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Vol. 16(18), pp. 1042-1047, 3 May, 2017
DOI: 10.5897/AJB2015.14975
Article Number: F12241F64055
ISSN 1684-5315

http://www.academicjournals.org/AJB

African Journal of Biotechnology

Full Length Research Paper

The African black soap from *Elaeis guineensis* (Palm kernel oil) and *Theobroma cacao* (Cocoa) and its transition metal complexes

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Received 17 September, 2015; Accepted 18 November, 2015

African black soap is an indigenous African organic soap formed by esterification. This was prepared by reacting palm kernel oil and the filtrate of cocoa pod ash. Chemical analyses revealed the moisture content was 26% (w/w), total fatty matter (TFM) was 44.75% (w/w), total fatty alkaline (TFA) was 0.22% (w/w), total alkaline (TA) was 11.78% (w/w) and pH was 10. The metal complexes were formed by the reaction of the synthesized black soap with some transition metal salts which included $Cu(CH_3COO)_2.H_2O$, $Pb(CH_3COO)_2.3H_2O$ and $FeCl_3$. The metal:ligand ratio, that is, M:L = 3:1, while the reaction was carried out in an aqueous medium to afford $[Pb(C_{11}H_{23}COO^-K^+)_2(C_{11}H_{23}COO^-)_2].9H_2O$, $[Cu(BL)_4(C_{11}H_{23}COO^-)_2].4H_2O$ and $[Fe(BL)_2(C_{11}H_{23}COO^-)Cl_2]$ with the percentage yield of 56, 48 and 41%, respectively. Characterization of the black soap and complexes was done by spectroscopic analyses and determination of physicochemical properties. The solubility of the metal complexes was determined at room temperature in various solvents. Results showed that solubility increased as polarity decreased and it was most effective with non-polar organic solvents. Potassium ester ($C_{11}H_{23}COO^-K^+$), commonly called African black soap, has acted either as a monodentate or bidentate ligand forming metal complexes by coordinating through one or two of its oxygen donor atoms and also by entirely replacing the potassium ion with the transition metal (displacement reaction). Spectra analyses corroborate an octahedral structure for the Pb(II), a distorted octahedral structure for the Cu(II) and an octahedral Fe(III) complex.

Key words: African black soap, esterification, metal complexes.

INTRODUCTION

Palm kernel oil is an edible plant oil derived from the kernel of the oil palm *Elaeis guineensis* (Poku, 2012). Palm kernel oil is high in lauric acid which has been shown to raise blood cholesterol levels, both as cholesterol contained in low-density lipoprotein (LDL-C) and cholesterol contained in high-density lipoprotein

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(HDL-C) (Rakel, 2012). Palm kernel oil does not contain cholesterol or trans fatty acids (Rakel, 2012). Lauric acid is important in soap making: a good soap must contain at least 15% laurate for quick lathering, while soap made for use in sea water is based on virtually 100% laurate (Musa, 2009). *Theobroma cacao* also called cacao tree, is a small (13 to 26 ft tall) evergreen tree in the family Malvaceae, whose parts are very useful to man's daily living (Encyclopedia of Life, 2012). Soaps are mainly used as surfactants for washing, bathing and cleaning, but they are also used in textile spinning and are important components of lubricants. Soaps for cleansing are obtained by treating vegetable oil or animal oils and fats with a strong alkaline solution. Fats and oils are composed of triglycerides; three molecules of fatty acids are attached to a single molecule of glycerol (Beetseh and Anza, 2013). Black soap (BL) widely used by different tribes in Nigeria has different names, such as Ose Dudu in Yoruba and Eko Zhiko in Nupe (Getradeghana, 2000). In the Western part of Africa, black soap is known as Anago soap or Alata simena in Ghana and in Hausa it is known as Sabulun salo. The making of soaps from ash-derived alkali has been an age-old craft in Nigeria and West African countries (Bella, 2008). African black soap or black soap is a natural source of vitamin A and E, and iron (Grieve, 1997). Depending on where it is manufactured, black soap contains leaves and plantain skins, shea tree bark, cocoa pods or palm tree leaves (Bella, 2008). Metal complexes or coordination complexes consist of an atom or ion (usually metallic), and surrounding array of bound molecules or anions, that are in turn known as ligands or complexing agents (IUPAC, 1997). Air stable Ag(I), Co(II) and Cu(II) complexes of pyrimethamine have been synthesized and characterized by Idemudia and Ajibade (2010). The structure of African black soap, a potassium ester, reveals it contains two oxygen donor atoms (Dunn, 2010). These oxygen donor atoms can coordinate to other transition metals. The objectives of this study were to prepare and chemically analyze the African black soap from *E. guineensis* (Palm Kernel Oil) and *T. cacao* (Cocoa) and its transition metal complexes. Therefore, this report serves as the first on the coordination of one or two of the oxygen donor atoms present in the potassium ester, African black soap, to other transition metals, as well as the substitution of the potassium cation with a transition metal.

