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N-Morpholine-*N'*-benzoylthiourea as an extractant for Pb(II) and Cu(II) in aqueous media: Crystal structure of bis(*N*-morpholine-*N'*-4-benzoylthioureato)lead(II)

Kenochukwu Johncross Ifeanyieze ¹, Obinna Chibueze Okpareke ¹,
 Uchechukwu Susan Oruma ¹, Nkechinyere Nwanneka Ukwueze ¹, Ilknur Babahan Bircan ²,
 and Jonnie Niyi Asegbeloyin ^{1,*}

¹ Department of Pure and Industrial Chemistry, Faculty of Physical Sciences, University of Nigeria, Nsukka, Enugu State, 410001, Nigeria

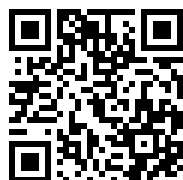
² Department of Chemistry, Faculty of Arts and Science, Adnan Menderes University, Aydin 09010, Turkey

* Corresponding author at: Department of Pure and Industrial Chemistry, Faculty of Physical Sciences, University of Nigeria, Nsukka, Enugu State, 410001, Nigeria.

e-mail: niyi.asegbeloyin@unn.edu.ng (J.N. Asegbeloyin).

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ABSTRACT



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The reaction of *N*-morpholine-*N'*-benzoylthiourea (L: HBMOR) and lead(II) acetate gave a neutral, stable metal(II) complex of type ML₂. The Pb(II) complex crystallized in a monoclinic crystal system with *P*2₁/*n* space group. The complex was further characterized by spectroscopic and microanalytic analyses. The solvent extraction behaviors of Pb(II) and Cu(II) ions were investigated in aqueous media containing HBMOR/CHCl₃ as extracting reagents. The solvent extraction of Pb(II) and Cu(II) ions from solutions of varying pH, varying concentrations of mineral acids (HCl, HNO₃ and H₂SO₄), varying concentrations of masking agents (EDTA, KCN and KH[C₈H₆O₄]) and varying concentrations of salting-out agents (NaCl, Na₂SO₄, KNO₃) in chloroform solutions of HBMOR were studied. Pb(II) and Cu(II) ions were quantitatively extracted at pH = 7 in 10 min (HCl = 0.01 M) and pH = 8 in 5 min (H₂SO₄ = 0.01 M), respectively. The Pb(II) ions were quantitatively extracted with minimal interference from EDTA (0.01 M), KCN (0.50 M), and potassium hydrogen phthalate (1.0 M), while the Cu(II) ions were extracted with EDTA (1.0 M), KCN (1.0 M) and potassium hydrogen phthalate (0.01 M). The order of increasing interference for the extraction of Pb(II) and Cu(II) ions was KCN > potassium hydrogen phthalate > EDTA. Sodium sulfate (0.01 M) in HCl enhanced the extraction of Pb(II) ions, while sodium chloride (0.50 M) in HCl enhanced the extraction of Cu(II) ions. p*H*_{0.5} values of 0.67 and 2.70 were obtained for Pb(II) and Cu(II) ions, respectively, indicating that the separation of the two metal ions is favorable with HBMOR.

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1. Introduction

Aqueous effluents from many technological processes often contain Cu(II) and Pb(II) ions. For example, Cu(II) ions are found in effluents from the electroplating and brass manufacturing industries, printed circuit boards, and copper-based agrochemical run-off from agricultural lands [1]. The presence of these effluents discharged into the environment has serious negative consequences on the ecosystem due to the persistence and nondegradable nature of the metal ions and their tendency to accumulate [2,3]. Lead has been implicated in a number of adverse health effects, including cancer, haematological, neurological, cardiac, renal, and digestive disorders [4-8]. Copper is a valuable metal due to its low toxicity, and it plays an essential biological role in the survival of life [9,10]; it also has antibacterial properties. However, very high concentrations of copper in the human body have been reported to cause adverse health effects such as lung cancer [10], stomach and intestinal

cancer, liver, and kidney damage [11,12]. The extraction, detection, and analysis of Pb(II) and Cu(II) ions are still considered necessary since the allowed limits in the aqueous effluent become progressively low. Solvent extraction has continued to be very attractive as a method for extracting and concentrating metal ions from aqueous media because of its ease of handling, high extraction efficiency, and good selectivity. Organic molecules that are often used for the extraction of metal ions from aqueous solutions are expected to have high chelating ability and selectivity. 1-(Acyl/aroyl)-3-(mono-substituted)thioureas and 1-(acyl/aroyl)-3,3-(di-substituted)thioureas, with the general formula R₁-C(O)-N(1)H-C(S)-N(3)R₂R₃ form metal complexes with ease [13-20], several reports are also available on the formation of stable Cu(II) complexes of these group of compounds [14-17,19]. Some 1-(acyl/aroyl)-3-(mono-substituted)thioureas and 1-(acyl/aroyl)-3,3-(di-substituted)thioureas have been reported in

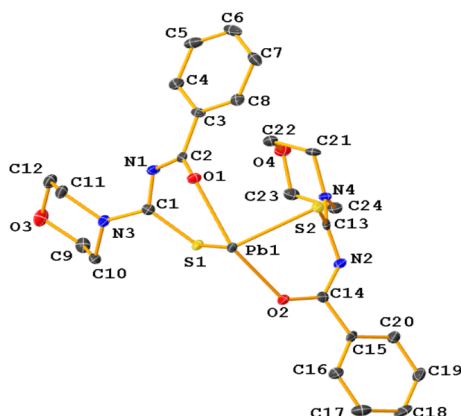


Figure 1. Molecular structure of PbBMOR with atom numbering scheme, H atoms were omitted for clarity.

effective liquid-liquid extraction of Au (III)[21] and potential extractants for Cd(II), Cu(II), Hg(II), Pd(II) and Pt(II) ions [22]. The ease of isolation of the thiourea ligands and the observed attractive metal-dependent colors of the metal complexes have prompted our interest in exploring the use of thiourea derivatives for the extraction and determination of metal ions in aqueous media. Herein, we present the solvent extraction studies of *N*-morpholine-*N'*-benzoylthiourea toward Pb(II) and Cu(II) ions in aqueous media. In addition, the crystal structure of bis(*N*-morpholine-*N'*-benzoylthioureaato)lead (II) is reported.

