Inorganica Chimica Acta, *167* (1990) 1–3

Inorganica Chimica Acta
LETTER

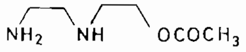
The Preparation of Copper(II) and Nickel(II) Complexes of 2-(2′-Acetoxyethylamino)ethylamine

KEVIN B. NOLAN* and HAJI RAHOO

Department of Chemistry, University of Surrey, Guildford GU2 5XH (U.K.)

(Received July 6, 1989)

In the course of our work on metal-promoted hydrolysis reactions, we decided to investigate systems for which accelerated rates might be observed due to the generation of better leaving groups through complex formation [1]. To do this, we first synthesised the title ligand (L) in the expectation



= L

that its hydrolysis in the presence of metal ions would afford $CH_3CO_2^-$ and the leaving group $NH_2(CH_2)_2NH(CH_2)_2OH$ which would be stabilised by complexation as a 2N bidentate ligand. In the course of our work, we isolated some copper(II) and nickel(II) complexes of L and in this note we describe their synthesis and physical properties.

Experimental

2-(2′-Acetoxyethylamino)ethylamine Dihydrochloride (L·2HCl) and Dihydrobromide (L·2HBr)

2-(2′-Aminoethylamino)ethanol, $NH_2(CH_2)_2NH(CH_2)_2OH$ (Aldrich, 10.0 g, 0.1 mol) was dissolved in glacial acetic acid (100 cm^3) which had previously been saturated with dry HCl gas. Further HCl gas was passed through the solution over a 10-min period, during which time precipitation of the dihydrochloride of the starting material occurred. The suspension was treated dropwise with acetyl chloride (25 cm^3) and refluxed until the solid had completely dissolved. On cooling, L·2HCl crystallised from solution. This was washed with ethanol, then ether and air dried. Recrystallisation from ethanol gave a product with melting point 171–173 °C (yield 9.5 g, 44%). *Anal.* Found: C, 32.8; H, 7.3; N, 12.8. Calc. for $C_6H_{16}N_2O_2Cl_2$: C, 32.9; H, 7.3; N, 12.8%. Mass spectrum $m/e = 147$ (= L): ^1H NMR (D_2O) 2.25 δ (singlet, 3H), 3.35 δ (broad, 6H), 4.45 δ (triplet, 2H); IR (Nujol): 2200–3300, 2010, 1740 cm^{-1}.

L·2HBr was obtained by dissolving L·2HCl (2.0 g, 9×10^{-3} mol) in 48% HBr solution (5 cm^3). Addition of ethanol resulted in the precipitation of L·2HBr which was collected by filtration, washed with ethanol, then ether and finally dried in a vacuum oven at 40 °C; yield 1.6 g (46%), melting point 150–152 °C. The spectroscopic properties of L·2HBr are very similar to those of L·2HCl.

$(LH_2\cdot Cl)_2[CuCl_4]$

To a refluxing solution of L·2HCl (1 g, 4.5×10^{-3} mol) in ethanol (100 cm^3) was added dropwise with stirring a solution of $CuCl_2\cdot 2H_2O$ (1.5 g, 9×10^{-3} mol) in ethanol (25 cm^3). During the addition, a yellow precipitate was deposited. The mixture was cooled and stirred for 30 min at room temperature. The precipitate was filtered, washed with ethanol, then ether and finally dried in a vacuum oven at 40 °C; yield 1.1 g (42.%). *Anal.* Found: C, 25.18; H, 5.55; N, 9.56. Calc. for $C_{12}H_{32}N_4O_4Cl_6\cdot Cu$: C, 25.15; H, 5.59; N, 9.78%. Cu (EDTA): Found 11.02; Calc. 11.09%. IR (Nujol): 3120, 3040, 2720, 2610, 2570, 2480, 2415, 1755, 1740 cm^{-1}; electronic spectrum: 400, 775 nm; μ_{eff} (room temp.) = 1.82 BM.

$(LH)_2[CuBr_4]$

This bronze-coloured complex was obtained as above except that $CuBr_2$ was used instead of $CuCl_2\cdot 2H_2O$; yield 1.4 g (46%). *Anal.* Found: C, 20.66; H, 4.57; N, 7.87. Calc. for $C_{12}H_{30}N_4O_4Br_4Cu$: C, 21.26; H, 4.43; N, 8.27%. Cu (EDTA): Found 9.29; Calc. 9.38%. IR (Nujol): 3090, 3030, 2700, 2400, 1735 cm^{-1}; electronic spectrum 417, 770 nm; μ_{eff} (room temp.) = 1.89 BM.

