

PREPARATION AND CHROMATOGRAPHIC ELUTION OF COPPER(II) AND NICKEL(II) COMPLEXES OF MESO AND DL-BIS(TRIFLUOROISOPROANOYLACETONE) STILBENEDIIMINE ON GLC AND ABSORPTION HPLC

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The copper and nickel complexes of new tetradentate ligands bis(trifluoroisopropanoylacetone) meso-stilbenediimine (meso- $H_2F_3PA_2S$) and bis(trifluoroisopropanoylacetone)dl-stilbenediimine (dl- $H_2F_3PA_2S$) are prepared and characterised. The metal complexes are fairly volatile as evaluated from recording their DTA and TG curves and the complexes could easily be eluted on stainlesssteel gas chromatographic column packed with OV101 and OV17, 3% on chromosorb 80-100 mesh size, with detection limits corresponding to 5-10ng of metal ions, but without separation of copper and nickel complexes. However copper and nickel complexes are completely separated on adsorption HPLC column (250x4mm) packed with Licrosorb Si 100 5μ and complexes are isocratically eluted using binary mixture of chloroform-*n*-hexane. Detection was achieved using UV detector at 310 nm and detection limit were obtained at sub ng levels of metal ions.

Key words: HPLC separation of copper and nickel complexes.

INTRODUCTION

The application of gas chromatography and liquid chromatography for the separation and quantitative determination of transition metal ions at trace levels using suitable complexing reagents has been recognized [1-3]. The tetradentate ketoamine Schiff bases have proved useful reagents for GLC and HPLC separation of a number of metal ions [4-7]. Thus in the present work two new fluoro substituted ligands have been prepared and their copper and nickel complexes are eluted on GLC and HPLC columns.

EXPERIMENTAL

Preparation of the ligands: Bis(trifluoroisopropanoylacetone)meso-stilbenediimine(meso- $H_2F_3PA_2S$) and bis(trifluoroisopropanoylacetone)dl-stilbenediimine(dl- $H_2F_3PA_2S$). Trifluoroisopropanoylacetone (0.02 mol) and meso

or dl-stilbenediamine (0.01 mol) dissolved in ethanol was refluxed for 30 min. and cooled. The precipitate obtained was recrystallised from ethanol. meso- $H_2F_3PA_2S$, MS m/e (rel. intensity %) 540(0.04), 521(0.42), 471(0.14), 360(0.32), 271(100), 202(16) 165(6), 106(22). dl- $H_2F_3PA_2S$, MS m/e (rel. intensity %) 540(0.1), 521(0.15), 471(0.12), 384(0.2), 360(0.5), 271(30), 270(100), 202(12), 165(3) and 106(18).

Preparation of copper(II) and nickel(II) complexes. Equimolar solution of copper(II) acetate and nickel(II) acetate dissolved in methanol was added to the reagent solution in methanol. The solutions were refluxed for 30 min and cooled. The precipitate was filtered and recrystallized from methanol. The results of micro-analysis are summarized in Table 1.

Trifluoroisopropanoylacetone was prepared using the

Table 1. Results of elemental micro-analysis of the reagents and their metal complexes.

Compound	Mol. formula	m.p. °C	Expected %			Found %		
			C	H	N	C	H	N
Meso- $H_2F_3PA_2S$	$C_{28}H_{28}N_2O_2F_6$	148	62.22	5.22	5.18	62.15	5.59	5.17
Meso- F_3PA_2SCu	$C_{28}H_{28}N_2O_2F_6Cu$	270	55.93	4.63	4.65	56.39	5.10	4.70
Meso- F_3PA_2SNi	$C_{28}H_{28}N_2O_2F_6Ni$	294	56.37	4.69	4.69	57.16	5.27	4.63
DL- $H_2F_3PA_2S$	$C_{28}H_{28}N_2O_2F_6$	192	62.22	5.55	5.18	62.12	5.70	5.27
DL- F_3PA_2SCu	$C_{28}H_{28}N_2O_2F_6Cu$	227	55.93	4.65	4.65	55.83	4.75	4.62
DL- F_3PA_2SNi	$C_{28}H_{28}N_2O_2F_6Ni$	245	56.37	4.69	4.69	56.63	5.10	4.84

