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# Stabilization of Oxidation State Two of Copper in Thiourea Complexes

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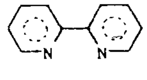
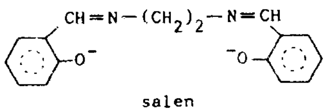
*Six new mixed thiourea-complexes of Cu$^{II}$, in which the oxidation state two for metal is stabilized by suitable ligands, have been obtained*: Cu(dip)$_2$tu(ClO$_4$)$_2$ (dip = *2,2'-bipyridyl;* tu = *thiourea*); Cu(fen)$_2$tu(ClO$_4$)$_2$H$_2$O (fen = *1,10-phenanthroline*); Cu(salen)tu (salen = *bis(salicylaldehyde)ethylenediimine*); Cu(pib)tu(ClO$_4$)$_2$ (pib = *N,N'-tetramethylenebis(2-pyridinaldimine)*); Cu(tac)tu½H$_2$O (tac = *bis(acetylacetone)trimethylenediimine*); Cu$_2$(pid)$_2$tu2H$_2$O (pid = *2,6-pyridinedicarboxylic anion*). *The electronic spectra and magnetic properties are discussed in terms of their probable structure. The main vibrational bands of coordinated thiourea are also assigned.*

## Introduction

The reducing properties of thiourea are well known and Cu$^I$ complexes are usually obtained with this ligand, even when Cu$^{II}$ is used.[1,2,3,4,5,6,7] Nevertheless, it was found that when copper is surrounded by suitable ligands (*e.g.*: picolinic acid),[8,9] the oxidation state two of the metal atom can be stabilized in the presence of thiourea. The present paper deals with the synthesis and characterisation of six new Cu$^{II}$-thiourea complexes, prepared from reaction of thiourea with Cu$^{II}$ chelated complexes with π-acceptor ligands: 1,10-phenanthroline (*fen*); 2,2'bipyridyl (*dip*); bis(salicylaldehyde)ethylenediimine(*salen*); *bis*(acetylacetone)trimethylenediimine(*tac*); N,N'-tetramethylenebis(2-pyridinaldimine)(*pib*); 2,6-pyridinedicarboxylic anion (*pid*).



dip



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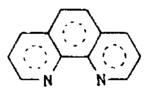

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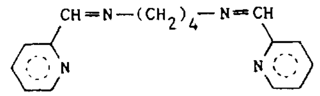

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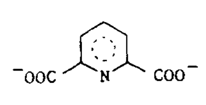

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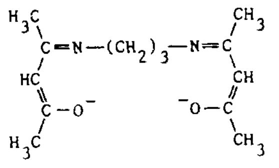

tac

The infrared and electronic spectra and magnetic properties for these complexes are discussed.

## Experimental Section

*Analyses.* Carbon, hydrogen, and nitrogen were determined with a Perkin-Elmer Mod. 240 automated equipment, metals gravimetrically by standard methods.

*Physical Measurements.* Magnetic measurements were carried out by the Gouy balance (Newport Instruments) using mercury(II) tetrathiocyanatocobaltate(II) as a standard.

Infrared spectra were obtained by a Perkin-Elmer Mod. 457 spectrophotometer using the KBr technique. The diffuse reflectance electronic spectra were measured on a Perkin-Elmer Mod. 402 spectrophotometer.

*Preparation of the Cu$^{II}$ complexes without thiourea.* The following compounds have been prepared as described in literature: N,N'-tetramethylenebis(2-pyridilaldimine)copper(II) perchlorate;[10] bis(1,10-phenanthroline)copper(II) perchlorate;[11] bis(2,2'-bipyridyl)-copper(II) perchlorate;[11] bis(avetylacetone)trimethylenediiminocopper(II);[12] bis(salicylaldehyde)ethylenediiminocopper(II);[13] 2,6-pyridinedicarboxylatecopper(II) dihydrate.[14]

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*Bis(1,10-phenanthroline)thioureacopper(II) Perchlorate.* Thiourea was added to a solution of bis(1,10-phenanthroline)copper(II) perchlorate in water. After stirring for several minutes, the colour changed from blue to green and by evaporating the solution yellow-green crystals of the complex were obtained. The complex was recrystallized from water-ethanol.