$CuLCl_2$

A stirred solution of L·2HCl (1.0 g, 4.5×10^{-3} mol) in ethanol (300 cm^3) was treated dropwise with triethylamine (1.25 cm^3, 9×10^{-3} mol). The resulting solution was added dropwise with stirring to a solution of $Cu(NO_3)_2\cdot 3H_2O$ (2.17 g, 9×10^{-3} mol) in ethanol at room temperature. After a few minutes a blue precipitate formed. This was filtered, washed with ethanol, then ether and finally air dried; yield 0.54 g (43%). *Anal.* Found: C, 25.96; H, 4.97; N, 9.94. Calc. for $C_6H_{14}N_2O_2Cl_2Cu$: C, 25.66;

---

*Author to whom correspondence should be addressed at: Department of Chemistry, Royal College of Surgeons in Ireland, St. Stephen's Green, Dublin 2 (Ireland).

0020-1693/90/$3.50

H, 4.99; N, 9.98%. Cu: Found 22.54; Calc. 22.64%. IR: 3335, 3260, 3195, 1745, 1730 sh cm^{-1}; electronic spectrum 350, 700 nm; μ_{eff} (room temp.) = 1.92 BM.

$CuLBr_2$

This was prepared by the method used for $CuLCl_2$ except that L·2HBr and $CuBr_2$ (2.0 g, 9 × 10^{-3} mol) were used as starting materials; yield 0.48 g (40%). *Anal.* Found: C, 20.08; H, 3.71; N, 7.58. Calc. for $C_6H_{14}N_2O_2Br_2Cu$: C, 19.50; H, 3.79; N, 7.58%. Cu: Found 17.29; Calc. 17.19%. IR: 3330, 3235, 3185, 1740 cm^{-1}; electronic spectrum: 400, 695 nm; μ_{eff} (room temp.) = 1.78 BM.

$CuLClBr \cdot H_2O$

This was prepared by the method used for $CuLCl_2$ except that $Cu(NO_3)_2 \cdot 3H_2O$ was replaced by $CuBr_2$ (2.0 g, 9 × 10^{-3} mol); yield 0.6 g (37%). *Anal.* Found: C, 21.39; H, 4.13; N, 8.19. Calc. for $C_6H_{16}N_2O_3ClBrCu$: C, 21.00; H, 4.66; N, 8.16%. Cu: Found 18.14; Calc. 18.52%. IR: 3500, 3320, 3235, 3185, 1737 cm^{-1}; electronic spectrum: 385, 690 nm; μ_{eff} (room temp.) = 1.73 BM.

$NiLCl_2 \cdot 0.5CH_3OH$

The method used for $CuLCl_2$ was again applied except that $NiCl_2$ (1.2 g, 9 × 10^{-3} mol) was used instead of $Cu(NO_3)_2 \cdot 3H_2O$ and methanol instead of ethanol; yield 0.4 g (31.%). *Anal.* Found: C, 26.54; H, 5.60; N, 9.99. Calc. for $C_6H_{14}N_2O_2Cl_2Ni \cdot 0.5CH_3OH$: C, 26.74; H, 5.48; N, 9.60%. Ni: Found 20.54; Calc. 20.13. IR: 3500, 3295, 3245, 3165, 1730 cm^{-1}; electronic spectrum: 375, 580, 700 nm; μ_{eff} (room temp.) = 3.08 BM.

$NiLBr_2 \cdot 0.25C_2H_5OH$

This complex was prepared by the method used for $CuLBr_2$ except that $NiBr_2 \cdot 3H_2O$ (1.31 g, 4 × 10^{-3} mol) was used instead of $CuBr_2$; yield 0.4 g (33%). *Anal.* Found: C, 20.73; H, 4.57; N, 7.93. Calc. for $C_6H_{14}N_2O_2Br_2Ni \cdot 0.25C_2H_5OH$: C, 20.74; H, 4.12; N, 7.45%. Ni: Found 15.45; Calc. 15.61%. IR: 3500, 3300, 3240, 3160, 1730 cm^{-1}; electronic spectrum: 390, 675 nm; μ_{eff} (room temp.) = 3.09 BM.

