Copper(II) Complexes with Some N-Methylated 3-Amino-1-propanols

T. LINDGREN, R. SILLANPÄÄ, T. NORTIA and K. PIHLAJA

Department of Chemistry and Biochemistry, University of Turku, SF-20500 Turku 50, Finland

Received June 1, 1983

Copper(II) chloride and bromide complexes with 3-methylamino-1-propanol, 2-methyl-3-methylamino-1-propanol and 4-methylamino-2-pentanol as ligands were prepared and characterized. The elemental analyses suggest that in all cases the molar ratio of copper to aminoalcohol is 1:1. The UV- and VIS- (50 000–10 000 cm^{-1}) and IR spectra (4000–100 cm^{-1}) of these six copper(II) complexes were measured.

The spectral data are compared with those previously reported for corresponding copper(II) complexes with 3-amino-1-propanols as ligands.

Introduction

In our previous report [1] we characterized the copper(II) complexes of some 3-amino-1-propanols as alkoxobridged square planar dimers with terminal halogen atoms: the amino-alcohols act as mono-anionic, bidentate ligands. In this study some N-methylated 3-amino-1-propanols have been chosen as ligands.

Experimental

Preparation of Ligands

3-Methylamino-1-propanol (*1*) was prepared from 3-chloro-1-propanol by a method described by Lehn *et al.* [2]. The product was boiling at 347–349 K/1.7 kPa (lit. 440–442 K/101.3 kPa [3], 327–331 K/0.4 kPa [4] and 364–366 K/3.3 kPa [5]).

2-Methyl-3-methylamino-1-propanol (*2*) was prepared from an equimolar mixture of the ethyl ester of methacrylic acid and methylamine (33% in ethanol) by a method described by Schönenberger [6]. The product was boiling at 346–349 K/1.3 kPa (lit. 358–360 K/0.9 kPa [7]).

4-Methylamino-2-pentanol (*3*) was prepared by the lithium-aluminiumhydride reduction of the condensation product of an equimolar mixture of 2,4-pentanedione and methylamine (33% in ethanol). The diastereomeric mixture of erythro- and threo-4-methylamino-2-pentanols was boiling at 343–348 K/1.5 kPa (erythro/threo 1:1 from the ^{13}C-NMR spectrum) (lit. 353–355 K/2.3 kPa [8], 348.5–349 K/1.9 kPa [9] and 336 K/0.8 kPa [10]).

Preparation of Complexes

The complexes were prepared using a method reported in the previous paper [1].

Analyses

The copper analyses of the complexes were performed electrolytically, and chloride and bromide were determined gravimetrically.

The relative molecular masses were measured with Knauer steam pressure osmometer in CH_2Cl_2 using benzil as reference at 298 K. The relative molecular masses could be measured for four complexes because of the low solubility of the compounds in all common organic solvents. The results of the analyses are shown in Table I.

Physical Measurements

IR spectra were measured with a Perkin Elmer 180 Grating Infrared spectrophotometer, either from KBr-pellets or by using Nujol or hexachlorobutadiene mull technics at 4000–400 cm^{-1}. The FIR spectra were measured from polyethylene pellets.

UV and VIS spectra were measured with a Cary 17 D spectrophotometer in CH_2Cl_2, and the solid state UV and VIS spectra from KBr-pellets.

Results and Discussion

Elemental analyses indicate that the complexes have the formula of $[Cu(aO)X]_n$, where aO is deprotonated aminoalcohol and X is Cl or Br. The relative molecular mass determinations suggest that the complexes are dimers in CH_2Cl_2 solutions.

The solubility of the complexes to different organic solvents increases with increasing size of the aOH molecule and N-methyl substitution makes them more soluble than the corresponding complexes of 3-amino-1-propanols [1]. This finds support in the literature, according to which N,N-di-substituted derivatives have been re-crystallized from benzene,

0020-1693/84/$3.00

TABLE I. Analyses of the Prepared Copper(II) Complexes.

Complexes	Cu %		Cl, Br %		Relative molecular mass	
	found	calc.	found	calc.	found	calc.
$[Cu(N-Me-ap)Cl]_2$	34.1	34.0	18.8	18.9		374.3
$[Cu(N-Me-ap)Br]_2$	27.3	27.4	34.4	34.5		463.2
$[Cu(N-Me-2\text{-}Me-ap)Cl]_2$	31.3	31.6	17.5	17.6	426	402.3
$[Cu(N-Me-2\text{-}Me-ap)Br]_2$	25.9	25.9	32.4	32.5	485	491.2
$[Cu(N-Me-1,3\text{-}diMe-ap)Cl]_2$	29.3	29.5	16.4	16.5	429	430.4
$[Cu(N-Me-1,3\text{-}diMe-ap)Br]_2$	24.4	24.5	30.7	30.8	525	519.3

where ap = OH-deprotonated 3-amino-1-propanol. (Ligands are (1), (2) and (3)).

methanol and ethanol, or from a mixture of the latter pair [11–14].

