



Solvent Extraction of Heavy Metals with a 23-Membered Macrocyclic Ionophore Attached with BF_2^+ -Capped Cobalt(III) Complex

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Abstract

A new (E, E)-dioxime cobalt(III) complex $[\text{Co}(\text{HL})_2\text{pyCl}]$ containing four 23-membered macrocyclic ionophores has been prepared. The cobalt(III) complex $[\text{Co}(\text{LBF}_2)_2\text{pyCl}]$ bridged with BF_2^+ was prepared using the precursor cobalt(III) complex and boron trifluoride ethyl ether complex. The solvent extraction of heavy metal cations such as Ni^{2+} , Cu^{2+} , Zn^{2+} , Hg^{2+} and Pb^{2+} by the BF_2^+ -capped cobalt(III) complex has been investigated. The structure of the complexes is proposed according to elemental analyses, ^1H and ^{13}C -NMR, IR and mass spectral data.

Introduction

Macrocyclic compounds have been of considerable interest in recent years because of their ability to form remarkable stable and selective complexes with a number of metal ions and their extraordinary solubility in some solvents such as chloroform and dichloromethane [1]. In designing synthetic ionophores, the presence of amide groups in their periphery is advantageous due to their dual ligating character. Metal complexes of ionophores can be considered to be in host–guest interactions in which the guest entity is shape entrapped in a cavity-like structure. In these complexes, interaction between host and guest is mainly achieved by hydrogen bonding and dipole-induced forces. Different macrocyclic compounds have been employed as ionophores in sensors for the determination of different metal ions such as alkali, alkaline earth and transition metal cations [2].

Metal complexes of vicinal dioxime ligands containing a number of synthetic mono and polymacrocycles of varying sizes with nitrogen, sulphur and oxygen as donor atom have been extensively investigated [3]. Recently, we have been exploring a group of macrocyclic dioximato complexes in which the original hydrogen-bridging protons of the bis(oximato) complexes have been replaced by BF_2^+ groups [4]. This substitution has markedly enhanced the solubility in common organic solvents such as acetonitrile chloroform and dichloromethane by removing the labile acidic protons from the H-bonded complexes. The *vic*-dioxime Co(III) complex containing synthetic ionophore is expected to have significant properties due to the ionophore which can be characterized as receptors that form stable, lipophilic complexes with charged hydrophilic species for metal cations and transporting them into lipophilic phases [5].

In this study, the extraction of some heavy metal cations from aqueous solution into organic media using the BF_2^+ bridged bis(dioximato) cobalt(III) complex containing tetrakis (benzo diaza-23-crown-7) moieties has been investigated.

Experimental

^1H and ^{13}C NMR spectra were recorded at ambient temperature on a Varian Mercury-200 spectrometer using DMSO- d_6 as solvent with TMS as the internal standard. IR spectra were obtained on a Perkin-Elmer 1600 FT-IR spectrometer with the samples in compressed KBr discs. The metal contents of the complexes and elemental analyses were determined on a Unicam 929 AA spectrometer and on a Hewlett-Packard 185CHN analyzer, respectively. Mass spectra of the complexes were measured on a Varian MAT 711 spectrometer. *N,N'*-Bis[2,3-(4'-aminobenzo)-1,4,11,14,17-pentaoxa-6,22-dioxo-7,21-diazacyclotricosane-2-ene]diaminoglyoxime (H_2L) was synthesized according to the reported method [5]. All the reagents used were of reagent grade and purified by conventional procedures [6].