Discussion

The addition of acetyl chloride to 2-(2′-aminoethylamino)ethanol in HCl/acetic acid results in acetylation of the OH group and gives crystalline L·2HCl. This was characterised by microanalysis and by spectroscopic methods. The ^{1}H NMR spectrum in D_2O shows signals at 2.25 δ (singlet, 3H) due to the methyl group, at 2.53 δ (broad, 6H) due to overlapping triplets for the $^+N{-}CH_2$ groups and at 4.45 δ (triplet, 2H) due to the $-CH_2{-}OCO$ group [2]. The IR spectrum of L·2HCl contains intense, broad overlapping bands in the 2200–3300 cm^{-1} region due to ν_{sym} and ν_{asym} ($^+NH_3$) and ($^+NH_2$) [3]. The medium band at 2000 cm^{-1} is typical of the N–H stretch of secondary amine salts. The position of ν(C=O) at 1740 cm^{-1} is typical of an aliphatic ester [3].

The product obtained as a result of addition of CuX_2 (X = Cl, Br) to L·2HX in ethanol depends on whether or not the sterically hindered (and in this case non-complexing) base triethylamine is added to the reaction mixture. In its absence, salts containing the complex anions $[CuCl_4]^{2-}$ and $[CuBr_4]^{2-}$ were obtained. The presence of conjugate acids of L as cations in these salts is confirmed by the IR spectra which clearly show the symmetric and asymmetric N–H stretching bands at 2000–3300 cm^{-1}, characteristic of protonated primary and secondary amines. Complex salts containing these anions have been widely investigated and the geometry of the anion varies between tetrahedral and square planar (most are flattened tetrahedral), depending on factors such as crystal packing forces, hydrogen bonding to the cation, and many others [4]. The complex $(LH_2 \cdot Cl)_2[CuCl_4]$ prepared in this work is analogous to bis(*N*-benzylpiperazinium chloride)tetrachlorocuprate(II); i.e. $(L'H_2 \cdot Cl)_2[CuCl_4]$ where L′ = *N*-benzylpiperazine, the crystal and molecular structure of which has been reported [5]. This complex contains a flattened tetrahedral $CuCl_4{}^{2-}$ anion, two *N*-benzylpiperazinium cations ($L'H_2{}^{2+}$) and two lattice Cl^- ions. Each $L'H_2{}^{2+}$ cation is hydrogen bonded to two adjacent $CuCl_4{}^{2-}$ anions and also to a lattice Cl^- ion. A similar type of structure is likely for the complex described in this paper with the dication $LH_2{}^{2+}$ replacing the *N*-benzylpiperazinium ion, $L'H_2{}^{2+}$.

The addition of 2 moles of the sterically hindered base triethylamine to the L·2HX/metal ion solution generates the free ligand L *in situ* by deprotonation and results in the formation of products in which L is complexed to the metal. The IR spectra of these complexes have NH stretching bands at 3200–3400 cm^{-1} and lack absorptions in the range 2000–3000 cm^{-1}, which confirms the absence of protonated forms of L as cations in these complexes. The CO stretching bands in the IR spectra of these complexes are in similar positions to the free ligand, indicating weak or non-coordination of these groups [6]. It therefore appears that in these complexes L is present as a bidentate 2N donor. The observed room-temperature magnetic moments and the positions of the band maxima in the electronic spectra are typical of those for complexes of copper(II) and for octahedral complexes of nickel(II) [4].

References

1 R. W. Hay, in G. Wilkinson, R. D. Gillard and J. A. McCleverty (eds.), *Comprehensive Coordination Chemistry,* Vol. 6, 61.4, Pergamon, Oxford, 1987, p. 437.
2 R. M. Silverstein and G. C. Bassler, in *Spectrometric Identification of Organic Compounds,* Wiley, New York, 2nd edn., 1967, Ch. 4.
3 R. M. Silverstein and G. C. Bassler, in *Spectrometric Identification of Organic Compounds,* Wiley, New York, 2nd edn., 1967, Ch. 3.
4 F. A. Cotton and G. Wilkinson, in *Advanced Inorganic Chemistry,* Wiley-Interscience, New York, 5th edn., 1988, Ch. 18.
5 L. Antolini, L. Menabue, G. C. Pellacani, M. Saladini and G. Marcotrigiano, *Inorg. Chim. Acta, 58* (1982) 193.
6 K. B. Nolan and A. A. Soudi, *J. Chem. Res. (S),* (1979) 210.