Synthesis, characterization, and sorption activity of novel azo-colorants derived from phloroglucinol and antipyrine and their metal complexes

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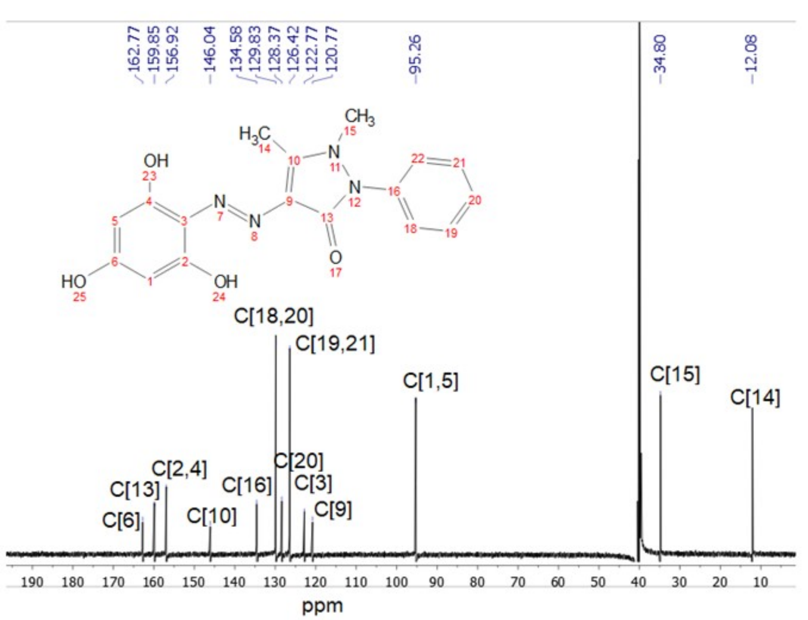
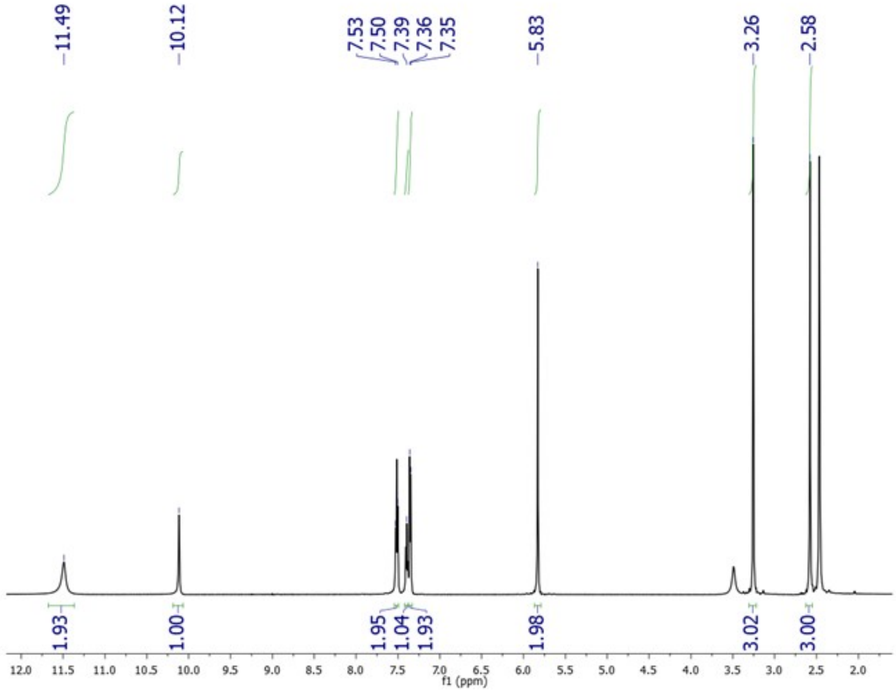


a)



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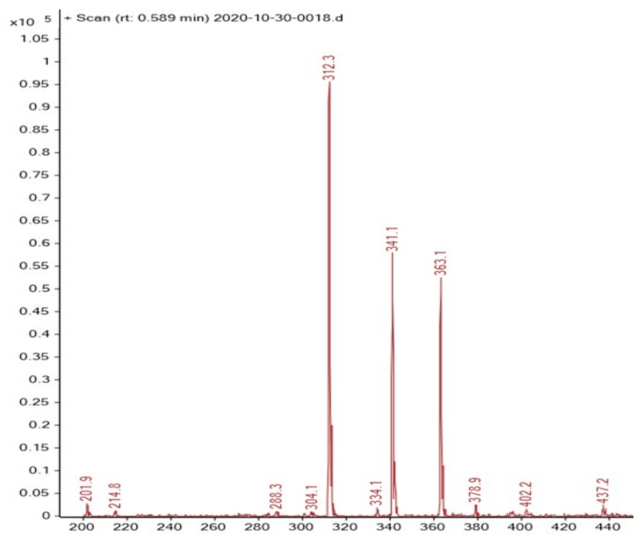


c)