2. Experimental

2.1. Chemicals and instrumentation

All reagents were used without further purification. Benzoylchloride and morpholine were obtained from Sigma-Aldrich Chemicals, USA, while lead(II)acetate trihydrate, copper(II)acetate dihydrate, and potassium thiocyanate were obtained from Fluka Chemicals. Dichloromethane, ethanol, methanol, hydrochloric acid, chloroform, sulphuric acid, nitric acid, sodium chloride, sodium sulphate, potassium hydrogen phthalate, potassium cyanide, EDTA, potassium nitrate, boric acid and sodium hydroxide were obtained from Fine Laboratory Chemicals, China.

The ^1H NMR and ^{13}C NMR spectrum of bis(*N*-morpholine-*N'*-benzoylthioureaato)lead (II) was obtained on a Bruker spectrometer; DMSO- d_6 was used as a solvent. The mass spectrum was obtained using micrOTOF ESI-MS. Infrared spectra were recorded in the range of 4000-400 cm^{-1} using KBr pellets on a Perkin Elmer 100 infrared spectrophotometer. The melting point was obtained with a Fisher-John melting point apparatus. UV/vis spectra were obtained using a UV-2500 PC series model spectrophotometer. Metal ion concentrations were measured using an atomic absorption spectrometer 210 VGP. Single crystal X-ray diffraction data of bis(*N*-morpholine-*N'*-benzoylthioureaato)lead (II) were obtained on an XtaLAB Synergy, Dualflex, Pilatus 200K diffractometer.

2.2. Synthesis of bis(*N*-morpholine-*N'*-benzoylthioureaato)lead(II) complex

N-Morpholine-*N'*-benzoylthiourea (HBMOR) was synthesized as previously reported [23]. Bis(*N*-morpholine-*N'*-benzoylthioureaato) lead(II) complex (PbBMOR) was synthesized as follows: A solution of lead acetate trihydrate (0.95 g, 0.0025 mol) in ethanol (20 mL) was added dropwise to a solution of the ligand (HBMOR) (0.46 g, 0.005 mol) in dichloromethane (30 mL) at room temperature and the

resulting mixture was stirred for 60 min, and a light gray solid product was formed. The precipitate was filtered and crystals suitable for X-ray studies were obtained by slow evaporation of a 1:1 dichloromethane:ethanol solution of PbBMOR for a few days. Color: Light gray. M.p.: 169-170 °C. Yield: 78.23 %. FT-IR (KBr, ν , cm^{-1}): 1479 ($\nu\text{C}=\text{O}$), 1349 ($\nu\text{C}=\text{S}$). ^1H NMR (400 MHz, DMSO- d_6 , δ , ppm): 8.02 (d, $J = 7.2$ Hz, 4H, Ar-H), 7.46 (t, $J = 7.2$ Hz, 2H, Ar-H), 7.37 (t, $J = 7.5$ Hz, 4H, Ar-H), 3.93 (t, $J = 4.4$ Hz, 8H, O-CH $_2$), 3.55 (t, $J = 4.4$ Hz, 8H, N-CH $_2$). ^{13}C NMR (101 MHz, DMSO- d_6 , δ , ppm): 178.0 (quat, N=C-N,S), 169.7 (quat, O=C-N,Ar), 137.7 (Ar-ipso), 130.9 (Ar-para), 129.1 (Ar-ortho), 127.8 (Ar-meta), 66.2 (O-CH $_2$), 47.8 (N-CH $_2$). MS (ESI, m/z (%)): calculated for $[\text{M}+\text{Na}]^+$ 728.83; found $[\text{M}+\text{Na}]^+$ 728.816. UV/Vis (CHCl_3 , λ_{max} , nm): 285 nm.

2.3. X-ray crystallography

Crystal of bis(*N*-morpholine-*N'*-benzoylthioureaato)lead(II) complex suitable for X-ray crystallography were mounted on the glass fibre with epoxy cement for X-ray measurement. The diffraction data was collected at 111.7(4) K on a XtaLAB SynergyDualflex Pilatus 200K diffractometer. Graphite monochromated Cu-K α radiation ($\lambda = 1.54184$ Å) was used. Data integration, scaling, and empirical absorption corrections were carried out using the CrysAlisPro program package [24]. The structure was solved with the SHELXT [25] structure solution program using intrinsic phasing and refined with the SHELXL [26] refinement package using least squares minimization in Olex2 [27].

2.4. Extraction studies

2.4.1. Preparation of metal stock and buffer solutions

1000 ppm of Pb(II) stock solution was prepared by dissolving 0.915 g of $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ in 500 mL of deionized water. 1000 ppm Cu(II) stock solution was prepared by dissolving 1.71 g of $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ in 500 mL of deionized water. A working solution of 18 $\mu\text{g}/\text{mL}$ was prepared from the stock solution, which was used for the extraction process. Clark and Lubs procedures [28] were used to prepare buffer solutions of pH values 1-13 with standard solutions of the following acid/salt systems; hydrochloric acid/potassium chloride, hydrochloric acid/potassium hydrogen phthalate, potassium hydrogen phthalate/sodium hydroxide, and boric acid/sodium hydroxide [29]. They were standardized with Jenway 3510 pH meter.

Table 1. Crystal data and refinement parameters of PbBMOR.