MATERIALS AND METHODS

Chemical

Palm kernel seeds and cocoa pods were locally sourced from a town called Ifeodan, Osun State, Nigeria. All solvents used (methanol, dimethylsulfoxide (DMSO), dimethylformamide (DMF), acetone, chloroform, ethanol and diethyl ether) were purchased as analytical grades from Sigma-Aldrich and SAARChem.

Instrumentation

Infrared spectra were recorded as KBR plates on a Nicolet Avatar FTIR 330 spectrophotometer. The UV-Visible spectra were recorded on a Schimadzu UV-1800 spectrometer. The percentage metal analyses were determined using Agilent 240FS AA spectrometer.

Preparation of black soap

The palm kernel oil was obtained from palm kernel seeds. These seeds were ground to extract the palm kernel oil locally by squeezing. Thereafter, 20 pieces of cocoa pods were burnt to ashes. 750 g of the ash was mixed with 1 L of water. The mixture was filtered to get the filtrate. A pot was placed on a burner prepared from local firewood, 1 L of the palm kernel oil was poured into the pot and it was allowed to boil. 0.5 L of the potash ash filtrate from cocoa pods was measured in a bowl. 0.3 L of the filtrate was poured gradually with the hand well above the pot into the boiling oil. As the filtrate was poured into the boiling oil, the mixture began to lather. The mixture was left to heat at a regulated temperature. The remaining 0.2 L of the filtrate was poured gradually into the mixture and allowed to boil at a regulated temperature. This process was repeated till the ash filtrate was used up. 10 min later, the mixture was stirred and as the stirring continued, the mixture began to solidify. 50 ml of water was added to the solid mixture and stirred thoroughly to form a dark brown soap. The solid soap was melted to obtain a much softer and feather weight soap, while the stove was maintained at a very low temperature to avoid burning or charring of the soap.

Preparation of the metal complexes of black soap

Various complexes were prepared by reacting metal salt:black soap in the ratio 3:1. 0.00132 mol (0.5 g) of $Pb(CH_3COO)_2.3H_2O$ was reacted with 0.000439 mol (0.105 g) of black soap, 0.0025 mol (0.5 g) of $Cu(CH_3COO)_2$ was reacted with 0.0008348 mol (0.199 g) of black soap and 0.00308 mol (0.5 g) of $FeCl_3$ was also separately reacted with 0.001027 mol (0.24 g) of black soap. Each metal salt was dissolved in 20 ml of distilled water and then added to a stirring solution of the black soap in 10 ml distilled water. The colour of each solution changed in a few minutes. The mixture was refluxed for 1 h and the products precipitated were filtered (after cooling), washed with 5 ml of distilled water, dried and stored in the desiccator.

RESULTS AND DISCUSSION

The reaction for the preparation of African black soap (Dunn, 2010) is presented as Equation 1.

$$\underset{\text{Lauric acid}}{\begin{array}{l} CH_2OCO(CH_2)_{10}CH_3 \\ | \\ CH_2OCO(CH_2)_{10}CH_3 \\ | \\ CH_2OCO(CH_2)_{10}CH_3 \end{array}} + 3KOH \longrightarrow \underset{\text{Black soap (BL)}}{3CH_3(CH_2)_{10}COOK} + \underset{\text{Glycerol}}{\begin{array}{l} CH_2OH \\ | \\ CH_2OH \\ | \\ CH_2OH \end{array}}$$

Equation 1: Preparation of African black soap

The general equation for the preparation of the transition metal complexes synthesized from the reaction of black soap and the hydrated acetate salts can be represented

$C_{11}H_{23}COO^{-}K^{+}$ (BL) $C_{11}H_{23}COO^{-}$ (L)

Figure 1. Structures of both ligands, that is, black soap (BL) and its hydrolyzed state (L).

