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Synthesis and Characterization of Novel Formazans and their Metal Complex Dyes Containing Crown Ether Moieties

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ABSTRACT

*4′-Formylbenzo(15-crown-5)-2-carboxyphenylhydrazone (CPH) was synthesized by the addition reaction of 2-carboxyphenylhydrazine and 4′-formylbenzo(15-crown-5). 1,5 Bis(2′-carboxyphenyl)-3-benzo(15-crown-5) formazan (CPF) and 1-(2′-carboxyphenyl)-5-(2′-hydroxy-4′-carboxyphenyl)-3-benzo(15-crown-5)formazan (HPF) were then synthesized by coupling the diazonium salts of 2-aminobenzoic acid and 3-amino-4-hydroxybenzoic acid with 4′-formylbenzo(15-crown-5)-2-carboxyphenylhydrazone in strong alkaline media. The copper(*II*) and cobalt(*III*) complexes of these formazans have also been isolated. The structure of the formazans and their Cu(*II*) and Co(*III*) complexes were evaluated by elemental analysis, ^{1}H-NMR, IR and UV-VIS spectra.*

1 INTRODUCTION

Hydrazone derivatives such as benzaldehydephenylhydrazone and benzaldehydephenylhydrazone-2-carboxylic acid[1,2] give formazans with the coupling reaction of diazonium salts under strong basic conditions.[3,4]

Metal complex formations by tetradentate formazans have been investigated by Wizinger and his coworkers, by the reaction of tetradentate formazans with transition metal salts. These compounds readily form nickel and copper complexes having 1:1 stoichiometry.[5]

Formazans and their metal complexes are of interest in the field of dyes,

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medicine and biochemistry.[6,7] The pharmacological effect of azo groups is also of importance.[8] Fischer and Schiess[9] prepared formazans with substituents such as in sulphonic acid and hydroxy groups, which rendered the formazans soluble in water, thus, allowing a study of their potential as dyestuffs. The intense colors of the metal complexes of the formazans have found some applications in analytical chemistry;[10] formazans have been reported to be excellent reagents for the colorimetric determination of copper and nickel.[11]

Macrocyclic compounds, especially crown ethers and their metal complexes, have been the focus of much interest,[12] and these compounds show very high cation binding ability and solubility in organic solvents.[13-16] Because of this, interest has been developed in the investigation of formazans containing crown ether moieties.[17]

In this present study, a new hydrazone derivative, two new tetradentate formazans and their metal complex dyes, which contain macrocyclic rings, were synthesized from 4′-formylbenzo(15-crown-5), 2-carboxyphenylhydrazine, 2-aminobenzoic acid and 3-amino-4-hydroxybenzoic acid.

2 EXPERIMENTAL

2.1 Equipment and reagents

The absorption spectra were measured in DMF using a GBC 911 spectrophotometer (1 cm quartz cells). Elemental analysis and atomic absorption data were performed on a Perkin-Elmer 240C and a Hilger-Watts A.A.H.1550 instrument. ^{1}H-NMR and IR spectra were recorded with a Bruker 200 MHz and a Perkin-Elmer FT-IR 1600 spectrophotometer, respectively. 4′-Formylbenzo(15-crown-5) was synthesized according to Ref. 18, 2-carboxyphenylhydrazine hydrochloride (Aldrich), 2-aminobenzoic acid (Koch-Light), and 3-amino-4-hydroxybenzoic acid (Fluka) were used without further purifications.

2.2 Synthesis of 4′-formylbenzo(15-crown-5)-2-carboxyphenylhydrazone (CPH)

To a solution of 2-carboxyphenylhydrazine (1·218 g, 8 mmol), which was prepared by mixing a solution of 2-carboxyphenylhydrazine hydrochloride (1·508 g, 8 mmol) in absolute ethanol (50 ml) with a solution of sodium (0·184 g, 8 mmol) in absolute ethanol (25 ml), 4′-formylbenzo(15-crown-5) (3·68 g, 8 mmol) in absolute ethanol (50 ml) was added in small portions. The mixture was then stirred for 3 h at room temperature. The white solid which precipitated was filtered, washed with ethanol, dried *in vacuo* and recrystallized from ethanol. Yield 2·90 g (84·3%); MP 196°C. Elemental analysis for $C_{22}H_{26}N_2O_7$: Calculated, C, 61·4; H, 6·0; N, 6·5; Found,: C, 61·1; H, 5·9; N, 6·4.