Empirical formula	C ₂₄ H ₂₆ N ₄ O ₄ PbS ₂
Formula weight	705.80
Temperature (K)	100.00(10)
Crystal system	Monoclinic
Space group	<i>P2₁/n</i>
<i>a</i> , (Å)	13.3922(2)
<i>b</i> , (Å)	7.97550(10)
<i>c</i> , (Å)	23.3368(3)
α (°)	90
β (°)	92.5820(10)
γ (°)	90
Volume (Å ³)	2490.06(6)
<i>Z</i>	4
ρ_{calc} (g/cm ³)	1.883
μ (mm ⁻¹)	15.072
F(000)	1376.0
Crystal size (mm ³)	0.22 × 0.2 × 0.16
Radiation	CuK α (λ = 1.54184)
2 θ range for data collection (°)	7.468 to 148.802
Index ranges	-16 ≤ <i>h</i> ≤ 16, -9 ≤ <i>k</i> ≤ 9, -28 ≤ <i>l</i> ≤ 29
Reflections collected	29913
Independent reflections	5010 [R _{int} = 0.0343, R _{sigma} = 0.0213]
Data/restraints/parameters	5010/0/316
Goodness-of-fit on F ²	1.251
Final R indexes [I ≥ 2 σ (I)]	R ₁ = 0.0248, wR ₂ = 0.0637
Final R indexes [all data]	R ₁ = 0.0250, wR ₂ = 0.0638
Largest diff. peak/hole (e.Å ⁻³)	1.28/-1.81

2.4.2. Preparation of acids, salting-out agents, and masking agents

The 5 M HCl, H₂SO₄, and HNO₃ solutions were prepared by the dilution method. Solutions of 2 M NaCl, Na₂SO₄, and KNO₃ were prepared by dissolving an appropriate amount of salts (11.89 g of NaCl, 28.409 g of Na₂SO₄, 20.221 g of KNO₃) in 100 mL of deionized water. 1.0 M solutions of KCN and potassium hydrogen phthalate (KH(C₈H₆O₄)) were prepared by dissolving an appropriate amount of salts (3.26 g of KCN and 10.21 g of KH(C₈H₆O₄)) in 50 mL of deionized water. 0.4 M solution of EDTA-disodium salt dehydrate was prepared by dissolving 7.45 g of the salt in 50 mL of deionized water.

2.4.3. Extraction procedure

Equal volumes (6 mL) of aqueous phase containing 18 ppm of either Pb(II) or Cu(II) ions and 1% solution of HBMOR in chloroform were shaken mechanically in stoppered extraction bottles at time intervals of 5, 10, 20, 30, 40, 50, 60 and 70 minutes. For each extraction process; after centrifugation, the phases are separated and the concentration of solutes in aqueous raffinate was determined by atomic absorption spectroscopy (AAS). Equal volumes (6 mL) of aqueous phase containing 18 ppm of either Pb(II) or Cu(II) ions and the relevant buffer solution (adjusted to the required pH using either dilute hydrochloric acid or ammonia solution) and 1% HBMOR solution in chloroform were mechanically shaken in stoppered extraction bottles at the appropriate time determined for each metal. For each extraction process; after centrifugation, the phases are separated and the concentration of solutes in aqueous raffinate was determined using AAS. These processes were repeated for equal volumes (6 mL) of aqueous phase containing 18 ppm of Pb(II) or Cu(II) ions and the appropriate acids, masking agents and salting-out agents and 1% solution of HBMOR in chloroform.

3. Results and discussion

3.1. Physical properties and spectroscopic analysis of PbBMOR

PbBMOR was isolated by recrystallization using suitable solvents. It is a light gray and non-hygroscopic, and an air stable

solid. It is insoluble in water and diethyl ether, slightly soluble in ethanol and methanol, but soluble in acetone, chloroform, dichloromethane, DMF and DMSO. It has a low molar conductivity value of 21 μ S/cm indicating that it is non-electrolyte.

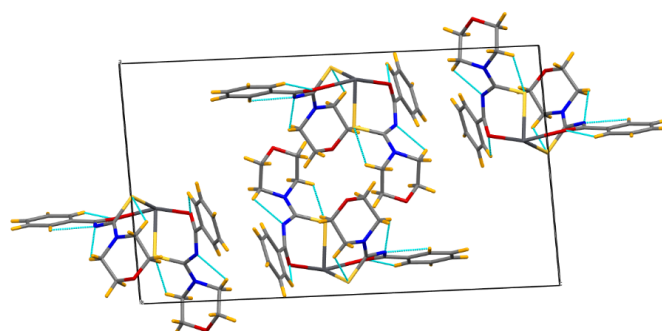
In the ¹H NMR spectra of the metal complex, there are characteristic peaks in the aromatic regions. Multiplets at δ 7.37-8.02 ppm were assigned to the aromatic protons of the phenyl moiety, however there were no peaks that are characteristic of NH protons because the ligand was deprotonated on complexation [30-33]. The δ 3.55-3.93 ppm bands have been assigned to the protons of the morpholine moiety. The ¹³C NMR spectra are also consistent with the structural information provided by the single crystal X-ray diffraction studies. The C=O group was observed at δ 169.7 ppm and the peak for C=N was observed at δ 178.0 ppm, while the O-CH₂ and N-CH₂ carbons were observed at δ 66.2 and 47.8, respectively. Chemical shifts of aromatic carbons were observed in the range δ 127.8-137.7. In the IR spectra, there are no characteristic vibration peaks of the N-H stretching [30-33]. The peak at 1479 cm⁻¹ has been assigned to the C=O stretching vibration. The UV/vis spectra of PbBMOR were recorded in acetone. The absorption band (nm) observed at 285 was assigned to the *n* → π^* electronic transition of the C=S bond [16].

3.2. Structural analysis of PbBMOR

The complex PbBMOR was synthesized and isolated at room temperature, showing a favorable energy interaction between Lewis acid Pb(II) and the thiourea derivative with a combination of hard O and soft S donors, consistent with Pearson's hard-soft acid-base principle [34]. PbBMOR crystallized in a monoclinic crystal system with *P2₁/n* space group. The molecular structure and unit cell packing of PbBMOR are presented in Figures 1 and 2, respectively. Crystallographic refinement parameters are presented in Table 1, while selected bond angles and bond length are shown in Table 2. Lead is in a +2 oxidation state and is coordinated to the S and O atoms of the BMOR with a four-coordination number. However, the Pb(II) complex was neither square planar nor tetrahedral geometry, which is commonly observed for *p*-block transition metals [31,32]. Pb is a *p*-block element in the periodic table, Pb(II) has an electronic configuration of [Xe]4f¹⁴5d¹⁰6s², the coordination geometry is affected by the lone pair of

Table 2. Bond lengths (Å) and bond angles (°) of PbBMOR.