Fig 1S. ^{1}H (a) and ^{13}C NMR (b) spectra and mass spectra (c) of H_3L^1

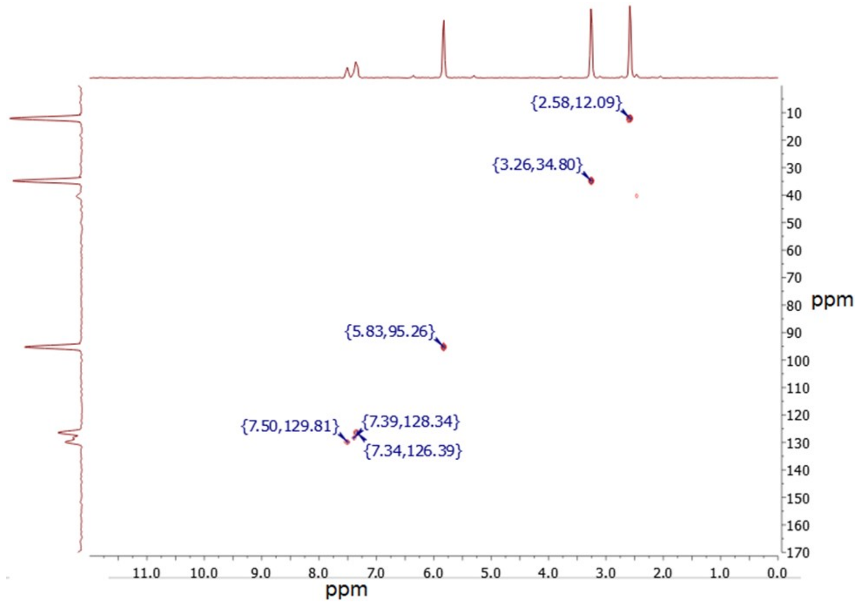


Fig 2S. COSY ^{1}H-^{1}H NMR spectra of H_3L^1

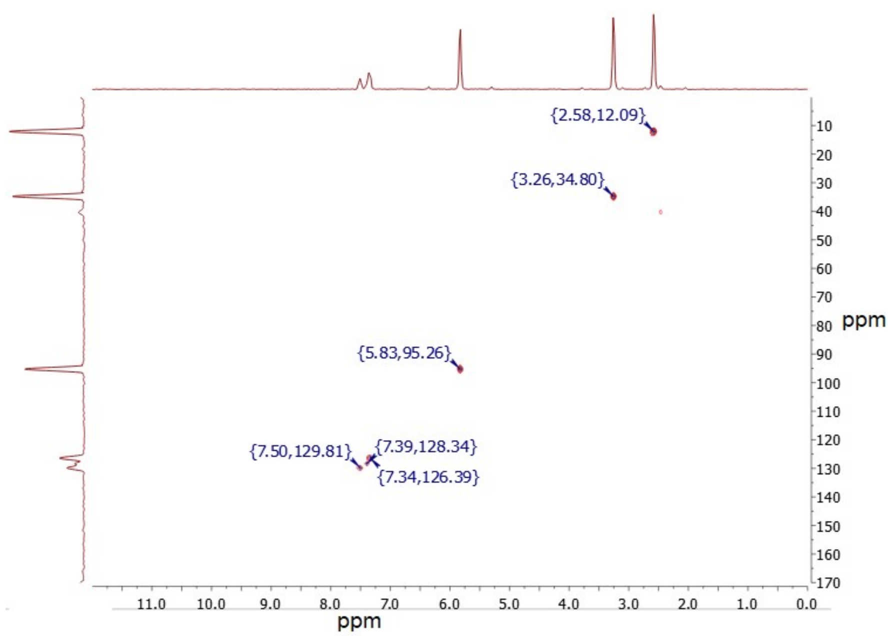


Fig 3S. HMBC ^{1}H-^{13}C NMR spectra of H_3L^1

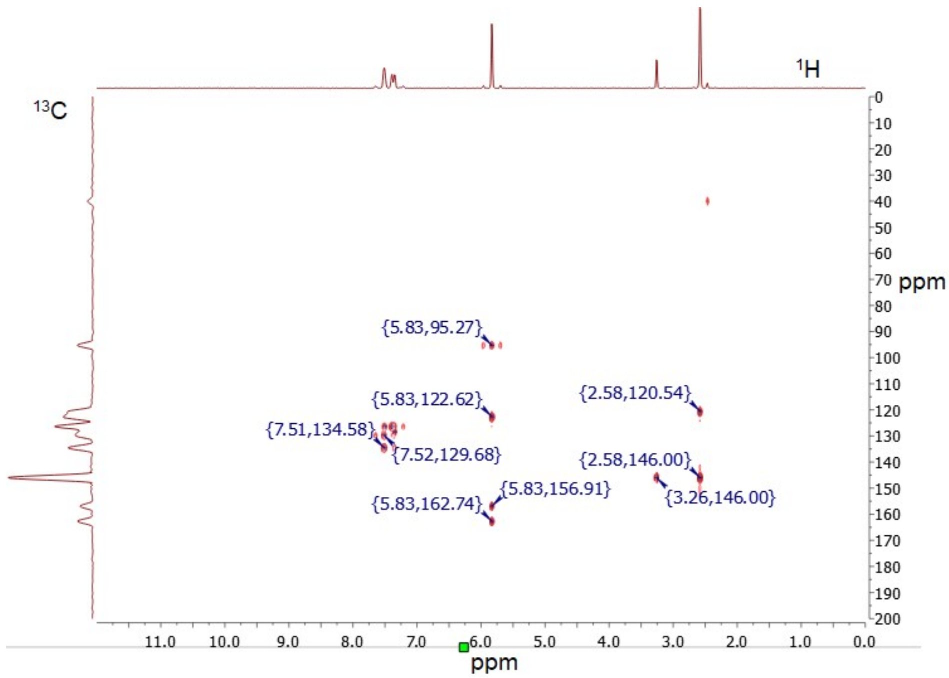


Fig 4S. HMQC ^{1}H-^{13}C NMR spectra of H_3L^1

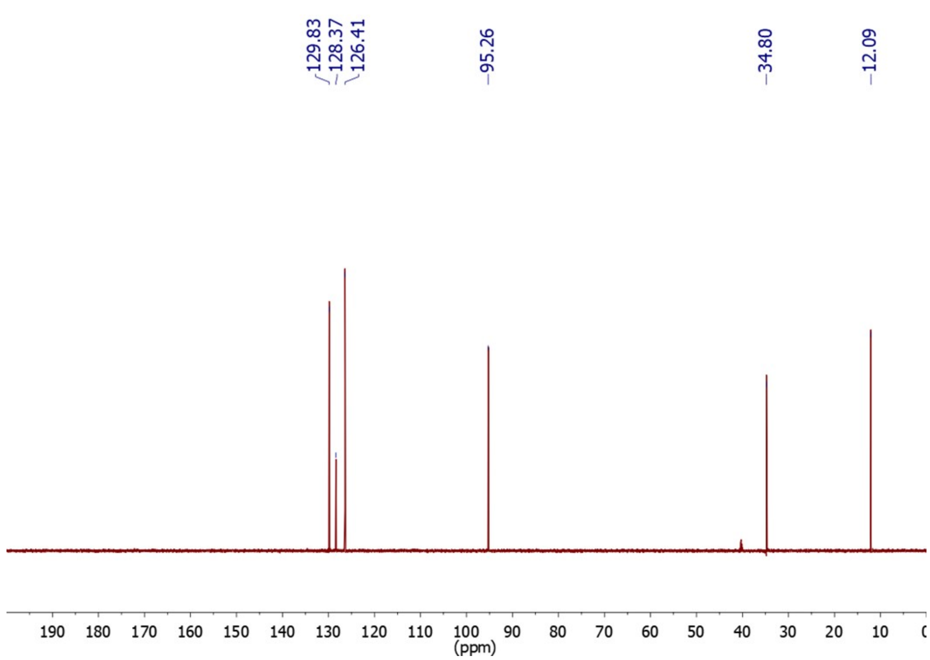
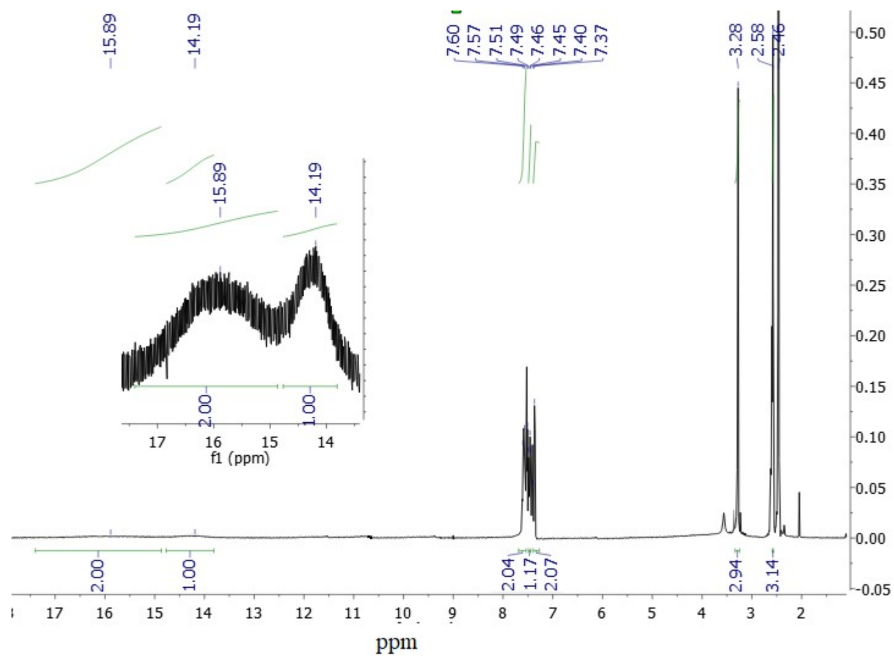
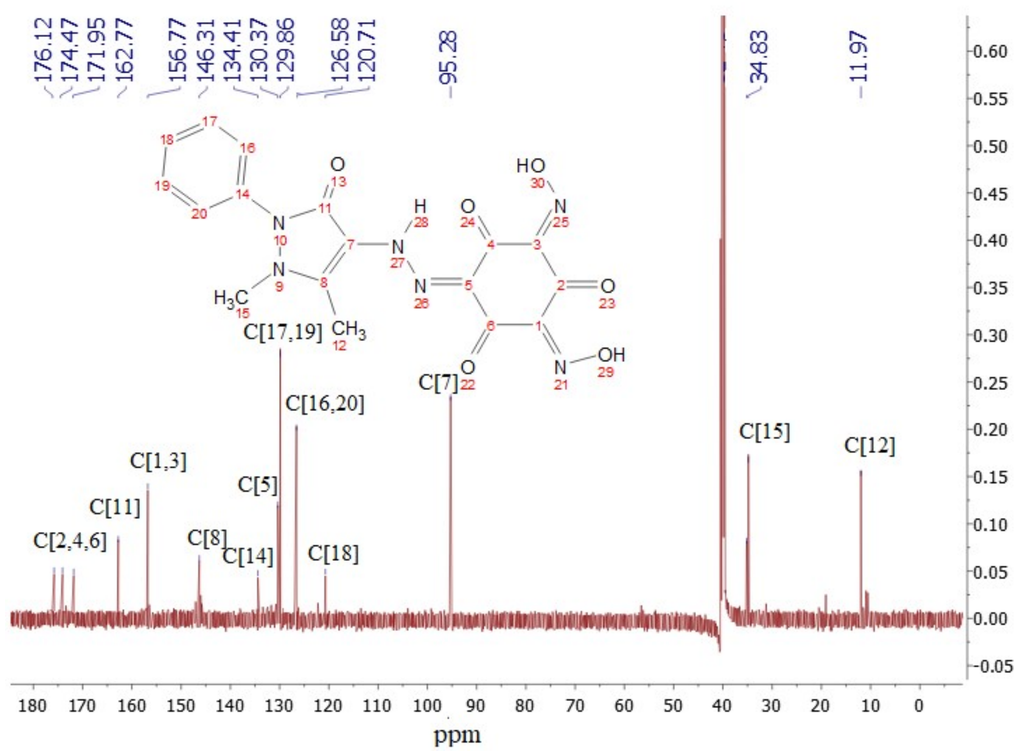


