

Copper(I) Complexes of Rhodanine

Antonio C. Fabretti, Giorgio Peyronel* and Gian Carlo Franchini

Istituto di Chimica Generale e Inorganica, University of Modena, 41100 Modena, Italy

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Summary

Some new crystalline copper(I) complexes of rhodanine (HL) have been prepared and studied by i.r. and conductometric methods. The neutral ligand is bonded to the metal atom through the thiocarbonylic sulphur atom. The $\text{Cu}(\text{HL})_2\text{OH} \cdot 0.5\text{H}_2\text{O}$ complex has a dimeric tetrahedral hydroxyl-bridged structure as have the isostructural halides $\text{Cu}(\text{HL})_2\text{X}$ ($\text{X} = \text{Cl}, \text{Br}$ and I) for which the halide-bridged stretching bands have been identified. The $\text{Cu}(\text{HL})_3\text{A}$ ($\text{A} = \text{ClO}_4, \text{BF}_4, 0.5\text{SO}_4$ and CF_3CO_2) complexes have monomeric distorted tetrahedral structures with the anion bonded to the metal.

Introduction

The copper(I) complexes of rhodanine, HL, $\text{Cu}(\text{HL})_2\text{X}$ ($\text{X} = \text{Cl}, \text{Br}$ and I) and $\text{Cu}(\text{HL})\text{Cl}$ have been investigated previously by i.r. ($4000\text{--}200\text{ cm}^{-1}$) and by n.m.r. spectroscopy⁽¹⁾ which shows that the ligand is bonded to the metal through the thiocarbonylic sulphur atom. Some new copper(I) complexes of rhodanine were prepared and the investigation of this class was extended to the far i.r. region (down to 60 cm^{-1}). Some new data is reported for already known complexes⁽¹⁾ in order to provide a comparison with the new complexes.

Experimental

$\text{Cu}(\text{HL})_2\text{X}$ ($\text{X} = \text{Cl}, \text{Br}$ and I)

These complexes were prepared by the method (c) described in the literature⁽¹⁾.

* Author to whom all correspondence should be directed.

$\text{Cu}(\text{HL})_2\text{OH} \cdot 0.5\text{H}_2\text{O}$

The compound was obtained by adding either a) a solution of HL (2 mmol) in EtOH (10 cm^3) to the brown suspension formed by adding an EtOH solution of NH_3 (2 mmol) to a solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (1 mmol) in EtOH (10 cm^3) or b) a solution of HL (2 mmol) in EtOH (20 cm^3) to a solution of $\text{Cu}(\text{O}_2\text{CMe})_2 \cdot \text{H}_2\text{O}$ (1 mmol) and sodium acetate (2 mmol) in 95% EtOH (140 cm^3); the microcrystalline yellow-brown precipitate was washed with EtOH and Et_2O and dried *in vacuo*.

$\text{Cu}(\text{HL})_3\text{A}$ ($\text{A} = \text{ClO}_4, \text{BF}_4$ and CF_3CO_2)

A solution of the copper(II) salt (1 mmol) in the corresponding concentrated acid ($1.5\text{--}2.0\text{ cm}^3$) was added to a solution of HL (6 mmol) in glacial acetic acid (30 cm^3); the brown microcrystalline products were washed with HOAc, EtOH and Et_2O .

$\text{Cu}_2(\text{HL})_4\text{SO}_4$

A warm solution of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (1 mmol) in HOAc (2 cm^3) was added to a warm solution of HL (6 mmol) in HOAc (30 cm^3) + H_2SO_4 (1 cm^3). Upon cooling, a microcrystalline light brown product precipitated and was washed with HOAc and EtOH.

The compounds were analysed by standard methods (Table 1). The molar conductivities were determined in DMF solution at 25° with a WTW conductivity bridge. The i.r. spectra were recorded on solids in KBr disks ($4000\text{--}250\text{ cm}^{-1}$) with a Perkin-Elmer 521 spectrophotometer and in nujol mulls on polythene ($400\text{--}60\text{ cm}^{-1}$) with an Hitachi FIS3 spectrophotometer.

Results and discussion

In DMF solution, the perchlorato and fluoroborato complexes behave (Table 1) as 1:1 electrolytes

Table 1. Analytical data and molar conductivities at 25° in DMF solution for the copper(I) complexes of rhodanine (HL)