Atom	Atom	Bond lengths (Å)	Atom	Atom	Atom	Bond angles (°)
Pb	S1	2.680(1)	S2	Pb1	S1	96.24(3)
Pb	S2	2.679(1)	S2	Pb1	O2	76.07(7)
Pb	O1	2.441(3)	S2	Pb1	O1	85.35(7)
Pb	O2	2.452(3)	S1	Pb1	O2	76.90(7)
S1	C1	1.747(4)	S1	Pb1	O1	79.53(7)
S2	C13	1.747(4)	O2	Pb1	O1	148.0(1)
O1	C2	1.254(5)	Pb1	S2	C13	98.2(1)
O2	C14	1.265(5)	Pb1	S1	C1	103.6(1)
N1	C1	1.329(5)	Pb1	O2	C14	132.8(3)
N1	C2	1.333(5)	Pb1	O1	C2	127.4(3)
N3	C9	1.471(5)	S1	C1	N1	124.0(3)
N3	C12	1.470(5)	S1	C1	N3	118.2(3)
N3	C1	1.345(5)	S2	C13	N2	122.9(3)
N2	C14	1.324(5)	S2	C13	N4	119.8(3)
N2	C13	1.345(5)	N2	C13	N4	116.9(3)
N4	C13	1.329(5)	C1	N1	C2	124.8(3)
N4	C24	1.470(5)	C9	N3	C12	112.0(3)
O3	C10	1.433(5)	C12	N3	C1	121.5(3)
O3	C11	1.414(5)	C13	N4	C24	123.1(3)
O4	C23	1.427(5)	C24	N4	C21	111.7(3)
O4	C22	1.428(5)	N2	C14	C15	116.7(3)
C11	C12	1.517(6)	C20	C15	C16	119.6(4)
C5	C6	1.386(7)	N3	C9	C10	108.0(3)

**Figure 2.** Molecular packing arrangement of PbBMOR in the unit cell, showing intramolecular and intermolecular contacts.

electrons on the 6s orbital. Thus, Pb(II) in PbBMOR is in a square pyramidal geometry distorted mainly by the repulsion between the 6s² electrons and the Pb-S and Pb-O bonding electrons as clearly predicted by the valence shell electron pair repulsion theory. As a result of this distortion, the bond angles of S2-Pb1-O2, S2-Pb1-O1, S1-Pb1-O2, and S1-Pb1-O1 were 76.07, 85.35, 76.90 and 79.53°, respectively, which deviated from the 90° angle expected for an ideal square pyramidal geometry. Because of the large orbital size of sulfur compared to that of oxygen, the Pb-S bonding electrons experienced more repulsion than the Pb-O bonding electrons. This led to the shrinking of the S2-Pb-S1 bond angle from 180° to 96.24°, whereas the O2-Pb-O1 bond angle was 148.0°. The Pb(II) complex adopted a *trans* geometry with the S atoms, morpholine, and phenyl rings on alternate sides to minimize repulsion.

Acylthioureas are known to form metal complexes by deprotonation of the N-H group of the thiourea moiety [16]. This hypothesis is supported by the elongated C1-S1 bond of 1.747 Å and the C14-O2 bond of 1.265 Å compared to the average length of the C-S and C-O bond in acyl thioureas of 1.67 and 1.23 Å [16]. The elongation of the C-S and C-O bonds indicated that the deprotonation of the N-H protons was followed by the delocalization of electrons around the OC-N-CS moiety prior to coordination to Pb(II) as demonstrated in an earlier report [13], thus metal complexation and potential extraction will be favored above neutral pH. The C-N bonds in the acylthiourea moiety were C1-N3, C1-N1, C2-N1, C13-N2, and C13-N4 of 1.345, 1.324, 1.345 and 1.329 Å, respectively. The Pb-S bond length in PbBMOR of ~1.680 Å is much shorter than that reported for Pb(II) coordinated to

thiourea with Pb-S bond length of 2.65-3.23 Å [35]. This might be due to the stronger interaction between Pb(II) and negatively charged S in PbBMOR compared to (NH₂)₂C=S coordinated to Pb(II) through the lone pair of electrons on the sulfur. The four-molecule aggregate packing structure of the molecule in Figure 2 does not show any conventional hydrogen bond, but some phenyl-C-H...O (morpholine) intermolecular contacts link the four-aggregate structure in the three-dimensional space and are stabilized by some intramolecular phenyl-C-H...N (morpholine) and phenyl-C-H...S (thiol) contacts.

3.3. Extraction studies

3.3.1. Equilibration time

The equilibration time for efficient extraction of Pb(II) and Cu(II) ions was examined in the presence of 1% HBMOR in chloroform. The percentage yield of the extracted ions at different time intervals were determined. For the extraction of Pb(II) ions, the optimum extraction was obtained at an equilibration time of 10 min, while for the extraction of Cu(II) ions, the optimum extraction was obtained at an equilibration time of 5 min. All subsequent extraction processes were conducted in the appropriate time for each metal ion.

3.3.2. Effect of pH on the extraction of Pb(II) and Cu(II)

The extraction of Pb(II) and Cu(II) ions with HBMOR was studied as a function of pH in the range of 1-13.

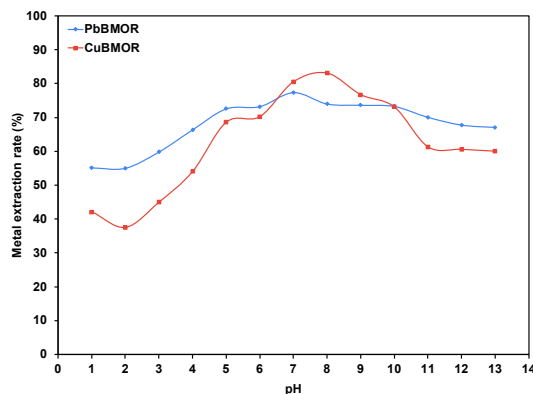


Figure 3. The effect of pH on the extraction of Pb (II) and Cu(II) ions.