Fig. 5S. DEPT 135 ^{13}C NMR spectra of H_3L^1



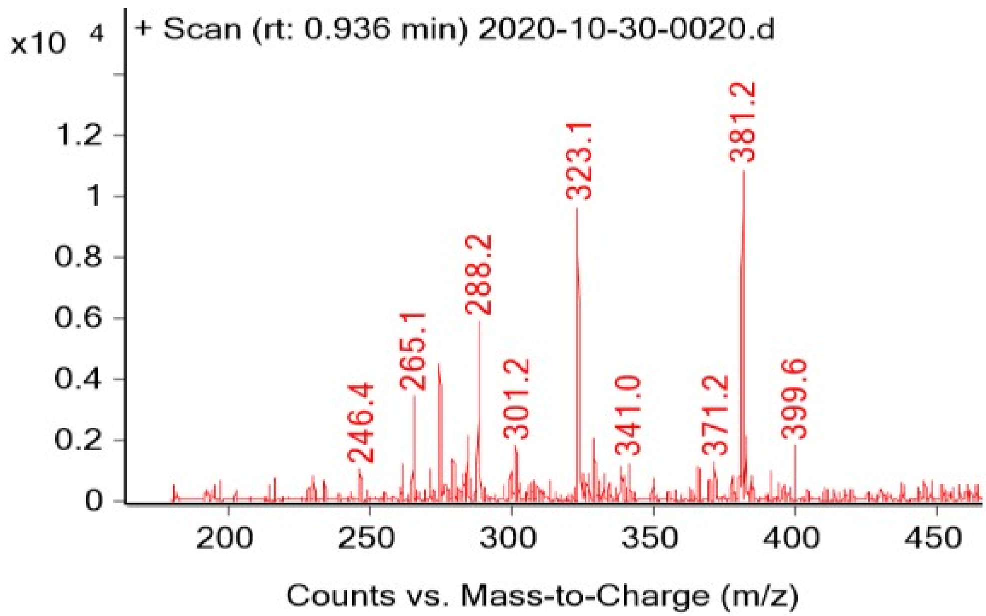
15.89
14.19
7.60
7.57
7.51
7.49
7.46
7.45
7.40
7.37
3.28
2.58
2.46
2.00
1.00
2.04
1.17
2.07
2.94
3.14
f1 (ppm)
ppm

a



176.12
174.47
171.95
162.77
156.77
146.31
134.41
130.37
129.86
126.58
120.71
95.28
34.83
11.97
C[2,4,6]
C[11]
C[1,3]
C[8]
C[14]
C[5]
C[17,19]
C[16,20]
C[18]
C[7]
C[15]
C[12]
ppm

b



c

Fig 6S. [1]H (a) and [13]C (b) NMR spectra of H_3L^2 and mass spectra (c)

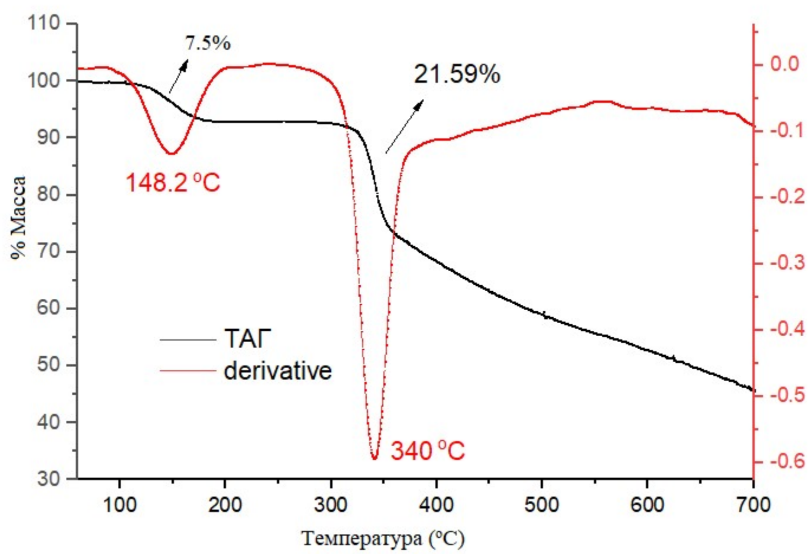


Fig 7S. Thermogravimetric analysis $[ZnH_2L^1Cl.2H_2O]$ (4)

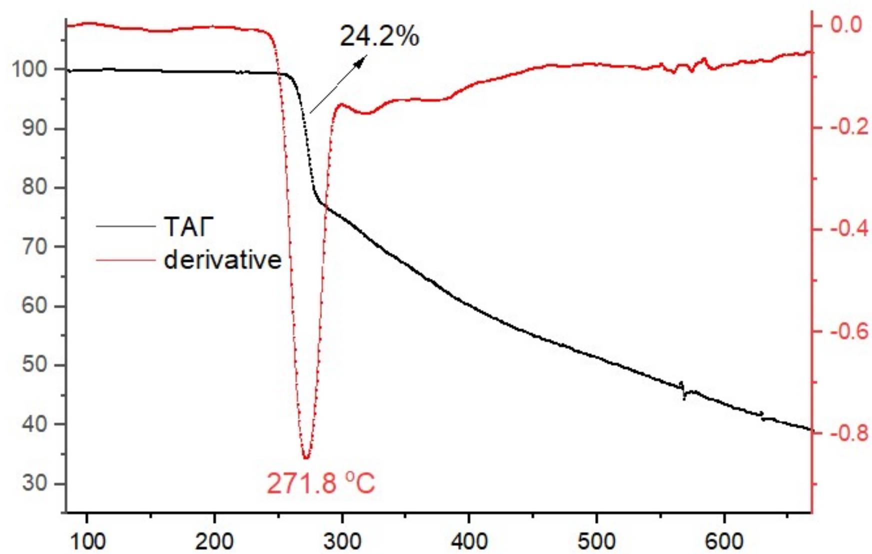
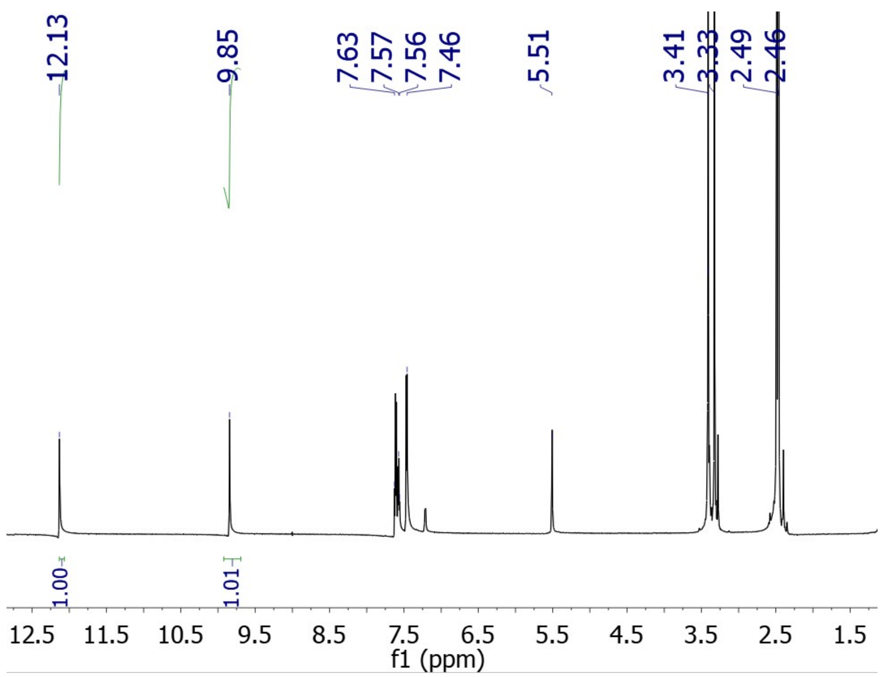
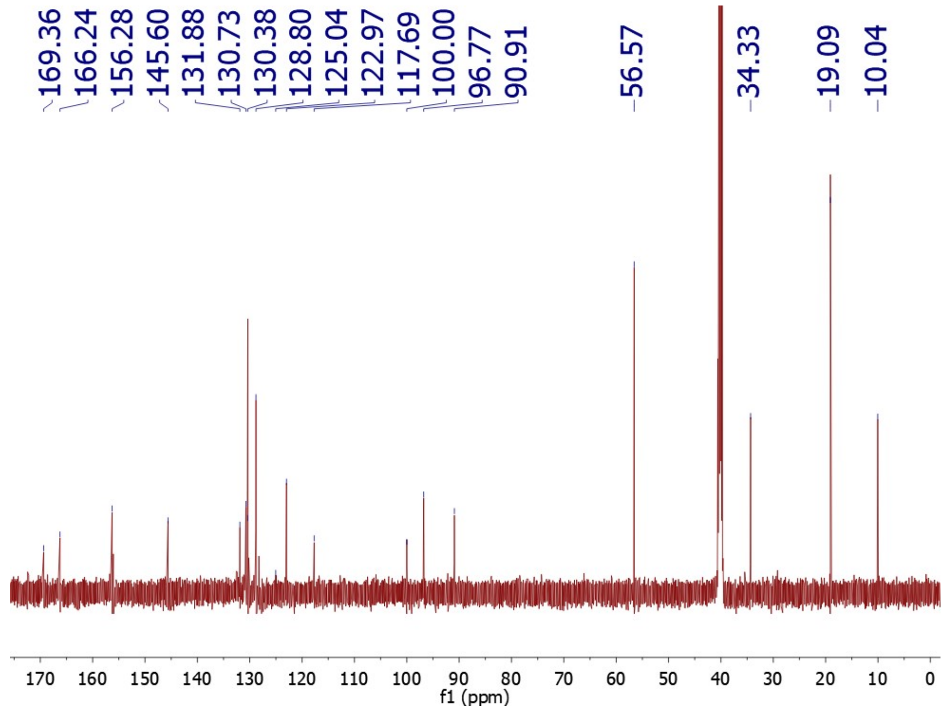