general procedure of Belcher *et al.* [8], and meso and dl-stilbenediamines were prepared as reported [9,17]. Elemental micro-analysis was carried out by Elemental Micro-Analysis Ltd., UK. IR were recorded on Hitachi 260-30 and Unicam SP-1025 IR Spectrophotometer using KBr and mujol mull techniques within 4000-250cm and 3800-625 cm^{-1} respectively. Mass spectra of the reagents on Finnigan Mat 1125, ^1H NMR on Bruker AM 300 were carried out at HEJ Research Institute of Chemistry, University of Karachi and ^1H NMR on Jeol FX-100 were recorded at PINSTECH, Islamabad. Spectrophotometric studies were carried out on Hitachi 220-Spectrophotometer. DTA and TG of metal complexes were recorded on Shimadzu TG-30 Thermal Analyser at a heating rate of $15^\circ/\text{min}$. and nitrogen flow rate $50 \text{ cm}^3/\text{min}$.

Hitachi 163 gas chromatograph equipped with FID system and recorder Hitachi 056 was used. Stainlesssteel columns (2mx3mm) packed with OV-101, 3% and OV-17, 3% on Chromosorb WHP80-100 mesh size (Attach Assoc.) were used.

Hitachi 665A liquid chromatograph, connected with variable wavelength UV monitor, recorder 561 and Rheodyne Injector 7125 were used throughout the study. Stainless steel column 250x4mm was packed with liorosorb Si 100 5μ using usual procedure.

RESULTS AND DISCUSSION

The reagents and metal complexes are prepared in good yield. Their IR spectra follow a similar pattern as observed with their related compounds [11]. The metal complexes show bands at 530-40 cm and 440 cm due to metal ligand vibrations. The mass spectra of the reagents show molecular ion peak at m/e 540 and a peak at m/e 471 due to loss of CF_3 group followed by $\text{C}_6\text{H}_9\text{NO}$ to give a peak at m/e 360. Further loss of C_7H_6 fragment takes place to obtain base peak at m/e 270 at half the molecular ion peak. Similar pattern has also been reported by Belcher [10] and Lindoy [12].

^1H NMR spectra of both of the reagents and their diamagnetic nickel complexes slightly differ from each other, because of different arrangements of phenyl groups at bridge position. The reagents contain two isopropyl groups in each of the ligand, but methyl groups in both of the isopropyl are found to be chemical shift unequal in the reagents and their diamagnetic nickel complexes, and indicate two doublets within δ 0.38-1.18 ppm. The reagents show a multiplet at δ 4.93 ppm for bridge CH, which changes into singlet at δ 4.847 ppm and 4.478 ppm in meso- $\text{F}_3\text{PA}_2\text{SNi}$ and dl- $\text{F}_3\text{PA}_2\text{SNi}$ respectively, due to a fixed configuration and magnetic shielding effect of phenyl groups (Table 2). The doublet observed at δ 12.19 ppm and δ 12.47 ppm in meso- $\text{H}_2\text{F}_3\text{PA}_2\text{S}$ and dl- $\text{H}_2\text{F}_3\text{PA}_2\text{S}$.

Table 2. ^1H NMR spectra in δ ppm in CDCl_3 of the reagents and their nickel complexes with possible assignment.

Compound	CH_3 isopropyl	-CH isopropyl	-CH bridge	=CH	-NH	$\text{-C}_6\text{H}_5$
Meso- $\text{H}_2\text{F}_3\text{PA}_2\text{S}$	0.8102(d) 3.33Hz 0.8512(d) 7.66Hz	2.432(m)	5.936(m)	5.786(s)	12.19(d)	7.16(m), 7.30(m) 7.39(m), 7.38(m)
Meso- $\text{F}_3\text{PA}_2\text{SNi}$	0.3821(d) 6.6Hz 1.074(d) 3.75 Hz	2.1916(m)	4.8476(s)	5.4773(s)	—	7.082(m), 7.252(s)
dl- $\text{H}_2\text{F}_3\text{PA}_2\text{S}$	0.96(d) 6.9 Hz 1.183(d) 6.3 Hz	2.911(m)	4.935(m)	5.446(s)	12.471(d)	7.034(m), 7.23(m) 7.32(m)
dl- $\text{F}_3\text{PA}_2\text{S}$	0.5768(d) 6.77 Hz 0.6913(d) 6.66Hz	2.6053(m)	4.4782(s)	5.4481(s)	—	7.389(m), 7.565(m) 8.3021(m)

PA₂S respectively, disappear in nickel complexes as expected [11-13].