Preparation of the cobalt(III) complex $[\text{Co}(\text{HL})_2\text{pyCl}]$ (1)

A solution of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.24 g, 1 mmol) in absolute ethanol (40 mL) was added to a hot solution of H_2L (1.87 g, 2 mmol) in absolute ethanol (100 mL). Pyridine (0.079 g, 1 mmol) in absolute ethanol (2 mL) was added to the above solution while heating. The reaction mixture was heated and stirred for 45 minutes at 60 °C then cooled to room temperature and a stream of air was bubbled through the solution for 4 h. The brown solution was evaporated to 30 mL under

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reduced pressure and then cooled in a refrigerator overnight whereupon the product crystallized from the solution. The brown solid was collected, washed with cold ethanol and diethyl ether and then dried *in vacuo*. Yield: 1.5 g (74.5%), m.p. 265–267 °C (dec.). ¹H-NMR (DMSO-*d*₆): (δ) 16.82 (s, 2H, O—H···O), 8.84 (s, 4H, NH), 8.28 (s, 8H, NH), 7.88 (d, *J* = 5.4 Hz, 2H, py-H), 7.52 (t, *J* = 7.6 Hz, 1H, py-H), 7.06 (m, 4H, Ar—H), 6.87–6.69 (m, 9H, Ar—H, py-H), 4.43 (m, 16H, Ar—OCH₂), 3.76–3.54 (m, 48H, CH₂O), 3.28 (m, 16H, HNCH₂), 1.75 (m, 16H, CH₂). ¹³C-NMR (DMSO-*d*₆): (δ) 164.02, 149.16, 148.44, 146.93, 144.88, 140.41, 134.78, 124.03, 121.17, 108.32, 103.19, 70.47–69.09, 68.25, 37.83, 31.27. IR (KBr pellets, cm⁻¹): 3376 (N—H), 3067 (Ar—H), 2922–2834 (C—H), 1705 (O—H···O), 1670 (HNC=O), 1618 (C=N), 1603 (N—H), 1254 (Ar—OCH₂), 1158 (CH₂OCH₂), 974 (N—O), MS(FAB): *m/z* = 2038.2 [M]⁺, 1959 [M-py]⁺.

Anal. Calcd. for C₈₉H₁₂₇N₁₇O₃₂ClCo: C, 52.36; H, 6.22; N, 11.67; Co, 2.88. *Found:* C, 52.54; H, 6.40; N, 11.43; Co, 2.58.

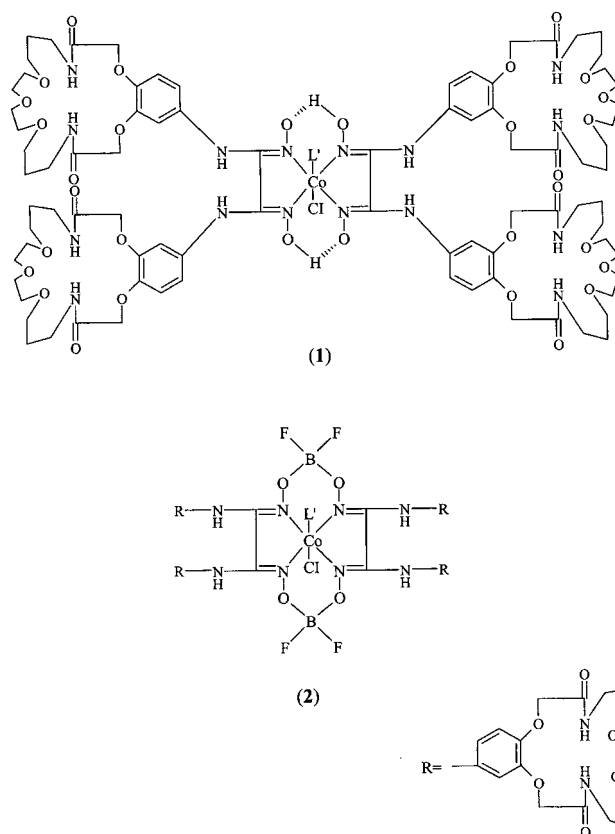
Preparation of BF₂⁺-capped cobalt(III) complex [Co(LBF₂)₂pyCl] (2)