Table 1. Some physical properties of black soap and its metal complexes.

Compound	Colour	Formula weight	Yield (% Yield)	% Metal calculated (Found)
$C_{11}H_{23}COO^{-}K^{+}$ (BL)	Dark Brown	238	0.31 g (56)	ND
$[Pb(BL)_2(C_{11}H_{23}COO^{-})_2].9H_2O$	White	1243	0.31 g (56)	16.67 (16.70)
$[Cu(BL)_4(C_{11}H_{23}COO^{-})_2].4H_2O$	Blue	1489	0.59 g (48)	4.28 (4.30)
$[Fe(BL)_2(C_{11}H_{23}COO^{-})Cl_2]$	Red	802	0.42 g (51)	6.97 (7.0)

ND: Not determined.

Table 2. FTIR spectra analyses of the metal complexes and black soap.

Compound	υ (OH) (cm^{-1})	υ (C-H) (cm^{-1})	υ (C=O) (cm^{-1})	υ (C-O) (cm^{-1})	Others
$C_{11}H_{23}COO^{-}K^{+}$ (BL)	3250 s 3170 s	2995 s 2877 s	1770 s 1688 s	1305 s	1435 s
Pb(II) complex; $[Pb(BL)_2(C_{11}H_{23}COO^{-})_2].9H_2O$	3522 bw	2925 s 2863 s	-	-	1524 s 1411 s
Cu(II) complex; $[Cu(BL)_4(C_{11}H_{23}COO^{-})_2].4H_2O$	3472 bm	2932 s 2866 s	-	-	1555 s 1423 s
Fe(III) complex; $[Fe(BL)_2(C_{11}H_{23}COO^{-})Cl_2]$	3460 bm	2931 s 2866 s	-	-	1591 s 1448 s

as Equation 2.

$$M(CH_3COO)_2.xH_2O \ + \ yBL \xrightarrow{H_2O} [M(BL)_{2m}L_2].\ nH_2O \ + \ 2CH_3COOK$$

where BL is black soap ($C_{11}H_{23}COO^{-}K^{+}$) and L is the $C_{11}H_{23}COO^{-}$ when $M^{2+} = Pb^{2+}$; x = 3, y = 4, m = 1 and n = 9; when $M^{2+} = Cu^{2+}$; x = 1, y = 6, m = 2 and n = 4.

Equation 2: General equation for the reaction of black soap with hydrated acetate salts

But when the salt was changed to anhydrous $FeCl_3$, the equation of the reaction with the prepared black soap is presented as Equation 3.

$$FeCl_3 \ + \ yBL \xrightarrow{H_2O} [Fe(BL)_{2m}LCl_2] \ + \ KCl$$

where BL is the black soap ($C_{11}H_{23}COO^{-}K^{+}$) and L is the $C_{11}H_{23}COO^{-}$ for y = 2 and m = 1.

Equation 2: The reaction of black soap with anhydrous metal chloride salt

Figure 1 presents the structures of both ligands, that is, black soap and its hydrolyzed state (L).

Some of the physical properties of black soap and its metal complexes are shown in Table 1.

Infrared spectra analysis

The FTIR spectra analyses of the prepared black soap and its metal complexes are shown in Table 2. The characteristic vibrational frequencies have been identified

Table 3. Electronic spectra data for the metal complexes and black soap.

