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Synthesis and characterization of novel pigments derived from Lithol Rubine

W. M. A. Abdelmaksoud [(1)*], M. M. M. Abdaly [(2)], Said M. Teleb [(3)] , A. M. El-Din [(4)] , and Mostafa A. Sayed [(5)*]

[(1)] *Paint and Chemicals Industries (Pachin) Co., Cairo, Egypt*
[(2)] *Chem. Dept., Faculty of Science, Ain Shames Univ., Cairo, Egypt*
[(3)] *Chem. Dept., Faculty of Science, Zagazig Univ., Zagazig, Egypt*
[(4)] *Paint and Chemicals Industries (Pachin) Co., Cairo, Egypt*
[(5)] *Chem. Dept., Faculty of Science, Ain Shames Univ., Cairo, Egypt*

Abstract

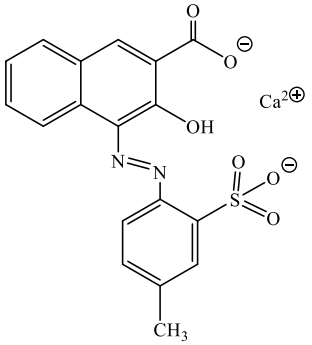
This article was designed to synthesize new pigments derived from Lithol Rubine (LR) important in inks industry and to investigate their physical properties. Several pigments, used as special inks for printing and essential in inks industry, were successfully prepared via the reaction of Lithol Rubine (LR) with salts of Cu (II) and Zn (II) ions in ethanolic solutions. The obtained pigments were isolated as solid compounds and characterized through elemental analysis, UV-Vis, FT- IR, ^{1}HNMR spectra, specific gravity, melting point, molar conductivity and magnetic moments measurements. Their physical properties related to dyeing were investigated using "American Standard Testing Methods (ASTM)" and the pigments were then applied to ink formulations. The results of this study showed that the output of newly prepared pigments is comparable to currently used commercial pigments. Lithol Rubine currently used, and the new pigments can be vital in other different industries such as coated papers, crayons, rubber, Paints, ink, and baking enamels. The prepared pigments would be a cost-effective and good substitute for the original commercially available and costly pigments used in the inks industry.

Keywords: Lithol Rubine, Pigments, Printing inks, Spectroscopic analysis

1. Introduction

Inks play a significant role in our current life and find several uses in the field of printing books, calendars, photocopies, and computer prints. Generally, an organic or inorganic pigment or dye that has been dissolved or suspended in a solvent is known as ink. Chemically, however, it is regarded as a colloidal system of fine pigment particles, colored or uncolored, dispersed in an aqueous or organic solvent in the presence of resin and additives **(Gajadhur M., 2017, Kunjappu J.T., 2001, Michel B., 2001, Othmer K., 1981)**. Pigments are the principal constituent of ink and contribute about 50% of its cost. A pigment is essentially any colored insoluble fluorescent solid due to light scattering. They can also provide gloss and resistance to attack by environmental factors. Special pigments known as transparent extenders and white opaque pigments are also used. The mainly ordinary pigments used in the of printing ink make up are red pigments **(Buxbaum G., 2005, Rapp G., 2009 Gawish S.M., Mashaly H.M., Mosleh S. and Helmy H.M. 2019).**

Many of the red pigments used in inks industry fall into the chemical category of azo pigments because the azo chromophore —N=N— is a feature of the molecule as Red Lake C and Lithol Rubine.



(E)-3-hydroxy-4-((4-methyl-2-sulfonatophenyl)diazenyl)-2-naphthoate

*Corresponding author e-mail: chem.wael@gmail.com.; (W. M. A. Abdelmaksoud).
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Structure (I): Lithol Rubin (LR)

Lithol Rubine (LR) as shown in structure (I) is a type of pigment that widely used in printing inks. It has been used broadly in letterpress and offset inks and in gravure inks. It is bright red with high tint strength and good dispersion characteristics **(Belai N., 2012, Marmion D.M., 1991, Tracton A.A., 2006, Nagla S. El-Shemy , Nancy S. El-Hawary , Karima Haggag, and Hosam ElSayed 2020).**

In the present work, new pigments were prepared by reaction of Lithol Rubine with Cu (II) and Zn (II) ions. These solid pigments were identified through elemental analysis, vibrational, electronic and ^{1}HNMR spectra together with their melting points, molar conductivity, and magnetic moment properties. Physical properties of the obtained pigments were investigated using American Standard Test Methods (ASTM).