A suspension of complex (1) (1.43 g, 0.70 mmol) in 80 mL of freshly distilled acetonitrile was refluxed in an oxygen-free nitrogen atmosphere. The boron-trifluoride ethyl etherate (0.35 mL, 2.8 mmol) was added with stirring of the above suspension which immediately converted the colour of the reaction mixture to a red solution. The reaction was allowed to stand at reflux temperature for 20 mm. Then the solvent was removed under vacuum and the residue was dissolved in 40 mL of dry acetonitrile and then evaporated to dryness. The last step was repeated and the residue was dissolved in 25 mL of dry acetonitrile and then allowed to cool in a refrigerator at -18 °C overnight whereupon the product was crystallized from the solution. The product was filtered off, washed with cold acetonitrile and diethyl ether and then dried *in vacuo*. Yield: 0.63 g (42.3%), m.p. 198–200 °C. ¹H-NMR (DMSO-*d*₆): (δ) 8.75 (s, 4H, NH), 8.17 (s, 8H, NH), 7.96 (d, *J* = 5.4 Hz, 2H, py-H), 7.59 (t, *J* = 7.4 Hz, 1H, py-H), 7.15 (m, 4H, Ar, H), 6.82–6.70 (m, 9H, Ar—H, py-H), 4.53 (m, 16H, Ar—OCH₂), 3.71–3.54 (m, 48H, CH₂O), 3.33 (m, 16H, HNCH₂), 1.86 (m, 16H, CH₂). ¹³C-NMR (DMSO-*d*₆): (δ) 164.29, 149.33, 148.40, 147.14, 145.71, 140.27, 135.20, 124.54, 121.35, 108.68, 103.58, 70.52–69.13, 68.45, 38.07, 31.40. IR (KBr pellets, cm⁻¹): 3362 (N—H), 3048 (Ar—H), 2917–2848 (C—H), 1678 (HNC=O), 1634 (C=N), 1601 (N—H), 1265 (Ar—OCH₂), 1158 (CH₂OCH₂), 1145 (B—O), 965 (N—O), 889 (B—F). MS (FAB): *m/z* = 2132 [M]⁺, 2018 [M-py-Cl]⁺.

Anal. Calcd. for C₈₉H₁₂₅N₁₇O₃₂B₂F₄ClCo: C, 50.02; H, 5.85; N, 11.14; Co, 2.75. *Found:* C, 49.81; H, 6.01; N, 11.32; Co, 2.57.

Extraction measurements

The chemicals were of analytical grade and water was ion-exchanged and bidistilled. The solvents were washed and



Scheme 1.

equilibrated with bidistilled water before use. The extraction experiments were carried out at 25 °C (±0.01 °C) with equal phase volumes in an overhead shaker. The aqueous phase contained 5 × 10⁻⁵ M of metal nitrate in single ion extraction (Hg²⁺, Pb²⁺, Zn²⁺) or 5 × 10⁻⁵ M each of Ni²⁺ and Cu²⁺ nitrate, as well as various amounts of HNO₃. The organic phase contained 5 × 10⁻⁵ M BF₂⁺-capped Co(III) complex (2) in chloroform. The extraction values (%) were determined for Hg(II), Pb(II), Zn(II), Ni(II) and Cu(II) nitrates with ionophore (2) by using chloroform as an apolar membrane. The equilibrium pH of the aqueous phase was measured by using a combination glass electrode (Orion). Metal analysis was done with an AA Spectrophotometer, using commercially available standard solutions.

Results and discussion

The starting compound *N,N'*-bis[2,3-(4'-aminobenzo)-1,4,11,14,17-pentaoxa-6,22-dioxo-7,21-diazacyclotricosane-2-ene]diaminoglyoxime (H₂L) was obtained by a multistep reaction sequence [5]. The novel hydrogen-bridged Co(III) complex of H₂L (1) was also prepared using the standard procedure [7] in high yield (74.5%). Elemental analysis, NMR, IR and MS spectral data confirmed the Co(III) complex structure. As an axial ligand and being related with Co(III) complex it was necessary for pyridine to be used Li in the exact stoichiometry amount because the presence of excessive base in the reaction mixture was reported to yield a complex in which one of the linking protons