UV–VIS Spectra

The UV–VIS absorption spectral data of the prepared compounds are presented in Table II.

The band maxima observed in the region 15 500–17 700 cm^{-1} are due to the d–d transitions [1] and are consistent with a square planar or tetragonal structure around the copper ion in the complexes. The envelopes of the bands are nearly symmetrical and have only one peak. The complexes of 4-methylamino-2-pentanols, however, make an exception: there are in the solid state spectra two d–d bands (see Table II), and the d–d band envelopes of the spectra measured in CH_2Cl_2 are very broad. Since the ligand is a mixture of erythro and threo isomers there is the possibility that a mixture of the complexes of both isomers is in question. Similar splitting is seen in the spectra of copper(II) complexes of some N,N-dialkyl-2-aminoethanols [14] and N,N-dialkyl-2-amino-ethanol–N–oxides [14, 15].

A second absorption band is found for these complexes in the region 24 500–26 300 cm^{-1}, as for the corresponding copper(II) complexes of 3-amino-1-propanols [1], and this suggests that both have an alkoxobridged binuclear structure. Furthermore, this band is rather strong in CH_2Cl_2 whereas in the solid state spectra it is very weak or only a shoulder. Hence we conclude that the complexes are dimers in the solution but tetramers or polymers in the solid state.

A third absorption band is found at 30 000–31 200 cm^{-1} in the CH_2Cl_2 solution spectra whereas in the solid state spectra only a small shoulder is seen at this area. This can be a normal charge transfer band or it might be due to a simultaneous pair excitation in coupled Cu(II) system [1].

The last, strong band found in the solution and in the solid state spectra between 35 600 cm^{-1} and 37 700 cm^{-1} is probably due to the charge transfer from chloride (bromide) ion to copper.

TABLE II. The UV–VIS Absorption Spectral Data of the Prepared Copper(II) Complexes.

Complexes	Band maxima/nm (cm^{-1})	
	solid state	in CH_2Cl_2
$[Cu(N-Me-ap)Cl]_2$	272 (36800)	265 (37700)
		322 (31100)
	395 (25300)	380 (26300)
	640 (15600)	629 (15900)
$[Cu(N-Me-ap)Br]_2$	269 (37200)	277 (36100)
		332 (30100)
	402 (24900)	400 (25000)
	642 (15600)	629 (15900)
$[Cu(N-Me-2\text{-}Me-ap)Cl]_2$	268 (37300)	268 (37300)
		321 (31200)
	396 (25300)	380 (26300)
	646 (15500)	645 (15500)
$[Cu(N-Me-2\text{-}Me-ap)Br]_2$	270 (37000)	278 (36000)
		330 (30300)
	403 (24800)	400 (25000)
	641 (15600)	633 (15800)
$[Cu(N-Me-1,3\text{-}diMe-ap)Cl]_2$	265 (37700)	269 (37200)
		325 (30800)
	400 (25000)	386 (25900)
	565 (17700)	610 (16400)
	643 (15600)	
$[Cu(N-Me-1,3\text{-}diMe-ap)Br]_2$	265 (37700)	281 (35600)
		333 (30000)
	408 (24500)	405 (24700)
	565 (17700)	617 (16200)
	640 (15600)	

In the solution spectra the maximum of the halogen-copper charge transfer band moves to lower energy when the chloride ion is changed to the bromide ion. In 3-amino-1-propanol derivatives this shift was found to be larger [1]. The UV–VIS spectra are consistent with a square planar structure around copper and with oxygen bridges between the two copper(II) ions.

Infrared Spectra

The IR frequencies of the ligands and the complexes in the region 3500–3100 cm^{-1} are shown in Table III. The broad O–H stretching band (3400–3200 cm^{-1}) of the amino-alcohols is not seen in the spectra of the complexes, pointing out that the OH-group of the aminoalcohol has been deprotonated on coordination to copper.

The N–H stretching vibration has its maximum at 3305–3300 cm^{-1} in the spectra of the free ligands [16]. This maximum is shifted to lower frequencies in the spectra of the complexes, suggesting that the methylamino group is also coordinated to copper. On coordination this band is in some cases split to more than one band, and the complexes have one to three bands in the region 3260–3185 cm^{-1}.

