Available online at www.sciencedirect.com

SCIENCE DIRECT®

Thermochimica Acta 406 (2003) 245–248

thermochimica acta

www.elsevier.com/locate/tca

Short communication

Synthesis, characterization and TG–DSC study of cadmium halides adducts with caffeine

Robson F. de Farias [a,*], Ademir O. da Silva [b], Umberto G. da Silva Jr. [c]

[a] *Departamento de Química, Universidade Fedral de Roraima, 69310-270 Boa Vista, Roraima, Brazil*
[b] *Departamento de Química, Universidade Federal do Rio Grande do Norte, CP 1662, 59078-970 Natal, Rio Grande do Norte, Brazil*
[c] *Centro Federal de Educação Tecnológica da Paraíba, Av. 10 de maio 720, Jaguaribe, 58015-430 João Pessoa, Paraíba, Brazil*

Received 14 January 2003; received in revised form 28 March 2003; accepted 30 March 2003

Abstract

The synthesis, characterization and TG–DSC study of the compounds $CdX_2 \cdot n$caff, for which X: Cl, Br and I; $n = 1$ and 2 and caff: caffeine is reported. It is verified that caffeine is coordinated through more than one coordination site, despite the fact that the nitrogen of the imidazole ring is the main coordination site. The following thermal stability trend is observed: Cl > Br > I and monoadducts are more stable than bisadducts. The thermal degradation (td) enthalpies have the values ($kJ\,mol^{-1}$): 58.2 and 71.5; 74.9 and 91.4; 31.1 and 47.5 for Cl, Br and I mono and bisadducts, respectively.

Keywords: Caffeine; Cadmium halides; Adducts; Thermogravimetry

---

1. Introduction

The interaction between metal cations, such as Cu(II), Co(II), Mn(II), Sn(II), Zn(II), Ni(II), Cd(II) and Ce(IV) and molecules of biological interest have been successfully studied employing thermal techniques [1–15]. Such kind of study enables a better understanding of the physical–chemical behavior of adducts, as recently shown for zinc halides adducts, for which a close quantitative relationship between calorimetric, thermogravimetric and infrared data is observed [16]. The present work is in the same context, and reports the synthesis, characterization and TG–DSC study of the coordination compounds $CdX_2 \cdot n$caff, for which X: Cl, Br and I; $n = 1$ and 2 and caff: caffeine. Caffeine (1,3,7-trimethyl-2,6-dioxopurine), whose structural formula is shown in Fig. 1, is one of a purine alkaloids, present in many beverages, such as coffee and tea, which exerts stimulating effects on the nervous system. Caffeine causes the inhibition of the action of cyclic adenosine monophosphate (cAMP) [17].

2. Experimental

Cadmium halides (Aldrich) and caffeine (Aldrich) were of analytical grade and were used without further purification.

All adducts were synthesized through the same experimental procedure, as follows: caffeine (0.01 or 0.02 mol) was previously dissolved in deionized water (100 cm^3) at 60 °C, and then, after cooling of the caffeine solution, a desired amount of cadmium halide

---

[*] Corresponding author. Present address: Instituto de Química, Universidade Estadual de Campinas, CP 6154, 13083-970 Campinas, São Paulo, Brazil. Fax: +55-19-3788-3109.
E-mail address: robsonfarias@aol.com (R.F. de Farias).

doi:10.1016/S0040-6031(03)00229-6

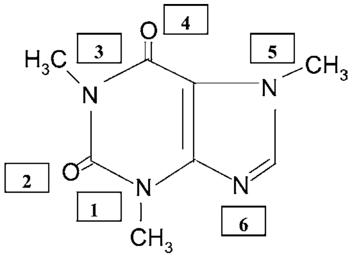

Fig. 1. Structural formula of caffeine.

solution (0.01 mol in 100 cm^3 of deionized water) was added. The resulting solution was slowly evaporated in a fume hood, at room temperature, for 8 days until the formation of white crystals. The obtained white crystalline compounds were then dried under vacuum at room temperature for 12 h.

C, N and H contents were determined using a Perkin-Elmer microelemental analyzer model 2400. Infrared spectra were recorded on a Bomem MB series apparatus in the 4000–400 cm^{-1} range, by using KBr discs.

The TG and DSC curves were obtained under nitrogen atmosphere at a heating rate of 10 °C min^{-1} in Shimadzu apparatus (TGA-50 and DSC-50, respectively).

3. Results and discussion

The C, H and N elemental analysis results for the adducts, and the main IR bands for free caffeine and adducts, are summarized in Tables 1 and 2, respectively. The CHN results are in good agreement with the proposed formulas.