The spectrophotometric studies of the reagents and their coloured metal complexes were carried out in acetone. The complexes meso-F₃PA₂SNi, dl-F₃PA₂SCu and dl-F₃PA₂SNi show a symmetrical band in visible region, due to d-d transitions at 575nm, 550nm and 562nm with molar absorptivity of 173, 158 and 17 l.mole⁻¹ cm⁻¹ respectively, but meso-F₃PA₂SCu shows a band at 580nm and a sholder at 640nm with molar absorptivity of 122 and 108 l.mole⁻¹ cm⁻¹ respectively. The nickel complex also show a charge transfer band at 360 nm and 383 nm with molar absorptivity of 3.9x10³ and 3.8x10³ l.mole⁻¹ cm⁻¹ for meso-F₃PA₂SNi and dl-F₃PA₂SNi respectively, and make possible insensitive spectrophotometric determination of metal ions.

DTA and TG of the copper and nickel complexes (Table 3) (Figs. 1 and 2) indicate that the metal complexes are considerably volatile above 225° and less in weight is almost quantitative except meso-F₃PA₂SCu, which leave certain residue behind.

The reasonable volatility of the metal complexes encouraged to inject the copper and nickel complexes on a gas chromatograph mounted on stainless steel column

Table 3. DTA and TGA of metalchelates.

Complexing agent	Cu (II) chelate	Ni(II) chelate
Meso-H ₂ F ₃ PA ₂ S	10.85 mg samples loss in weight starts 235° and loss of 88 % by 330° with maximum rate of loss by 295°. Loss of 92 % by 500°.	7 mg sample loss in weight starts by 225° and 100 % loss by 350° with maximum rate of loss of 300°.
	DTA shows melting endotherm at 270° and vaporization endotherm at 300° and an exotherm at 420°.	DTA shows melting endotherm at 285° and vaporisation endotherm at 340°.
DI-H ₂ F ₃ PA ₂ S	5.6 mg sample loss starts by 225° and 100 % loss in weight by 325° with maximum rate of loss at 295°.	Sample 5.0 mg loss in weight starts 230° and loss of 99 % by 340° with maximum rate of loss by 295°.
	DTA show melting endotherm at 205 and vaporisation endotherm at 220, 322 and 365°.	DTA show melting endotherm at 219° and endotherm at 320° and exotherm at 360°.

(2m x 3mm) packed with OV17, 3% or OV101, 3% on chromosorb WHP 80-100 mesh size, and the copper and nickel complexes eluted as symmetrical peaks at column temperature within 250-75°, injection port 260-90 and a nitrogen flow rate 30 cm³/min. But when a mixture of copper and nickel complexes of meso-H₂F₃PA₂S and dl-H₂F₃PA₂S was injected, no separation between copper and nickel complexes was obtained and each time slightly broader peak was obtained, inspite of a difference between the volatility of copper and nickel complexes (Fig. 1). However the metal complexes of meso and dl-isomers could easily be separated.

In order to check the response of the detector versus the amount of the complex injected on the column OV

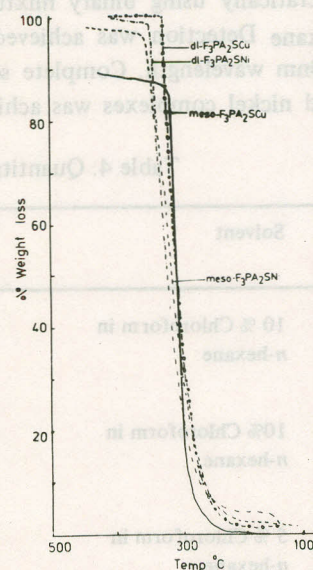


Fig. 1. TG of copper and nickel complexes, at a heating rate of 15°/min and nitrogen flow rate of 50 cm³/min.

