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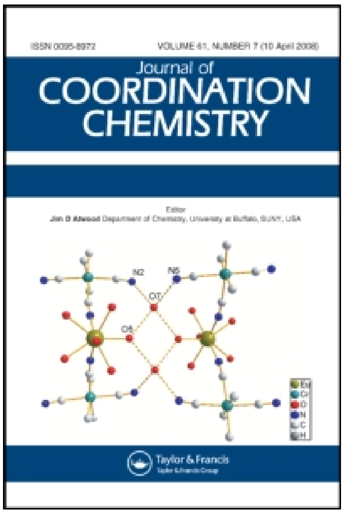

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COORDINATION COMPOUNDS OF 4,4′ -BIPYRIDYL WITH COPPER(I) HALIDES

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The reaction of 4,4′-bipyridyl (L) with copper(I) halides in different solvent yields coordination compounds of the type CuXL or $(CuX)_2L$ where X is Cl, Br, or I. The CuXL complexes are red and transform thermally into the yellow species $(CuX)_2L$. This reaction and subsequent thermal decomposition has been investigated. Polymeric structures for the two kinds of complexes are proposed, based on spectral measurements and other observations.

Key words: Copper(I), 4,4′-bipyridyl, halides, polymers, thermal stability

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INTRODUCTION

Coordination compounds of copper(I) halides of the type CuXL where L is a phosphine or arsine are well known.[1–5] In most cases these possess a cubane or chair (with halogen bridges) tetrameric structures.[6,7]

In $Cu_4I_4(AsR_3)_4$ where R is ethyl, Mann *et al.*,[2] have found that the Cu-Cu bond distance is only 0.04 A larger than in metallic copper and hence in these complexes the coordination sphere is rather complicated and strongly depends on the nature of the ligand.

The reaction of $[CuCl(PPh_2)]_4$ with $NaBH(OMe)_3$ in dimethylformamide produces the red octaheral cluster $[CuH(PPh_3)]_6$. The copper-copper bond distance is 2.60 A, exactly the distance found in tetrameric $Cu_4I_4(AsR_3)_4$, implying that in this compound metal-metal interaction is also important.[3] Tetrameric molecules such as $[CuI(PBu_3)L]$ can be cleared by reaction with 4,4′-bipyridyl to produce $[CuI(PBu_3)L]$.

The coordination capability of 4,4′-bipyridyl has not been as extensively studied as its 2,2′ isomer. Bukowska-Strzyzewsk *et al.*,[8] have prepared a piezoelectric Ce(III) complex in which the cerium atoms are eleven-coordinate by eight oxygens from four bidentate nitrate ligands, two oxygens atoms from two water molecules and one nitrogen from the 4,4′-bipyridyl ligand. DTA-DTG studies[9] of some lanthanide(III) complexes have been reported. All these complexes are of the type $Ln(NO_3)_3L \cdot nH_2O$ where Ln is a lanthanide(III) ion. The Eu(III), Ho(III) and Dy(III) complexes show a pink luminescence at room temperature. Although no structural studies have been carried out on these species, the low solubility of all compounds suggests polymeric structures.

The ligand 4,4′-bipyridyl also form 2:1 complexes with cobalt(II) and nickel(II) nitrates whereas a 1:1 stoichiometry was found for the Zn(II), Cd(II) and silver(I) nitrates.[10] In all cases the nitrogen base acts as a bridging ligand.

In an attempt to further explore the coordination properties of this ligand, we have prepared a series of compounds of the type CuXL and $(CuX)_2L$ where X = Cl, Br or I and characterized them spectroscopically.

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EXPERIMENTAL

Synthesis of the complexes

The compounds CuIL and $(CuI)_2L$ were prepared by dissolving CuI in the minimum required amount of an aqueous solution of KI. This solution was treated either with hot aqueous or ethanolic solutions of the nitrogen ligand. From the aqueous solution a red solid precipitated, whereas from the ethanolic solution a yellow solid was immediately obtained. The solids were filtered off, washed with water or ethanol and dried under vacuum.

The bromide and chloride derivatives were prepared by directly reacting the appropriate copper(I) halide with the ligand dissolved either in hot water or ethanol. The reaction mixtures were left stirring for 24 hours and the corresponding solids filtered off, washed and dried under vacuum. As in the case of the iodide complexes, a red solid was isolated from the aqueous reaction medium, whereas a yellow one was obtained from ethanol. In all cases the solids were insoluble in most common solvents.