Fig 8S. Thermogravimetric analysis $Cd_2Cl_4(H_3L^1)_2$ (5)

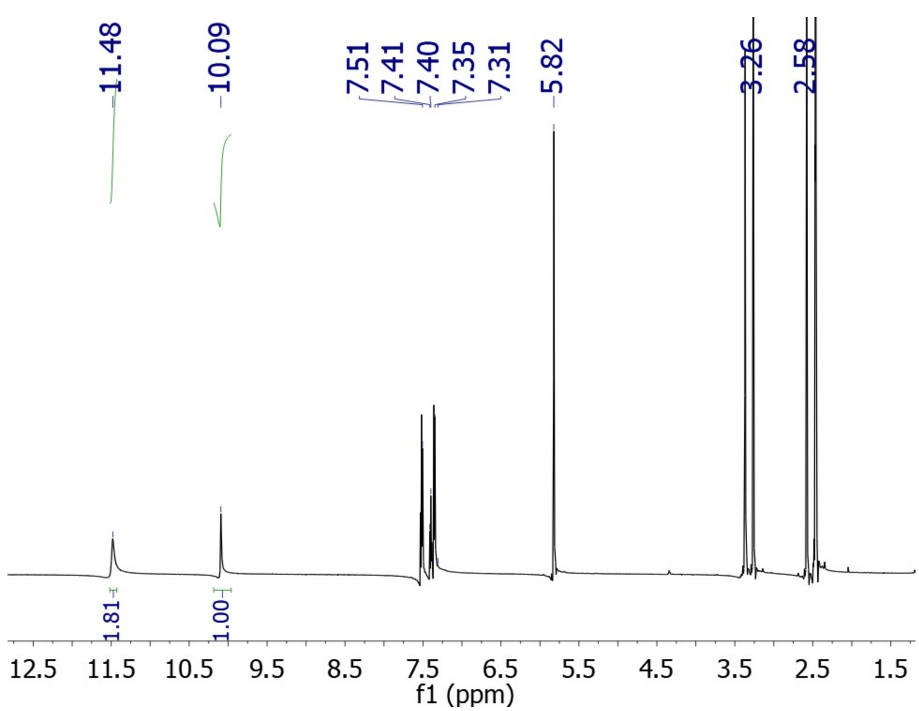


a

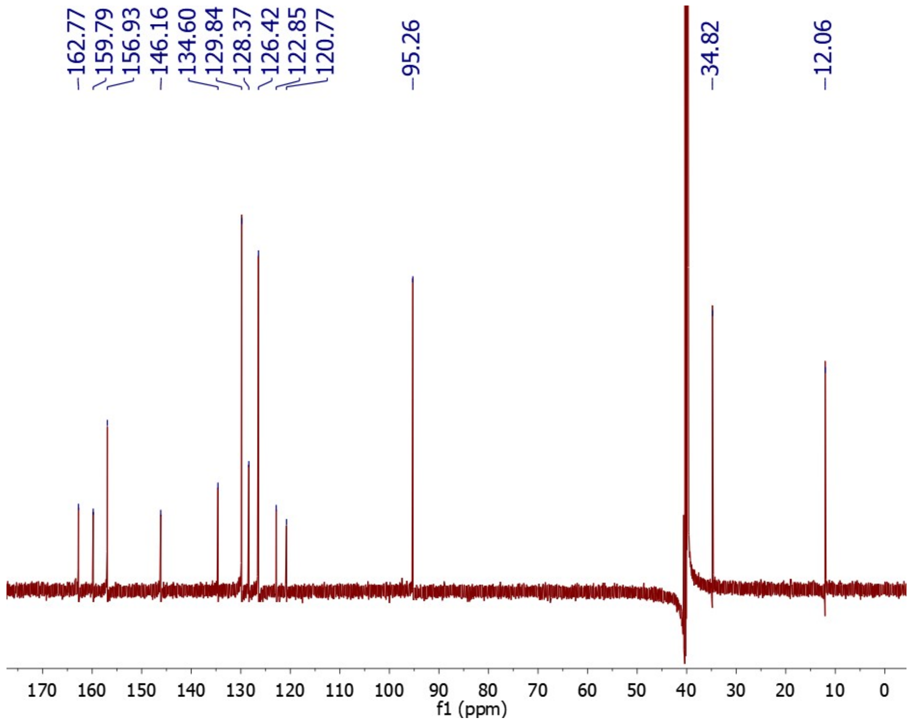


b

Fig 9S. [1]H (a) and [13]C (b) NMR spectra of $ZnH_2L^1Cl.2H_2O$ (4)



a



b

Fig 10S. ^{1}H (a) and ^{13}C (b) NMR spectra of $Cd_2Cl_4(H_3L^1)_2$ (5)

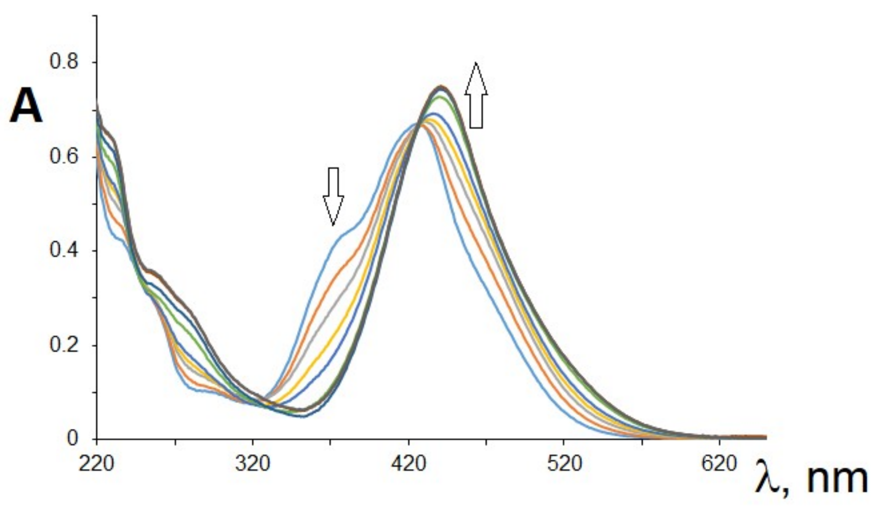


Fig 11S. Changes in electronic absorption spectra of ethanol solutions of H_3L^1 at stepwise addition of the solution $CuCl_2$

