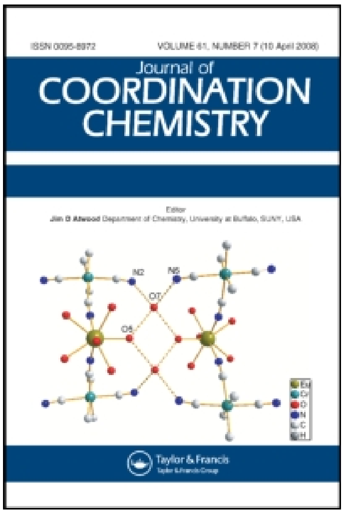

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COPPER(I) AND COPPER(II) COMPLEXES OF CREATININE

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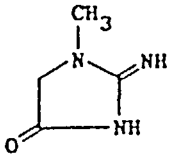
A Cu(II) complex of creatinine (creat) was prepared, with formula $Cu(creat)_2Cl_2$, as well as a Cu(I) creatinine complex, $Cu(creat\ H_{-1})(EtNH_2).H_2O(EtNH_2 = $ ethylamine). The Cu(II) adduct is complexed with neutral creatinine and IR evidence suggests a tetrahedral geometry for the complex with bonding to the ring amino nitrogen atom. Diamagnetic $Cu(creat\ H_{-1})(EtNH_2).H_2O$, formed from a redox reaction between Cu(II) and creatinine, is composed of Cu(I) atoms bonded to the deprotonated ring amino nitrogen, with the exocyclic carbonyl group hydrogen bonded to coordinated ethylamine molecules.

Keywords: Copper(I), copper(II), creatinine, IR

INTRODUCTION

Creatinine (creat), the cyclic anhydride of creatine, is a major source of urinary nitrogen. Formed from creatine in the body, its concentration in the urine provides an indication of proper renal function. Creatinine has a number of possible sites for metal ion coordination; complexes with Hg(II),[1,6] Cu(II),[2,5] Ag(I),[3] Co(II),[4] Zn(II),[6] Cd(II),[6] Pt(II),[7-9] Pd(II),[7,8] and Ni(II)[10] have been reported in recent years. Several crystal structures have been solved, including that of creatininium tetrachlorocuprate(II),[2] in which centrosymmetric $CuCl_4^{-2}$ ions are linked to cationic creatininium units through N–H · · · Cl hydrogen bonding involving imino and amino nitrogen atoms. Structures of monomeric Pt(II) and Pd(II) creatinine complexes have recently been reported in which the metal ion, bound to creatinine ring amino nitrogens, exhibits square planar coordination geometry.[7-9] In addition, bis(creatinine) silver(I) perchlorate dihydrate[3] shows centrosymmetric Ag atoms linearly coordinated through ring amino nitrogen atoms of two creatinine ligands.



Creatinine

We have prepared two new creatinine complexes starting with Cu(II); the first, $Cu(creat)_2Cl_2$, with 2/1 neutral creatinine to Cu(II) stoichiometry, is similar to previously reported complexes.[6] The second complex however, $Cu(creat\ H_{-1})$-$(EtNH_2).H_2O$ ($EtNH_2$ = ethylamine), contains Cu(I) and is the result of an

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interesting redox reaction. We now report the syntheses and characterization of these complexes, and discuss their bonding on the basis of IR and magnetic susceptibility evidence.

EXPERIMENTAL

Preparation of Cu(creat)$_2$Cl$_2$

The synthetic procedure was similar to that used for previously reported copper halide–purine complexes.[11,12] Some 10 mmol creat was dissolved in methanol and mixed with a methanol solution containing 10 mmol $CuCl_2.2H_2O$. A greenish yellow powder separated immediately; this was filtered by vacuum and washed with methanol (yield: 87%). Found: C, 26.9; H, 4.0; N, 23.2; Cu, 17.6%. Calc. for $(C_4H_7N_3O)_2CuCl_2$: C, 26.6; H, 3.9; N, 23.3; Cu, 17.4%.

Preparation of Cu(creat H$_{-1}$)(EtNH$_2$).H$_2$O

The synthetic procedure was similar to that employed for previously reported copper–purine complexes with primary amines.[11,12] Some 20 mmol creat and 10 mmol $CuSO_4.5H_2O$ were dissolved separately in 35% ethylamine in H_2O and then mixed with stirring. After approximately 10 minutes, the dark blue solution became clear, but with a faint yellow colouration, then slowly turned cloudy white over several hours. A white powder precipitated from solution after 12 hours; this was filtered by vacuum, washed with aqueous amine and H_2O, and dried with acetone (yield: 76%). Found: C, 30.0; H, 5.2; N, 23.8; Cu, 26.0%. Calc. for $(C_4H_6N_3O)Cu(C_2H_7N).H_2O$: C, 30.2; H, 6.2; N, 23.5; Cu, 26.6%.

