an isobestic point at 365 nm, indicating that a first-order reaction is taking place in the system. Treatment of the kinetic plot as described in [14], for the reaction in chloroform freed from ethanol and redistilled over P_4O_{10} gives a rate constant of $(2.11 \pm 0.41) \cdot 10^{-5} sec^{-1}$ (25°C) (the error figure was obtained by least squares). The need for complete removal of ethanol from the chloroform is dictated by the considerable increase in the reaction rate as the alcohol concentration is increased. When solutions of $[Cu(OH)L^1]$ in chloroform are stored, a precipitate of $[Cu(OH)L^3]$ separates, the composition of which corresponds to the addition of a CCl_3 group to $[Cu(OH)L^1]$. The mass spectrum of $[Cu(OH)L^3]$ shows a peak for the molecular ion with m/z 533. The IR spectrum of $[Cu(OH)L^3]$, which is similar to that of $[Cu(OH)L^1]$, shows strong νC–Cl absorption at 747 cm^{-1}. The EAS spectral characteristics of a solution of pure $[Cu(OH)L^3]$ are identical with those of a solution of $[Cu(OH)L^1]$ which has been kept for 2-3 days. These observations provide a rationale for the first-order reaction of $[Cu(OH)L^1]$ in chloroform. The kinetic measurements were carried out in solutions of CC concentration $1.7 \cdot 10^{-4}$ M, the concentration of chloroform remaining unchanged. so that in practice the kinetic plot was obtained under pseudo-first-order conditions.

Unlike $[Cu(OH)L^1]$, $[Cu(OH)L^3]$ is paramagnetic (Table 2), the μ_{eff} value corresponding to the presence of a single unpaired electron in the CC molecule, this value remaining virtually constant as the temperature was reduced from 293 to 77°K. The EPR spectrum of a solution of this compound showed one signal only due to Cu(II) ions. It appears that the trichloromethyl group is bonded to the nitroxyl group to form the grouping $>N-O-CCl_3$. The probable structure of $[Cu(OH)L^3]$ may be represented as follows:



In order to compare the chemical behavior of the diamagnetic L^2H with the paramagnetic L^1H, the product of the reaction of L^2H in chloroform with freshly prepared Cu(II) hydroxide was studied. It was found to be identical in its structure and properties to $[Cu(OH)L^1]$, i.e., L^2H is oxidized to L^1H during complex formation. The conversion into $[Cu(OH)L^1]$ and $[CuCl_2(L^2H)]$ on treatment with aqueous or aqueous-alcoholic alkali is virtually instantaneous. Rapid, and on addition of alkali almost instantaneous, conversion into $[Cu(OH)L^1]$ is also undergone by $[Cu(AcO)L^2 \cdot H_2O]$ when treated with water, methanol, or ethanol. These reactions of compounds of Cu(II) with L^1H and L^2H may be represented as follows:



R = Me, Et.

The conversion of $[CuCl_2(L^2H)]$ and $[Cu(AcO)L^2 \cdot H_2O]$, obtained in neutral and slightly acid solution, respectively, into CCs with L^1 on addition of alkali leads to the conclusion that the alkaline medium facilitates the oxidation of the hydroxylamino group to nitroxyl in the presence of Cu(II) salts. This effect of Cu(II) salts on the efficient oxidation of a hydroxylamino derivative of imidazoline to the NR in alkaline medium, as noted previously [15], is of a similar type to that occurring with piperidine derivatives [16]. This leads to the conclusion that the efficient oxidation of hydroxylamines to the corresponding nitroxyls in alkaline media in the presence of Cu(II) salts is a fairly general reaction.

CONCLUSIONS

1. During the formation of complexes of Cu(II) with 2-acetyl-2,5,5-trimethyl-4-phenyl-3-imidazoline-3-oxide-1-oxyl thiosemicarbazone, which has a donor functional group adjacent

to the radical center, in methanol, chloroform, CH_2Cl_2, or acetone, the nitroxyl group of the ligand is reduced to the hydroxylamine. In alkaline solution, on the other hand, in the presence of Cu(II) salts the hydroxylamine group of 2-acetyl-2,5,5-trimethyl-4-phenyl-3-imidazoline-1-hydroxy-3-oxide thiosemicarbazone is converted into the nitroxyl.

2. The coordination compound with the nitroxyl radical is diamagnetic, apparently owing to strong antiferromagnetic interaction between the unpaired electrons of the paramagnetic centers arising as a result of coordination of the $>\mathrm{N}\dot{-}\mathrm{O}$ group by the Cu(II) ion.

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