Pergamon

PII: S0277-5387(97)00067-3

Polyhedron Vol. 16, No. 19, pp. 3379–3383, 1997

0277-5387/97 $17.00+0.00

Crystal structure, IR-spectrum and electrochemical behaviour of $Cu(creatinine)_2Cl_2$

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(Received 13 November 1996; accepted 4 February 1997)

Abstract—The crystal structure of the title compound has been solved by single-crystal X-ray diffractometry. The Cu^{II} ion is located on a two-fold crystallographic axis in a quasi-tetrahedral coordination. The infrared spectrum of the complex was recorded and briefly analyzed in relation to its structural peculiarities. Its electrochemical behaviour was investigated by cyclic voltammetry in methanolic solutions. © 1997 Elsevier Science Ltd

Keywords: $CuCl_2$/creatinine complex; crystal structure; IR-spectrum; cyclic voltammetry.

Creatinine (creat, Fig. 1) is the final degradation product of phosphocreatine, a high energy phosphate which plays an important role in the energetics of muscle tissues [1]. It is also an important end product of nitrogen metabolism in vertebrates and its level in urine and serum is recognized as an indicator of certain diseases [2]. Several tautomeric forms for this molecule have been proposed, that depicted in Fig. 1 seems to be the most probable [2].

As part of our present studies on copper(II) complexes of bioligands and related molecules [3–10], we have attempted to investigate in detail $Cu(creat)_2Cl_2$, one of the few simple creatinine complexes so far described [2,11]. It became possible to solve the crystal structure of this complex using single-crystal methods. On the basis of this information, we have also reinvestigated the vibrational behaviour of the complex and gained a first insight into its redox characteristics.

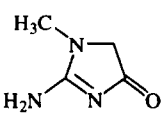

Fig. 1. Structure of creatinine (creat).

This investigation was also interesting from the general structural point of view of creatinine complexes because only a very limited number of structural data on complexes involving this ligand and first-row transition metals is known [2].

EXPERIMENTAL

Synthesis of the complex

The complex was obtained following the procedure described by Birdsall and Weber [11] by reaction of methanolic solutions of creatinine (Sigma) and $CuCl_2 \cdot 2H_2O$ (Merck) in a 1 : 1 molar ratio. The complex immediately precipitates as a microcrystalline greenish powder. During one of these preparations, we could obtain a small quantity of single crystals adequate for a structure determination.

Determination of the crystal structure

Crystal data. $[C_8H_{14}N_6O_2Cl_2Cu]$, $M = 360.69$, monoclinic, space group $P2/c$ (Nr.13), $a = 7.1825(5)$, $b = 7.7965(4)$, $c = 12.428(2)$ Å, $\beta = 94.952(8)°$, $V = 693.3(1)$ Å^3, $Z = 2$, $D_{calc.} = 1.73$ g cm^{-3}, μ(Mo-K_α) = 1.97 mm^{-1}, $F(000) = 366$.

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Data processing and structure solution. A single crystal with approximate dimensions 0.15 × 0.2 × 0.35 mm was used. Intensity data were collected at 293(2) K on an Enraf-Nonius CAD-4 diffractometer, using monochromated Mo-K_α radiation ($\lambda = 0.71069$ Å) with a scan mode of $\omega-2\theta$. 1831 independent reflections were collected in the range $2.61 < 2\theta < 29.95°$ and 1391 independent reflections with $I > 2\sigma(I)$ were used for further computations. The intensity data were corrected for Lorentz and polarization effects and for absorption [12]. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares techniques. SDP [13], SHELX-76 [14], SHELX-86 [15] and SHELX-93 [16] and program systems were used.

All hydrogen atoms but one of the methyl group were located in a difference Fourier map. However, they were all positioned on a stereochemical basis and included in the refinement riding on the atom to which they are bonded with three independent isotropic thermal parameters, one common to the CH_2 hydrogens (which converged to $U = 0.050(7)$ Å^2), another common to the amine hydrogens ($U = 0.060(7)$ Å^2) and a third one common to the methyl hydrogens ($U = 0.13(1)$ Å^2). During the refinement, the methyl hydrogen atoms were allowed to rotate as a rigid group around the corresponding C—N bond so as to maximize the sum of the electron density at the three calculated hydrogen positions. The somewhat large corresponding U-value seems to indicate that the CH_3-group is rotating fairly freely (low potential barrier). However, there is a single different electron maximum after the three-fold averaging.