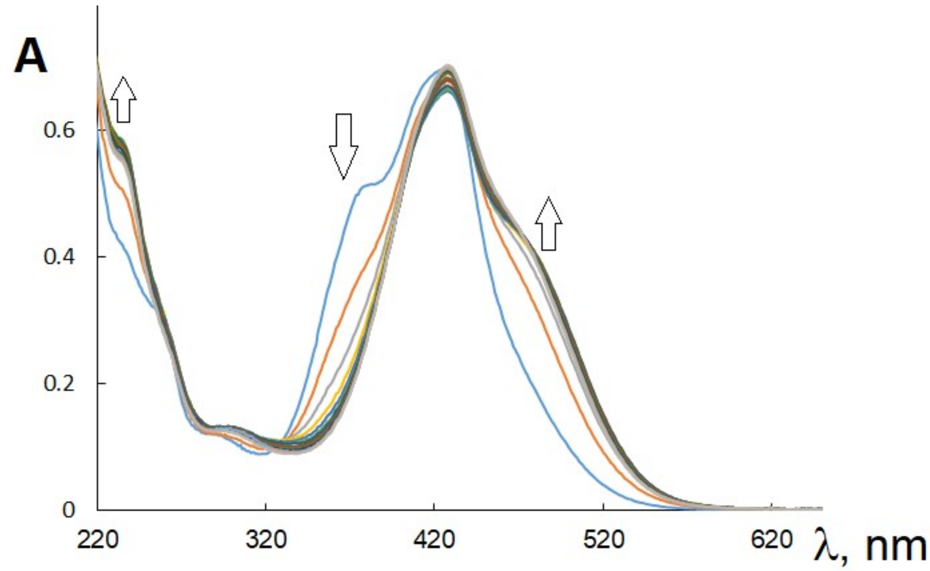


Fig 12S. Changes in electronic absorption spectra of ethanol solutions of H_3L^1 at stepwise addition of the solution $NiCl_2$

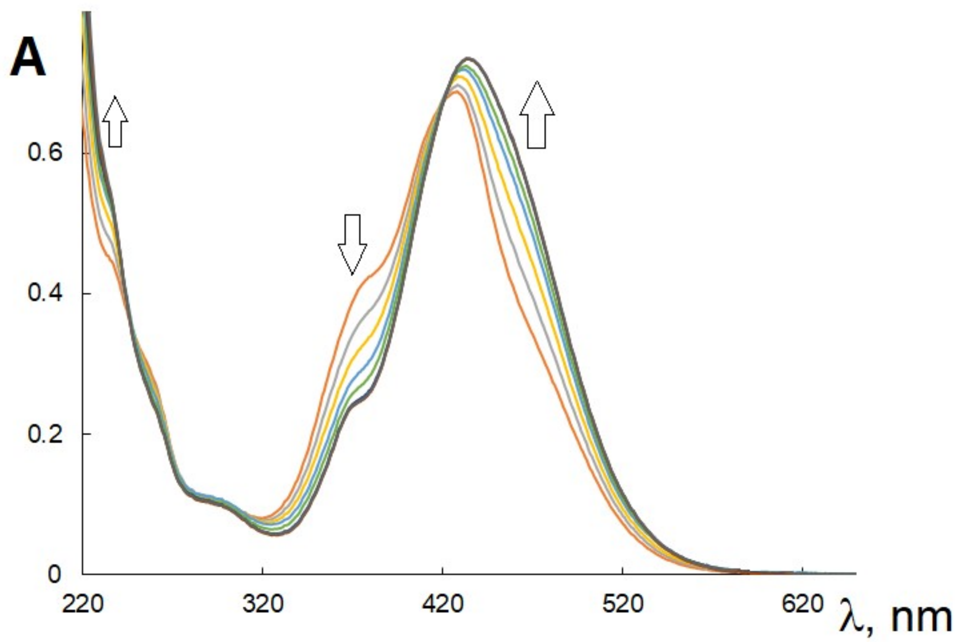


Fig 13S. Changes in electronic absorption spectra of ethanol solutions of H_3L^1 at stepwise addition of the solution $ZnCl_2$

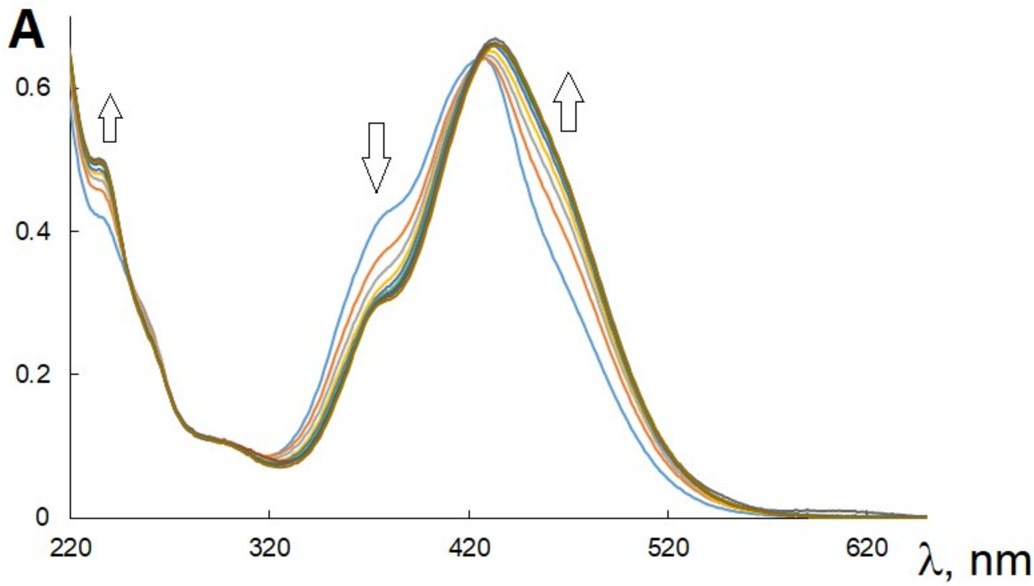


Fig 14S. Changes in electronic absorption spectra of ethanol solutions of H_3L^1 at stepwise addition of the solution $CdCl_2$