Experimental

Materials

All chemicals used were of commercially analytical reagent grade, obtainable from different sources and used without additional purification. Lithol Rubine (LR) is a red powder of high purity was procured from UK SEUNG CHEMICAL Co. chemical reagents grade. Cu $(COOCH_3)_2.2H_2O$ was obtained from ADWIC; Egypt and $ZnCl_2$ were obtained from Sigma Aldrich, USA.

Synthesis

Two new pigments with a general chemical formula $[MC_{18}H_{12}N_2O_6.2H_2O]$, (LR – M) where M = Cu(II) or Zn(II) were synthesized by addition the appropriate metal salt (copper acetate, or zinc chloride), ethanolic solution, (25 mL, 10 mmol) to a hot ethanolic solution of the Lithol Rubine, (25 mL 10 mmol). The equimolecular mixture was refluxed for 6h to ensure complete formation. The precipitated solid was filtered, washed several times with ethanol (5 × ½ mL), and finally dried under vacuum over P_2O_5. The purity of the synthesized complexes was checked by measuring their melting point.

Analyses *(Calculated values are shown in parenthesis)*

LR, $[Ca(C_{18}H_{16}N_2O_8S)].2H_2O$, ($C_{18}H_{16}CaN_2O_8S$, 460.4); C, 50.28, (46.9); H, 3.02 ,(3.47); N,7.24 (6.08); S, 7.62, (7.90); Ca, 9.02 (8.69); ^{1}H NMR, δ values (ppm): 7.143 - 8.4 (aromatic protons), 2.31 (CH_3), 3.3 (H_2O) and 8.6 (N – H ---- O).

$[Cu(C_{18}H_{16}N_2O_8S)].2H_2O$, (LR – Cu), ($C_{18}H_{16}CuN_2O_8S$, 483.94); C, 43.92, (44.67); H, 2.67, (3.33); N, 6.13, (5.79); S, 6.98, (6.62); Cu, 12.98 (13.13), paramagnetic.

$[Zn (C_{18}H_{16}N_2O_8S)].2H_2O$, (LR – Zn), ($C_{18}H_{16}ZnN_2O_8S$ – 485.77); C,45.16, (44.51); H,2.57, (3.32); N, 6.11, (5.77); S, 6.34, (6.60); Zn, 13.27 (13.46); ^{1}H NMR, δ values (ppm): 7.143 - 8.4 (aromatic protons), 3.3 (H_2O) and 2.3 (CH_3), 8.6 (N – H ---- O), diamagnetic.

Pigment evaluation

The prepared complex pigments were investigated according to American Standard Test Methods for specific gravity (ASTM D 5,965-96, 2007), oil absorption (ASTM D 281-95, 2007), density (ASTM D 1475-13), (ASTM D387-00, 2017) and melting point (ASTM D87- 09,2014).

Instrumentation

Elemental analyses (CHN) were performed on a Perkin Elmer - 2400 mass spectrometer. Metal contents were determined gravimetrically as $CaSO_4$ for Ca and by EDTA titrations for Ca, Cu and Zn (Pella, 1984). or by atomic absorption method using a spectrometer model PYE-UNICAM SP 1900 fitted with the corresponding lamp.

The IR spectra were carried out on a Unicam-Mattson 1000 FT-IR as KBr pellets in the range (4000-400 cm^{-1}).

Electronic spectra were measured in DMSO solvent with a concentration (1.0×10^{-4} M) for Lithol Rubine and complexes using Shimadzu UV-Vis 1800, Spectrophotometer in the range of 800-200 nm.

