



Saccharinate–metal complexes with 1,10-phenanthroline (phen) or 2,2'-bipyridine (bipy) as co-ligands; the synthesis, crystal and molecular structures of five new compounds of divalent metals

Andrei S. Batsanov^a, Clair Bilton^a, Robert M.K. Deng^{b,*}, Keith B. Dillon^{a,*}, Andrés E. Goeta^a, Judith A.K. Howard^a, Helena J. Shepherd^{a,2}, Sabitha Simon^b, Inonge Tembwe^b

^a Chemistry Department, University of Durham, South Road, Durham DH1 3LE, UK

^b Chemistry Department, University of Botswana, Private Bag 0022, Gaborone, Botswana

ARTICLE INFO

Article history:

Received 25 May 2010

Received in revised form 10 September 2010

Accepted 15 September 2010

Available online 14 October 2010

Keywords:

Metal complexes
Saccharinate
Bipy
Phen
Molecular structure

ABSTRACT

Five new saccharinate complexes of divalent metals with either phen or bipy as co-ligands have been synthesised, and fully characterised by single crystal X-ray diffraction at low temperature. The complexes $[M(\text{phen})_2(\text{H}_2\text{O})_2](\text{sac})_2 \cdot \text{H}_2\text{O}$ ($M = \text{Co}$ or Zn) are isostructural, while $[\text{Hg}(\text{bipy})_2(\text{sac})_2]$ is isostructural with the analogous cadmium(II) compound, which has been described previously in the literature. Cadmium(II) complex $[\text{Cd}(\text{phen})_2(\text{sac})(\text{H}_2\text{O})](\text{sac}) \cdot \text{H}_2\text{O}$ has an octahedral cation with the unidentate ligands in *cis*-positions, while $[\text{Hg}(\text{phen})_2(\text{sac})](\text{sac}) \cdot 2.5 \text{H}_2\text{O}$ provides a rare example of a distorted *tbp* structure for the cation, with five nitrogen donors. The structures are compared with those of related saccharinate complexes. In general, the more sterically demanding phen, when compared with bipy, forces more of the saccharinate anions to be uncoordinated, and for smaller ligands such as H_2O to be coordinated to the metal, despite the electrostatic attraction between the positively charged metal and the anion. Intramolecular hydrogen bonding involving saccharinate groups plays an important role in all the hydrated complexes.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

In recent years, several saccharinate complexes of divalent metals with the bidentate nitrogen donors 2,2'-bipyridine (bipy) or 1,10-phenanthroline (phen) as co-ligands have been described, many of which have been characterised crystallographically [1–21]. Indeed the topic of metal saccharinates and their complexes with N-donor ligands has been reviewed [22], while a crystallographic survey and theoretical study of the geometry of the saccharinato-ligand/counter-ion in metal saccharinates has been published [23]. More recently, a major review on metal complexes of saccharin has appeared [24]. Specifically, structures have been elucidated for monomeric manganese(II) [1–4], iron(II) [5–7], cobalt(II) [2], nickel(II) [8], copper(II) [9–13], zinc(II) [8,14,15], cadmium(II) [8], mercury(II) [16], lead(II) [17,18], silver(I) [19], cobalt(III) [20] and recently palladium(II) and platinum(II) [21] saccharinates with either bipy or phen as co-ligands. The com-

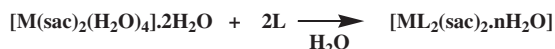
plexes $[M(\text{phen})_2(\text{sac})_2] \cdot 3\text{H}_2\text{O}$ ($M = \text{Co}$, Ni or Zn) have also been reported, and octahedral structures suggested for these on the basis of spectroscopic and magnetic measurements, with two *trans*-saccharinate ligands attached to the metal [25]. In an important paper, Johns et al. have extended our earlier work on Mn(II) [1] and Co(II) [2] bipy derivatives to some Ni(II), Zn(II) and Cd(II) complexes, the crystal and molecular structures of which were determined at 293 K [8]. We have similarly ascertained the low-temperature (150 K for the Ni and Cd compounds, 120 K for the Zn salt) structures of these complexes [26], which do not show any significant differences from their room temperature structures. There has been no systematic study and comparison of the structures of corresponding pairs of bipy and phen saccharinate complexes for a particular metal, however. Thermoanalytical data have been recorded for a number of divalent metal saccharinates with bipy [27] or phen [28] as co-ligands. A five-coordinate structure was originally suggested for the isomorphous Co^{2+} , Ni^{2+} and Zn^{2+} -bipy saccharinate complexes, $[M(\text{bipy})_2(\text{sac})](\text{sac}) \cdot \text{H}_2\text{O}$, from limited crystallographic data [29], but in later work the metal was regarded as six-coordinate $[M(\text{bipy})_2(\text{sac})\text{H}_2\text{O}]\text{sac}$ [27], in accord with more recent structure determinations [2,8,14]. The phen complexes were formulated as $M(\text{phen})_2(\text{sac})_2 \cdot \text{H}_2\text{O}$ ($M = \text{Co}$, Ni or Zn), $\text{Cu}(\text{phen})_2(\text{sac})_2$ and $\text{Pb}(\text{phen})(\text{sac})_2 \cdot 2\text{H}_2\text{O}$ from the results [28].

