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Extraction and Characterization of *Bis*(nioximato)diiodocobaltate(III)-Mixed Complex by Different Organic Solvents

ELBASHIR ENNAGEH ALI-SHATTLE*, A.R. JAFAR and ASSIYA HANDALIBA
Department of Chemistry, Faculty of Science, University of Alfateh, P.O. Box 84303, Tripoli, Libya
E-mail: elbnali@hotmail.com

This paper reports the studies on extraction of cobalt ion from aqueous solution using 1,2-cyclohexanedione dioxime (nioxime) by different organic solvents, such as, *n*-hexane, cyclohexane, isoamyl alcohol, chloroform and ethyl acetate at pH 3, in the presence of different halide ions, F^-, Cl^-, Br^-, I^--I_2 solutions and in the presence of appreciable concentrations of other transition metal ions up to 1/1000 ratio of Co/M, where M is Ni, Cu or Fe. Metal nioxime-iodide complexes were extracted into different organic solvents and the absorption at 470 nm was measured for each system by means of spectrophotometry. It was found that the extraction efficiency was enhanced in the presence of I^--I_2 solution among the halide ions. The optimum extraction was achieved by ethyl acetate as an organic solvent and with cobalt concentration of 0.07 M. where the optical density was 0.8. To isolate the extracted complex, higher concentration of cobalt salt solution was used. The complex *Bis*(nioximato)diiodocobaltate(III) was isolated and characterized by CHN elemental analysis, UV-Vis and ESR spectroscopy. From the study of the spectra, the proposed structure was deduced. It is a distorted octahedral (tetragonally distorted) with elongation along the z-axis toward the weak ligands of iodide, $K[Co(NH)_2I_2]$; where NH^- is nioximato ligand.

Key Words: Solvent extraction, Nioxime, diiodonioximatocobaltate, Mixed complexs.

INTRODUCTION

Extraction and determination of cobalt(II) as cobalt dioxime complex from aqueous solutions (pH 1-3) into organic solvents in presence of complexing ligand such as SCN^- and Cl^- has been reported[1,2]. The extract was used for determination of Co(II) by means of spectrophotometry (at wavelength 625 nm). A number of high molecular weight amines and quaternary ammonium salts have been used for the extraction of various anionic metal-thiocyanate complexes[3,4] such as $M(SCN)_4^{2-}$ where M = Co, Ni, Fe. The results show that the extraction efficiency enhanced in the presence of complexing agent or other oxidant ligands, such as NO_2^-, I^--I_2 (iodine-iodide solution). Effect of pH, diverse ions and masking agents are reported[5]. This method has been applied to determination of cobalt in the presence of other transition metal ions such as Fe, Ni and Cu.The stability constants of the mixed cobalt complexes formed between iodide and the cobalt(III)-dioxime parent complexes were determined by spectrophotometeric studies. in dioxan-water solvent[6].

Determination of cobalt in the presence of transition ion such as Fe, Ni and Cu, depends on the formation of the complex with the proper reagents such as SCN^-, nioxime and other complexing agents. It is found that the addition of an oxidant ligand to the cobalt complexes enhances the extraction efficiency. This enhancement is due to the oxidation of Co(II) to Co(III) in the complexes, which adds more stability to the extracted complex. The efficiency of extraction also depends on pH of the aqueous solution and the type of the extracting organic solvent, such as *n*-hexane, amyl alcohol, cyclohexane, ethyl acetate, *etc*.

Studies of extraction and determination of cobalt by dimethyl glyoxime (DH_2) is reported. This method is capable of determination of cobalt at low concentration, as low as 0.5 mg/mL. The results show that the presence of iron and copper did not affect the efficiency of determination and nickel complex will be precipitated and need to be separated prior to the determination[7].