The white product was insoluble in H_2O and nonpolar organic solvents, but swelled in EtOH and could be recovered as a glass after dissolution in DMF. The presence of creatinine in the product was confirmed by its isolation employing published methods.[13] The presence of methylguanidine, a known oxidation product of creatinine,[14] was indicated by IR analysis of the concentrated supernatant solution following the reaction.

IR spectra were obtained as KBr pellets (4000–200 cm^{-1}) on a Perkin-Elmer 1430 spectrometer. Room temperature magnetic susceptibility measurements were conducted on a Gouy balance of standard design. Elemental analyses (C,H,N) were performed by Galbraith Laboratories.

RESULTS AND DISCUSSION

Table I lists assigned IR absorbances for creatinine[15] as well as for the two new complexes. Assigned creatinine bands can still be recognized in Cu(creat)$_2$Cl$_2$, although imino and amino N–H frequencies shift significantly to higher wave numbers, with the energy of C=N also increasing but to a lesser extent. Udupa and Krebs[3] have reported the structure of $[Ag(C_4H_7N_3O)_2]^+$ and find that the H atom of the cyclic amino group now bonded to a silver atom is transferred to the exocyclic imino group, with extensive intermolecular hydrogen bonding present in the complex. N–H assignments from the IR in the present compound must therefore be seen as tentative. In addition, C=O shifts slightly to lower energies, while the in-plane imino N–H deformation remains constant. Martin-Gil and Martin-Gil[7] have reported crystal structure information on Pt(II) and Pd(II) halide complexes of creatinine in which the metal atom is coordinated to the ring nitrogen atom with no metal coordination from exocyclic imine or carbonyl groups. They also report similar IR shifts to those observed for $Cu(creat)_2Cl_2$. Indeed, other crystal structures of creatinine–metal complexes indicate the metal atom is bonded to the ring nitrogen atom with no coordination from exocyclic carbonyl or imine groups.[8,9] Mitewa, Bontchev and Kabassanov,[5] however, have synthesized a Cu(II)–creatinine complex and propose its structure to contain a four-membered chelate ring involving copper bonding to the ring nitrogen atom as well as the carbonyl oxygen atom; this bonding model is possible in the present complex as well on the basis of IR evidence. To date, no X-ray structures have been accomplished on copper–creatinine adducts exhibiting direct metal coordination to creatinine ring or exocyclic atoms. $Cu(creat)_2Cl_2$ exhibits a well-defined Cu–Cl doublet at 305 and 288 cm^{-1}, which suggests a tetrahedral or *cis*-square planar geometry around the metal centre.[11,16,17] The complex has a slightly subnormal magnetic susceptibility value (1.65 BM), in keeping with many other Cu(II) coordination compounds of this type.

TABLE I

Selected IR frequencies (cm^{-1}) of the copper complexes of creatinine.

Creat	$Cu(creat)_2Cl_2$	$Cu(creat\ H_{-1})(EtNH_2){\cdot}H_2O$	Assignment
3250	3346	3282	imino N–H stretching fundamental
3040	3215, 3180		amino N–H stretching fundamental
1690	1714	1690	C=N stretching fundamental
1665	1645	1610	C=O stretching fundamental
1500	1503	1482	imino N–H in-plane deformation
	305, 288		Cu–Cl stretching fundamental
		3440	water O–H stretching

The interpretation of the IR spectrum of $Cu(creat\ H_{-1})(EtNH_2).H_2O$ is straightforward. Creatinine ring amino N–H stretching disappears upon complexation, while imino N–H and C=N stretching and N–H in-plane deformation remain largely unchanged. Further, C=O stretching shifts 55 cm^{-1} to lower frequencies in the complex which suggests carbonyl involvement in bonding, probably through hydrogen bonding to the coordinated ethylamine group. This situation has been proposed for other complexes of this type.[11,12] Copper is therefore bonded to the deprotonated ring amino nitrogen atom, a type of bonding which has been observed in several creatinine–metal complexes whose structures have been determined.[3,7–9]

White $Cu(creat\ H_{-1})(EtNH_2).H_2O$ is diamagnetic, it slowly turns green due to surface oxidation. The compound swells in alcohol and can be recovered from a DMF solution as a glass which suggests its polymeric nature. Creatinine was isolated from the complex upon decomposition under neutral conditions, while evidence of an oxidation product of creatinine was observed in the supernatant liquid after the initial synthesis. Two moles of creatinine are therefore required for each Cu(II) ion, one to reduce Cu(II) to Cu(I), and a second to complex with Cu(I) to form the product. Indeed, no products result if Zn(II) is substituted for Cu(II) in the initial reaction. Certain metal ions such as Hg(II) can oxidize creatinine,[13] and radical formation has been reported during the interaction of Ni(II) with creatinine,[10] but $Cu(creat\ H_{-1})(EtNH_2).H_2O$ presents an interesting example of creatinine acting as a reducing as well as a complexing agent to effect the synthesis of a novel Cu(I)-creatinine adduct.

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