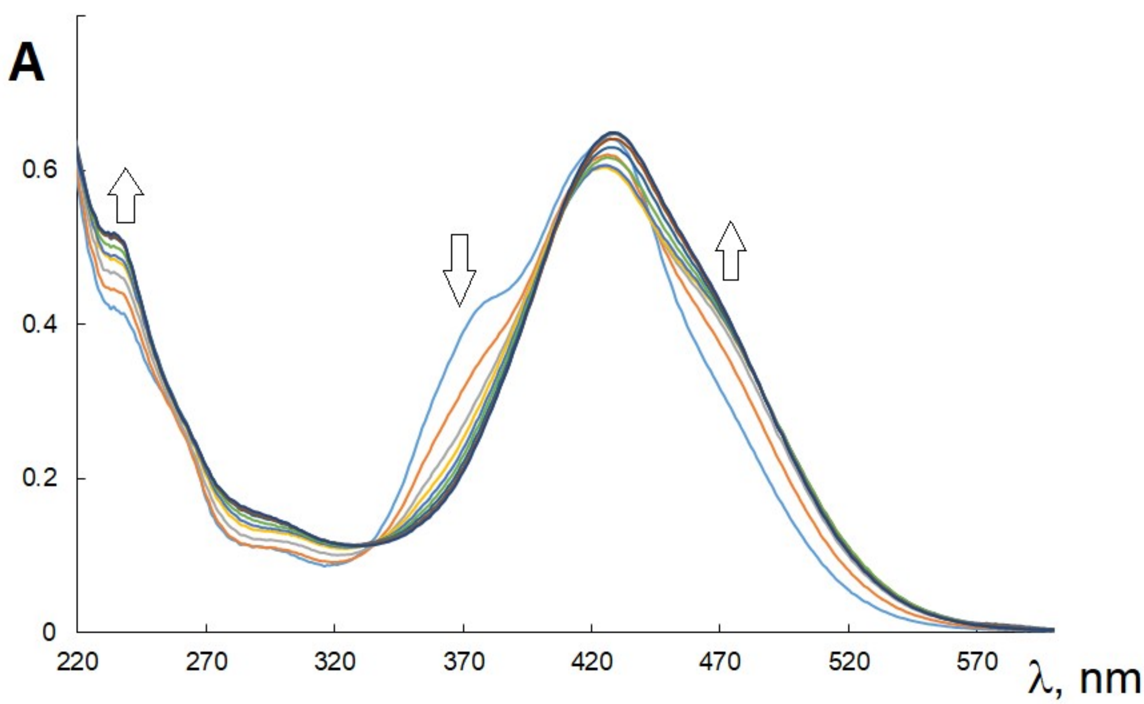


Fig 15S. Changes in electronic absorption spectra of ethanol solutions of H_3L^1 at stepwise addition of the solution $CoCl_2$

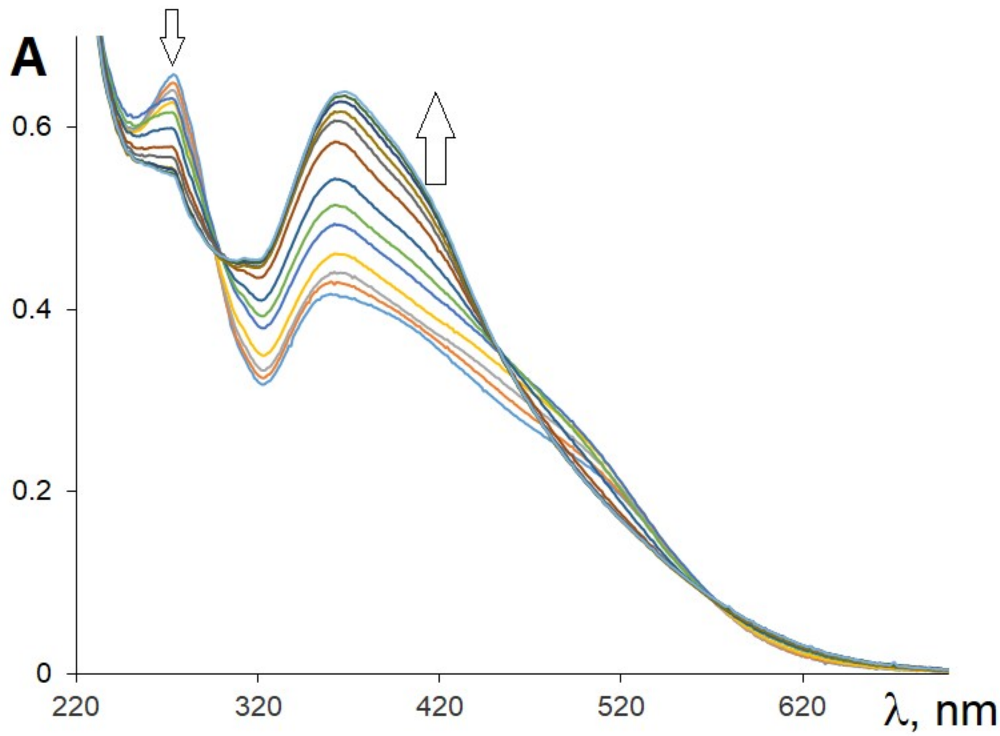


Fig 16S. Changes in electronic absorption spectra of ethanol solutions of H_3L^2 at stepwise addition of the solution $NiCl_2$

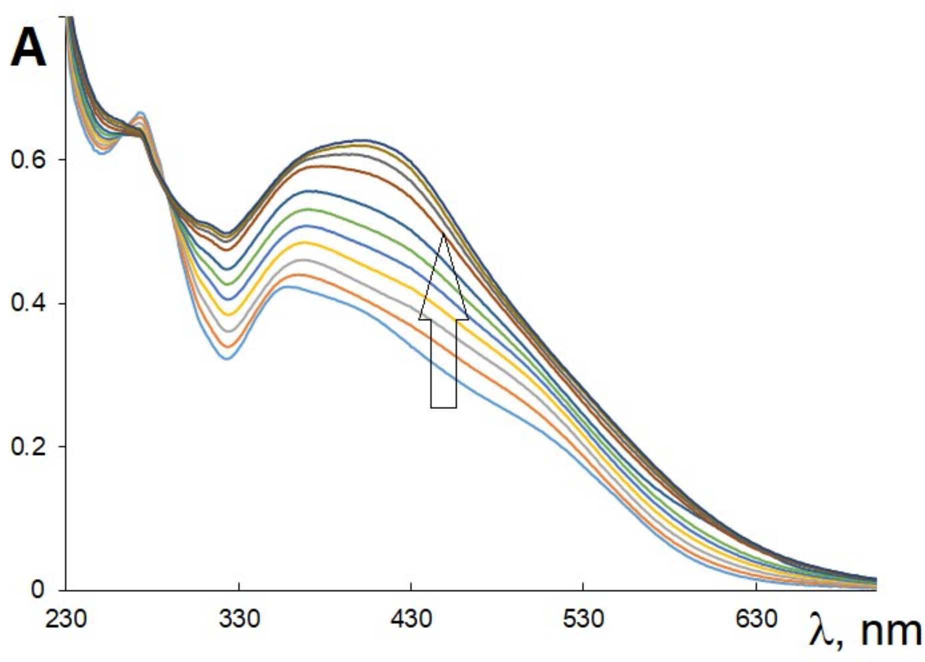


Fig 17S. Changes in electronic absorption spectra of ethanol solutions of H_3L^2 at stepwise addition of the solution $CoCl_2$

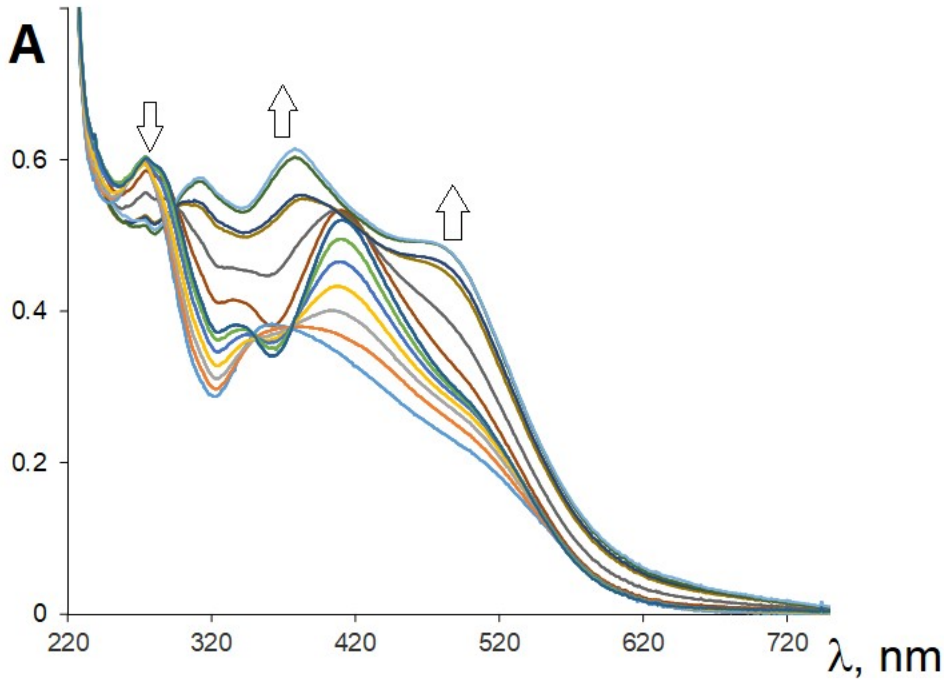


Fig 18S. Changes in electronic absorption spectra of ethanol solutions of H_3L^2 at stepwise addition of the solution $CuCl_2$