Table 1
Elemental analysis results for cadmium halides adducts with caffeine

Compound	C (%)	H (%)	N (%)
$CdCl_2$·caff	25.3 (25.4)	2.6 (2.6)	14.5 (14.8)
$CdCl_2$·2caff	33.2 (33.6)	3.3 (3.5)	19.2 (19.6)
$CdBr_2$·caff	20.9 (20.6)	1.7 (2.1)	12.3 (12.0)
$CdBr_2$·2caff	29.4 (29.1)	2.5 (3.0)	16.8 (17.0)
CdI_2·caff	17.5 (17.1)	1.8 (1.8)	10.2 (10.0)
CdI_2·2caff	25.7 (25.4)	2.4 (2.7)	14.4 (14.8)

Calculated values are in parenthesis.

Table 2
Main infrared bands (cm^{-1}) for free caffeine and its compounds with cadmium halides

Compound	ν(C=O)	Pyr	Im	A[a]
Caffeine	1698[b], 1646[c]	1544	1481, 1241	608
$CdCl_2$·caff	1703, 1646	1546	1480, 1242	612
$CdCl_2$·2caff	1705, 1646	1544	1486, 1240	606
$CdBr_2$·caff	1694, 1652	1549	1486, 1230	604
$CdBr_2$·2caff	1696, 1654	1547	1485, 1230	604
CdI_2·caff	1696, 1643	1547	1485, 1228	606
CdI_2·2caff	1694, 1641	1547	1486, 1230	604

Pyr: mainly a pyrimidic ring vibration; Im: mainly an imidazolic ring vibration.

[a] In-plane and out-of-plane deformation coupled with δ(C=O).

[b] Carbonyl group 2.

[c] Carbonyl group 4 (see Fig. 1).

To help in the infrared data interpretation, a comparison with a previously reported specific infrared study on caffeine [18] will be used. However, is worth noting that despite the use, in both cases ([18] and this work) of analytical grade caffeine samples, the two sets of infrared data do not matches perfectly. At a first look, one can see that caffeine exhibits six possible coordination sites, labeled from 1 to 6 in Fig. 1, i.e. two oxygen atoms and four nitrogen atoms. At a first reasoning, is possible to suppose that the sites 1–5 are affected in a larger extent by steric hindrance than site 6 and so, we expect that this site will be employed.

The upward shift of the caffeine C=O bands could be associated with a lower electron delocalization in the two carbonyl groups [18]. Furthermore, in molecules with groups with structures similar to those of the six member ring of caffeine, such as ethyleneurea and propyleneurea [7–15] a negative shift of the C=O band is associated with a coordination involving the oxygen atoms of the carbonyl group, whereas an increase of this band is associated with a coordination through nitrogen. So, based on Table 2 data, could be supposed that, for all compounds, the carbonyl groups are always involved in the coordination to cadmium. However, it can be noted that the infrared bands associated mainly with the imidazole ring are the most affected (mainly for cadmium bromide and cadmium iodide adducts), whereas the band associated mainly with the pyrimidinic ring remains practically unchanged. So, as a general remark, could be supposed that, for all six synthesized adducts, caffeine is coordinated through more than one coordination site, despite the fact that the nitrogen (6) of the imidazole ring is the main (producing most effective bonds) coordination site. Such proposal is in agreement with the obtained infrared data, with the existence of multiple coordination sites in caffeine, as well as with the tendency of cadmium compounds to polymerize [19].

All adducts exhibits a single mass loss step associated with the release of caffeine molecules, as verified by inspection of TG–DTG curves. For all adducts, the thermal degradation (td) sequence steps are: $CdX_2 \cdot n\text{caff}\ (s) \rightarrow CdX_2(s) + n\text{caff}(g)$; $CdX_2(s) \rightarrow CdX_2(g)$. Since even for the bisadducts a single mass loss step for caffeine release is observed, could be inferred that in such adducts both caffeine molecules are located at equivalent (from an energetic point of view) coordination sites. The experimental mass losses for caffeine are in good agreement (±3%) with the calculated values, taking into account the proposed formulas. The following thermal stability trend is observed: Cl > Br > I and monoadducts are more stable than bisadducts: $CdCl_2 \cdot$caff (250 °C), $CdCl_2 \cdot 2$caff (240 °C), $CdBr_2 \cdot$caff (220 °C), $CdBr_2 \cdot 2$caff (200 °C), $CdI_2 \cdot$caff (200 °C) and $CdI_2 \cdot 2$caff (190 °C).

As previously observed for cadmium halides adducts with cyclic amides and thioamides [10] (infrared data) the metal–ligand bond strength is related with the hardness of cadmium and the halides. In this case, since Cl^- is a hard base and taking into account that Cd^{2+} could be considered a soft or borderline base, weaker Cd–Cl bonds are expected, and so, stronger Cd–caffeine bonds, implying in a more stable compound, as is indeed observed.