Compound	Band position (nm)	Band position (cm^{-1})	Transition
$C_{11}H_{23}COO^-K^+$ (BL)	350	28,571	n - π*
	277; 299	36,101; 33,445	π - π*
$[Pb(BL)_2(C_{11}H_{23}COO^-)_2].9H_2O$	259	38,610	π - π*
	466; 496	21,459; 20,161	d-d
$[Cu(BL)_4(C_{11}H_{23}COO^-)_2].4H_2O$	262	38,168	π - π*
	688; 721	14,535; 13,870	d-d
$[Fe(BL)_2(C_{11}H_{23}COO^-)Cl_2]$	340	29,411	n- π*
	288	34,722	π - π*
	466; 544	21,459; 18,382	d-d

by comparing the spectra of the complexes with the free ligand. There are two potential donor sites in black soap. These are the keto-oxygen and ester oxygen. The infrared spectrum of the prepared black soap shows two strong bands at 3250 and 3170 cm^{-1} attributed to the stretching vibration of υ (OH) due to hydrogen bonding. This bands appeared as a broad either medium or weak band having undergone a shift to higher frequencies between 3460 and 3522 in the metal complexes due to the presence of the water molecules. The strong bands appearing at 1770 and 1688 cm^{-1} in the spectrum of black soap were attributed to the υ (C=O) frequency of the keto group. These bands have disappeared in all its metal complexes signifying the involvement of the oxygen of the keto group in chelation. The strong band appearing at 1305 cm^{-1} attributable to υ (C-O) frequency has also disappeared in all its metal complexes. This also signifies the involvement of the oxygen of the ester group in chelation (Osowole et al., 2005; Adetoye et al., 2009; Ikotun et al., 2011; Oladipo et al., 2012).

Electronic spectra analyses

The electronic spectra data for black soap and the metal complexes are shown in Table 3. The solid reflectance spectra of these compounds were determined. The ultraviolet spectrum of black soap showed an absorption at 28,571 cm^{-1}, which has been attributed to n - π* transition. This band disappeared in the spectra of its Cu(II) and Pb(II) complexes, but appeared at a higher frequency of 29,411 cm^{-1} in the spectrum of its Fe(III) complex. The bands appearing at 36,101 and 33,445 cm^{-1} have been attributed to π - π* transitions. This π - π* transition appeared as a single band in all its complexes, moving to higher frequencies. It appeared at 38,610 cm^{-1} in complex $[Pb(BL)_2(C_{11}H_{23}COO^-)_2].9H_2O$; 38,168 cm^{-1} in complex $[Cu(BL)_4(C_{11}H_{23}COO^-)_2].4H_2O$ and 34,965 cm^{-1} in complex $[Fe(BL)_2(C_{11}H_{23}COO^-)Cl_2]$. The visible spectrum of the complex $[Pb(BL)_2(C_{11}H_{23}COO^-)_2].9H_2O$ showed d-d transitions at 21,459 and 20,161 cm^{-1} (Lever, 1980). These d-d transitions appeared at 14,535 and 13,870 cm^{-1} in the spectrum of $[Cu(BL)_4(C_{11}H_{23}COO^-)_2].4H_2O$, while also appearing at 21,459 and 18,382 cm^{-1} in the spectrum of $[Fe(BL)_2(C_{11}H_{23}COO^-)Cl_2]$ (Lever, 1980; Oladipo et al., 2012).

Solubility test

The results of the solubility test of black soap and its metal complexes are shown in Table 4. The solubility of the prepared compounds was determined at room temperature (25°C) in water, methanol, ethanol, dimethylsulfoxide (DMSO), dimethylformamide (DMF), acetone, chloroform and diethyl ether, with a decreasing order of polarity. Solubility test results revealed that black soap was soluble in water and diethyl ether, sparingly soluble in the alcohols, while insoluble in all other tested solvents. The Pb(II) complex was only soluble in diethyl ether, sparingly soluble in chloroform and insoluble in all other tested solvents. Cu(II) complex was soluble in DMSO, DMF, chloroform and diethyl ether, but insoluble in water, methanol, ethanol and acetone. Fe(III) complex was soluble in chloroform and diethyl ether. It was sparingly soluble in DMSO and DMF, while it was insoluble in all other tested solvents.

