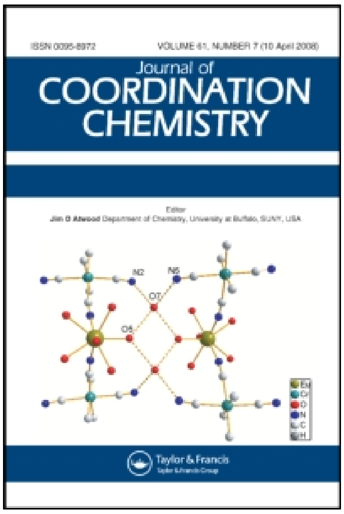

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Synthesis, structural, spectroscopic, thermal and voltammetric properties of 5,5-diethylbarbiturato complexes of zinc with 2-(2-aminoethyl)pyridine and 2-(2-hydroxyethyl)pyridine

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Synthesis, structural, spectroscopic, thermal and voltammetric properties of 5,5-diethylbarbiturato complexes of zinc with 2-(2-aminoethyl)pyridine and 2-(2-hydroxyethyl)pyridine

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Two new *bis*(5,5-diethylbarbiturato) (barb) complexes of zinc, [Zn(barb)$_2$(aepy)] (**1**), [Zn(barb)$_2$(hepy)] (**2**) [aepy = 2-(2-aminoethyl)pyridine and hepy = 2-(2-hydroxyethyl)pyridine], have been prepared and characterized by elemental analysis, FT-IR spectroscopy, thermal analysis and single crystal X-ray diffraction. Complex **1** crystallizes in the triclinic $P\bar{1}$ space group; crystals of complex **2** could not be obtained. The zinc(II) in complex **1** is tetrahedrally coordinated by two barb and an aepy ligand. The barb ligands are *N*-coordinated while the en ligand acts as a bidentate *N*,*N*′ chelate. One of the carbonyl oxygen atoms of each barb ligand makes a remarkably long bond to zinc and in this case, coordination geometry can be considered as a highly distorted octahedron. The molecules of complex **1** are connected *via* N–H $\cdots$ O hydrogen bonds, involving hydrogen atoms of both barb and aepy ligands. The voltammetric behavior of complexes **1** and **2** was investigated in aqueous solution by cyclic voltammetry using a NH_3/NH_4Cl buffer. The cyclic voltammograms of both complexes are similar, showing well-defined cathodic and anodic peaks at -1.29 and -1.10 V, respectively, due to a quasi-reversible two-electron transfer of the complexed zinc(II) ions.

Keywords: 5,5-Diethylbarbiturate; 2-(2-Aminoethyl)pyridine; 2-(2-Hydroxyethyl)pyridine; Zinc(II); Crystal structure

1. Introduction

Barbiturates are widely used as sedative hypnotic drugs and also employed for anesthesia since their discovery at the beginning of the last century [1]. Because of their potential use in clinical detection and estimation of these drugs, several such metal complexes of barbiturates have been prepared [2–4]. Among barbiturates, 5,5-diethylbarbituric acid (barbH) (also known as barbital, veronal or diemal) is the simplest derivative used especially in the form of Na(barb). Barb contains several

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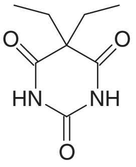
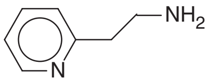
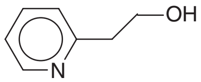
potential donor sites such as two amine nitrogen and three carbonyl oxygen atoms and can act as a polyfunctional ligand. Various metal-barb complexes with different metal ions such as Co^{II} [5], Ni^{II} [6], Cu^{II} [7–9], Zn^{II} [5, 10], Pd^{II} [11] and Pt^{II} [12] appeared.

Recently, we have started a research project on the synthesis and characterization of metal complexes of barb and two zinc(II) and two cadmium(II) complexes, namely $[Zn(barb)_2(en)]$ and $[Zn(barb)_2(bpy)] \cdot H_2O$ [13] and *cis*-$[Cu(barb)_2(en)]$ and $\{[Cd(barb)_2(\mu\text{-en})] \cdot 2H_2O\}_n$ [14] [en = ethylenediamine, bpy = 2,2′-bipyridine] were reported. As continuation of this work, in this article, we report the syntheses, structural characterization and redox behavior of two new zinc-barb complexes with the bidentate chelating ligands, 2-(2-aminoethyl)pyridine (aepy) and 2-(2-hydroxyethyl)-pyridine (hepy), namely $[Zn(barb)_2(aepy)]$ (**1**) and $[Zn(barb)_2(hepy)]$ (**2**).


barb


aepy


hepy

2. Experimental

2.1. *Materials and measurements*

All reagents were commercially available and used without further purification. Elemental analyses (C, H, N) were carried out on an Elementar Vario EL elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range 4000–400 cm^{-1} by using a Mattson 100 FT-IR spectrophotometer. Thermal analysis curves (TG and DTA) were obtained using a Rigaku TG8110 thermal analyzer in a static air atmosphere at a heating rate of 10°C min^{-1}.