had been removed and which contained two axially bound nitrogen bases [8]. In the $^1\text{H-NMR}$ spectrum of **1**, the singlet which indicates the hydroxyimino groups disappeared and a new resonance appeared at $\delta = 16.82$ ppm, as expected, belonging to the hydrogen-bridge, which indicated complexation. This resonance could easily be identified by deuterium exchange. Upon complexation, additional signals at $\delta = 7.88$ and 7.52 were caused by the coordinated pyridine molecule. The $^{13}\text{C-NMR}$ spectrum of this compound is very similar to that of the corresponding free ligand. Due to the coordination to Co(III) cation, the ligand resonances were slightly shifted but their numbers were unchanged. Additional resonances at $\delta = 149.16$, 134.78 and 124.03 ppm due to the presence of the coordinated pyridine molecule were also present. The usual hydrogen bridges of the pseudo-macrocyclic octahedral *vic*-dioxime complex were characterized by the weak deformation bands at 1705 cm^{-1} which indicates $\text{O-H}\cdots\text{O}$ bending vibrations, in the case of **1**. In addition, the C=N stretching vibrations were at lower wave numbers as expected for *N,N*-chelated *vic*-dioxime complexes [9]. The fast atom bombardment mass spectrum of this complex showed a peak at $m/z = 2038.2$ which confirms the proposed structure, and another at $m/z = 1959$ which is attributed to the loss of axial ligation $[\text{M-py}]^+$.

The synthesis of the extraction agent $[\text{Co}(\text{LBF}_2)_2\text{pyCl}]$ (**2**) was accomplished by adding the borontrifluoride ethyl etherate to a refluxing acetonitrile suspension containing the H-bonded precursor Co(III) complex and gave a moderate yield (42.3%). The bridging protons were replaced by BF_2^+ groups and pyridine, and chlorine and both of the axial ligands were retained. In the $^1\text{H-NMR}$ spectrum of this complex, the bridging boron groups caused the resonances of the other groups to shift down field relative to those of complex (**1**) [10]. Similar trends were observed in the $^{13}\text{C-NMR}$ spectrum as observed in the $^1\text{H-NMR}$ spectrum of this complex. In the IR spectrum of **2**, the broad band at 1705 cm^{-1} due to $\text{O-H}\cdots\text{O}$ bending vibrations, disappeared upon encapsulation of the hydrogen-bridged complex with BF_2^+ with the concomitant appearance of peaks at 1158 and 825 cm^{-1} for the B-O and B-F vibrations, respectively. The fast atom bombardment mass spectrum of this compound showed a peak at $m/z = 2132$ which is caused by $[\text{M}]^+$ and another peak at $m/z = 2018$ which is attributed to the loss of pyridine and chloride $[\text{M-py}]^+$ which is in accord with the proposed formulation.

The extraction of the above-mentioned transition metal cations could be achieved using only one ionophore which contains ionophore attached with BF_2^+ -capped Co(III) complex due to the extraordinary solubility of this compound in chloroform medium. The role of the amide group in directing the binding selectivity of macrocycles towards alkali or earth alkaline metal cations has stressed the importance of ionophore studies on azooxa group containing macrocycles [11]. However, the relations with ionophore and cations through a nonpolar membrane contain complexation and de-complexation steps, and extraction is related to these step properties. In view of the available evidence, most of the

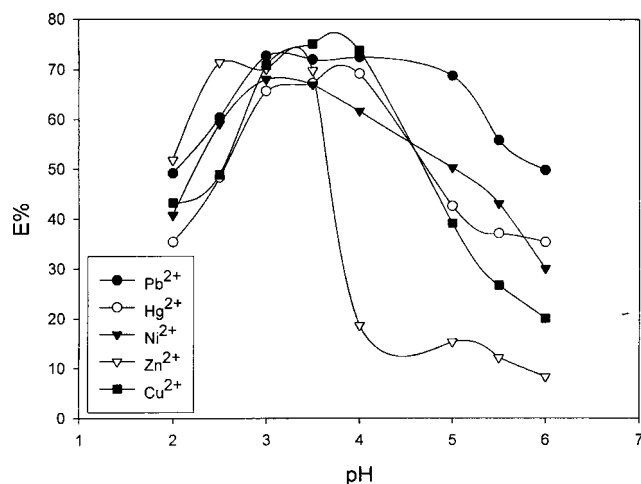


Figure 1.