* Corresponding authors.

E-mail address: k.b.dillon@durham.ac.uk (K.B. Dillon).

¹ Present address: Chemistry Department, University of Juba, Sudan.

² Present address: Laboratoire de Chimie de Coordination, 205, Route de Narbonne, 31077 Toulouse Cédex 04, France.



M = Co, L = phen	n = 3	1
M = Zn, L = phen	n = 3	2
M = Cd, L = phen	n = 2	3
M = Hg, L = phen	n = 2.5	4
M = Hg, L = bipy	n = 0	5

Scheme 1. Synthesis of new complexes.

The crystal and molecular structures of a zinc(II) complex corresponding to this overall formula, $[\text{Zn}(\text{phen})_2(\text{sac})\text{H}_2\text{O}]\text{sac}$, have been ascertained very recently [15].

In the present work, new isomorphous trihydrate complexes $[\text{M}(\text{phen})_2(\text{H}_2\text{O})_2]\text{sac}_2 \cdot \text{H}_2\text{O}$ (M = Co **1** or Zn **2**), with no sac ligands coordinated to the metal, have been structurally characterised at low temperature, together with $[\text{Cd}(\text{phen})_2(\text{sac})(\text{H}_2\text{O})](\text{sac}) \cdot \text{H}_2\text{O}$ **3**, $[\text{Hg}(\text{phen})_2(\text{sac})](\text{sac}) \cdot 2.5\text{H}_2\text{O}$ **4** and $[\text{Hg}(\text{bipy})_2(\text{sac})_2]$ **5**, as described below. More significantly, we have established an important correlation for corresponding pairs of bipy and phen complexes of the same metal.

2. Results and discussion

2.1. Synthesis

In general the new complexes were prepared by adding a warm aqueous solution of the appropriate bidentate ligand (phen or bipy) in a 2:1 molar ratio to a warm aqueous solution of the metal saccharinate hexahydrate, $[\text{M}(\text{sac})_2(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$ [30,31] as shown in Scheme 1. The only exception was the $\text{Hg}(\text{sac})_2$ –phen complex **4**, which was prepared in dichloromethane as solvent (M = Hg, L = phen, $n = 2.5$ in Scheme 1). Elemental analyses for all of the products are given in Section 4. Crystals suitable for X-ray diffraction were obtained in each case.

2.2. Crystal structures

The crystal and molecular structures of complexes **1** and **2** are depicted in Figs. 1 and 2, respectively. The cobalt(II) and zinc(II) derivatives **1** and **2** are isostructural, and have no saccharinate moieties bound to the metal, although they are present as counter-ions. Selected bond distances and angles for **1** and **2** are listed in Table 1. The cations are approximately octahedral, with the two coordinated water molecules occupying *cis* positions. Both anions