Other physicochemical properties of black soap

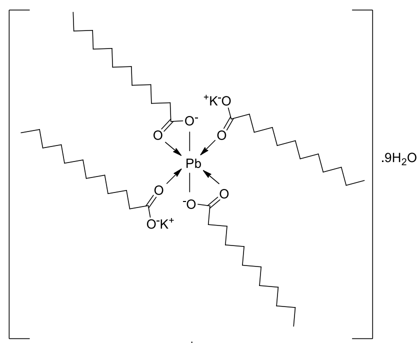
Table 5 presents the results for some other determined physicochemical parameters for the prepared black soap. The total fatty matter (TFM) as determined was 44.75% (w/w), total fatty alkaline (TFA) was 0.22% (w/w), the moisture content was 26% (w/w), the pH was 10 and the total alkaline (TA) was 11.78% (w/w). Figure 2 presents the proposed structures for the prepared transition metal complexes of black soap based on spectra analyses.

Table 4. The solubility test of the black soap and its metal complexes.

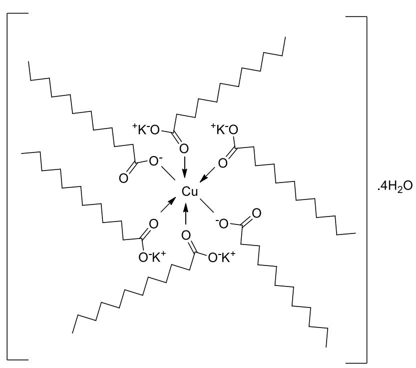
Compound	Water	Methanol	Ethanol	DMSO	DMF	Acetone	Chloroform	Diethyl ether
$C_{11}H_{23}COO^-K^+$ (BL)	Soluble	Sparingly soluble	Sparingly soluble	Insoluble	Insoluble	Insoluble	Insoluble	Soluble
Pb(II) complex	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble	Sparingly soluble	Soluble
Cu(II) complex	Insoluble	Insoluble	Insoluble	Soluble	Soluble	Insoluble	Soluble	Soluble
Fe(III) complex	Insoluble	Insoluble	Insoluble	Sparingly soluble	Sparingly soluble	Insoluble	Soluble	Soluble

Table 5. Results of the percentage composition of various parameters of black soap).

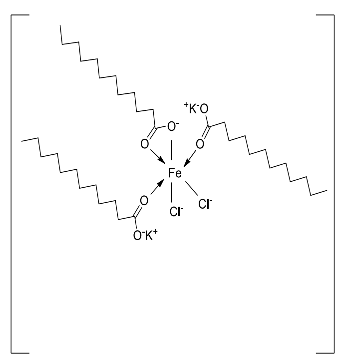
Parameter	Composition (%)
Total fatty matter	44.75
Total fatty alkaline	0.22
Moisture content	26
pH	10
Total alkaline	11.78



$[Pb(C_{11}H_{23}COO^-K^+)_2(C_{11}H_{23}COO^-)_2].9H_2O$



$[Cu(C_{11}H_{23}COO^-K^+)_4(C_{11}H_{23}COO^-)_2].4H_2O$



$[Fe(C_{11}H_{23}COO^-K^+)_2(C_{11}H_{23}COO^-)Cl_2]$

Figure 2. Proposed structures for transition metal complexes of black soap.

Conclusion

African black Soap from *E. guineensis* (Palm Kernel Oil) and *T. cacao* (Cocoa) and its transition metal complexes have been successfully prepared. Physicochemical analyses of this black soap revealed that the moisture content was 26% (w/w), TFM was 44.75% (w/w), TFA was 0.22% (w/w), TA was 11.78% (w/w) and pH was 10. Potassium ester, commonly called African black soap, $C_{11}H_{23}COO^-K^+$ (BL), has also acted either as a monodentate or a bidentate ligand forming metal complexes by either coordinating through one or two of its oxygen donor atoms or entirely replacing the potassium cation with the transition metal (displacement reaction). Spectra analyses corroborate an octahedral structure for the prepared Pb(II), Cu(II), and Fe(III) complexes, with Pb(II) and Cu(II) complexes possessing some water of hydration. This report presents an arousing interest in the possibility of this ligand to form more complexes with other transition metals, as well as mixed ligand complexes with further studies.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

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