Mononuclear nickel(II) and copper(II) complexes of metal to dioxime ligand (H_2L) ratio 1:2 were synthesized. The mononuclear cobalt(III) complex with dioxime (H_2L) ligand, $[Co(HL)_2Clpy]$, where py = pyridine, has been isolated[8]. The mononuclear distorted octahedral cobalt-nioximatic complexes based on 2,3-butanedione dioxime or dimethylglyoxime with identical or mixed axial ligands such as, $[Co(Hdmg)_2Ipy]$, $H[Co(Hdmg)_2I_2]$, $[Co(Hdmg)_2py_2]NO_3$ have been isolated[9]. Electrochemical studies (cyclic voltametry) and UV-vis spectroscopy of these complexes show some absorptions at low energy, which are attributed to either π-π^* transition, to *d-d* transition or metal-to-ligand charge transfer.

This paper reports an optimum condition for extraction of cobalt by 1,2-cyclohexanedione dioxime (nioxime) as diiodo,*bis*-dioximato-cobalt(III) complex into different organic solvents from an aqueous solvents in the presence of different ligands such as F^-, Cl^-, I^--I_2, Br^- at low pH 3 and in the presence of other transition metals such as Ni. Fe, Cu, which did not interfere in the extraction. An attempt has also been made to identify the extracted complex by UV-Vis. spectrophotometry, IR spectroscopy, elemental analysis and ESR spectroscopy.

EXPERIMENTAL

1,2-Cyclohexanedione dioxime (nioxime = H_2N, m.p. 189 ºC) was used as obtained. All inorganic chemicals were of analytical grade. The organic solvents were of reagent grade except chloroform which was of analytical purity.

For this investigation the following solutions were prepared: 0.02 M potassium halide aqueous solutions (KF, KCl and KBr) were prepared by dissolving a suitable weight of potassium halide (0.59 g of KF, 0.755g of KCl or 1.2 g of KBr) in 500 mL of distilled water.

0.01 M metal ions aqueous solutions (Co^{2+}, Ni^{2+}, Fe^{2+} and Cu^{2+}) were prepared by dissolving a suitable weight of metal salt {2.37 g of $CoCl_2·6H_2O$, 2.8 g of $NiSO_4·7H_2O$, 1.519 g of $FeSO_4$ or 1.875 g of $Cu(NO_3)_2$} in 1000 mL of distilled water. Oxidant solution was prepared by dissolving excess of iodine in 0.02 N potassium iodide aqueous solution and rapidly shaken then the solution was filtered. 0.01 M nioxime aqueous solution was prepared by dissolving suitable amount of nioxime in distilled water.

Effect of different halide ions on the extraction efficiency of cobalt-nioxime (1,2-cyclohexanedione dioxime) into chloroform solvent was investigated: To 2 mL of 0.010 M $CoCl_2·6H_2O$ aqueous solution, 8 mL of 1 % hydrochloric acid (1 + 99 v), 4 mL of 0.02 N halide ions solution F^-, Cl^-, Br^- or I^--I_2 and 6 mL of 0.01 M solution of 1,2-cyclohexanedione dioxime (nioxime) solution in distilled water, were added to make up the total volume to 20 mL. To this mixture of solutions, an equal volume (20 mL) of chloroform solvent was added in a separating funnel. The mixture was mechanically shaken for 0.5 h at room temperature (*ca.* 25 ºC) and pH *ca.* 1-3, a time found to be adequate for the establishment of equilibrium in all systems studied. After clear separation of the two phases, the two phases drained into separate tubes (in case I^--I_2 solution, to the organic phase 2 g of $Na_2S_2O_3$ were added to destroy the excess of iodine and the solution was filtered), 5 mL of aliquots of the organic and aqueous layers (phases) were pipetted into separate tubes to perform UV-Vis measurements of absorbance against a blank solution at wavelength λ = 470 nm.