Voltammetric experiments were performed with an EG&G PAR Model 384B polarographic analyzer connected to an EG&G PARC Model 303A polarographic stand. A hanging mercury drop electrode and a $Ag/AgCl/KCl_{sat}$ reference electrode were used, while the auxiliary electrode was a platinum wire. The measurements were carried out at room temperature. Stock solutions of the complexes were prepared in triply distilled and deionized water, including 20% (v/v) 2-propanol and used immediately. 0.1 M NH_3/NH_4Cl buffer (pH 9.60) was used as supporting electrolyte. Before each measurement, the solution within the electrochemical cell was deaerated by purging with pure nitrogen gas for 5 min, and during measurements a stream of nitrogen gas was passed over the solution. The voltammograms were recorded in the potential scan range from −0.6 to −1.6 V, using the following conditions: an equilibrium time of 5 s, a drop size of medium and the scan rate ranging from 100 to 1000 mV s^{-1}.

2.2. *Preparation of the zinc complexes*

Na(barb) (5,5-diethylbarbituric acid sodium salt) (0.82 g, 4 mmol) dissolved in water (10 mL) was mixed with $Zn(NO_3)_2$ (0.60 g, 2 mmol) dissolved in water (10 mL) with stirring. The solution immediately became milky. 2-(2-Aminoethyl)pyridine (aepy) (0.25 mL, 2 mmol) was added to the milky suspension and then, addition of 10 mL of 2-propanol resulted in a clear solution. The resulting solution was stirred for 30 min at room temperature and allowed to stand at room temperature. Colorless crystals of **1** were obtained after 2 days. Yield 72% (Found: C, 49.8; H, 6.0; N, 15.3; $C_{23}H_{32}N_6O_6Zn$ Calcd: C, 49.9; H, 5.8; N, 15.2).

The preparation method of **2** was the same as described for **1** with 2-(2-hydroxyethyl)pyridine (hepy) replacing aepy. Yield 64% (Found: C, 49.8; H, 5.6; N, 12.7; $C_{23}H_{31}N_5O_7Zn$ Calcd: C, 50.0; H, 5.3; N, 12.4).

2.3. *X-ray structure determination*

Intensity data for complex **1** were collected using a STOE IPDS 2 diffractometer at 100 K. The structure was solved and refined using SHELXS-97 and SHELXL-97 [15]. All non-hydrogen atoms were found on the difference Fourier map and refined anisotropically. All hydrogen atoms were included using a riding model. The details of data collection, refinement and crystallographic data are summarized in table 1.

3. Results and discussion

3.1. *Synthesis*

Na(barb) was reacted with $Zn(NO_3)_2$ in aqueous solution in the presence of aepy or hepy at room temperature, and complexes **1** and **2** were obtained in high yields. Complex **1** was obtained as well-shaped prisms, but all attempts for the crystallization of complex **2** failed. The analytical data (C, H, and N) are consistent with the expected formulations of these complexes. The title complexes are non-hygroscopic and stable in air at room temperature. Both complexes are slightly soluble in water, methanol, ethanol, and 2-propanol, whereas highly soluble in the mixture of water and 2-propanol (5 : 1). Complexes **1** and **2** melt with decomposition at 255 and 177°C, respectively.

3.2. *Description of the crystal structure of 1*

The molecular structure of complex **1** with the atom labeling scheme is shown in figure 1. Selected bond distances and angles are listed in table 2. The complex crystallizes in the triclinic crystal system $P\bar{1}$. The zinc(II) ion is coordinated by an aepy ligand and two barb anions. The coordination geometry around zinc(II) is basically a distorted ZnN_4 tetrahedron determined by the deprotonated nitrogen atoms of each barb anion and by two nitrogen atoms of a neutral aepy ligand. However, one carbonyl oxygen atom of each barb ligand bond with the zinc(II) ion with significantly long

Table 1. Crystallographic data for **1**.