By inspection of DSC curves, is verified that with exception of the cadmium bromide monoadduct, all compounds melt before suffers the thermal degradation. The enthalpy variations associated with the melting and release of caffeine molecules are summarized in Table 3. By inspection of Table 3 data, can be verified that cadmium chloride monoadduct and cadmium bromide bisadduct exhibits very similar melting enthalpies, suggesting that for those adducts the intermolecular forces have similar magnitude. Furthermore, $CdCl_2$ and $CdBr_2$ adducts exhibits the same percentage increase in the thermal degradation enthalpy values from monoadducts to bisadducts: $71.5/58.2 = 91.4/74.9 = 1.22$. Cadmium iodide adducts are those with lower thermal degradation enthalpy values and those with the lower (with exception of $CdCl_2 \cdot 2$caff adduct) thermal degradation enthalpy/melting enthalpy ratios suggesting that for this compounds the intermolecular and intra-molecular forces have similar magnitudes.

Table 3
Enthalpy values (from DSC data) for melting (m) and thermal degradation (td) for caffeine adducts with cadmium halides

Compound	ΔH_m (kJ mol^{-1})	ΔH_{td} (kJ mol^{-1})
$CdCl_2 \cdot$caff	16.7	58.2
$CdCl_2 \cdot 2$caff	80.9	71.5
$CdBr_2 \cdot$caff	–	74.9
$CdBr_2 \cdot 2$caff	16.2	91.4
$CdI_2 \cdot$caff	29.0	31.1
$CdI_2 \cdot 2$caff	33.2	47.5

Taking into account the previous argument about the influences of cadmium and halides hardness on the metal–caffeine bond strength, the fact that the $CdBr_2$ adducts are those with the higher thermal degradation enthalpy values is unexpected: Cd^{2+} (a borderline acid) could make most strong bonds with Br^- (a borderline base) an so, weaker bonds with the caffeine molecules. However, one must remember that in the energetic of the thermal degradation process not only the rupture of the metal–ligand bonds are involved: the grain sizes and shapes, the diffusion of the gaseous products through the solid phase as well as the possible caffeine–caffeine interactions into an adduct molecule could exerts remarkable effects on the ligand release process.

4. Conclusion

Based on the obtained experimental results could be concluded that:

(1) When interacting with cadmium halides to form solid adducts, caffeine molecules links to Cd^{2+} by using mainly the nitrogen atom of the imidazole ring.
(2) The thermal stability and thermal degradation enthalpies for the studied adducts seems to be affected by the metal and halides hardness.
(3) For cadmium iodide–caffeine adducts, the intermolecular and intra-molecular forces should have similar magnitudes.

References

[1] R.F. de Farias, H. Scatena Jr., C. Airoldi, J. Inorg. Biochem. 73 (1999) 253.
[2] R.F. de Farias, C. Airoldi, J. Inorg. Biochem. 76 (1999) 273.
[3] R.F. de Farias, L. Martínez, C. Airoldi, Transition Met. Chem. 27 (2002) 253.
[4] R.F. de Farias, Transition Met. Chem. 27 (2002) 594.
[5] R.F. de Farias, L.M. Nunes, C. Airoldi, J. Therm. Anal. Calom., in press.
[6] L. Martinez, R.F. de Farias, C. Airoldi, Thermochim. Acta, in press.
[7] R.F. de Farias, O.A. de Oliveira, J.V. de Medeiros, C. Airoldi, Thermochim. Acta 328 (1999) 241.
[8] R.F. de Farias, C. Airoldi, Thermochim. Acta 378 (2001) 113.
[9] R.F. de Farias, G.C. Petrucelli, C. Airoldi, Thermochim. Acta 376 (2001) 1.
[10] R.F. de Farias, Thermochim. Acta 376 (2001) 63.
[11] R.F. de Farias, L. Martínez, C. Airoldi, Thermochim. Acta 376 (2001) 91.
[12] R.F. de Farias, L.M. Nunes, Transition Met. Chem. 26 (2001) 477.
[13] R.F. de Farias, L. Martínez, C. Airoldi, Transition Met. Chem. 27 (2002) 748.
[14] R.F. de Farias, A.O. da Silva, Transition Met. Chem., in press.
[15] R.F. de Farias, C. Airoldi, Thermochim. Acta 390 (2002) 213.
[16] R.F. de Farias, C. Airoldi, H. Scatena Jr., Polyhedron 21 (2002) 1677.
[17] P. Ritter, Biochemistry—A Foundation, Brooks/Cole, Pacific Grove, 1996.
[18] J. De Taeye, Th. Zeegers-Huyskens, Spectrosc. Lett. 19 (1986) 299.
[19] N.N. Greenwood, A. Earnshaw, Chemistry of the Elements, Butterworths–Heinemann, Oxford, 1995, pp. 1395–1420.