^{1}HNMR spectra were performed on a Spectrospin-Bruker AC 300MHz spectrometer using DMSO-d_6 as a solvent and TMS as an internal reference. Chemical shifts are given in δ values and were related to that of the solvents.

Molar conductivities of $1x10^{-3}$M DMSO complexes were measured by using Jenway 4010 conductivity meter.

Magnetic moments were determined on a Sherwood Scientific magnetic moment balance (Model No.: MK1) at room temperature (25 ^oC) using $Hg[Co(SCN)_4]$ as a calibrant. The solid sample is firmly crowded into a weighed sample tube with a suitable length (l) and noted the sample weight (m). Then the packed sample tube was placed into tube lead of the balance and the reading (R) was noted. The mass susceptibility, χ_g, is calculated using the following equation:

$\chi_g = C_{Bal} * l * (R- R_0)/10^9 * m$, where; l = the sample length (cm).m = the sample mass (g).R = the reading for the tube plus sample. R_0 = the empty tube reading. C_{Bal} = the balance calibration constant = 2.082. Then molar susceptibility $\chi_m = \chi_g *$ molecular formula of the complex. The molar susceptibility is corrected with diamagnetic contribution. The effective magnetic moment μ_{eff} is then calculated using the following equation: $\mu_{eff} = 2.83 * (T * X_A)^{1/2}$, Where: X_A = the corrected molar susceptibility.

Results and discussion

Characterization of synthesized pigments

The molar conductivity measurements of Lithol Rubine pigment suggest its covalent character. Table (1) shows the non-electrolytic pigment character.

Table (1): Physical properties of Lithol Rubine 4B and new pigment complexes

Compound	Color	Specific Gravity	Oil Absorption (g/100g)	Density (gm/cm$^{3)}$	Melting point(°C)	Molar. Conductivity Λ_m ($\mu s.cm^2.mol^{-1}$)
LR	Red	1.902	49	1.82	364	0
LR-Cu	Worm red	1.84	57	1.31	382	0
LR-Zn	Magenta red	1.794	59	1.37	375	0

The infrared spectra of lithol rubine pigment Figure (1) provide a further verification support for the covalent bonding of calcium ion with COO^- and SO_3^- groups. The carboxylate group exhibits several modes for binding metal ions **(Nakamoto, K., 1997)**. For the monodentate mode of carboxylate group the antisymmetric stretch ν_{as}(COO) will increase and the symmetric stretch ν_S(COO) will decrease as the metal – oxygen bond become stronger (more covalent character) in the complexes. The ν_{as}(COO) motion of the carboxylate group in the spectrum of LR pigment is observed at 1623 cm^{-1} as a strong band while, the symmetric motion, ν_S(COO) is assigned at 1405 cm^{-1} which is the typical behavior for a monodentate carboxylate group **(Silambarasan S., 2013; Hadjikostas C.C., 1987; Franchini G.C.,1985; Jasim R.H., 2017).** Furthermore, the separation between the asymmetric and symmetric stretch of the carboxylate group in the pigment spectrum is given in Table (2) and is shown to be > 200 cm^{-1}, which is further indication for the monodentate nature of the carboxylate group in these complexes **(Nakamoto, K., 1997).** The sulfonyl, gives two absorption bands at 1290 cm^{-1} and 1157 cm^{-1}, corresponding to the asymmetric and symmetric stretching motion of S=O bond. The appearances of these two bands at these frequencies indicate oxygen bonded monodentate sulphonyl group. The absorption band at 2923 cm^{-1} may be attributed due to intramolecular hydrogen bonding of the type N–H---O **(Guzler H., Germlich H., 2002; Nakamoto, K., 1997).**

Table (2): Characteristic Infrared Frequencies* (cm^{-1})