Compound	**1**
Empirical formula	$C_{23}H_{32}N_6O_6Zn$
Molecular formula	553.92
T (K)	100(2)
Radiation, λ (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions (Å, °)	
a	9.4951(14)
b	11.762(2)
c	12.8259(16)
α	70.490(12)
β	76.817(11)
γ	76.047(13)
V	1293.2(4)
Z	2
D_c ($g\,cm^{-3}$)	1.422
μ (mm^{-1})	0.999
$F(000)$	580
Crystal size (mm^3)	$0.34 \times 0.28 \times 0.22$
θ range (°)	2.13/27.99
Index range (h, k, l)	−12/12, −15/15, −16/15
Reflections collected	19428
Independent reflections (R_{int})	6167 (0.0439)
Absorption correction	Numerical
Min. and max. transmissions	0.733 and 0.881
Data/restraints/parameters	6167/325
Goodness-of-fit on F^2	1.022
R indices [$I > 2\sigma(I)$]	0.0271
R indices (all data)	0.0316
wR indices (all data)	0.0696
Largest diff. peak and hole ($e\,Å^{-3}$)	0.425 and −0.409

Zn–O bonds (ranging from 2.82 to 2.90 Å). Therefore, each barb ligand behaves as a N,O donor chelating ligand as observed in $[Zn(barb)_2(bpy)] \cdot H_2O$ [13] and *cis*-$[Cu(barb)_2(en)]$ [14], and the geometry around the zinc(II) ion in **1** may be considered as a highly distorted ZnN_4O_2 octahedral geometry.

The $Zn–N_{barb}$ bond distances in complex **1** are similar and in good agreement with the corresponding distances reported for $[Zn(barb)_2(im)_2]$ at 2.009(2) Å [5], $[Zn(barb)_2(pic)_2]$ at 1.987(3) and 2.006(3) Å [10], $[Zn(barb)_2(en)]$ at 1.980(2) Å, and $[Zn(barb)_2(bpy)] \cdot H_2O$ at 1.982(2) and 1.978(1) Å [13]. The two Zn–O bond distances in complex **1** are comparable to the analogous bonds found in $[Zn(barb)_2(bpy)] \cdot H_2O$ at 2.813(1) and 2.839(1) Å [13]. The $Zn–N_{aepy}$ bond distances are slightly longer than those of the $Zn–N_{barb}$ bond distances.

The pyrimidine rings of the barb ligands and the py ring of the aepy ligand are essentially planar. The dihedral angle between the mean planes of barb1 with atoms N1–N2 and barb2 with atoms N3–N4 is 71.68(5)°. The dihedral angles between py and barb1, and py and barb2, are 86.83(5) and 64.61(5)°, respectively. Crystal packing of complex **1** is governed by N–H···O hydrogen bonds, involving hydrogen atoms of both barb and aepy ligands (see table 2 and figure 2).

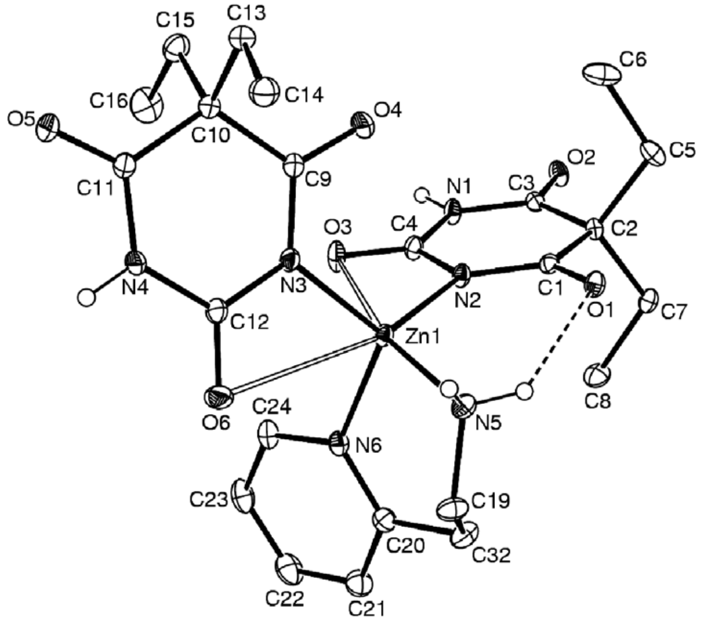


Figure 1. Molecular structure of **1** with the atom labelling scheme and 50% displacement ellipsoids (arbitrary spheres for the H atoms). All the C–H hydrogen atoms are omitted for clarity.