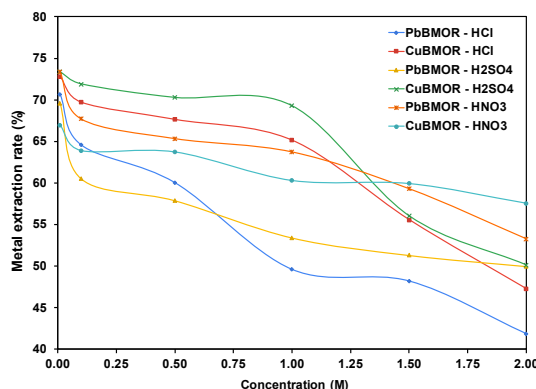


Figure 4. The effect of mineral acids on the extraction of Pb(II) and Cu(II) ions.

Figure 3 shows the profile of the effect of pH on the extraction of Pb(II) and Cu(II) ions. Between pH = 1 and 4, the percentage of Pb(II) ions extracted ranged from 55.13-73.23%. However, the percentage extraction increased at pH = 5, reaching a peak at pH = 7 where a quantitative extraction of 77.37% was observed. The low extraction between pH = 1 and 4 is likely due to incomplete dissociation of the ligand leading to poor formation of the extractable metal complex [36]. Quantitative extraction at pH = 7 is likely due to the formation of a complex completely extractable into the organic phase. Furthermore, between pH = 8 and 13, a decrease in the amount of Pb(II) ions extracted was observed. The low extraction in this pH range could be attributed to the ease of hydrolysis of the metal ion, and the masking effect of the buffer contributes to decreasing metal extraction [37].

The extraction of Cu(II) ions with HBMOR was also studied as a function of pH in the range 1-13. There was quantitative extraction at pH = 8 with 83.10% extraction. The low extraction at pH = 1-5 may be due to competition between proton and Cu(II) ions for the ligand coordination sites. A $pH_{0.5}$ for Pb was observed at 0.67 while that of Cu was observed at 2.70. The difference in the $pH_{0.5}$ value of 2.03 indicated the possibility of separating Pb and Cu in aqueous medium [38].

3.3.3. Effect of mineral acids on the extraction of Pb(II) and Cu(II)

The variation of the acid concentration on the percentage of extracted Pb (II) and Cu(II) ions is shown in Figure 4. The result shows that acid concentrations of 0.01-0.10 M support the formation of extractable complex of Pb(II). In addition, it shows that there is a decrease in the amount of Pb(II) extracted as the acidity increases. The % extraction was up to 73.33 in 0.01 M

HNO₃. Low extraction was observed in HCl as compared to that in any other acid.

The acid concentrations of 0.01-0.10 M also support the formation of extractable complex of Cu(II) ions. At an acid concentration of 0.01 M H₂SO₄, 73.37% of Cu(II) ions were extracted. It also shows that the percentage extraction decreases with an increase in acidity. Low extraction was also observed in HCl than in any other acid; however, the extraction efficiency is better than in 0.01 M HNO₃.

3.3.4. Effect of salting-out agents on the extraction of Pb(II) and Cu(II)

The effect of salting-out agents on the extraction of Pb(II) and Cu(II) ions at varying concentrations of salting-out agents was studied. Figure 5 shows the profile of the effect of the salting-out agents on the extraction of Pb(II) and Cu(II) ions. The extraction of Pb(II) ions with HBMOR in chloroform was studied between 0.01 and 1.00 M concentration of salting-out agents (NaCl, Na₂SO₄ and KNO₃) and different acid concentrations. The results show that HCl/NaSO₄ showed an improvement in the percentage extraction of 41.87 to 87.83%. This is attributable to the formation of extractable species. The percentage extracted decreased with an increase in the concentration of the salting-out agents. In HCl/KNO₃, a relatively small percentage of extraction was observed (41.87-51.53%). Generally, it was observed that the amount of metal ions extracted was higher at a lower concentration of the salting-out agent. Therefore, 0.01 M Na₂SO₄ and NaCl are good salting-out agents for the extraction of Pb(II) ions.

Extraction of Cu(II) ions with 1% HBMOR was studied at different concentrations of salting-out agents (NaCl, Na₂SO₄ and KNO₃) at an acid concentration where partial extraction was obtained.

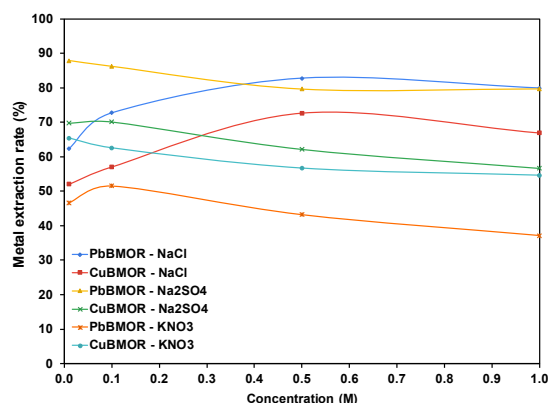


Figure 5. The effect of salting-out agents on the extraction of Pb(II) and Cu(II) ions.

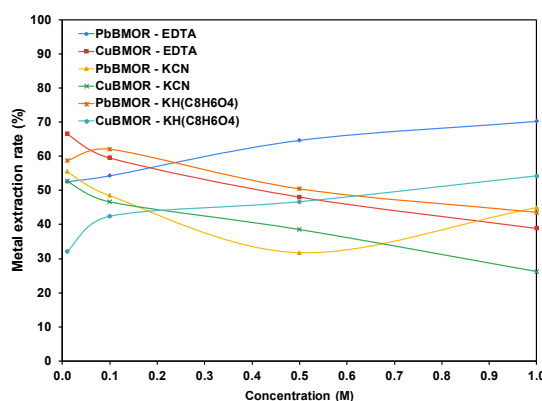


Figure 6. The effect of masking agents on the extraction of Pb(II) and Cu(II) ions with HBMOR.