The copper(II) chloro complex of the 2-methyl-3-methylamino-1-propanol has only one sharp peak, while the bromo complex has three peaks in this region. The difference might be due to different packing of the dimeric units of the complexes. The main reason for the various packing models could lie in the different orientations of the N–methyl group with respect to the Cu_2O_2 ring plane (Fig. 1). The chloro complex might be more symmetric and hence cause only one sharp peak at 3250 cm^{-1}. There are also small differences in other regions of the spectra of these two complexes.

The same phenomenon is seen in the spectra of the copper(II) halide complexes of 3-methylamino-1-propanol. The bromo complex is more symmetric and has only one sharp peak at 3240 cm^{-1}, while the chloro complex has two sharp peaks at 3230 cm^{-1} and 3185 cm^{-1}. In the region 3100–500 cm^{-1} the spectra of both derivatives are nearly the same, indicating that the ligands have similar structures in both despite the differences in the 3500–3100 cm^{-1} region.

The spectra of the copper(II) chloro and bromo complexes of the 4-methylamino-2-pentanols are nearly identical, both having two sharp peaks at 3240 cm^{-1} and 3210 cm^{-1}. In the case of the corresponding 4-amino-2-pentanols the Cu(II) halides reacted preferably with threo-4-amino-2-pentanol [1]. In the present case the complexation does not resolve the threo- and erythro-forms from each other. Therefore the two N–H stretching vibrations could in this case be due to the different conformations (erythro and threo) of the ligands, the copper complexes of both being symmetrical enough to cause only one peak in this region.

The C–H stretching bands occur as strong sharp peaks in the region 3000–2850 cm^{-1}. All free N-methylated aminoalcohols have one more band at 2800 cm^{-1} which is due to the N–methyl group [17]. In the spectra of the complexes this C–H band is probably shifted to higher frequencies as a result of the coordination of the nitrogen atom and is hence found among the other C–H stretching bands.

TABLE III. The Infrared Bands of Copper(II) Complexes of 3-methylamino-1-propanols in the Region 3500–3100 cm^{-1}.

	ν(OH)	ν(NH)
Free ligands (liquid state)	3400–3200	~3300
Complex (solid state)		
$[\mathrm{Cu(N{-}Me{-}ap)Cl}]_2$		3230, 3185
$[\mathrm{Cu(N{-}Me{-}ap)Br}]_2$		3240
$[\mathrm{Cu(N{-}Me{-}2{-}Me{-}ap)Cl}]_2$		3250
$[\mathrm{Cu(N{-}Me{-}2{-}Me{-}ap)Br}]_2$		3260, 3225, 3195
$[\mathrm{Cu(N{-}Me{-}1{,}3{-}diMe{-}ap)Cl}]_2$		3240, 3210
$[\mathrm{Cu(N{-}Me{-}1{,}3{-}diMe{-}ap)Br}]_2$		3240, 3210

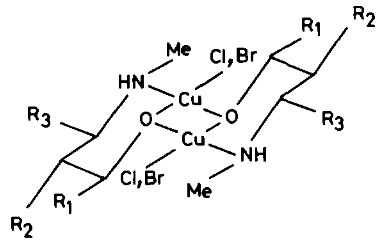

Fig. 1. Schematic picture of the basic structure unit of the complexes (where the ligand is (*1*) when $R_1 = R_2 = R_3 = H$, (*2*) when $R_1 = R_3 = H$, $R_2 = Me$ and (*3*) when $R_1 = R_3 = Me$, $R_2 = H$).

The C–C, C–N and C–O stretching vibrations occur between 1200–800 cm^{-1} but it is not possible to assign them exactly.

From the IR spectra we can conclude that the aminoalcohols coordinate to copper(II) ion as monoanionic, bidentate ligands.

The most important frequencies of the FIR spectra of the complexes are listed in Table IV. They are mainly due to metal–ligand vibrations which are coupled with the skeletal vibrations of the chelates. This makes the assignment of the absorption bands difficult.

In the region 525–440 cm^{-1} there are two rather strong absorption bands, the stronger of which is near to 450 cm^{-1}. In two cases both bands are nearly equal. Uhlig and Staiger [18] have stated that in the related Cu(II) complexes of N,N-dibutylamino ethanol these bands originate from the Cu_2O_2-ring. According to Thornton *et al.* [19, 20] the ν(Cu–O) vibration exists in this region in square planar compounds.

Around 300 cm^{-1} there are several absorption bands, some of which might be assigned to ν(Cu–O) vibrations.

TABLE IV. Selected FIR Spectral Frequencies (cm^{-1}) and Their Assignments of the Solid Copper(II) Complexes.