Compound	Found (Calcd)%			Λ_M (mhos $\text{mole}^{-1}\text{cm}^2$)
	C	H	N	
$\text{Cu}(\text{HL})_2\text{OH} \cdot 0.5\text{H}_2\text{O}$	20.3 (20.3)	1.8(2.0)	7.95(7.9)	
$\text{Cu}(\text{HL})_2\text{Cl}$	20.35(19.7)	1.8(1.7)	7.5 (7.7)	
$\text{Cu}(\text{HL})_2\text{Br}$	17.8 (17.6)	1.8(1.5)	6.6 (6.8)	
$\text{Cu}(\text{HL})_2\text{I}$	16.0 (15.8)	1.7(1.3)	5.6 (6.1)	
$\text{Cu}(\text{HL})_3\text{ClO}_4$	19.2 (19.2)	1.5(1.6)	7.4 (7.45)	69
$\text{Cu}(\text{HL})_3\text{BF}_4$	19.8 (19.7)	1.5(1.65)	7.5 (7.6)	60
$[\text{Cu}(\text{HL})_3]_2\text{SO}_4$	21.05(21.15)	1.6(1.8)	7.9 (8.2)	17
$\text{Cu}(\text{HL})_3\text{O}_2\text{CCF}_3$	22.2 (22.9)	1.6(1.6)	7.7 (7.3)	17

Table 2. Principal i.r. bands (cm^{-1}) of rhodanine (HL) and its copper(II) complexes

Band	HL	Cu(HL) ₂ OH · 0.5 H ₂ O	Cu(HL) ₂ Cl	Cu(HL) ₂ Br	Cu(HL) ₂ I	Cu(HL) ₃ ClO ₄	Cu(HL) ₃ BF ₄	Cu(HL) ₃ · 0.5 SO ₄	Cu(HL) ₃ O ₂ CCF ₃
$\nu(\text{NH})$	3150m	3080m,sh.	3085s,sh.	3104ms	3140sh	3200sh	3220mb		3225wb
	3070mb	3020mb	3030s	3050s	3113s	3132msb	3130vw		3110wb
$\nu(\text{CO})$	1770m	1734s	1737ms,sh	1742vs	1750vs	1754vs	1753vs		1750vs
	1712ms,sh								
$\nu(\text{CNC})_{\text{as}} + \nu(\text{CS})$	1708sb	1704s	1708vs	1712vs	1724vs	1725vs	1714vsb		1695vsb
	1230sb	1215sb	1210vs	1215vs	1220vs	1218vs	1212vs		1210vs
	1183sb	1170sb	1168vs	1170vs	1170vs	1172vs	1167vsb		1172vs
III Thioam. $\nu(\text{CS})$	1082s	1060s	1060vs	1060vs	1060vs	1062vs	1050vsb		1060sh
						1022ms	1010sh		1015m
IV Thioam. $\nu(\text{CS})$	820mb	773ms	772s	770m	770m	770m	778m		783m
	785m	745m	742ms	748ms	715sh		750vw		724w
				728ms	706ms		722w		
$\nu(\text{CuS})$		308m	294w	295w	298wm	297m	305m		302wmb
		275vw	270w	272w	286w,sh	282sh	278vw		273wmb
$\nu(\text{CuX})$ (X = OH, Cl, Br, I)		201vs	206sb	143mw	117w				
		150s	154s	112mw	(90vb)				
def.		158vw,sh	158vw,sh			158mw	155wm,sh		156msh
							147ms		143m,sh

($\Lambda_M = 60-69 \text{ mhos mole}^{-1} \text{ cm}^2$)⁽²⁾ while the sulphato and the trifluoroacetato complexes ($\Lambda_M = 17 \text{ mhos mole}^{-1} \text{ cm}^2$) behave as nonelectrolytes⁽²⁾

The i.r. spectra of the copper(I) complexes (Table 2) are similar to those of the silver(I) and gold(I) complexes of rhodanine already discussed previously⁽³⁾. The $\nu(\text{NH})$ and $\nu(\text{CO})$ frequencies of the complexes do not indicate nitrogen or C=O coordination of the neutral ligand molecule to the metal ion. However the $\nu(\text{NH})$ frequencies are influenced by the electronegativity of the anion, the decrease of the ligand values being in the order:

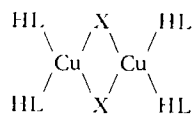
$\text{HO}^- \approx \text{Cl}^- > \text{Br}^- > \text{I}^- > \text{ClO}_4^- \approx \text{BF}_4^-$. The decrease in $\nu(\text{CS})$ frequencies confirms that in all these complexes, as for the halides⁽¹⁾, the coordination occurs through the thiocarbonylic sulphur atom. The small frequency decrease of the band at 1230 cm^{-1} assigned to the $\nu(\text{C}-\text{N}-\text{C})_{\text{as}}$ mode may be due to some $\nu(\text{CS})$ contribution. Similar behaviour applies to the band at 1183 cm^{-1} .

Two $\nu(\text{CuS})$ bands, distinct from the ligand bands and independent from the anion bonded to the metal ion, may be recognized in the $310-295$ ⁽¹⁾ and $280-270 \text{ cm}^{-1}$ regions in agreement with other literature values for copper(I) complexes of thioamidic ligands, such as dithiomalonamides⁽⁴⁾, dithiobiuret⁽⁵⁾ and *N*-ethylthiourea⁽⁶⁾.