The results show that the percentage extraction increased from 47.27 to 72.67% in 0.01 M HCl with the addition of 0.5 M NaCl. This may be due to the decrease in the activity of water, consequent on the hydration of the added salt, enabling the formation of extractable species. The amount extracted decreased with an increase in the concentration of Na₂SO₄, and the reverse was the case in other salts. In HCl/ Na₂SO₄, there was an enhancement in percentage extraction from 47.27 to 70.07%. This may likely be due to the increase in the dielectric constant of the aqueous medium, which enhances the extractability of the metal complex into the organic phase [36]. Analysis of the results revealed that 0.50 M NaCl and 0.10 M Na₂SO₄ are good salting-out agents for the extraction of Cu(II) ions.

3.3.5. Effect of masking agents on the extraction of Pb(II) and Cu(II)

The effect of masking agents on the degree of extraction was investigated at an acid concentration for quantitative extraction of the metal ions. Figure 6 shows the effects of masking agents on the extraction of Pb(II) and Cu(II) ions. EDTA, potassium cyanide and potassium hydrogen phthalate greatly contributed to decrease in the % extraction of Pb(II) ions in 0.01 M acid concentration. 0.5 M KCN reduced the % extraction of Pb(II) to 31.67. The % extraction of Pb(II) was decreased to 43.57 at 1.0 M potassium hydrogen phthalate.

Potassium cyanide and potassium hydrogen phthalate greatly decreased the % extraction of Cu(II) ions. 1.0 M potassium cyanide reduced the % extraction of Cu(II) to 26.23, while 0.01 M potassium cyanide reduced the % extraction to 52.77. For potassium hydrogen phthalate, at 0.01 M, the % extraction of Cu(II) was reduced to 32.03, and at 0.5 M, it was

reduced to 46.67. EDTA 1 M, on the other hand, reduced the % extraction of Cu(II) to 38.9. The high reduction in extraction as observed in both metals is likely to be the result of the formation of non-extractable complex species formed in the aqueous phase [36].

4. Conclusions

The crystal structure of the *bis*(*N*-morpholine-*N'*-benzoyl thioureato)lead(II) complex has been reported. The complex crystallized in a monoclinic crystal system with *P2₁/n* space group, as an ML₂ type metal complex. Expectedly, the four-coordinate complex has a square pyramidal geometry distorted mainly by the repulsion between the 6s² electrons and the Pb-S and Pb-O bonding electrons, considering the fact that the lead belongs to the *p* block in the periodic table, with an electronic configuration of [Xe]4f¹⁴5d¹⁰6s² and the coordination geometry is mainly affected by the lone pair of electrons in the 6s orbital.

Extraction studies at a pH range 1-13, indicated that maximum extraction of Pb(II) ions using 1% HBMOR/CHCl₃ was attained at pH = 7 in 10 minutes. Furthermore, quantitative extraction was observed at acid concentrations of 0.01 to 2.00 M. HNO₃ and HCl quantitatively extracted Pb(II) ions at lower concentrations, with an observed decrease in percentage extraction as the acid concentration increased. Na₂SO₄ proved to be a good salting-out agent at 0.01 M for the extraction of Pb(II) ions. The interference of potassium cyanide was high at 0.5 M and low for EDTA at 1.0 M.

The Cu(II) ion was extracted using 1% HBMOR/CHCl₃ under a pH range of 1-13 and maximum extraction was observed at pH = 8 under 5 minutes. Quantitative extraction of Cu(II) ions was observed at 0.01 M to 2.0 M acid concentrations. H₂SO₄ and HCl quantitatively extracted Cu(II) ions at lower

concentrations, with an observed decrease in percentage extraction as the acid concentration increased. Na₂SO₄ also proved to be a good salting-out agent at 0.1 M for the extraction of Cu(II) ions. Potassium hydrogen phthalate had a high masking action on the extraction of Cu(II), but EDTA and potassium cyanide had a moderate effect. 1% HBMOR/CHCl₃ has been shown to be a promising extractant for the extraction of Pb(II) ions at pH = 7, 0.01 M HCl, and 0.01 M Na₂SO₄. The optimal extraction conditions for the extraction of Cu(II) ions with 1% HBMOR/CHCl₃ are pH = 8, 0.01 M H₂SO₄, and 0.01 M Na₂SO₄. The pH_{0.5} values of 0.67 and 2.70 were obtained for Pb(II) and Cu(II) ions, respectively, indicating that the two ions can be effectively extracted in aqueous media.

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Supporting information

CCDC-2102001 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033.

Disclosure statement


Conflict of interest: The authors declare that they have no conflict of interest. Ethical approval: All ethical guidelines have been adhered. Sample availability: Samples of the compounds are available from the author.

CRedit authorship contribution statement

Conceptualization: Jonnie Niyi Asegbeloyin, Kenechukwu Johncross Ifeanyieze; Methodology: Kenechukwu Johncross Ifeanyieze, Obinna Chibueze Okpareke; Software: Kenechukwu Johncross Ifeanyieze, Obinna Chibueze Okpareke; Validation: Obinna Chibueze Okpareke, Kenechukwu Johncross Ifeanyieze; Formal Analysis: Kenechukwu Johncross Ifeanyieze, Obinna Chibueze Okpareke; Investigation: Kenechukwu Johncross Ifeanyieze, Jonnie Niyi Asegbeloyin; Resources: Kenechukwu Johncross Ifeanyieze, Nkechinyere Nwanneka Ukwueze; Data Curation: Kenechukwu Johncross Ifeanyieze, Uchechukwu Susan Oruma; Writing - Original Draft: Kenechukwu Johncross Ifeanyieze, Jonnie Niyi Asegbeloyin; Writing - Review and Editing: Jonnie Niyi Asegbeloyin, Ilknur Babahan Bircan, Uchechukwu Susan Oruma; Visualization: Uchechukwu Susan Oruma, Nkechinyere Nwanneka Ukwueze; Supervision: Jonnie Niyi Asegbeloyin, Ilknur Babahan Bircan; Project Administration: Jonnie Niyi Asegbeloyin, Ilknur Babahan Bircan.