extractions for d and f elements should be regarded as valid only for a certain pH range [12]. A description of this was possible only for a narrow pH range. Experimentally, pH curves observed by extraction are normally dome-shaped (Figure 1). The results of the extraction of divalent Pb, Ni, Hg, Cu and Zn from weakly acidic media, in the pH range of 2.75 to 4.05, into chloroform were obtained as shown in Table 1, by using the BF_2^+ -capped Co(III) complex as ionophore. The effect of pH on the determination of metal cations in aqueous media was investigated spectrophotometrically. For this purpose, the absorbances of the complex solution containing 5×10^{-5} M cations and ionophore (**2**) were measured in a pH range of 0–14 [13]. The pH at which the highest extractability occurred was determined. The behaviour of these measured pH degrees showed nonlinearity, which is probably due to the extraction mechanism. The highest extractability among the divalent cations is observed for Pb(II). This can be related to the macrocycle size, because on increasing the macrocycle size (23 membered macrocycle), the extraction of metals from aqueous media to organic phase is significantly higher than for smaller ones (17-membered one) [14]. In fact, the extraction by compound **2** has a considerable percentage above $\text{pH} = 3.15$ for Pb(II) and above $\text{pH} = 4.0$ for Hg(II). It is seen that ionophore (**2**) preferentially extracts the larger cations with larger ion radii, with a preference for Pb(II) over Hg(II) [15]. The value related to Hg(II) is lower than expected for divalent ions and can be explained by the extraction of hydrolyzed Hg(II) species above $\text{pH} = 4.05$ and the extraction of nitrate anions at lower pH [16]. This appears to be a consequence of the greater affinity of Hg(II) for nitrogen donors and Pb(II) for oxygen donors as demonstrated in the literature concerning [2.2.2] cryptands [16]. On the other hand, Hg(II) (0.11 nm radius), is a “soft” Lewis acid, Pb(II) (0.12 nm), Ni(II) (0.069 nm), Cu(II) (0.074 nm) and Zn(II) (0.074 nm) are of intermediate nature according to the hard and soft acids [17]. It is obvious that, the “hard” polyether moiety prefers “hard” cations and the “softer” amide group increases the selectivity towards “soft” or intermediate nature between “soft” and “hard” cations expect Hg(II)

Table 1. Solvent extraction of divalent metal ions by compound **2** from aqueous into chloroform media

Cation	pH	Extraction (%) [*]	Radius (nm)
Pb(II)	3.15	72.7 ± 0.9	0.12
Hg(II)	4.05	69.2 ± 1.1	0.11
Ni(II)	2.82	68.1 ± 0.8	0.069
Cu(II)	2.75	70.8 ± 1.2	0.074
Zn(II)	2.80	71.4 ± 0.7	0.074

* The extraction values are the means of four independent extraction experiments.

in this investigated system. Although the ionophore used in this study contains 0-donor atoms and amide groups, there is no clear discrimination between the hard or soft nature. However, the amide nitrogen participates more effectively in complexation with soft cations [14]. The complex stabilities depend on the nature of the substituents at the nitrogen donors. If the carbonyl group is a neighbor of the nitrogen donors, the complex stabilities are lower. Due to the carbonyl groups, the electron density at the nitrogen donors is reduced [18]. Similar extraction values among the cations can be explained by the cavity size of the macrocycle being the nondominant factor for extraction in this investigated system.

However, not only alkali or alkaline earth metal cations but also some of the other metal ions such as Ag(I), Pb(II), Cu(II), Tl(I) can form stable complexes with some ionophores and dioxocyclam [19]. The mentioned ionophores generally show the highest selectivity towards Ag(I) cation among other cations [20]. As stated above, the extraction studies done with ligands of complete ionophore characteristic were generally made with alkali and alkaline earth cations and few transition metal ions. There is no study in the literature with the ligand and metal cations with the characteristics in this study. Therefore, the comparison of the finding will not be significant.

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