*Bis(2,2′-bipyridyl)thioureacopper(II) Perchlorate.* This preparation was similar to that described above except that bis(2,2′-bipyridyl)copper(II) perchlorate was introduced instead of the phenanthroline derivative. The complex was isolated as green elongated crystals.

*Bis(salicylaldehyde)ethylenediiminothioureacopper-(II).* Thiourea was added to a suspension of bis(salicylaldehyde)ethylenediiminocopper(II) in ethanol, and the mixture was stirred at about 70°C, for three hours. After a day the colour changed from yellow-green to mauve-brown. The cristalline product was separated by evaporating the solvent.

*Bis(acetylacetone)trimethylenediiminothioureacopper(II) Hemihydrate.* A methanol solution of thiourea and bis(acetylacetone)trimethylenediiminocopper-(II) was strired for an hour; after cooling in an ice-bath, the grey-green complex was isolated and collected by filtration.

*N,N′-Tetramethylenebis(2-pyridinaldimine)thioureacopper(II) Perchlorate.* Thiourea in ethanol was added, with stirring, to N,N′-tetramethylenebis(2-pyridinaldimine)copper(II) perchlorate, suspended in ethanol. After two days, green crystals of the complex were separated.

*Bis(2,6-pyridinedicarboxylate)thioureadicopper(II) Dihydrate.* Thiourea and 2,6-pyridinedicarboxylate-copper(II) dihydrate, in ethanol suspension, were stirred for about three hours. The resulting green product was collected by filtration and recrystallized from ethanol.

**Table I.** Analytical Data.

| Complex | | %Cu | %C | %H | %N |
|---|---|---|---|---|---|
| $Cu(\mathit{dip})_2\mathit{tu}(ClO_4)_2$ | calc. | 9.8 | 38.7 | 3.1 | 12.9 |
| | obs. | 10.1 | 38.3 | 3.0 | 13.0 |
| $Cu(\mathit{fen})_2\mathit{tu}(ClO_4)_2H_2O$ | calc. | 8.9 | 41.9 | 3.1 | 11.7 |
| | obs. | 8.9 | 41.5 | 3.0 | 11.5 |
| $Cu(\mathit{salen})\mathit{tu}$ | calc. | 15.7 | 50.3 | 4.5 | 13.8 |
| | obs. | 15.9 | 49.9 | 4.6 | 13.6 |
| $Cu(\mathit{pib})\mathit{tu}(ClO_4)_2$ | calc. | 10.5 | 33.7 | 3.7 | 13.9 |
| | obs. | 10.9 | 33.9 | 3.8 | 13.8 |
| $Cu(\mathit{tac})\mathit{tu}\frac{1}{2}H_2O$ | calc. | 16.5 | 43.7 | 6.6 | 14.6 |
| | obs. | 16.9 | 44.1 | 6.8 | 14.1 |
| $Cu_2(\mathit{pid})_2\mathit{tu}2H_2O$ | calc. | 22.3 | 31.9 | 3.2 | 9.8 |
| | obs. | 21.9 | 31.7 | 2.8 | 10.2 |

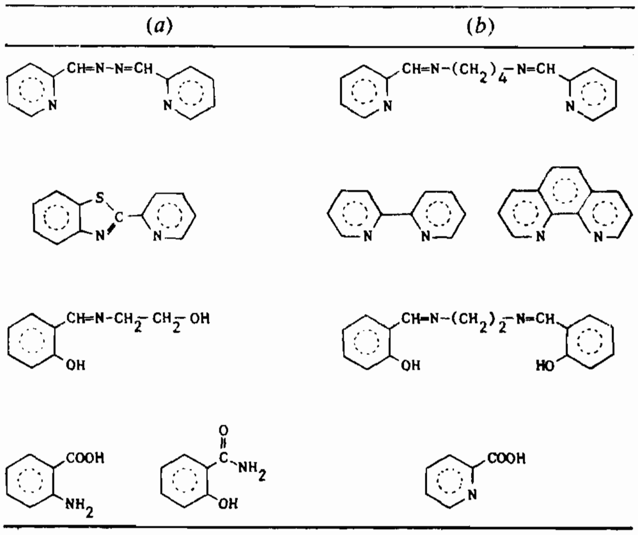
*tu* = thiourea; *dip* = 2,2′-bipyridyl; *fen* = 1,10-phenanthroline; *salen* = bis(salicylaldehyde)ethylenediimine; *pib* = N,N′-tetramethylenebis(2-pyridinaldimine); *tac* = bis(acetylacetone)-trimethylenediimine; *pid* = 2,6-pyridinedicarboxylic anion.