UV-VIS λ_{max} (log ε) (in DMF): 360 nm (3·76), 330 nm (4·13), 275 nm (4·43), 245 nm (4·74).

Synthesis of 1,5-bis(2′-carboxyphenyl)-3-benzo(15-crown-5)formazan (CPF)

2-Aminobenzoic acid (0·908 g, 6·6 mmol) was dissolved in 1·5 ml of concentrated HCl (ice-bath) and sodium nitrite (0·458 g, 6·6 mmol) was then added in small portions. A solution of 4′-formylbenzo(15-crown-5)-2-carboxyphenylhydrazone (1·72 g, 4 mmol) in 40 ml of 5% aq. NaOH at 0°C, was added to the above diazonium solution, during which procedure the dark yellow solution turned red. After stirring for 5 h at 0°C, the solution was acidified with 0·2 M HCl to pH 4·90 and the dark red formazan was precipitated. The crude product was filtered, washed with water and dried *in vacuo*. The product was purified by dissolving in alkali and precipitating with 0·2 M HCl. Yield 0·786 g (34%); MP 166°C. Elemental analysis $C_{29}H_{30}N_4O_9$: Calculated: C, 60·2; H, 5·2; N, 9·7. Found: C, 60·0; H, 5·05; N, 9·5.

UV-VIS λ_{max} (log ε) (in DMF): 553 nm (4·08), 514 nm (4·32), 393 nm (3·91), 363 nm (3·85), 328 nm (4·17), 276 nm (4·41), 247 nm (4·86).

2.4 Synthesis of 1-(2′-carboxyphenyl)-5-(2′-hydroxy-4′-carboxyphenyl)-3-benzo(15-crown-5) formazan (HPF)

This dark-brown compound was synthesized from 4′-formylbenzo(15-crown-5)-2-carboxyphenylhydrazone (1·72 g, 4 mmol) and 3-amino-4-hydroxybenzoic acid (1·08 g, 6·6 mmol) by the same precedure as above. Yield 0·546 g (46%); MP 197°C. Elemental analysis $C_{29}H_{30}N_4O_{10}$: Calculated, C, 58·6; H, 5·05; N, 9·4; Found: C, 58·2; H, 4·8; N, 9·2.

UV-VIS λ_{max} (log ε) (in DMF): 554 nm (4·27), 520 nm (4·15), 405 nm (4·09), 354 nm (4·33), 316 nm (4·07), 264 nm (4·18).

2.5 Cu^{2+} complex of CPF

A solution of $Cu(CH_3COO)_2 . 2H_2O$ (0·0543 g, 0·25 mmol) in ethanol (15 ml was added to a solution of CPF (0·1445 g 0·25 mmol) in ethanol (20 ml). The mixture was refluxed with stirring for 3 h, and the reaction liquor then reduced to 15 ml. The purple crystalline product was filtered, washed with cold ethanol and diethyl ether, and then dried *in vacuo*. Yield 0·115 g (72·32%); MP > 300°C. Elemental analysis, $C_{29}H_{28}N_4O_9Cu$: Calculated, C, 54·4; H, 4·4; N, 8·75; Cu, 9·9. Found: C, 54·2; H, 4·2; N, 8·6; Cu, 9·6.

UV-VIS λ_{max} (log ε) (in DMF): 595 nm (4·19), 560 nm (4·29), 525 nm (4·26), 484 mm (4·13), 367 mm (4·15), 348 nm (4·12), 322 nm (4·42), 286 nm (4·45), 275 nm (4·49), 245 nm (4·40).

2.6 Cu^{2+} complex of HPF

This dark-red compound was prepared from HPF and $Cu(CH_3COO)_2 . 2H_2O$ by the same procedure as described above. Yield 0·112 g (74·84%); MP 287°C. Elemental analysis, $C_{29}H_{28}N_4O_{10}Cu$: Calculated C, 53·1; H, 4·3; N, 8·5; Cu, 9·7. Found: C, 52·8; H, 4·1; N, 8·4; Cu, 9·4.