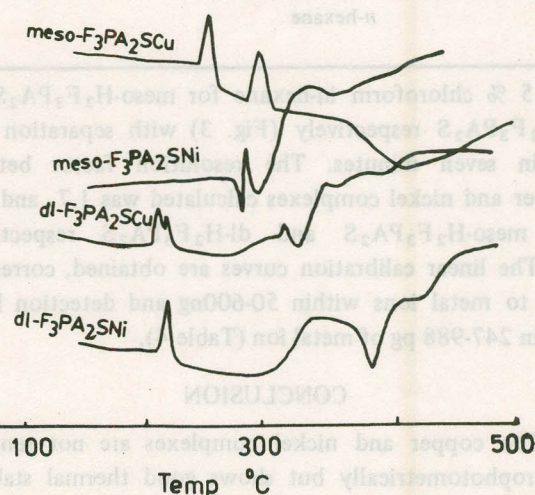


Fig. 2. DTA of copper and nickel complexes at a heating rate of 15°/min. and nitrogen flow rate of 50 cm³/min.

101, 3 % on Chromosorb 80-100, at a column temperature of 270°, injection port 280° and nitrogen flow rate of 30 cm³/min and average peak height of at least two injection was measured. The linear calibration curves were obtained within 1-5 µg of the complex, corresponding to 105-528 ng of copper and 99-494 ng of nickel. The detection limits measured as thrice the background noise were 0.1 µg and 0.05 µg of complexes of meso-H₂F₃PA₂S and dl-H₂F₃PA₂S respectively.

The lack of GLC resolution of copper and nickel complexes on nonpolar stationary phase led to explore the possible use of adsorption HPLC and the resolution of copper and nickel complexes using normal phase HPLC was tried, using Licosorb Si 100 5µ column. The complexes were eluted isocratically using binary mixture of chloroform and *n*-hexane. Detection was achieved using detector fixed at 310 nm wavelength. Complete separation between copper and nickel complexes was achieved at 10 %

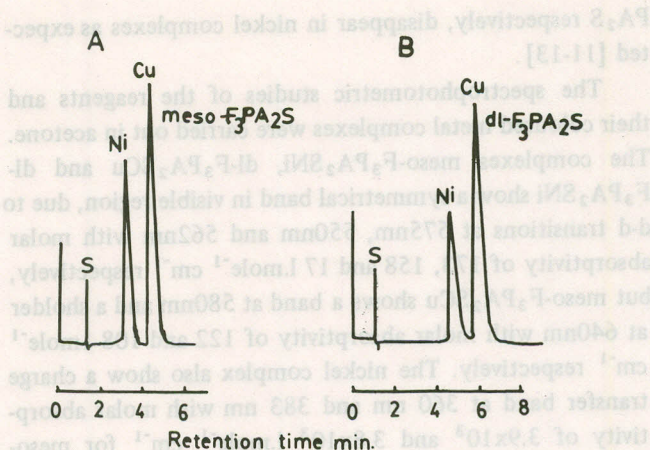


Fig. 3. HPLC separation of copper and nickel complexes on stainless steel column 250x4mm packed with Licosorb Si 100, 5µ. Elution (A) 10 % Chloroform (B) 5 % Chloroform in *n*-hexane flow rate (A) = 2 ml/min (B) 2.5 ml/min. Detection UV detector at 310 nm.

Table 4. Quantitative normal phase HPLC on Licosorb Si 100, 5µ.