ORCID and Email

Kenechukwu Johncross Ifeanyieze

 kenechukwu.ifeanyieze.pg00135@unn.edu.ng

 <https://orcid.org/0000-0002-3801-872X>

Obinna Chibueze Okpareke

 obinna.okpareke@unn.edu.ng

 <https://orcid.org/0000-0003-0815-8198>

Uchechukwu Susan Oruma

 susan.oruma@unn.edu.ng

 <https://orcid.org/0000-0002-9226-2512>

Nkechinyere Nwanneka Ukwueze

 nkechinyere.ukwueze@unn.edu.ng


 <https://orcid.org/0000-0003-1707-0438>

Ilknur Babahan Bircan

 ibabahan@adu.edu.tr

 <https://orcid.org/0000-0002-1336-671X>

Jonnie Niyi Asegbeloyin

 niyi.asegbeloyin@unn.edu.ng

 <https://orcid.org/0000-0002-5710-7613>

References

- Boujelben, N.; Bouzid, J.; Elouear, Z. Adsorption of nickel and copper onto natural iron oxide-coated sand from aqueous solutions: Study in single and binary systems. *J. Hazard. Mater.* **2009**, *163*, 376–382.
- Khan, M. A.; Ahmad, I.; Rahman, I. U. Effect of environmental pollution on heavy metals content of *Withania somnifera*. *J. Chin. Chem. Soc.* **2007**, *54*, 339–343.
- Ahmaruzzaman, M. Industrial wastes as low-cost potential adsorbents for the treatment of wastewater laden with heavy metals. *Adv. Colloid Interface Sci.* **2011**, *166*, 36–59.
- Mudgal, V.; Madaan, N.; Mudgal, A.; Singh, R. B.; Mishra, S. Effect of toxic metals on human health. *Open Nutraceuticals J.* **2010**, *3*, 94–99.
- Tandon, S. K.; Chatterjee, M.; Bhargava, A.; Shukla, V.; Bihari, V. Lead poisoning in Indian silver refiners. *Sci. Total Environ.* **2001**, *281*, 177–182.
- Pizent, A.; Čolak, B.; Kljaković, Z.; Telišman, S. Prostate-Specific Antigen (PSA) in serum in Relation to Blood Lead Concentration and Alcohol Consumption in men. *Arh. Hig. Rada Toksikol.* **2009**, *60*, 69–78.
- Lindbohm, M. L.; Sallmen, M.; Anttila, A.; Taskinen, H.; Hemminki, K. Paternal occupational lead exposure and spontaneous abortion. *Scand. J. Work Environ. Health* **1991**, *17*, 95–103.
- Tang, S.; Yu, X.; Wu, C. Comparison of the levels of five heavy metals in human urine and sweat after strenuous exercise by ICP-MS. *J. Appl. Math. Phys.* **2016**, *04*, 183–188.
- Rai, P. K.; Lee, S. S.; Zhang, M.; Tsang, Y. F.; Kim, K.-H. Heavy metals in food crops: Health risks, fate, mechanisms, and management. *Environ. Int.* **2019**, *125*, 365–385.
- Yu, B.; Zhang, Y.; Shukla, A.; Shukla, S. S.; Dorris, K. L. The removal of heavy metal from aqueous solutions by sawdust adsorption — removal of copper. *J. Hazard. Mater.* **2000**, *80*, 33–42.
- Wuana, R. A.; Okieimen, F. E. Heavy metals in contaminated soils: A review of sources, chemistry, risks and best available strategies for remediation. *ISRN Ecol.* **2011**, *2011*, 1–20.
- Dixit, R.; Wasiullah; Malaviya, D.; Pandiyan, K.; Singh, U.; Sahu, A.; Shukla, R.; Singh, B.; Rai, J.; Sharma, P.; Lade, H.; Paul, D. Bioremediation of heavy metals from soil and aquatic environment: An overview of principles and criteria of fundamental processes. *Sustainability* **2015**, *7*, 2189–2212.
- Saeed, A.; Flörke, U.; Erben, M. F. A review on the chemistry, coordination, structure and biological properties of 1-(acyl/aroyl)-3-(substituted) thioureas. *J. Sulphur Chem.* **2014**, *35*, 318–355.
- Binzet, G.; Gumus, I.; Dogen, A.; Flörke, U.; Kulcu, N.; Arslan, H. Nickel(II) and copper(II) complexes of N,N-dialkyl-N'-3-chlorobenzoylthiourea: Synthesis, characterization, crystal structures, Hirshfeld surfaces and antimicrobial activity. *J. Mol. Struct.* **2018**, *1161*, 519–529.
- Binzet, G.; Kavak, G.; Külcü, N.; Özbey, S.; Flörke, U.; Arslan, H. Synthesis and characterization of novel thiourea derivatives and their nickel and copper complexes. *J. Chem.* **2013**, *2013*, 1–9.
- Oyeka, E. E.; Asegbeloyin, J. N.; Babahan, I.; Eboma, B.; Okpareke, O.; Lane, J.; Ibezim, A.; Biyik, H. H.; Törün, B.; Izuogu, D. C. Synthesis, crystal structure, computational analysis and biological properties of 1-(4-chlorobenzoyl)-3-[2-(2-(3-(4-chlorobenzoyl)-thioureido)-ethoxyethoxy)ethyl]-thiourea and its Ni(II) and Cu(II) complexes. *J. Mol. Struct.* **2018**, *1168*, 153–164.
- Oyeka, E. E.; Babahan, I.; Eboma, B.; Ifeanyieze, K. J.; Okpareke, O. C.; Coban, E. P.; Özmen, A.; Coban, B.; Aksel, M.; Özdemir, N.; Groutso, T. V.; Ayogu, J. I.; Yildiz, U.; Dinçer Bilgin, M.; Halil Biyik, H.; Schrage, B. R.; Ziegler, C. J.; Asegbeloyin, J. N. Biologically active acylthioureas and their Ni(II) and Cu(II) Complexes: Structural, spectroscopic, anti-proliferative, nucleolytic and antimicrobial studies. *Inorganica Chim. Acta* **2021**, *528*, 120590.
- Ghazal, K.; Shoaib, S.; Khan, M.; Khan, S.; Rauf, M. K.; Khan, N.; Badshah, A.; Tahir, M. N.; Ali, I.; Rehman, A.-U.- Synthesis, characterization, X-ray diffraction study, in-vitro cytotoxicity, antibacterial and antifungal activities of nickel(II) and copper(II) complexes with acyl thiourea ligand. *J. Mol. Struct.* **2019**, *1177*, 124–130.
- Arslan, H.; Külcü, N.; Flörke, U. Synthesis and characterization of copper(II), nickel(II) and cobalt(II) complexes with novel thiourea derivatives. *Transit. Met. Chem.* **2003**, *28*, 816–819.
- Binzet, G.; Flörke, U.; Külcü, N.; Arslan, H. Crystal and molecular structure of bis(4-bromo-N-(diethylcarbamothioyl)benzamide)nickel(II) complex. *Eur. J. Chem.* **2012**, *3*, 37–39.
- Luckay, R. C.; Mebrahtu, F.; Esterhuysen, C.; Koch, K. R. Extraction and transport of gold(III) using some acyl(aroyl)thiourea ligands and a crystal structure of one of the complexes. *Inorg. Chem. Commun.* **2010**, *13*, 468–470.
- Koch, K. R. New chemistry with old ligands: N-alkyl- and N,N-dialkyl-N'-acyl(aroyl)thioureas in co-ordination, analytical and process chemistry of the platinum group metals. *Coord. Chem. Rev.* **2001**, *216–217*, 473–488.