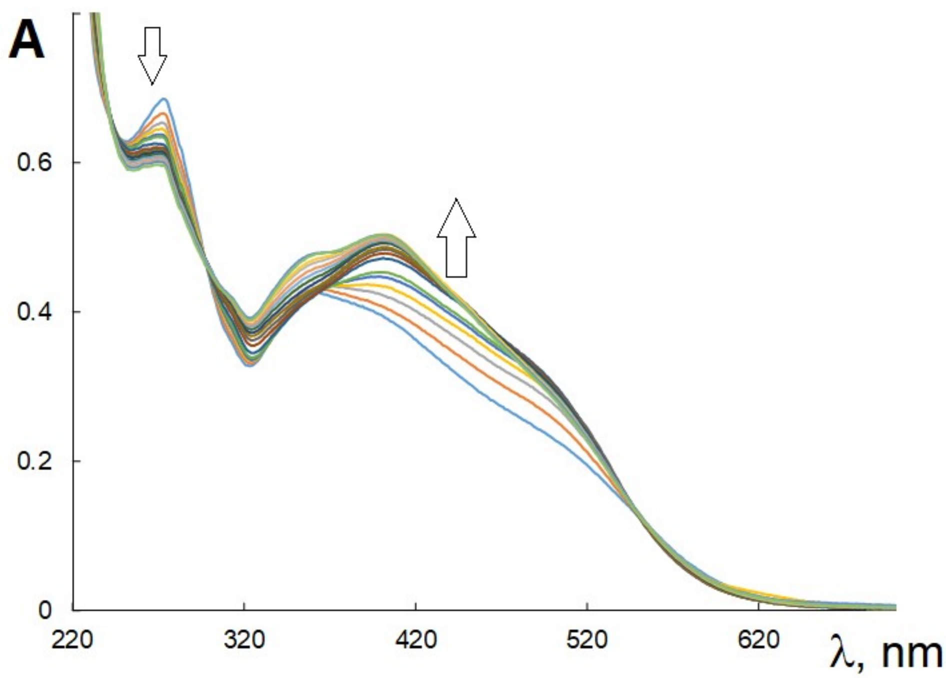


Fig 19S. Changes in electronic absorption spectra of ethanol solutions of H_3L^2 at stepwise addition of the solution $ZnCl_2$

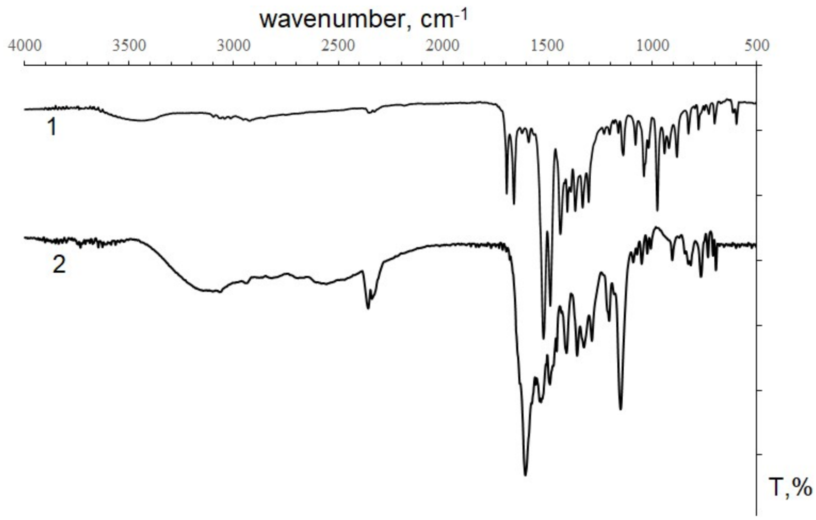


Fig 20S. IR spectra of H_3L^1(2) and H_3L^2 (1)

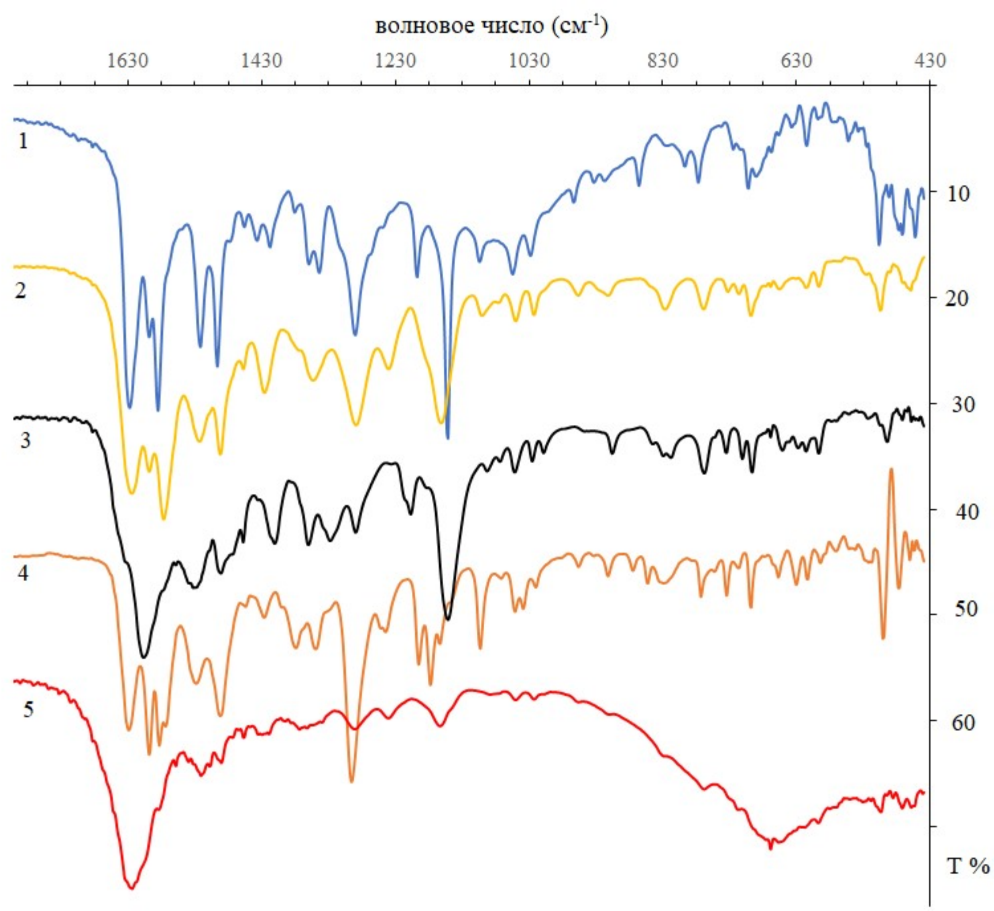


Fig 21S. IR spectra in the range 430 - 1800 cm1 of metal complexes: 1 - $Cu(H_2L^1)Cl$ (3); 2 - $Zn(H_2L^1)Cl.2H_2O$ (4); 3 – $Cd_2Cl_4(H_3L^1)_2$ (5); 4 - $Co(H_3L^1)Cl_2.3H_2O$ (1); $Ni(H_2L^1)Cl$ (2)

The determination of the dissociation constants of three ligands was archived by pH metric titration in aqueous solution. The ionic strength was controlled constant at 0.1 M by adding a calculated amount of KCl, and the Schwarzenbach algebraic method was used.

$$K_1 = \frac{[H^+]\{ac_{Ligan} + [H^+] - [OH^-]\}}{(1-\alpha)c_{Ligan} - [H^+] + [OH^-]};\qquad K_2 = \frac{[H^+]\{(a-1)c_{Ligan} + [H^+] - [OH^-]\}}{(2-a)c_{Ligan} - [H^+] + [OH^-]},$$

$$K_3 = \frac{[H^+]\{(a-2)c_{Ligan} + [H^+] - [OH^-]\}}{(3-a)c_{Ligan} - [H^+] + [OH^-]}$$

where c_{Ligan} is the total concentration of H_3L^i (i=1,2) and *a* is the neutralization point.

We titrated 25 mL 4.22×10^{-4} M solution of ligands (H_3L^1 and H_3L^2) with 5.15×10^{-3} M solution of NaOH (figure 20S).