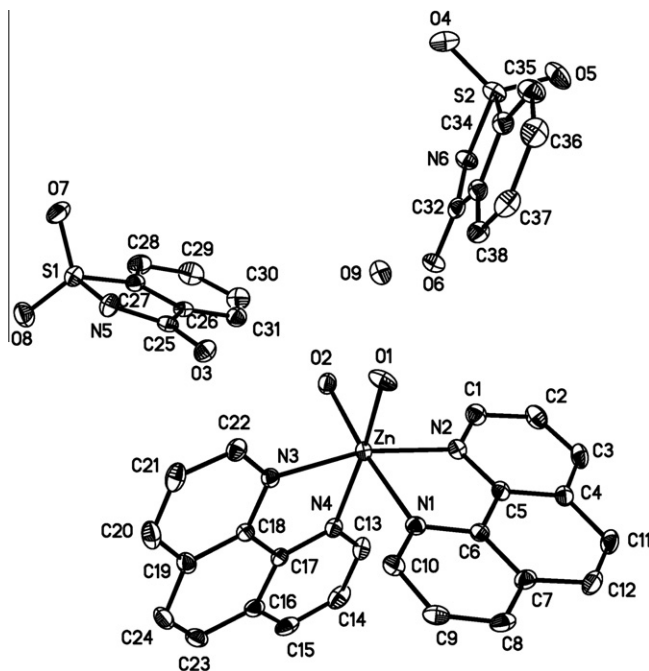


Fig. 2. Molecular structure of $[\text{Zn}(\text{phen})_2(\text{H}_2\text{O})_2] \text{sac}_2 \cdot \text{H}_2\text{O}$, **2**, at 120 K. Atomic displacement parameters are shown at 50% probability, and hydrogen atoms are omitted for clarity.

act as hydrogen bond acceptors via the carbonyl oxygen atoms, and ribbons formed through intermolecular H-bonding interactions extend parallel to the *c* axis. The average Co–N distance for the phen ligands of 2.145(2) Å is significantly longer than that of 1.934(2) Å in $[\text{Co}(\text{phen})_3](\text{sac})_3 \cdot 8.5 \text{H}_2\text{O}$ [20], as expected for the change in oxidation state. The zinc-containing cation has been structurally characterised previously in the complex *cis*- $[\text{Zn}(\text{phen})_2(\text{H}_2\text{O})_2](\text{H}_2\text{Or})_2 \cdot (\text{H}_2\text{O})_{2.125}$, where $\text{H}_3\text{Or} = \text{orotic acid}$ [32]. In this compound the octahedral arrangement around Zn is somewhat more symmetrical than in **2**, with a Zn–O distance of 2.124(2) Å and an average Zn–N distance of 2.145(2) Å [32], compared with average Zn–O and Zn–N bond lengths of 2.090(2) and 2.170(2) Å, respectively, in **2**.

The anhydrous mercury(II)–bipy complex **5** (Fig. 5) is isostructural with its cadmium(II) analogue, the room temperature structure of which has been published [8]. The metal is octahedrally

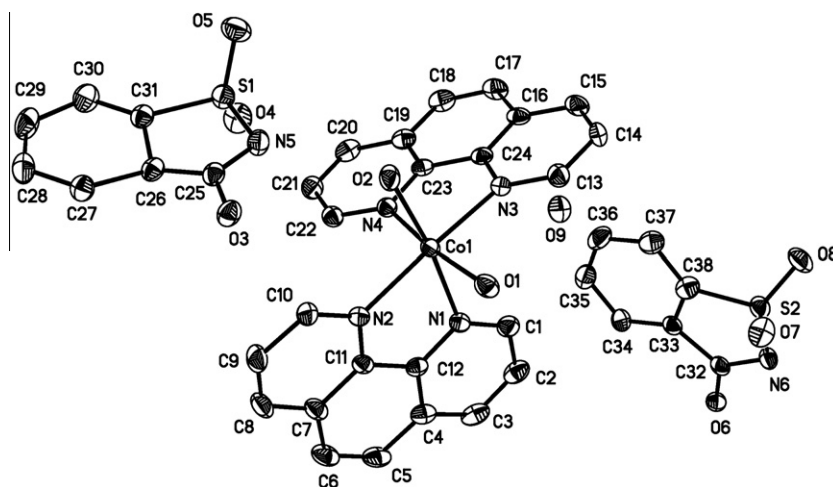


Fig. 1. Molecular structure of $[\text{Co}(\text{phen})_2(\text{H}_2\text{O})_2] \text{sac}_2 \cdot \text{H}_2\text{O}$, **1**, at 150 K. Atomic displacement parameters are shown at 50% probability, and hydrogen atoms are omitted for clarity.

Download English Version:

<https://daneshyari.com/en/article/1306548>

Download Persian Version:

<https://daneshyari.com/article/1306548>

[Daneshyari.com](https://daneshyari.com)