Final agreement indices were $R_1 = 0.0355$ and $wR_2 = 0.0853$. Tables of atomic coordinates, anisotropic thermal parameters, and calculated and observed structure factor amplitudes are available from the authors on request. Coordinates have been deposited at the Cambridge Crystallographic Data Centre.

IR-spectra

They were recorded with a Bruker FTIR spectrometer, model 113v, dispersing the samples either in KBr or in polyethylene pellets.

Electrochemical measurements

Cyclic voltammetric experiments were performed in methanolic solutions on a Bioanalytical Systems Inc. CV-1B assembly using a three-electrode cell. The working electrode was a glassy carbon disk, a platinum wire was used as a counterelectrode and a Ag/0.01 M $AgNO_3$ (in CH_3CN) electrode as reference. The system was calibrated against the $[Fe(C_5H_5)_2]^+/Fe(C_5H_5)_2]$ redox couple for which a redox potential of 0.4 V *vs* the normal hydrogen electrode (NHE) was assumed [17,18]. Potentials are given *vs* NHE in volts. $LiClO_4$ was employed as a supporting electrolyte. The response for all scan rate experiments was recorded on a Houston Instrument Omnigraphic 2000 XY recorder.

RESULTS AND DISCUSSION

Crystal and molecular structure

An ORTEP [19] drawing of the complex, showing the labelling of the non-hydrogen atoms and their vibrational ellipsoids, is presented in Fig. 2. Bond distances and angles are given in Table 1.

The Cu^{II} ion is located on a crystallographic two-fold axis and quasi-tetrahedrally coordinated to two creatinine ligands (d(Cu—N) = 1.982(2) Å and N—Cu—N′ angle = 92.3(1)°) and two chlorine ions (d(Cu—Cl) = 2.2381(8) Å, Cl—Cu—Cl′, N—Cu—Cl and N—Cu—Cl′ angles of 97.55(5), 100.25(6) and 137.32(6)° respectively). The N—Cu—N′ and Cl—Cu—Cl′ planes subtend a dihedral angle of 59.10(6)°.

There is a relatively weak and bent N—H···Cl intramolecular hydrogen-bond (d(N···Cl) = 3.183(3) Å, N—H···Cl angle of 152.2(3)°). Neighbouring molecules related by a unit cell translation along **a** are linked through a N—H···O bond of medium strength (d(N···O) = 2.895(3) Å, N—H···O angle of 161.9(3)°).

Similar structures have recently been reported for $Zn(creat)_2Cl_2$ [20] and $Cd(creat)_2Cl_2$ [21]. Also in these cases, as well as in some Pt^{II} complexes of creatinine [22–24] and in the lineal $[Ag(creat)_2]^+$ complex [25], the metal-to-ligand interaction occurs in the same way, i.e. through the cyclic nitrogen atom of the ligand in its amino form (Fig. 1).

Infrared spectra

The infrared spectra of creatinine, and of some of its metal complexes, have been often reported in the recent literature [11,22,23,26–29]. Therefore, in Table

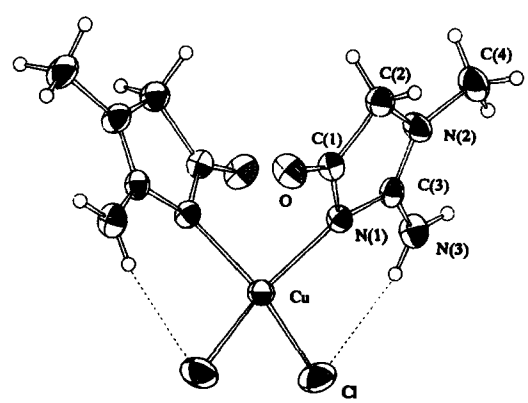

Fig. 2. ORTEP plot of $Cu(creat)_2Cl_2$ showing the non-H atoms labelling and their vibrational ellipsoids.