LR	LR-Cu	LR -Zn	Assignment
3441 br	3440 br	3430 br	ν(OH); H_2O
3248 w	3253 w	3273 w	ν(NH)
3069 w	3073 W	3064 w	ν(C–H); aromatic
3047 w	3058 W	3028 w	N–H-H, intramolecular
2923w	2923 w	2920 w	hydrogen bonding
1653 sh	1649 sh	1656 s	ν(C=O), ring
1623 m	1619 m	1620 m	ν_{as} (COO)
1600 sh	1602 sh	1604 m	δ(H_2O
1483 m	1438 m	1438 m	ν(C = N)
1450 m	1451 m	1450 ms	ν(N = N)
1405 s	1405 s	1405 s	ν_s(COO)
11290 m	1291 ms	1299 ms	ν_{as}(S = O)
1157 s	1159 s	1156 s	ν_s(S = O)

*w: Weak, m: Medium, s: Strong, br: Broad and sh: shoulder

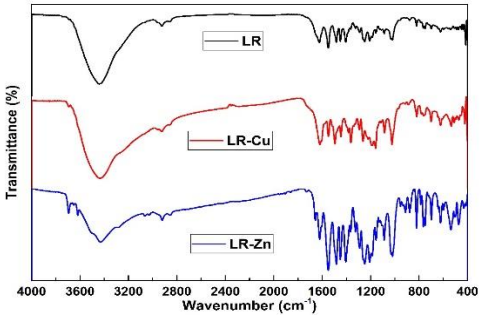


Fig. (1) FTIR spectra of LR, LR-Cu, and LR -Zn pigments

The electronic spectra of the pigment LR and its complexes LR – Cu and LR – Zn given in Figure (2) show analogous absorption patterns suggesting analogous composition for the three compounds. Absorption bands in the region 200 – 400 nm may be due to the electronic transition $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ **(Gajadhur M., 2017; Kunjappu J.T., 2001; Michel B., 2001; Othmer K., 1981, Tanaka D., 2017),** whereas the very intense absorption in the region 500 – 600 nm may be attributed due to charge-transfer transitions **(Housecroft K., 2008; Brisdon A., 1998; Huheey A., 1993; Drago M., 1992; Miessler H., 2004; Paris J. P., 1959).**

^{1}H NMR spectrum of the LR pigment and LR – Zn showed in Figures (3, 4) that present additional evidence about the structure of the pigment. The spectrum lakes any signal may be attributed due to -OH proton but instead a singlet at 8.6 ppm, attributed to a proton engaged in intramolecular hydrogen bonding, N–H---O (**Mohammed I. A. and Mustapha A., 2010).** This suggests that pigment undergoes a structural enol – keto form isomerism and the keto form is more stable. The spectrum reveals a singlet at 3.3 ppm attributed to the protons of two coordinated water molecules as well.

The molar conductivity measurements revealed a non-electrolytic nature for the two compounds LR – Cu and LR – Zn. Furthermore, their infrared, electronic and ^{1}H NMR spectral pattern almost the same as the pigment LR shows. Therefore, we suggest that the pigment LR and its Cu and Zn derivative have approximated the same structure and the reaction of pigment with metal salt involve only the displacement of calcium by cupper or zinc, according to the following reaction:

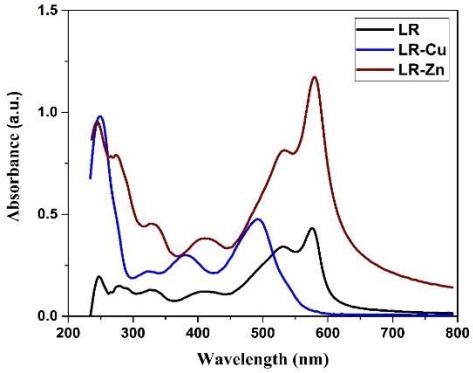


Fig. (2) UV-Vis's spectra of LR, LR-Cu, and LR-Zn pigments

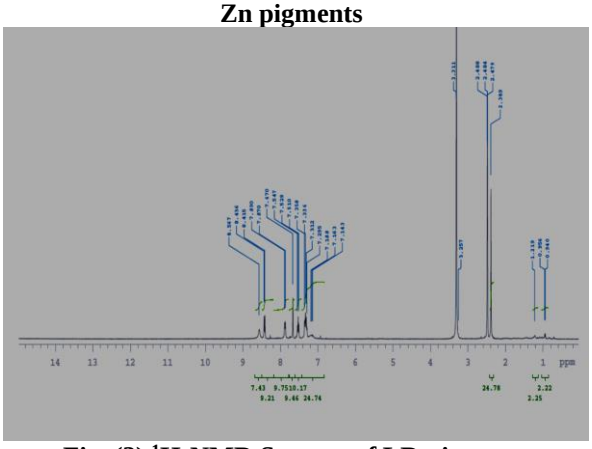


Fig. (3) ^{1}H-NMR Spectra of LR pigment

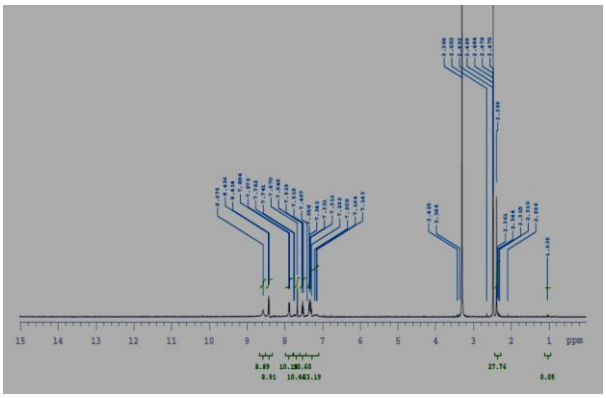
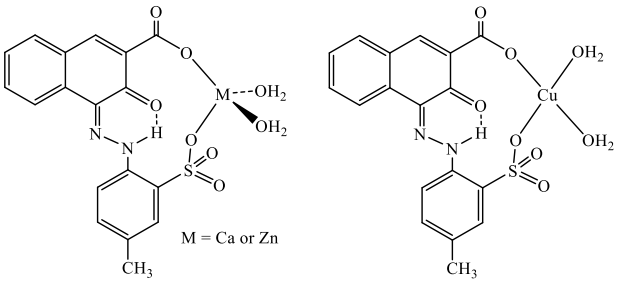


Fig. (4) ^{1}H-NMR Spectra of LR-Zn pigment

$$[Ca\ (C_{18}H_{16}N_2O_8S)].\ 2H_2O + MX_2 \xrightarrow[\text{ethanol}]{\text{reflux (6h)}} [M(C_{18}H_{16}N_2O_8S)].\ 2H_2O + CaX_2$$

(Where M = Cu or Zn and X = Cl or CH_3COO^-).

The most probable structure associated with LR and LR – Zn compounds is tetrahedral as expected according to their electronic structures d^0 and d^{10} for Ca and Zn, respectively. LR – Cu compound shows a square planar geometry in consistent with d^9 electronic structure, as shown in scheme (I).



Scheme (I) Physical studies of the new prepared pigments

The pigment characteristics are measured according to ASTM and are given in Table (1), several observations emerge from the obtained;

- Specific gravity and density of the prepared pigments is very near to those of Lithol Rubine and approximately the same.
- The oil absorption of the prepared pigments is somewhat higher than of Lithol Rubine. In general, as it is well known that the oil absorption is an indication of the binder that pigment can be consumed when applied in formulations.
- The melting point of pigments containing Zn is the highest.
- The color of the prepared pigments showed in Figure (5). The Figure indicates that the color changed on going from free LR to its complexes. Changing in colors is a further support on the formation of the new pigments and these pigments can be used in ink industry.