Physical measurements

Carbon, hydrogen and nitrogen analyses were performed in the microanalytical laboratory of the Departamento de Quimica of the Universidad de Concepcion. Copper was analyzed by atomic absorption. IR spectra were measured in CsI pellets on a Perkin Elmer 547 spectrophotometer. The electronic spectra were recorded in nujol mulls on a Perkin Elmer 550-S spectrophotometer using nujol as reference. Room temperature magnetic measurements were made on a Cahn RM-2 Faraday electrobalance calibrated with $HgCo(NCS)_4$. The DTA-DTG measurements were carried out on a Netzch thermogravimetric system using Kaolin as standard. The samples were heated to 500°C at a rate of 10° per minute.

RESULTS AND DISCUSSION

Elemental analyses of a number of batches isolated (see Table I) reveal that no matter what the ligand/metal ratio is used in the reactions, the products are the red complex CuXL when the reaction is carried out in water or the yellow complex $(CuX)_2L$ if the reaction is performed in ethanol. The red and yellow solids are quite stable and no apparent decomposition upon exposure to light, air or water is observed. All compounds are insoluble in most solvents and hence conductivity and ^{1}nmr measurements have not been possible.

TABLE I
Analytical data for the complexes of copper(I) halides with 4,4′-bipyridyl[a]

Compound	Colour	% C	% H	% N	% Cu
CuIL	red	35.15(34.65)	2.15(2.33)	8.00(8.08)	18.91(18.33)
$(CuI)_2L$	yellow	22.02(22.36)	1.35(1.50)	4.97(5.21)	23.79(23.66)
CuBrL	red	39.62(40.08)	2.60(2.69)	9.15(9.35)	20.90(21.20)
$(CuBr)_2L$	yellow	27.01(27.11)	1.83(1.82)	6.21(6.32)	28.50(28.68)
CuClL	red	46.85(47.07)	3.09(3.16)	10.75(10.93)	24.80(24.90)
$(CuCl)_2L$	yellow	33.02(33.91)	2.27(2.28)	7.36(7.91)	35.65(35.66)

[a] Calculated values are given in parentheses.

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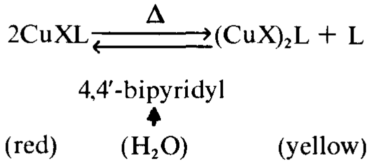
The red solids do not have a characteristic melting point and they convert to yellow complexes on heating. These yellow compounds are identical to the yellow $(\mathrm{CuX})_2\mathrm{L}$ complexes isolated from ethanol. If the yellow compounds are reacted with an excess of 4,4'-bipyridyl dissolved in water the red complexes are again obtained as shown below.



$$\underset{\text{(red)}}{2\mathrm{CuXL}} \underset{\substack{\text{4,4'-bipyridyl}\\ \uparrow \\ (\mathrm{H_2O})}}{\overset{\Delta}{\rightleftarrows}} \underset{\text{(yellow)}}{(\mathrm{CuX})_2\mathrm{L} + \mathrm{L}}$$

The DTA curves of the CuXL complexes show one general feature. There is an endothermic peak centred at 296, 325 and 308°C for the iodide, bromide and chloride respectively. This peak is associated with the loss of a molecule of 4,4'-bipyridyl in keeping with DTG studies that show that the change from red to yellow complexes occurs at these same temperatures. The DTA curves also have exothermic peaks located at 374 and 416°C the iodide, 425 and 472°C for the bromide and 415 and 447°C for the chloride. These peaks are associated with the loss of a molecule of 4,4'-bipyridyl from the $(\mathrm{CuX})_2\mathrm{L}$ species and the formation of the copper halides respectively. A similar mode of behaviour has been observed for some lanthanide(III) complexes of this ligand.[11] Table II gives the thermal behaviour of the CuXL complexes.

The IR spectra of the CuXL and $(\mathrm{CuX})_2\mathrm{L}$ complexes were compared with the spectra of the free ligand and pyridine. The assignment of the IR bands of the ligands is that given by Ahuya *et al.*,[10] and Corrsin *et al.*,[12] respectively. Table III gives IR spectral data for the compounds reported here. The band at *ca* 1600 cm^{-1} has been assigned to a pyridine ring vibration. This assignment differs from that given by Corrsin since we believe this band is a fundamental and not a combination band. The mode appears consistently in the free ligand and its complexes. The pyridine ring vibration at 1490 cm^{-1} in free 4,4'-bipyridyl is lowered in frequency by *ca* 10 cm^{-1} in the complexes as expected. The coordination to Cu(I) ions will perturb strongly this mode only if the Cu-N stretching force constant is large.