Compound	Solvent	Retention volume ml	Calibration range	Detection limit
Meso-F ₃ PA ₂ S. Ni	10 % Chloroform in <i>n</i> -hexane	6.4	0.5-4.0 µg of Ni. complex corresponding to 49-395 ng Ni	2.5 ng of nickel complex, corresponding to 247 pg of nickel.
Meso-F ₃ PA ₂ S. Cu	10% Chloroform in <i>n</i> -hexane	8.5	0.5-4.0 µg of Cu complex corresponding to 53-422 ng copper.	2.5 ng of copper complex corresponding to 263 pg of copper.
dl-F ₃ PA ₂ S. Ni	5 % Chloroform in <i>n</i> -hexane	10.62	0.5-4.0 µg of Ni complex corresponding to 49-395 ng Ni	10 ng of Nickel complex corresponding to 988 pg of nickel.
dl-F ₃ PA ₂ S. Cu	5 % Chloroform in <i>n</i> -hexane	13.33	0.5-3.5 µg of Copper complex corresponding to 53-369 ng of copper.	5 ng of copper complex, corresponding to 527 pg of copper.

and 5 % chloroform in-hexane for meso-H₂F₃PA₂S and dl-H₂F₃PA₂S respectively (Fig. 3) with separation time within seven minutes. The resolution factor between copper and nickel complexes calculated was 1.7 and 1.65 for meso-H₂F₃PA₂S and dl-H₂F₃PA₂S respectively.

The linear calibration curves are obtained, corresponding to metal ions within 50-600 ng and detection limits within 247-988 pg of metal ion (Table 4).

CONCLUSION

The copper and nickel complexes are not sensitive spectrophotometrically but shows good thermal stability and elute on GLC column easily with calibration range at ng level of metal ion, but the resolution of copper and

nickel complexes on nonpolar phases was poor. However complete separations between copper and nickel complexes are achieved on normal phase HPLC, with better detection limits at sub ng levels than GLC using UV monitor.

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Preparation of hydroxysulphite (stipendamine) chromium (III) hemihydrate-sodium sulphite [Cr(en)₂(SO₃H)₂·1/2H₂O]·2NaCl (B). Dichloro (2, 2'-bipyridine) (OH)₂·3H₂O·2NaCl (B). Dichloro (2, 2'-bipyridine) chromium (III) chloride dihydrate (1 g, 2.0 mmol) was dissolved in 30 ml acetate buffer solution, pH = 3.2. Successive amounts of sodium sulphite (0.25 g, 2.0 mmol), dissolved in the least amount of water, were added to the former solution to reach the ratios 1:1, 1:2, 1:3 and finally 1:4, whereas the changes of the pH of the solution were 4.7, 5.4, 6.3 and 6.6, respectively. The solution was then stirred for 4 hours. Excess acetone was added to precipitate sodium chloride, sodium acetate and excess sodium sulphite and was filtered. The filtrate left in the open to evaporate slowly resulting in a red solid. The yield was 0.9 g (82%). m.p. 170° (decomp.) at 110° the colour changes to deep brown. Analysis for [Cr(C₁₀H₈N₂)₂(SO₃H)₂·1/2H₂O]·2NaCl. Calcd. Na, 7.3, C, 38.0, H, 3.6, N, 8.9, Cl, 11.2, S, 2.1%. Found: Na, 8.1, C, 38.0, H, 4.3, N, 8.2, Cl, 11.2, S, 2.1%.

Preparation of hydroxysulphite (stipendamine) chromium (III) hemihydrate-sodium sulphite [Cr(en)₂(SO₃H)₂·1/2H₂O]·2NaCl (A). Potassium cis-bis (oxalato) diacetate (III) hemihydrate (1 g, 2.2 mmol) was dissolved in 30 ml acetate buffer solution, pH = 3.2. Successive amounts of sodium sulphite (0.4 g, 3.2 mmol), dissolved in the least amount of water, were added to the former solution to reach the molar ratio 1:1, 1:2, 1:3 and finally 1:4. The pH was 4.7, 5.1, 6.4 and 6.6, respectively. During these additions the colour of the solution changed gradually from purple to green. Addition of acetone yielded a green oil which was washed several times with ethanol then ether until the product solidified. The green solid was further washed with a mixture of cold water and methanol. The yield was 0.7 g (43.0%) m.p. > 240°. Analysis for Na[Cr(en)₂(SO₃H)₂·1/2H₂O]·2NaCl. Calcd. Na, 17.1, K, 7.3, Cr, 9.7, C, 8.7, H, 0.4, S, 11.9%. Found: Na, 17.9, K, 7.1, Cr, 9.9, C, 8.8, H, 0.7, S, 12.1%.