Effect of organic solvents on the extraction efficiency of cobalt-nioxime in the presence of iodine-iodide solution, into different organic solvent was investigated: To 2 mL of 0.010 M $CoCl_2·6H_2O$ aqueous solution, 8 mL of 1 % hydrochloric acid (1 + 99 v), 4 mL of 0.02 N, I^--I_2 ions solution and 6 mL of 0.01 M solution of 1,2-cyclohexanedione dioxime (nioxime) solution in distilled water, were added to make up the total volume to 20 mL. To this mixture of solutions, an equal volume (20 mL) of organic solvent (*n*-hexane, cyclohexane, isoamyl alcohol, chloroform or ethyl acetate) was added in a separating funnel and proceeded with the same steps as in the preceding extraction experiment and UV-Vis measurements of absorbance against a blank solution at wave length λ = 470 nm were performed.

Extraction of cobalt ion from pure solution and in the presence of other metal ions M, where M = Fe^{2+}, Ni^{2+} and Cu^{2+} ions was studied. A series of different ratio of cobalt solutions with; Co/M ratio = 1/1, 1/10, 1/100, 1/1000 and 1/10000 (five solution for each metal) were used. To each of these solutions, 1 % hydrochloric acid (1 + 99 v) was added to maintain pH 1-3, then an equivalent amount of 0.02 N oxidant solution (I^--I_2) and of 0.01 M solution of 1,2-cyclohexanedione dioxime (nioxime) were added. Subsequently an equal volume of chloroform solvent was added. The mixture of solutions, were transferred into separating funnel and preceded with the same steps as in the preceding extraction experiments. UV-Vis absorbance of the organic phases were measured against a blank solution at wavelength λ =

470 nm. The optical densities of all solutions (of cobalt solution or metals mixture) were found almost the same *ca.* 0.680-0.685. This result show no interference from the added metal ions.

Isolation of *bis* nioximato diiodocobaltate: A solution of 1.19 g (0.005 mol) of $CoCl_2 \cdot 6H_2O$ in 50 mL of distilled water was heated to *ca.* 60 ºC in the reaction flask. Under magnetic stirring, 50 mL of 0.02 M nioxime in distilled water was added slowly. Stirrig was continued for 5 min at this temperature and 50 mL of 0.02 M iodine-iodide solution was added. Stirring was continued for several minutes and the solution was allowed to cool down to room temperature. The precipitate was filtered and kept to dry in the desiccators. The complex was identified by elemental analysis and its characteristic UV-vis EPR spectra.

RESULTS AND DISCUSSION

Effect of halide on extraction of cobalt nioxime complex: The effect of iodine-iodide, bromide, chloride and fluoride on the formation of cobalt complex with nioxime in acidic medium at 25 ºC were investigated spectrophotometrically. The UV-Vis absorption spectra of the complex in the presence of different halides are shown in Fig. 1. It is seen that there is a principal absorption maxima at 470 nm only in the case of iodine-iodide solution. Whereas there is no absorptions in the corresponding region for the other halide systems, bromide, chloride and fluoride. Nioxime practically has no absorption in this region. This indicates that, the extraction happens only if the iodine is added. These results suggest that, iodine-iodide solution works as a ligand and an oxidant at the same time to enhance the extraction of cobalt.

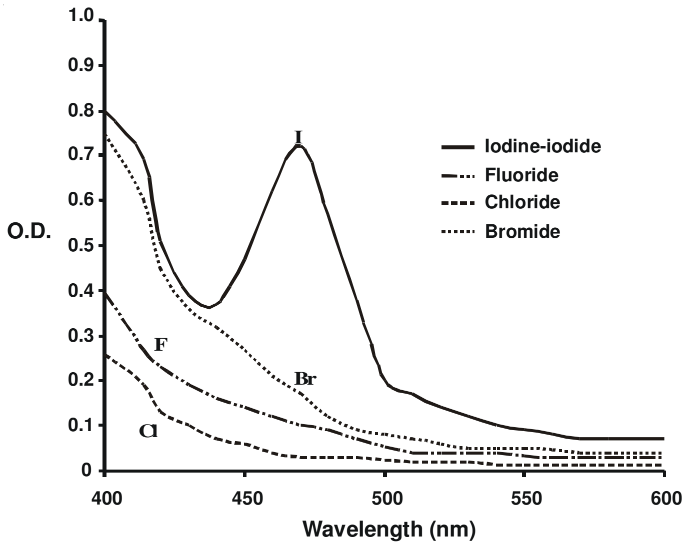

Fig. 1. Effect of halides on the formation of cobalt complex, spectra of cobalt nioxime complex in presence of iodine-iodide, bromide, fluoride