Application of the new prepared pigments in printing ink

The new pigments (LR-Cu and LR-Zn) were formulated with Nitro-cellulose Ink as Nitro-cellulose a binder and ethanol as solvent as shown in Table (3). These printing inks have been applied on polypropylene substrate at room temperature (25°C). Their competence was compared to the commercial printing inks which already exist in Pachin Company as the new printing inks containing the new pigments (LR-Cu and LR -Zn) compared to (GF 22-601/2 and GF 22-603/2), respectively **(Elshemy N. S., Haggage K., El-Sayed H. 2022)**. Figure (6) shows the results of the new printing inks containing the new pigments (LR-Cu and LR -Zn). These two prepared inks were stable at the room temperature lacking any change or decomposition. The visual inspection of the printing ink containing (LR-Cu) showed that its color was like to the color of the commercial ink (GF 22-601/2), and the inspection of the printing ink containing (LR -Zn) indicated that it has a stronger color than the commercial ink (GF 22-603/2). These results are excellent and prove that the prepared pigments have high efficiency.

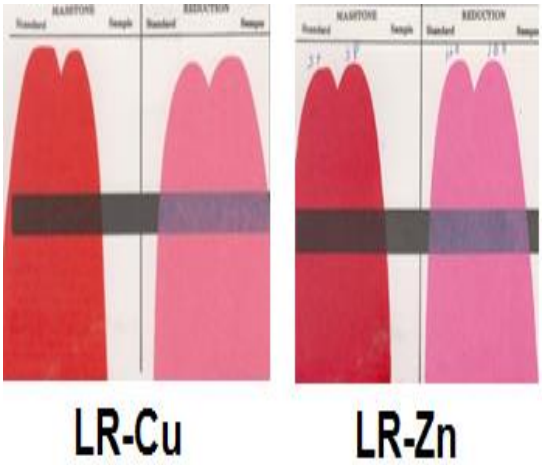


Fig. (5) The color test of the new prepared pigments

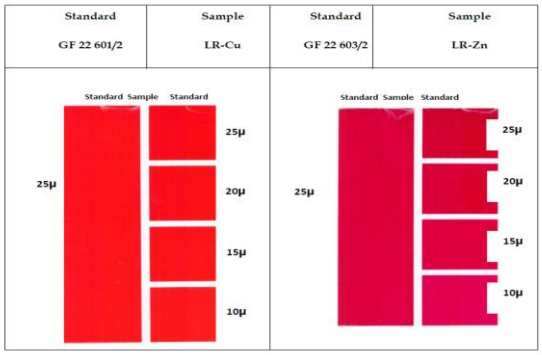


Fig. (6) The visual inspection of the prepared printing inks containing (LR-Cu and LR-Zn)

Beside the high efficiency of the prepared pigments (LR-Cu and (LR -Zn) in printing ink industry, they are economically practicable.

Conclusions

- New prepared pigments Cu (II) and Zn (II) complexes have been synthesized from the reactions of the corresponding metal salt with Lithol Rubine.
- Physical and spectroscopic properties of the new prepared pigments were studied to prove the formation of the new prepared pigments.
- Studying of spectroscopic properties of the new prepared pigments revealed that; the new pigments were prepared and confirmed their structure by using IR, H NMR, UV and mass spectroscopy.
- After the preparation of the pigments and studying their physical and spectroscopic properties, they were applied in printing ink formulations.
- The results of the visual inspection of the printing ink color test were satisfied and can be comparable with the commercial inks which already exist in Pachin Company.
- Finally, it can be concluded that the new prepared pigments have high efficiency and are economically feasible.

Table (3): Ink formulations of water ink according to Pachin Company

Row Material	**GF 22-601/2**		**GF 22-603/2**	
	standard	Sample	standard	Sample
LR-Cu	0	10	0	0
LR-Zn	0	0	0	9
NITRO CELLULOSE VARNISH	40	42	40	43
ETHANOL	12	12	12	12
METHOXY PROPANOL	2	2	2	2
DIOCTYL PHTHALATE	5	5	5	5
PIGMENT RED(59:1)	0	8	4	0
Pigment Red 57: 1 Lithol Rubine	12	0	8	0
NITRO CELLULOSE VARNISH	16	16	16	16
POLY ETHYLEN WAX SOLUTION.	1	1	1	1
ISO PROPYL ALCOHOL	7	7	7	7
ETHYL ACETATE	5	5	5	5
Total	100	100	100	100

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