Table I lists the analytical data.

## Results and Discussion

The stabilization of the oxidation state two for copper is probably due to the strong chelating ability of the ligands with π bonding from metal to ligand which produces some electron delocalisation in the chelate ring. This seems the main property the ligand must show in order to get mixed thiourea-complexes of $Cu^{II}$, as can be seen from the comparison given in Table II for the ligands which are able to do this and those giving $Cu^{II}$-complexes easily reduced by thiourea.

**Table II.** Ligands giving: (*a*) $Cu^{II}$-Complexes which are easily reduced by Thiourea to $Cu^{I}$, (*b*) $Cu^{II}$ Mixed-Complexes with Thiourea.



The infrared bands, due to the organic molecule and observed in the spectra of the six $Cu^{II}$ complexes without thiourea, are present at almost the same frequencies in the spectra of the corresponding $Cu^{II}$-thiourea complexes; the only significant differences are due to the presence of the thiourea vibrational bands. The bands, in the 3500-3100 cm$^{-1}$ region, are assigned to the N–H stretching vibrations, excepting for the water bands which appear in $Cu(\mathit{fen})_2\mathit{tu}(ClO_4)_2H_2O$ (3500 cm$^{-1}$), $Cu(\mathit{tac})\mathit{tu}\frac{1}{2}H_2O$( 3505 cm$^{-1}$), and $Cu_2(\mathit{pid})_2\mathit{tu}2H_2O$ (3500 cm$^{-1}$). A higher number of bands, which can be also assigned to the N–H stretching vibrations, is observed in the $Cu(\mathit{dip})_2\mathit{tu}(ClO_4)_2$ spectrum. The band observed at about 1600 cm$^{-1}$ can be assigned to the $NH_2$ bending vibrations, and that near to 1400 cm$^{-1}$ to the $NH_2$ rocking and to N–C–N and C=S stretching modes. A band occurs at 730 cm$^{-1}$ which can be attributed primarily to C–S stretching with some contribution from N–C–N stretching.[15,16] The main infrared bands for uncoordinated and complexed thiourea are compared in Table III. The free thiourea bands at 1412 and 730 cm$^{-1}$ are shifted by 10 cm$^{-1}$ in the case of $Cu^{II}$-complexes and by 15-20 cm$^{-1}$ in the case of $Cu^{I}$-

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**Table III.** Selected Infrared Absorption Bands (cm$^{-1}$) of Thiourea and Copper Complexes.

| Compound | δ($NH_2$) | ν(C=S), ν(NCN) | ν(C=S) ν(NCN) |
|---|---|---|---|
| *tu* | 1618s | 1412s | 730s |
| $\mathrm{Cu}(\mathit{tu})_3\mathrm{Cl}$ | 1592s | 1379br | 710s |
| $\mathrm{Cu}_2(\mathit{tu})_5\mathrm{SO}_4.2\mathrm{H}_2\mathrm{O}$ | 1600s | 1385s | 710s |
| $\mathrm{Cu}(\mathit{dip})_2\mathit{tu}(\mathrm{ClO}_4)_2$ | 1625s | 1423sh | 715sh |
| $\mathrm{Cu}(\mathit{fen})_2\mathit{tu}(\mathrm{ClO}_4)_2\mathrm{H}_2\mathrm{O}$ | 1613s | 1415sh | (720)s |
| $\mathrm{Cu}(\mathit{salen})\mathit{tu}$ | 1620s | 1400w | 730s |
| $\mathrm{Cu}(\mathit{pib})\mathit{tu}(\mathrm{ClO}_4)_2$ | 1618s | 1405s | 721m |
| $\mathrm{Cu}(\mathit{tac})\mathit{tu}½\mathrm{H}_2\mathrm{O}$ | 1620s | 1407sh | (742)s |
| $\mathrm{Cu}_2(\mathit{pid})_2\mathit{tu}2\mathrm{H}_2\mathrm{O}$ | (1615)sh | 1420m | 720sh |

s = strong; sh = shoulder; br = broad; w = weak; m = medium.