Preparation of hydroxysulphite (2, 2'-bipyridine) chromium (III) trihydrate-sodium chloride [Cr(bpy)₂(SO₃H)₂·3H₂O]·2NaCl (B). Dichloro (2, 2'-bipyridine) chromium (III) chloride dihydrate (1 g, 2.0 mmol) was dissolved in 30 ml acetate buffer solution, pH = 3.2. Successive amounts of sodium sulphite (0.25 g, 2.0 mmol), dissolved in the least amount of water, were added to the former solution to reach the ratios 1:1, 1:2, 1:3 and finally 1:4, whereas the changes of the pH of the solution were 4.7, 5.4, 6.3 and 6.6, respectively. The solution was then stirred for 4 hours. Excess acetone was added to precipitate sodium chloride, sodium acetate and excess sodium sulphite and was filtered. The filtrate left in the open to evaporate slowly resulting in a red solid. The yield was 0.9 g (82%). m.p. 170° (decomp.) at 110° the colour changes to deep brown. Analysis for [Cr(C₁₀H₈N₂)₂(SO₃H)₂·1/2H₂O]·2NaCl. Calcd. Na, 7.3, C, 38.0, H, 3.6, N, 8.9, Cl, 11.2, S, 2.1%. Found: Na, 8.1, C, 38.0, H, 4.3, N, 8.2, Cl, 11.2, S, 2.1%.

INTRODUCTION

Cobalt (III) sulphite complexes were previously investigated in much detail [1-3], however, the corresponding chromium (III) compounds have received less attention. Sulphite and sulphite-chromium (III) complexes were obtained initially as the O-bonded sulphite intermediates which rapidly rearranged to the stable S-bonded isomers [4, 5].

We have prepared the following starting complexes: K[Cr(en)₂(SO₃H)₂·1/2H₂O], [Cr(bpy)₂Cl₂·3H₂O] and [Cr(en)₂Cl₂·1.5H₂O] and reacted them with Na₂SO₃ in acidic acetate buffer solution to avoid the formation of bridging hydroxo products quite common with Cr (III) complexes. However, in spite of this precaution, hydroxysulphite products are obtained in the case of bipyridine and ethylenediamine containing complexes.

EXPERIMENTAL

Chemicals. Potassium dichromate, chromium chloride hexahydrate, oxalic acid, bipyridine, ethylenediamine, sodium sulphite and other chemicals used were all reagent grade.

Preparation of the starting complexes. The following complexes were prepared: K[Cr(en)₂(SO₃H)₂·1/2H₂O] [8], [Cr(bpy)₂Cl₂·3H₂O] [9] and [Cr(en)₂Cl₂·1.5H₂O] [10]. (bpy = bipyridine, en = ethylenediamine). Their analysis was satisfactory.

Preparation of sodium potassium bis (oxalato) diacetate (III) monohydrate, Na₂Cr(C₂O₄)₂(SO₃H)₂·H₂O (A). Potassium cis-bis (oxalato) diacetate (III) hemihydrate (1 g, 2.2 mmol) was dissolved in 30 ml acetate buffer solution, pH = 3.2. Successive amounts of sodium sulphite (0.4 g, 3.2 mmol), dissolved in the least amount of water, were added to the former solution to reach the molar ratio 1:1, 1:2, 1:3 and finally 1:4. The pH was 4.7, 5.1, 6.4 and 6.6, respectively. During these additions the colour of the solution changed gradually from purple to green. Addition of acetone yielded a green oil which was washed several times with ethanol then ether until the product solidified. The green solid was further washed with a mixture of cold water and methanol. The yield was 0.7 g (43.0%) m.p. > 240°. Analysis for Na[Cr(en)₂(SO₃H)₂·1/2H₂O]·2NaCl. Calcd. Na, 17.1, K, 7.3, Cr, 9.7, C, 8.7, H, 0.4, S, 11.9%. Found: Na, 17.9, K, 7.1, Cr, 9.9, C, 8.8, H, 0.7, S, 12.1%.