UV-VIS λ_{max} (log ε) (in DMF): 553 nm (4·41), 517 nm (4·35), 472 nm (4·31), 436 nm (4·28), 395 nm (4·29), 352 nm (4·66), 315 nm (4·36), 276 nm (4·59), 265 nm (4·69).

2.7 Co^{3+} complex of CPF

A solution of $Co(CH_3COO)_2 . 4H_2O$ (0·0622 g, 0·25 mmol) in ethanol (40 ml) was added to a solution of CPF (0·1445 g, 0·25 mmol) in ethanol (20 ml). Pyridine (0·24 g, 3 mmol) in ethanol (10 ml) was added and air was bubbled through the solution for 3 h whilst refluxing and stirring. The reaction mixture was then reduced to 20 ml and the dark-green complex filtered, washed with cold ethanol and diethyl ether, and dried *in vacuo*. Yield 0·104 g (65·8%); MP > 300°C. Elemental analysis $C_{39}H_{37}N_6O_9Co$: Calculated, C, 59·1; H, 4·7; N, 10·6; Co, 7·4. Found: C, 59·8; H, 4·4; N, 10·4; Co, 7·2.

UV-VIS λ_{max} (log ε) (in DMF): 554 nm (4·38), 517 nm (4·32), 472 nm (4·38), 437 nm (4·40), 396 nm (4·51), 355 nm (4·70), 314 nm (4·64), 275 nm (4·73), 270 nm (4·59).

Co^{3+} complex of HPF

This dark-brown complex was prepared from HPF and $Co(CH_3COO)_2 . 4H_2O$ by the same procedure as above. Yield 0·129 g (79·6%); MP > 300°C. Elemental analysis $C_{39}H_{37}N_6O_{10}Co$: Calculated, C, 57·9; H, 4·6; N, 10·4; Co, 7·3. Found: C, 57·7; H, 4·3; N, 10·2; Co, 7·1.

UV-VIS λ_{max} (log ε) (in DMF): 615 nm (4·19), 552 nm (4·61), 518 nm (4·52), 474 nm (4·55), 436 nm (4·58), 395 nm (4·63), 353 nm (4·68), 318 nm (4·58), 275 nm (4·69), 270 nm (4·73).

RESULTS AND DISCUSSION

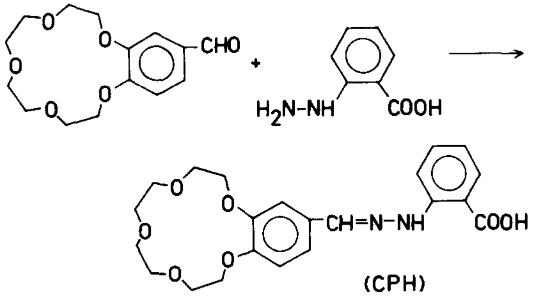
4′-Formylbenzo (15-crown-5)-2-carboxyphenylhydrazone (CPF) (Scheme 1) was synthesized from 4′-Formylbenzo(15-crown-5) and 2-carboxyphenylhydrazine in absolute ethanol at room temperature.

In the ^{1}H-NMR spectrum of 2-carboxyphenylhydrazine, there are singlets at $\delta = 3{\cdot}80$ ppm and $\delta = 7{\cdot}40$ ppm for NH_2 and NH protons, respectively. The singlet for the NH_2 protons disappears after the condensation reaction with 4′-Formylbenzo(15-crown-5) and the NH proton of the hydrazine group appears at $\delta = 7{\cdot}30$ ppm. The NH proton is also readily identified on D_2O exchange.[19] Two multiplets at $\delta = 7{\cdot}34$–$6{\cdot}64$ ppm and $\delta = 4{\cdot}08$–$3{\cdot}63$ ppm correspond to aromatic and ethanol protons.[20,21] The carbonyl protons shift upfield as expected and appear at $\delta = 9{\cdot}85$ ppm; a singlet at $\delta = 7{\cdot}90$ ppm corresponds to the carboxyl protons.[22]