In the 1100–800 cm^{-1} region, the spectrum of 4,4'-bipyridyl is difficult to interpret since upon coordination some bands vanish, others have decreased intensity and a few are only observed for the red CuXL complexes. The non-observation of certain bands has been taken as a criterion of coordination.[9] Amongst these bands it can be seen that those at 1176, 1102 and 968 cm^{-1} are totally absent in the complexes. This effect can be attributed to an increase in the rigidity of the 4,4'-bipyridyl ligand upon coordination and to steric effects.[13] These effects are also probably the responsable for the increase in the frequency of the band at *ca* 995 cm^{-1}.

TABLE II
Thermal Behaviour of the CuXL complexes

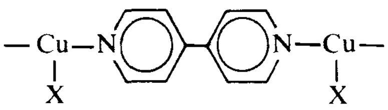
Reaction	Weight lost %		Temperature range °C	DTA peak °C
	Obs.	Calc.		
$2\mathrm{CuIL} \rightarrow (\mathrm{CuI})_2\mathrm{L} + \mathrm{L}$	23.38	22.53	240–300	296 (endo)
$(\mathrm{CuI})_2\mathrm{L} \rightarrow 2\mathrm{CuI} + \mathrm{L}$	29.38	29.08	360–380	374 (exo)
$2\mathrm{CuBrL} \rightarrow (\mathrm{CuBr})_2\mathrm{L} + \mathrm{L}$	25.90	26.06	300–355	325 (endo)
$(\mathrm{CuBr})_2\mathrm{L} \rightarrow 2\mathrm{CuBr} + \mathrm{L}$	35.05	35.25	380–450	425 (exo)
$2\mathrm{CuCL} \rightarrow (\mathrm{CuCl})_2\mathrm{L}$	30.40	30.60	300–450	308 (endo)
$(\mathrm{CuCl})_2\mathrm{L} \rightarrow 2\mathrm{CuCl} + \mathrm{L}$	44.00	44.10	400–480	447 (exo)

TABLE III
Selected IR Data for the CuXL and $(CuX)_2L$ complexes.

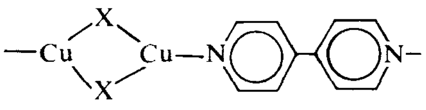
L	CuIL	$(CuI)_2L$	CuBrL	$(CuBr)_2L$	CuClL	$(CuCl)_2L$	Assignment
1593s	1596s	1600s	1600s	1603s	1600s	1605s	Py-ring vib.
1535s	1540w	1550m	1540m	1543m	1535w	1540m	py-ring vib.
1490s	1482s	1480m	1480s	1480s	1480m	1480m	py-ring vib.
1416m	1405mw	1405w	1405w	1410m	1408mw	1405m	ring vib.
1221s	1215s	1215s	1215s	1215s	1218s	1218s	CH in-plane bend
1176w							CH in-plane bend
1102m							CH in-plane bend
1079s	1070s	1068s	1065s	1070s	1080s	1080s	CH in-plane bend
1043m	1040m	1038m	1040m	1040m	1060m	1060m	ring breathing
995s	1005s	1010s	1005s	1005s	1005s	1005s	ring breathing
982m	980m		980m		980m		ring breathing
968m							ring deform.
882m							CH out-of-plane bend
853w	855w		855w		855w		CH out-of-plane bend
	815w	810mw	815w	815w	820w	815w	Coordination
800vs	800vs	800vs	800vs	800vs	800vs	800vs	CH out-of-plane bend
736s	730m	730w	725m	725m	725mw	730m	
	675m	675m	660mw	660m	650w	650m	Coordination
618s	640s	645s	638s	645s	640s	645s	Coordination
508s		508s		508s		510s	
369m							

The ligand band at 982 cm^{-1} is observed only in the CuXL species implying that these possess a less rigid structure as compared with $(CuX)_2L$. This same situation is observed for the 853 cm^{-1} absorption. The band at 618 cm^{-1} in the free ligand is very sensitive to coordination and in the complexes reported here shifts by *ca* 20 cm^{-1}.

Finally, the IR spectra of the CuXL and $(CuX)_2L$ complexes indicate that both nitrogen atoms of the ligand are bonded to copper(I) ions. Since the position of the nitrogen atoms precludes chelation, the ligand must be bridged between two metal ions in such a way as to favour the formation of polymeric chains. Thus for the CuXL complexes the structure I is likely, whereas a halogen and L-bridged structure II is probable for the $(CuX)_2L$ species.



(I)



(II)

The electronic spectra of some of the solids were recorded in nujol mull. Since the magnetic measurements clearly show that the compounds are diamagnetic, the oxidation state of the metal has not changed during reaction and the absorption bands located between 540–560 nm in the red CuXL complexes and between 440–480 nm in the yellow $(CuX)_2L$ complexes can be attributed to metal-to-ligand change transfer.

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