Table 2. Selected bond lengths (Å) and angles (°), and the hydrogen bonding geometry of **1**.[a]

Zn1–N2	2.002(1)	N2–Zn1–N3	117.79(5)	
Zn1–N3	1.962(1)	N2–Zn1– N5	109.79(5)	
Zn1–N5	2.032(1)	N2–Zn1–N6	102.65(5)	
Zn1–N6	2.069(1)	N3–Zn1–N5	110.05(5)	
Zn1–O3	2.820(1)	N3–Zn1– N6	116.75(5)	
Zn1–O6	2.898(1)	N5–Zn1–N6	97.83(5)	
D–H $\cdots$ A	D–H (Å)	H $\cdots$ A (Å)	D $\cdots$ A (Å)	∠D–H $\cdots$ A (°)
N5–H51 $\cdots$ O1	0.90	2.41	3.096(2)	134
N1–H1 $\cdots$ O3$^{\mathrm{i}}$	0.86	1.93	2.781(2)	171
N4–H4 $\cdots$ O2$^{\mathrm{ii}}$	0.86	1.95	2.799(2)	168
N5–H52 $\cdots$ O1$^{\mathrm{iii}}$	0.90	2.08	2.958(2)	164

[a] Symmetry operations: (i) $1-x$, $1-y$, $2-z$; (ii) x, $y-1$, z; (iii) $1-x$, $1-y$, $1-z$.

3.3. *IR spectra*

In the IR spectra of complex **1**, the strong absorption bands at 3316 and 3222 cm^{-1} correspond to the ν(NH) vibrations of the aepy and barb ligands, respectively, while the ν(OH) band of the hepy overlapped with the ν(NH) band giving a strong and broad band centered at 3176 cm^{-1}. The weak bands in the range ca 2850–3090 cm^{-1} are characteristic of the ν(CH) vibrations. The stretching vibrations of the carbonyl groups of barb in **1** appear as two very strong absorption bands at 1697 and 1618 cm^{-1}, similar to those observed for [Zn(barb)$_2$(en)] [13]. In contrast to complex **1**, the carbonyl vibrations in the spectra of **2** were observed as three strong bands at 1725, 1683 and

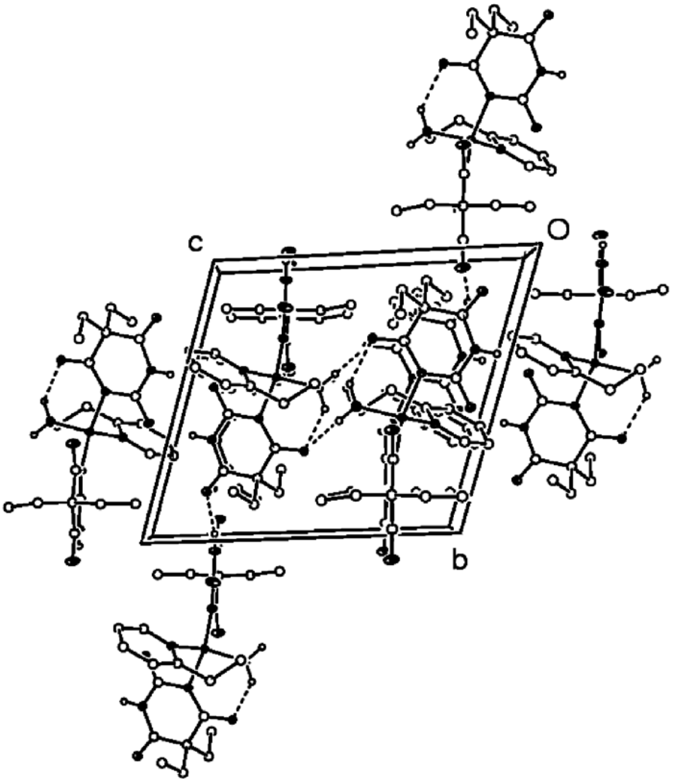


Figure 2. Crystal packing of **1**.

1631 cm^{-1}, indicating that the interaction of the carbonyl group differs from that of **1**. The bands with strong intensity between 1490 and 1423 cm^{-1} correspond to the C–C vibrations and the very strong band centred at ca 1255 cm^{-1} is attributed to the C–N stretching vibrations.