Table 1. Interatomic bond distances (Å) and angles (°) for $Cu(creat)_2Cl_2$

Cu—N(1)	1.982(2)	N(2)—C(4)	1.450(3)
Cu—Cl	2.2381(8)	N(2)—C(2)	1.453(3)
N(1)—C(3)	1.368(3)	N(3)—C(3)	1.310(3)
N(1)—C(1)	1.367(3)	O(1)—C(1)	1.217(3)
N(2)—C(3)	1.329(4)	C(1)—C(2)	1.507(4)
N(1)—Cu—Cl	100.25(6)	C(3)—N(2)—C(2)	109.3(2)
N(1)—Cu—N(1)#1	92.31(12)	C(4)—N(2)—C(2)	123.8(2)
N(1)—Cu—Cl#1	137.32(6)	O(1)—C(1)—N(1)	125.0(2)
Cl—Cu—Cl#1	97.55(5)	O(1)—C(1)—C(2)	125.7(2)
C(3)—N(1)—C(1)	107.1(2)	N(1)—C(1)—C(2)	109.3(2)
C(3)—N(1)—Cu	131.8(2)	N(2)—C(2)—C(1)	101.3(2)
C(1)—N(1)—Cu	117.5(2)	N(3)—C(3)—N(2)	124.8(2)
C(3)—N(2)—C(4)	126.9(2)	N(3)—C(3)—N(1)	122.2(3)
		N(2)—C(3)—N(1)	112.9(2)

Symmetry transformations used to generate equivalent atoms: (#1) $-x,y,-z+1/2$.

2, we only compare some of the most characteristic bands of the free ligand with those of the investigated complex. The spectral behaviour is totally consistent with the structural characteristics of the complex. Interestingly, and although the C=O bond distance found in the complex is practically identical to that found in the free ligand $d(C{=}O) = 1.22$ Å [30], the stretching frequency of this group is clearly displaced to higher frequencies in the complex. A similar behaviour has been reported for other N(1) bonded creatinine complexes [20, 21].

In order to attain a wider insight into the characteristics of the metal–ligand interactions, we have analyzed in detail the low frequency region of the IR spectra, shown in Fig. 3. The exact band positions measured in this region are also included in Table 2. As can be seen from these data, the Cu—N and Cu—Cl stretchings could be clearly identified. They lie in similar ranges as in the $Co(creat)_2Cl_2$ complex [27]. Also a group of bending vibrations of the metal–ligand linkage could be identified at 178/169 cm^{-1}.

Table 2. Some characteristic IR bands of creatinine and of $Cu(creat)_2Cl_2$ (values in cm^{-1})

Creatinine	$Cu(creat)_2Cl_2$	Assignment
3254vs	3212s	$\nu_{as}(NH_2)$
3033s	3178s	$\nu_s(NH_2)$
1690sh	1715vs	$\nu(C{=}O)$
1670vs	1648vs	$\delta(NH_2)+\nu(C{=}N)$
1591vs	1598vs	$\nu(C{=}N)$
1440sh	1436s/1426s	$\delta(CH_3)$
1245vs	1235vs	
1212m	1204m	$\nu(C{-}NH_2)$
1204sh	*ca* 1185sh	
841s/813m	847m	$(NH_2)_{wagg}$
Low frequency IR-spectra (450–100 cm^{-1})		
407vs	402s	
324s	*ca* 324sh	
	304vs/287vs	ν(Cu—Cl)
	253s/241s	ν(Cu—N)
246vs		
218m	210w	
198w	206w	
	178m/169m	δ(Cu—ligands)
150m	154m	
	145sh	
128w	137w/130w/124w	
115vs	113m/108sh	

vs: very strong; s: strong; m: medium; w: weak; sh: shoulder.

Electrochemical behaviour

Voltammetric experiments were effected at different scan rates, starting from +0.75 V in the negative direction (reduction of the complex).

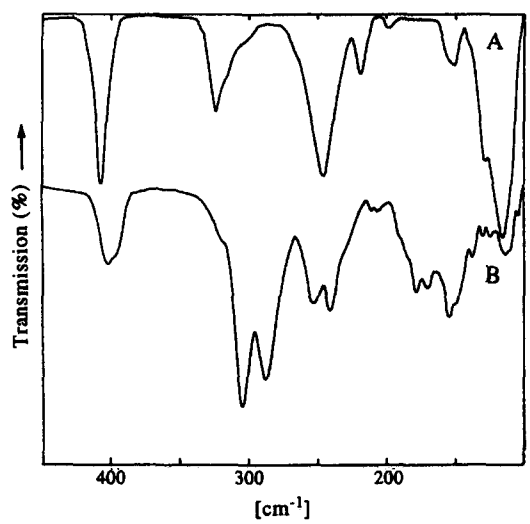

Fig. 3. FTIR spectra of creatinine (**A**) and $Cu(creat)_2Cl_2$ (**B**) between 450 and 100 cm^{-1}.