The $\text{Cu}(\text{HL})_2\text{X}$ (X = OH and Cl) complexes have almost identical i.r. spectra indicating that they must have an equivalent chemical constitution and the same structure. For the first complex, no i.r. bands characteristic for coordinated water⁽⁷⁾ could be recognized and the ligand bands are identical to those of the chloride; the $\text{CuL} \cdot \text{HL} \cdot \text{H}_2\text{O}$ formula containing a coordinated rhodanidato anion should have different i.r. bands and must be excluded. The two strong far i.r. bands of these complexes at $201-206$ and $150-154 \text{ cm}^{-1}$, not present in the other complexes, may therefore be assigned to Cu-X (X = OH, and Cl) vibration modes.

The $\text{Cu}(\text{HL})_2\text{X}$ (X = Br and I) complexes show two mass-dependent bands related to those assignable to Cu-Cl vibration modes by the ratios, $206:143:117 = 1:0.69:0.57$ and $154:112:90 = 1:0.73:0.58$, which are in the range accepted for complexes having similar coordination⁽⁸⁾. Stretching frequencies of bridging Cu^{II}-X bonds are reported for tetrahedral $[\text{CuCl}_3]_2$ at $236-222$ and $193-180 \text{ cm}^{-1}$ and for $[\text{CuBr}_3]_2$ at 168 and 122 cm^{-1} ⁽⁹⁾. A $\nu(\text{MX})$ frequency lowering is normal for a lowered oxidation number of the same cation with the same type of coordination⁽⁹⁾ and the $\nu(\text{CuX})$ bands may be assigned therefore to halide bridged bonds in agreement with other literature values for copper(I) complexes⁽¹⁰⁻¹²⁾.

A $\nu(\text{CuO})$ frequency of 201 cm^{-1} for the $\text{Cu}(\text{HL})_2\text{OH}$ complex, much lower than those reported for copper(II) hydroxyl-bridged complexes⁽⁹⁾, may be due either to the steric hindrance of the two cumbersome ligand molecules bonded to the metal or to hydrogen bonds between the OH group and the NH or CO groups of neighbouring ligand molecules. For the above four complexes a dimeric tetrahedral structure (I) may be proposed.



(I)

In the $Cu(HL)_3A$ ($A = ClO_4, BF_4, 0.5 SO_4$ and CF_3CO_2) complexes the anion bands are mostly superposed on ligand bands. The $\nu_3(ClO_4^-)$ band (1158sh, 1088w, 1055sh) and $[BF_4]^-$ (1076sh, 1010sh) ions and the ν_4 band (581w, 530w) of the $[BF_4]^-$ ion are split; both these ions show the ν_1 and ν_2 bands ($ClO_4 = 920vw, 440sh; BF_4 = 750w, 345wb$) which are forbidden for a T_d symmetry^(7,9). They may be considered to be at least weakly coordinated in the solid state even if their complexes behave as 1:1 electrolytes in the strong solvating DMF. The bands (1173vsb, 1055sh, 1014ms, 582w) assignable to the $[SO_4]^{2-}$ group are in part superimposed on other bands of the complex but seem to correspond to a bridging $[SO_4]^{2-}$ group⁽⁷⁾. No valuable information may be obtained on the trifluoroacetato anion however, as the sulphato and trifluoroacetato complexes behave in DMF solution as nonelectrolytes, it is reasonable to assume that they are coordinated in the solid state.

The strong band at 171 cm^{-1} for the perchlorate and the medium bands at 220 cm^{-1} for the sulphate and the trifluoroacetate are stronger than the much weaker bands assignable to the ligand which appear in the same region. They may be assigned to $\nu(CuO)$ modes due to long metal-anion interactions; for copper(II) complexes $\nu(CuO)$ frequencies (anion: NO_3^-, ClO_4^- and SO_4^{2-}) are reported at $240\text{--}280\text{ cm}^{-1}$ (13). A more or less distorted tetrahedral coordination is therefore likely for these complexes. The bands at $158\text{--}143\text{ cm}^{-1}$ may be assigned to M–C–S deformation modes⁽⁹⁾.

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Preparation of Halogen-Modified Titanium(II) Arene Complexes and their Electronic Spectra

Helena Antropiusová and Karel Mach*

J. Heyrovský Institute of Physical Chemistry and Electrochemistry of Czechoslovak Academy of Sciences, Máchova, 7, 12138 Praha 2, Czechoslovakia

Jaroslav Zelinka

Department of Organic Chemistry, Charles University, Albertov 2030, Praha 2, Czechoslovakia

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Summary

Complexes of overall formula $TiAl_2X_8 \cdot Ar$ ($X = Cl, Br$ or I , $Ar =$ benzene or hexamethylbenzene) and the complexes containing various amounts of Br or I in addition to Cl were

prepared both by a direct synthesis – the reduction of titanium tetrahalide by aluminium in the aromatic solvent and in excess of the corresponding aluminium halide – and by halogen exchange between the complexes and aluminium halides. The interpretation of the electronic spectra of the complexes is given on the assumption of pseudo-octahedral symmetry of the ligand field. The values of $10 Dq$ and B obtained are compatible with the assignment.

* To whom all correspondence should be directed.