Effect of the organic solvent on the extraction of the complex: Extraction of cobalt nioxime complex in the presence of iodide-iodine solution in acidic medium at 25 ºC by different organic solvents, *n*-hexane, cyclohexane, isoamyl alcohol, chloroform, or ethyl acetate was investigated spectrophotometricaly. It is apparent from Fig. 2 that the optical density increases as the concentration of cobalt increases, in accordance to Beer's law. The results also show that, the best extraction was achieved by ethyl acetate and chloroform.

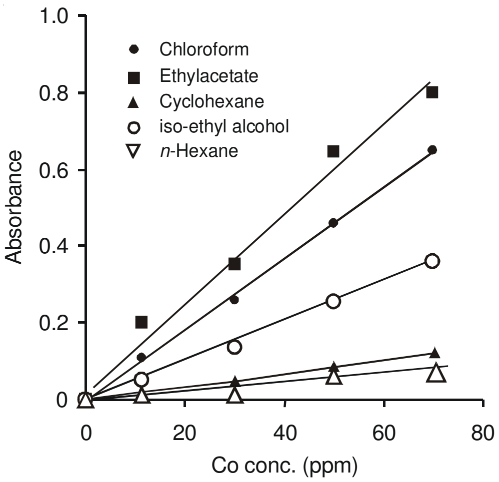

Fig. 2. Dependence of Co(III) nioxime (I_2) extraction by different organic solvents on cobalt concentration

Identification of the extracted complex: An attempt to identify the extracted complex was made. The complex was isolated and UV-Vis and ESR spectra were recorded. The results of elemental analysis are shown in Table-1. The results are in agreement with the empirical formula, $C_{12}H_{18}N_4O_4I_2KCo$.

TABLE-1
ELEMENTAL ANALYSIS OF DIIODO-BIS NIOXIMATO COBALT(III)

Element	Theor. (%)	Exp. (%)
C	22.18	22.71
H	02.41	2.840
I	40.46	40.06
N	09.20	08.83
Co	09.89	09.31
O	9.740	10.09
K	06.12	06.16

Electron paramagnetic resonance spectra of the complex at room temperature (Fig. 3), shows a multiple signal with a hyperfine splitting of $^{59}Co^{10}$. These results suggest that the complex is paramagnetic and the cobalt oxidation state is Co(III).

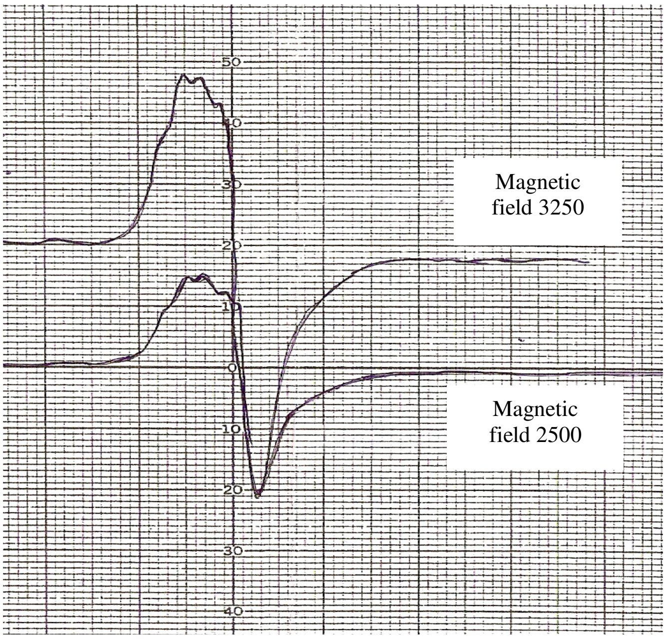

Fig. 3. EPR spectra were recorded on X-band EPR spectrometer using 10 KHz magnetic field modulation at 9.15 GHz and at room temperature