A cyclic voltammogram obtained at 0.1 V/s is shown in Fig. 4. On the forward scan, one reduction peak at +0.32 V and one broad wave at −0.75 V are observed. On the reverse (anodic) scan two oxidation peaks at +0.425 and +0.025 V appear. The first one is the counterpart of the first reduction peak, whereas the sharp anodic peak observed at +0.025 V is typical for a species stripped from the electrode surface.

The first redox couple (A/A′) was investigated at scan rates between 0.01 to 0.8 V/s, over a reduced potential range (+1.12 to −0.075 V). In this potential range, the species undergoes a quasi-reversible redox process. The difference $\Delta E_p = E_{pc} - E_{p\alpha}$ exceeds the Nernstian requirement of $59/n$ mV. The deviation from this value is scan-rate dependent and only at slower scan rates the ΔE_p-value approaches the reversible behaviour. In addition, at scan rates higher than 0.04 V/s, anodic and cathodic peak currents are not equal, and loss of cathodic current is observed.

Therefore, and for diagnostic purposes, and taking into account that it was difficult to define proper basis lines from the experimental data, the variation of $i_{p\alpha}/i_{pc}$ as a function of the scan rate was analyzed using an empirical relation derived by Nicholson [31]. These analyses show that the current ratio increases from 1.0 to 1.4 when the scan rate increases from 0.01 to 0.8 V/s. On the other hand, the peak/current function $i_{pc}/v^{1/2}$ depends also on the scan rate and decreases as v increases.

These two trends indicate that a chemical reaction occurs before the first reduction of the complex, a behaviour known as CE-mechanism or case III, using the Nicholson and Shain nomenclature [32]. The interpretation of this behaviour is that a "$CuCl_2$" species is generated according to the following equilibria:

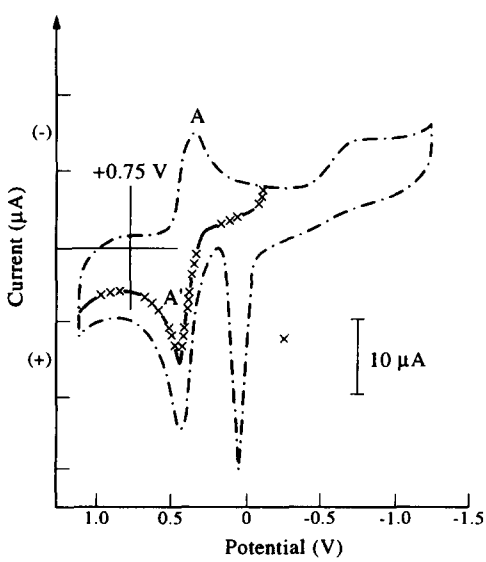

Fig. 4. Cyclic voltammetry experiment with a methanolic solution of the complex at $v = 0.1$ V/s. Supporting electrolyte: 0.1 M $LiClO_4$.

$$CuL_2Cl_2 \rightleftharpoons \text{"}CuCl_2\text{"} + 2L \quad (1)$$

This "$CuCl_2$" species is probably a pseudo-octahedral Cu^{II} complex with the cation coordinated by four solvent molecules and two chloride ions occupying both axial positions [33]. Evidence that the product of this chemical reaction is a $CuCl_2$ and not another species was obtained by additional measurements. When a 10^{-3} M $CuCl_2$ solution was investigated in identical experimental conditions, a qualitatively similar behaviour was observed. Notwithstanding, in this case, the oxidation/reduction process is quasi-reversible without chemical complications and the $i_{p\alpha}/i_{pc}$ ratio is constant and equal to 1.1 for all the employed scan rates. The couple is localized at a slightly more negative potential and the cathodic and anodic currents are greater than the currents obtained with the complex. Thus, these measurements confirm the above mentioned equilibria. Therefore, the "$CuCl_2$" obtained through the CE-mechanism is the electroactive species at this potential and the magnitude of the current is determined by the equilibrium concentration of this species.

On the basis that the first step is a reduction of "$CuCl_2$" to ["$CuCl_2$"]$^-$, the second cathodic process could be assigned to the reduction of the cuprous species to metallic copper, which is stripped from the electrode surface on the reverse scan. Nevertheless, the more negative potential obtained with the complex for this reduction step suggests that another competitive reduction process becomes operative. This may be the direct reduction of the complex (which is in equilibrium with the "$CuCl_2$" species according to eq. (1)) to metallic copper, or that of another CuL_xCl_y species also present in the mentioned equilibria.

Acknowledgements—This work was supported by CONICET and CIC-PBA. X-ray diffraction experiments were carried out at the National Diffraction Laboratory (LANADI), La Plata, Argentina.

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