3.4. *Thermal behavior*

The thermal decomposition behavior of the title complexes was studied in a static atmosphere of air. Complex **1** melts with decomposition at 255°C. The TG curve shows that it undergoes a continuous mass loss. The DTA curve presents an endothermic peak at 297°C, presumably elimination of the aepy ligand, and two highly exothermic peaks at 422 and 444°C, which may be attributed to the decomposition of the barb ligands. The decomposition of **1** is complete at 500°C and the total experimental mass loss value of 85.30% agrees well with the calculated value 86.1%, assuming that the remaining solid residue is ZnO.

Complex **2** follows a decomposition pathway similar to that of complex **1**. It melts with decomposition at 177°C and shows a continuous mass loss. The endothermic DTA peak at 236°C corresponds to the removal of the hepy ligand, while the two violently exothermic DTA peaks are due to the degradation of the barb moiety. Total mass loss

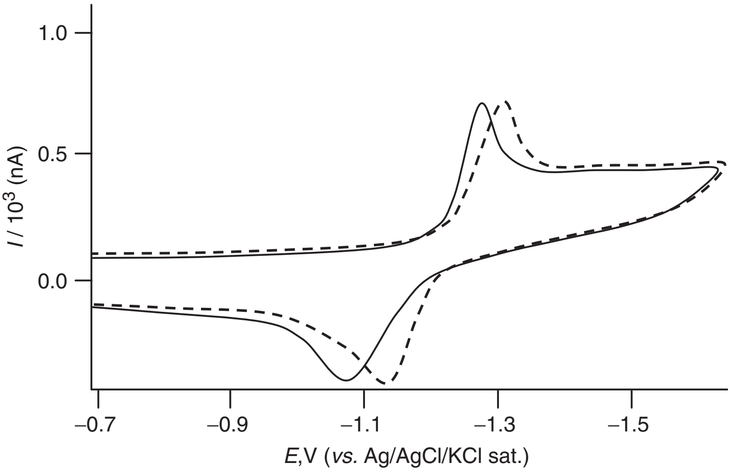


Figure 3. The cyclic voltammograms of complex **1** (solid line), and complex **2** (dashed line).

of 82.19% (Calcd 85.19%) suggests the formation of a ZnO bertolide residue deficient in oxygen as observed for $[Zn(barb)_2(bpy)] \cdot H_2O$ [13].

3.5. *Cyclic voltammetry*

The redox features of the ligands and the complexes are studied, using cyclic voltammetry in order to assign the voltammetric peaks and to elucidate the electrochemical process. The results obtained from the voltammograms of the ligand should allow easier interpretation of the electrochemical behavior of the complexes under similar experimental conditions. No peaks for the solutions of Na(barb), aepy and hepy could be identified in the voltammograms at the potential range studied (from −0.6 to −1.6 V), so the redox features of complexes **1** and **2** are metal-based reductions. Cyclic voltammograms for the aqueous solutions of complexes **1** and **2** in a 0.1 M NH_3/NH_4Cl buffer (pH 9.60) are given in figure 3. As can be seen in figure 3, both complexes display comparable voltammetric behavior, showing one well-defined reduction peak at around −1.29 V. The reverse scan showed the anodic counterpart of these reduction peaks on the voltammograms. $\Delta E_p = E_{pa} - E_{pc}$, the differences between anodic and cathodic peak potentials of complexes **1** and **2** are 156–212 and 104–164 mV, respectively. As can be seen, ΔE_p values are greater than $59/n$ mV, where n is electron number transferred. Therefore, the electron transfer processes are not in equilibrium and slow. Also, these differences increased with increasing scan rate (from 100 to 1000 mV s^{-1}). The slopes of linear equations of the log I_{pc}–log v relationships for **1** and **2** were determined as 0.60 and 0.50, respectively. According to these slope values, the reduction process of **2** was diffusion-controlled while that of **1** was mainly diffusion controlled with some adsorption contribution. Furthermore, the E_{pc} values for both complexes shifted more negative potentials with increasing scan rate. According to the diagnostic tests for quasi-reversible systems [16], these peak couples on figure 3 can correspond to a quasi-reversible two-electron transfer of the complexed zinc(II) ions.

Supplementary material

Crystallographic data for the structure reported in the article have been deposited at the CCDC as supplementary data, CCDC No. 292289 **1**. Copies of the data can be obtained on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. (E-mail: deposit@ccdc.cam.ac.uk.)

Acknowledgements

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