**Table IV.** Colour, Magnetic and Spectrophotometric Properties of Copper(II) Complexes.

| Complex | colour | μ(B.M.) | θ(°K) | $\lambda_{max}$(nm) |
|---|---|---|---|---|
| $\mathrm{Cu}(\mathit{dip})_2\mathit{tu}(\mathrm{ClO}_4)_2$ | green | 2.02 | 10.0 | 770 |
| $\mathrm{Cu}(\mathit{fen})_2\mathit{tu}(\mathrm{ClO}_4)_2\mathrm{H}_2\mathrm{O}$ | yellow-green | 1.91 | 2.1 | 840 |
| $\mathrm{Cu}(\mathit{salen})\mathit{tu}$ | mauve-brown | 1.88 | 8.1 | 555 |
| $\mathrm{Cu}(\mathit{pib})\mathit{tu}(\mathrm{ClO}_4)_2$ | green | 2.21 | 8.1 | 670 |
| $\mathrm{Cu}(\mathit{tac})\mathit{tu}½\mathrm{H}_2\mathrm{O}$ | grey-green | 1.81 | 8.2 | 620-630 |
| $\mathrm{Cu}_2(\mathit{pid})_2\mathit{tu}2\mathrm{H}_2\mathrm{O}$ | green | 1.94 | 4.8 | 680 |

complexes. This fact suggests that the M–S bonds in the $Cu^{II}$-complexes are probably weaker than those in the $Cu^{I}$-complexes.

Magnetic susceptibility was measured by using a Gouy's balance and the effective magnetic moment was calculated from the expression $\mu_{eff} = 2.83 \sqrt{\chi'_M T}$ ($\chi'_M$ = molar srusceptibility corrected using Pascal's constants).[17] All the copper(II)-complexes show normal magnetic moments for $d^9$ ions (see Table IV). The temperature dependence of susceptibility obeys the Curie-Weiss law; the positive values of the Weiss constant θ (Table IV) are all small, so ferromagnetic interactions are excluded.

The electronic spectra of all the complexes were examinated in the solid state (350-850 nm), as they are or slightly soluble in all the common solvents or unstable in solution.

$\mathrm{Cu}(\mathit{pib})\mathit{tu}(\mathrm{ClO}_4)_2$, $\mathrm{Cu}(\mathit{dip})_2\mathit{tu}(\mathrm{ClO}_4)_2$ and $\mathrm{Cu}_2(\mathit{pid})_2\mathit{tu}2\mathrm{H}_2\mathrm{O}$ show absorption maxima at 670, 770, and 680 nm respectively. These spectra show strong similarities to that of bis[pyridine-2-(N-cianocarboxamidato)]aquocopper(II)[18] and dichloro-N-2-methylthiophenyl-2′-pyridylmethyleneiminacopper(II),[19] in which pentacoordination around copper is present. Recently, the X-ray crystallographic analysis[20,21] has confirmed for $\mathrm{Cu}(\mathit{pib})\mathit{tu}(\mathrm{ClO}_4)_2$ and $\mathrm{Cu}(\mathit{dip})_2\mathit{tu}(\mathrm{ClO}_4)_2$ the presence of a distorted trigonal bipyramidal coordination. The complex $\mathrm{Cu}(\mathit{tac})\mathit{tu}½\mathrm{H}_2\mathrm{O}$ shows a band at 620-630 nm, which may be compared with that at 630 nm exhibited by bis(picolinato)bis(thiourea)copper(II) and bis(picolinato)bis(allylthiourea)copper(II),[22] where copper is surrounded by six atoms at the vertices of an elongated distorted tetragonal bipyramid.

The band observed at 555 nm in the spectrum of $\mathrm{Cu}(\mathit{salen})\mathit{tu}$ is consistent with a square-planar coordination.[23] The absorption maximum in the spectrum of $\mathrm{Cu}(\mathit{fen})_2\mathit{tu}(\mathrm{ClO}_4)_2$ appears at about 840 nm suggesting a distorted tetrahedral coordination.[23,24]

Since all the spectra, in the examinated region, show only one very broad absorption band and there is not a certain evidence of components, it is impossible to give an accurate assignment.

The X-ray structural analysis of the complexes described in the present communication, is going on in our Laboratory with the aim of defining the structural situation of thiourea in them.

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