For example: After addition of 0.35 mL $5.15\cdot10^{-3}$ M solution of NaOH to 25 mL $4.22\cdot10^{-4}$ M solution of H_3L^2, we observed that pH 4.04. So $[H^+]=9.12\cdot10^{-5}$; $[OH^-]=1.10\cdot10^{-10}$ M, and neutralization point: $a = \frac{0.35 \times 5.14 \times 10^{-3}}{25 \times 4.22 \times 10^{-4}} = 0.17$.

$$K_1 = \frac{[H^+]\left\{ac_{H_2L} + [H^+] - [OH^-]\right\}}{(1-\alpha)c_{H_2L} - [H^+] + [OH^-]} = \frac{[9.12\cdot10^{-5}]\{0.17\cdot4.22\cdot10^{-4} + 9.12\cdot10^{-5}}{(1-0.17)4.22\cdot10^{-4} - 9.12\cdot10^{-5} + 1.1} = 5.76\cdot10^{-5}$$

(See table 1)

Table 1. Calculation of the dissociation constants of H_3L^2 at 298K.

V_{NaOH}, mL	*a*	pH	$[H^+]$, M	$[OH^-]$, M	K_a, M	p*K*
0.35	0.17	4.04	9.12*10^{-5}	1.10*10^{-10}	5.76 10^{-5}	4.24
0.77	0.38	4.23	5.89 10^{-5}	1.69 10^{-10}	6.27 10^{-5}	4.20
1.01	0.49	4.37	4.27 10^{-5}	2.34 10^{-10}	6.25 10^{-5}	4.21

1.53	0.75	4.77	$1.69\ 10^{-5}$	$5.89\ 10^{-10}$	$6.29\ 10^{-5}$	4.21
1.82	0.89	5.19	$6.46\ 10^{-6}$	$1.55\ 10^{-10}$	$6.10\ 10^{-5}$	4.21
pK_1=4.21±0.03						
2.38	1.16	5.85	$1.41\ 10^{-6}$	$7.08\ 10^{-9}$	$2.81\ 10^{-7}$	6.55
2.62	1.28	6.15	$7.08\ 10^{-7}$	$1.41\ 10^{-8}$	$2.77\ 10^{-7}$	6.56
3.01	1.47	6.53	$2.95\ 10^{-7}$	$3.39\ 10^{-8}$	$2.63\ 10^{-7}$	6.58
3.65	1.78	7.10	$7.94\ 10^{-8}$	$1.26\ 10^{-7}$	$2.86\ 10^{-7}$	6.54
3.80	1.85	7.25	$5.62\ 10^{-8}$	$1.78\ 10^{-7}$	$3.33\ 10^{-7}$	6.48
pK_2=6.54±0.06						
5.02	2.45	9.13	$7.41\ 10^{-10}$	$1.73\ 10^{-5}$	$5.37\ 10^{-10}$	9.27
5.26	2.67	9.49	$3.23\ 10^{-10}$	$3.09\ 10^{-5}$	$3.18\ 10^{-10}$	9.49
5.50	2.69	9.76	$1.73\ 10^{-10}$	$5.75\ 10^{-5}$	$2.13\ 10^{-10}$	9.66
5.78	2.82	9.97	$1.07\ 10^{-10}$	$9.33\ 10^{-5}$	$1.62\ 10^{-10}$	9.79
pK_2=9.55±0.28						

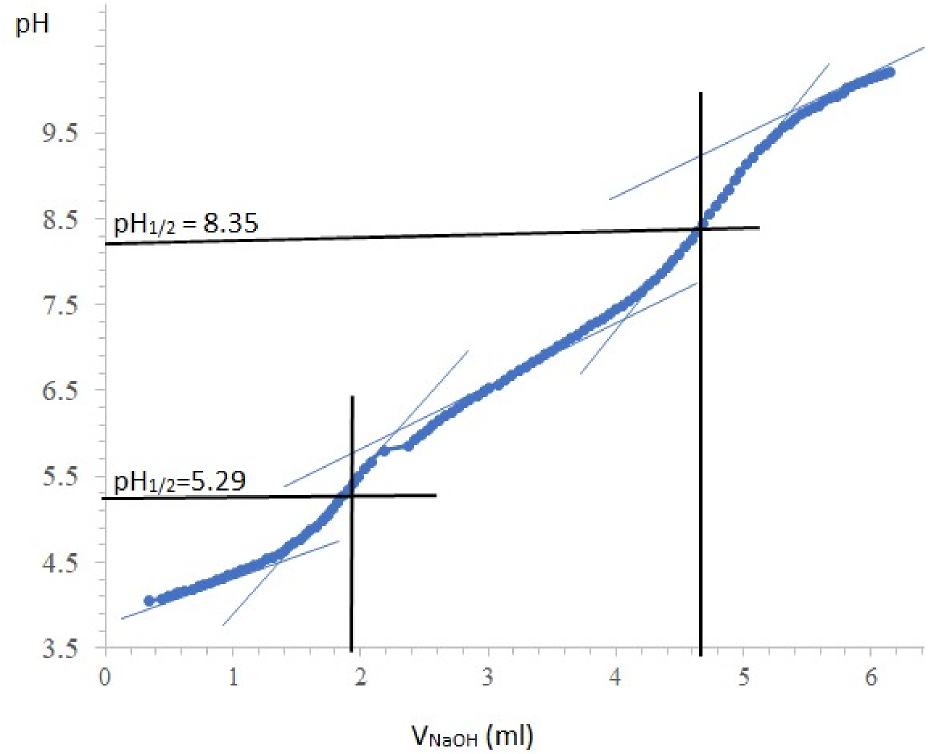


Fig 20S. Potentiometric titration curve H_3L^2 solution with NaOH 5.15×10^{-3} M at 298K

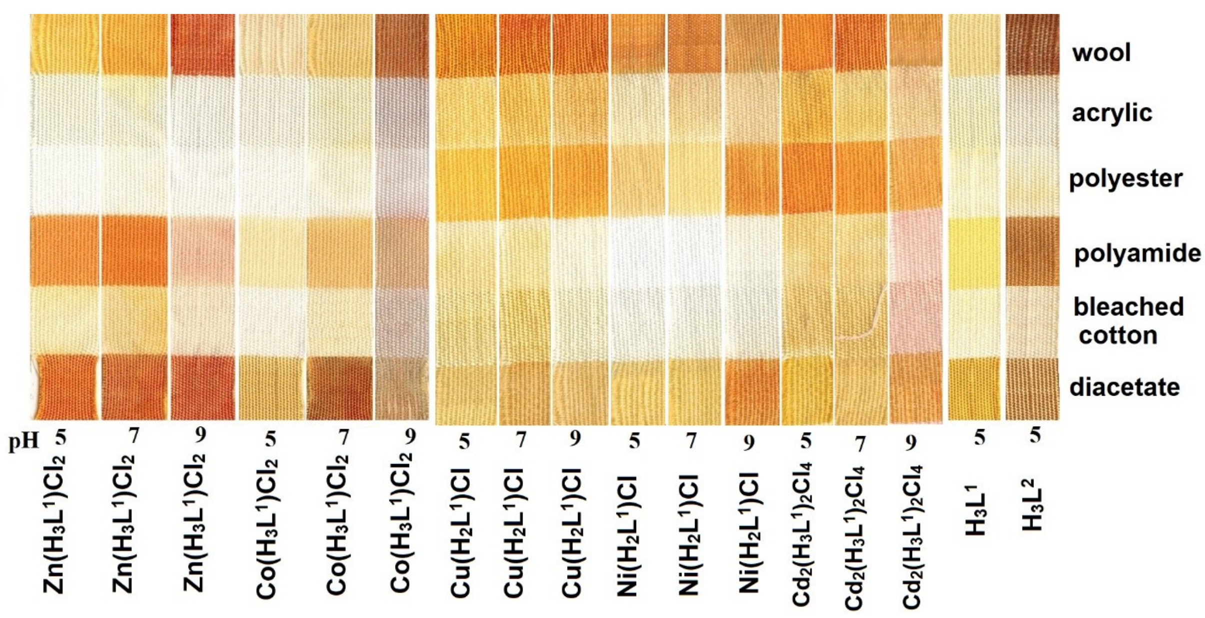


Fig 21S. Coloristic test of H_3L^1, H_3L^2 and their complexes