Complexes	ν(Cu–O) ligand	ν(Cu–N)	ν(Cu–Cl)	ν(Cu–Br)	ν(Cu–Br)/ ν(Cu–Cl)
[Cu(N–Me–ap)Cl]$_2$	442	373	230		0.80
[Cu(N–Me–ap)Br]$_2$	442	360		184	
[Cu(N–Me–2-Me–ap)Cl]$_2$	468	368	258		0.66
[Cu(N–Me–2-Me–ap)Br]$_2$	458	360		171	
[Cu(N–Me–1,3-diMe–ap)Cl]$_2$	512, 444	397	274		0.68
[Cu(N–Me–1,3-diMe–ap)Br]$_2$	510, 441	394		187	

The ν(Cu–N) vibrations of several related compounds have been found to be around 400 cm^{-1} [1, 18]. Therefore we assign the vibrations in the region 400–360 cm^{-1} to the ν(Cu–N) vibrations.

The copper–halogen stretching vibrations are easy to identify because of the shift which occur in their frequencies when the chloride atom is changed to the bromide atom. The ratio of the corresponding frequencies is Cu–Br/Cu–Cl $\sim$ 0.77 in various compounds [21]. The ν(Cu–Cl) vibration occur in the region 274–230 cm^{-1} and this band is probably due to the terminal chloride atom. The ν(Cu–Br) vibration of the terminal bromide atom occur in the region 187–171 cm^{-1}. From the FIR spectra we can conclude that the aminoalcohols coordinate to the copper atom as bidentate ligands and the oxygen atoms form bridges between two copper atoms. There is, in addition, one terminal halogen atom bonded to copper. The effective coordination number of the copper atom is four with a square planar symmetry.

The results obtained from FIR spectra are in good agreement with the conclusions made from UV and VIS spectral and IR spectral data, as well as with our previous work [1].

The basic structure unit of the complexes is thus a dimer [Cu(aO)X]$_2$ shown in Fig. 1.

Acknowledgements

Financial support from the Emil Aaltonen Foundation (T.L.) is acknowledged.

References

1 T. Lindgren, R. Sillanpää, T. Nortia and K. Pihlaja, *Inorganica Chimica Acta, 73*, 153 (1983).

2 J.-M. Lehn, P. Lindscheid and F. G. Riddell, *Bull. Soc. Chim. France*, 1172 (1968).

3 S. D. Goldberg and W. F. Whitmore, *J. Am. Chem. Soc., 59*, 2280 (1937).

4 S. Searles and P. Gregory, *J. Am. Chem. Soc., 76*, 2789 (1954).

5 S. R. Koepke, R. Kupper and C. J. Michejda, *J. Org. Chem., 44*, 2718 (1979).

6 H. Schönenberger, H. Vogel and E. Bamann, *Arch. Pharm., 298*, 371 (1965).

7 I. P. Boiko, O. I. Zhuk, Yu. F. Malina, Yu. Yu. Samitov and B. V. Unkovskii, *Zh. Org. Khim., 12*, 2107 (1976).

8 A. Skita and F. Keil, *Ber., 63*, 42 (1930).

9 R. Lukes, J. Kovar and K. Blaha, *Coll. Czech. Chem. Commun., 25*, 2179 (1960).

10 M. G. Andrews and J. A. Mosbo, *J. Org. Chem., 42*, 650 (1977).

11 R. Mergehenn and W. Haase, *Acta Cryst., B 33*, 1877 (1977).

12 A. Pajunen and M. Lehtonen, *Suomen Kemistilehti, B 44*, 200 (1971).

13 W. Haase, *Chem. Ber., 106*, 3132 (1973).

14 E. Uhlig and K. Staiger, *Z. anorg. allg. Chem., 346*, 21 (1966).

15 M. Okamura and S. Kida, *J. Inorg. Nucl. Chem., 36*, 1413 (1974).

16 R. Mathis, M. Maurette, C. Godechot and A. Lattes, *Bull. Soc. Chim. France*, 3047 (1970).

17 R. Mathis, A. M. Pellizzari, T. Bouissou, M. Revel and M. Chihaoui, *Spectrochim. Acta, A 37*, 677 (1981).

18 E. Uhlig and K. Staiger, *Z. anorg. allg. Chem., 360*, 39 (1968).

19 G. S. Shepard and D. A. Thornton, *J. Mol. Struct., 34*, 83 (1976).

20 P. R. Johnson and D. A. Thornton, *J. Inorg. Nucl. Chem., 37*, 461 (1975).

21 R. H. Nuttall, *Talanta, 15*, 157 (1968).