- [23]. Cunha, S.; Macedo, F. C., Jr; Costa, G. A. N.; Rodrigues, M. T., Jr; Verde, R. B. V.; de Souza Neta, L. C.; Vencato, I.; Lariucci, C.; Sá, F. P. Antimicrobial activity and structural study of disubstituted thiourea derivatives. *Monatsh. Chem.* **2007**, *138*, 511–516.
- [24]. Agilent (2014). CrysAlis PRO. Agilent Technologies Ltd, Yarnton, Oxfordshire, England.
- [25]. Sheldrick, G. M. *SHELXT*– Integrated space-group and crystal-structure determination. *Acta Crystallogr. A Found. Adv.* **2015**, *71*, 3–8.
- [26]. Sheldrick, G. M. Crystal structure refinement with *SHELXL*. *Acta Crystallogr. C Struct. Chem.* **2015**, *71*, 3–8.
- [27]. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *OLEX2*: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* **2009**, *42*, 339–341.
- [28]. Bower, V. E.; Bates, R. G. pH values of the Clark and Lubs buffer solutions at 25 C. *J. Res. Natl. Bur. Stand. (1934)* **1955**, *55*, 197.
- [29]. Kolthoff, I. M.; Sandell, E. B.; Mecham, E. J.; Eastern, S. P. *Quantitative chemical analysis*; Macmillan: London, 1969.
- [30]. Binzet, G.; Arslan, H.; Flörke, U.; Külcü, N.; Duran, N. Synthesis, characterization and antimicrobial activities of transition metal complexes of N,N -dialkyl- N' -(2-chlorobenzoyl)thiourea derivatives. *J. Coord. Chem.* **2006**, *59*, 1395–1406.
- [31]. Keskin, E.; Solmaz, U.; Binzet, G.; Gumus, I.; Arslan, H. Synthesis, characterization and crystal structure of platinum(II) complexes with thiourea derivative ligands. *Eur. J. Chem.* **2018**, *9*, 360–368.
- [32]. Gumus, I.; Solmaz, U.; Celik, O.; Binzet, G.; Balci, G. K.; Arslan, H. Synthesis, characterization and crystal structure of cis-bis[4-fluoro-N-(diethylcarbamothioyl)benzamido-κ2O,S]platinum(II). *Eur. J. Chem.* **2015**, *6*, 237–241.
- [33]. Plutín, A. M.; Ramos, R.; Mocelo, R.; Alvarez, A.; Castellano, E. E.; Cominetti, M. R.; Oliveira, K. M.; Donizeth de Oliveira, T.; Silva, T. E. M.; S. Correa, R.; Batista, A. A. Antitumor activity of Pd(II) complexes with N,S or O,S coordination modes of acylthiourea ligands. *Polyhedron* **2020**, *184*, 114543.
- [34]. Housecroft, C. E.; Sharpe, A. G. *Inorganic Chemistry*; Pearson Education: Philadelphia, PA, 2008.
- [35]. Schwade, V. D.; Kirsten, L.; Hagenbach, A.; Schulz Lang, E.; Abram, U. Indium(III), lead(II), gold(I) and copper(II) complexes with isophthaloylbis(thiourea) ligands. *Polyhedron* **2013**, *55*, 155–161.
- [36]. Ukoha, P. O.; Eker, N. R.; Opara, I. J. Studies on extraction of Co(II) ions from aqueous solution using 1,5-dimethyl-2 phenyl-4-[(e)-(2,3,4-trihydroxyphenyl)diazanyl]-1,2-dihydro-3h-pyrazol-3-one. *Journal of Chemical Society of Nigeria* **2017**, *40*, 12–18. www.journals.chemsociety.org.ng/index.php/jcsn/article/view/4
- [37]. Opara, I. J.; Ukoha, P. O.; Onunze, E. O. Extractive spectrophotometric determination of Fe(III) and Co(II) from steel sample using azo ligand 1,5-dimethyl-2-phenyl-4-[(E)-(2, 3, 4-trihydroxyl phenyl)diazanyl]-1,2-dihydro-3H-pyrazole-3-one. *Int. J. Chem. Mater. Environ. Res.* **2018**, *5(1)*, 148-154.
- [38]. Sinha, M.; Sahu, S.; Meshram, P.; Pandey, B.; Kumar, V. Solvent extraction and separation of copper and zinc from a pickling solution. *Int. J. Met. Eng.* **2012**, *1*, 28–34.



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