The IR spectra of 4′-Formylbenzo(15-crown-5) shows the stretching vibration of the carbonyl group at 1740 cm^{-1}. After the condensation reaction, this resonance disappears and a new band appears at 1660 cm^{-1}, characteristic of the cyano group. Stretching and bending vibrations of the NH_2 group do not appear. The stretching vibrations of the aromatic and the etheral groups of CPH are very similar for both 4′-formylbenzo(15-crown-5) and 2-carboxyphenylhydrazine, these bands appearing at 3040 and 1180–1120 cm^{-1}, respectively.

1,5-Bis(2′carboxyphenyl)-3-benzo(15-crown-5) formazan (CPF) and 1-(2′-carboxyphenyl)-5-(2′-hydroxy-4′-carboxyphenyl)-3-benzo(15-crown-5) formazan (HPF) were prepared by coupling the diazonium salts of 2-aminobenzoic acid and 3-amino-4-hydroxy benzoic acid with CPH in strongly alkaline media (Scheme 2).

In the ^{1}H-NMR spectra of CPF and HPF, the resonances of carbonyl proton disappear after the coupling reactions, but other resonances, for example, those for the aromatic, carboxy and crown ether residues, appear



Scheme 1

TABLE 1

^{1}H-NMR Chemical Shift δ (ppm) Data for CPH, CPF and HPF

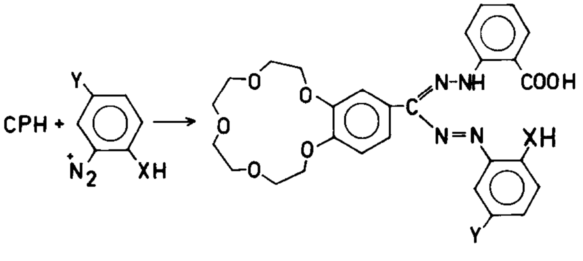
Compound	*NH*	*COOH*	*OH*	*Aromatic-H*	CH_2—CH_2—O	*CHO*
CPH[a]	7·30 (s, 1H)	7·90 (s, 1H)	—	7·34–6·64 (m, 7H)	4·08–3·63 (m, 16H)	9·85 (s, 1H)
CPF[a]	7·35 (s, 1H)	8·00 (s, 2H)	—	7·30–7·00 (m, 11H)	4·15–3·69 (m, 16H)	—
HPF[a]	7·28 (s, 1H)	8·10 (s, 1H) 7·95 (s, 1H)	8·85 (s, 1H)	7·28–7·16 (m, 11H)	4·19–3·69 (m, 16H)	—

[a] DMSO-d_6.

TABLE 2

IR absorptions of CPH, CPF, HPF and their Metal Complexes (cm^{-1}) (KBr)

Compound	$\nu(N—H)$	$\nu(COO)$	$\nu(OH)$	$\nu(COOH)$	$\nu(—CH_2—CH_2—)$	$\nu(CH_{arom})$	$\nu(C=N)$	$\nu(N—N)$	$\nu(C—O—C)$
CPH	3 300	1 700	—	3 120	2 910–2 810	3 040	1 660	—	1 180–1 120
CPF	3 280	1 720	—	3 140	2 920–2 820	3 025	1 670	1 420	1 170–1 120
HPF	3 330	1 720	3 200	3 170	2 925–2 840	3 030	1 660	1 440	1 145–1 125
(CPF) Cu(II)	3 360	1 720	—	—	2 920–2 810	3 040	1 640	1 435	1 150–1 120
(CPF) Co(III)	—	1 700	—	—	2 930–2 860	3 045	1 630	1 440	1 160–1 120
(HPF) Cu(II)	3 320	1 700	—	3 180	2 935–2 855	3 040	1 670	1 435	1 140–1 120
(HPF) Co(III)	—	1 710	—	3 220	2 940–2 850	3 045	1 670	1 445	1 145–1 120



CPF : XH=COOH , Y=H
HPF : XH=OH , Y=COOH
Scheme 2

at frequencies which are very similar to those of CPH (Table 1). The singlets at $\delta = 7{\cdot}35$ and 7·28 ppm, corresponding to NH protons, show significant upfield shifts due to the resonances for the formazan ring system.[3,23] The main differences in the ^{1}H-NMR spectra of HPF are the presence of the hydroxy group in the 2′-position ($\delta = 8{\cdot}85$ ppm) and the position of carboxy resonance.