Electronic absorption spectra (UV-Vis) show two peaks at 340 and 470 nm. These results are in agreement with cobalt(III) complex with a distorted octahedral (tetragonal distortion) environment as illustrated in Fig. 4, similar to $[Co(C_2O_4)(tn)_2]NO_3$[11] where cobalt is Co(III) and (tn) = trimethylenediamine.

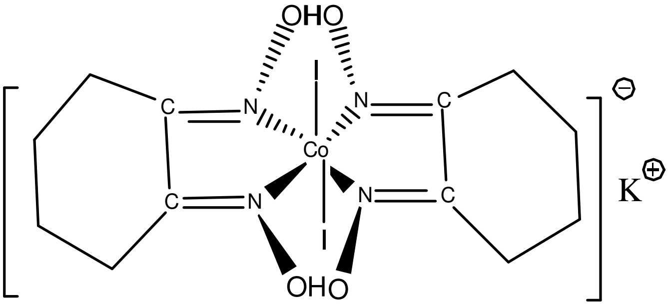

Fig. 4. Chemical formula: $KC_{12}H_{18}CoI_2N_4O_4$; molecular weight: 643.05

These results of elemental analysis, UV-vis and EPR suggest that the isolated compound is hexa-coordinated, paramagnetic cobalt complex and the structure of the complex is tetragonally distorted octahedral, where the *d*-orbitals split in a such way that it is very close to square planar pattern as shown in Fig. 5.

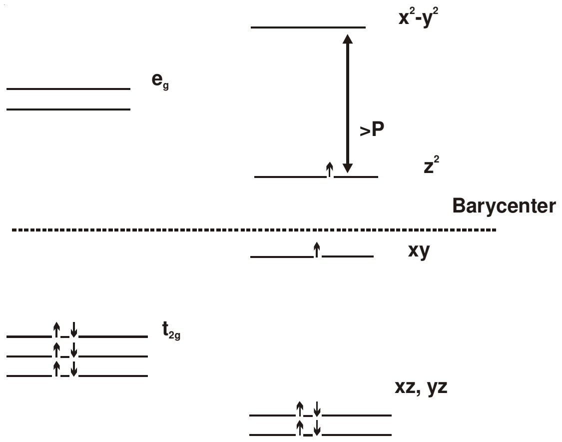

Fig. 5. Comparison of octahedral (left) *vs.* tetragonal distorted (right) symmetry

Conclusion

Extraction efficiency of cobalt from an aqueous solution by organic solvent reaches a maximum when 1,2-cyclohexanedione dioxime (nioxime) was used as a complexing agent in the presence of iodide-iodine solution and chloroform or ethyl acetate as an organic solvent where iodine-iodide solution was used as an oxidant ligand. Extraction efficiency of cobalt is the same, either in pure solution of cobalt or in the presence of other metals, M = (Fe, Ni or Cu), *i.e.* these metals do not interfere with the extraction of cobalt even at a high concentration $1/10^5$ of Co/M. The extracted complex was isolated and identified as potassium diiodido nioximato cobaltate(III), $K^+ [Co(HN)_2I_2]^-$; NH^- = neoximato ligand, where two iodide ligands are weakly coordinated to the axial position of the metal. Thus the structure of the complex is tetragonally distorted octahedral. The two axial iodide ligands of the octahedral structure are elongated along z-axis resulting in D_{2h} symmetry.

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