In the IR spectrum of CPF and HPF (Table 2), the stretching vibrations at 2945 cm^{-1} disappear after the coupling reactions and additional resonances for the N=N group appear at 1420–1440 cm^{-1}.[24,25] Although N=N stretching vibrations are infrared inactive for symmetrical trans-azo compounds, they do appear in the 1450–1400 cm^{-1} region for azo groups.[26] Skeleton vibrations of C—N=N—C or C=N—C—N groups appear at 1000 cm^{-1}.[24] In addition the ν(NH) broad vibration at 3280–3330 cm^{-1} indicates the presence of NH··N intramolecular hydrogen bonds.[27]

Reaction of CPF and HPF with $Cu(CH_3COO)_2 . 2H_2O$ and $Co(CH_3COO)_2 . 4H_2O$ were effected in ethanol. Elemental analysis data indicated a 1/1 metal:ligand ratio (Figs 1, 2). Complexes of 2,2′-disubstituted formazan dyes with Cu(II) and Co(III) ions give planar and octahedral complexes, respectively.[5,28] The six co-ordinated Co(III) complexes were obtained when air was bubbled through a mixture of cobalt–formazans in ethanol in the presence of pyridine.

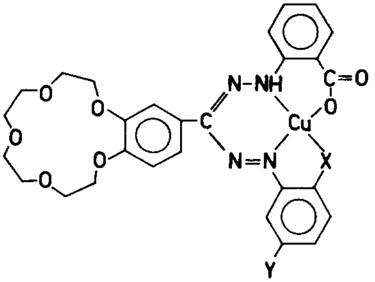


Fig. 1. Cu(II) complexes of CPF and HPF.

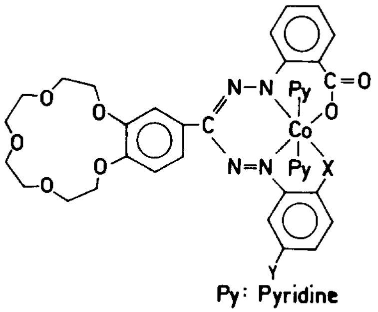


Fig. 2. Co(III) complexes of CPF and HPF.

The structures of the complexes of CPF and HPF were confirmed by IR. The ν(NH) vibrations at 3360 and 3320 cm^{-1} in the spectrum of the Cu(II) complexes was as anticipated, and the absence of both ν(COOH) and ν(OH) indicated the formation of the Cu(II) complexes shown in Fig. 1. The IR spectra of the tricyclic complexes of Co(III) with tetradentate formazans are in accord with the structure illustrated in Fig. 2. The coordination sphere of the Co(III) complexes are completed by monodentate pyridine ligands.

A color difference was observed in the complexes derived from CPF and HPF. These complexes also show grêat stability towards acids, as has been previously noted.[29]

The presence of the crown ether ring in the formazans results in significant bathochromic shifts in the visible absorption bands.[30] For example, in phenyl derivates of formazans, absorptions occur at 478 and 485 nm.[31] These values are shifted to 514 and 520 nm respectively by the macrocyclic effect. The nature and orientation of the substituents also influence the bathochromic shifts observed in CPF and HPF. A larger bathochromic shift for 2,5-disubstituted derivatives (2-hydroxy and 5-carboxy) of formazans (λ_{max} 520 nm) is observed compared to that of the 2-carboxy analogue ($\lambda_{max} = 514$nm). It is apparent that the shift in HPF is greater than in CPF due to the electron-donating character of the hydroxy group. In HPF, the lower electron-withdrawing character of the carboxy groups results in a slight decrease in both the absorption maximum and the extinction coefficient. Complexation of the formazans with Cu(II) and Co(III) also results in increased extinction coefficients.

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