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RESEARCH ARTICLE
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Synthesis, Characterization And Finger Print Application Of Zn(II) And Cobalt(II) Complexes With Schiff Base Ligands Derived From benzene-1,2-diamine

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ABSTRACT

Reaction of the o-phenene diamine with tert-butyl-salcyldehyde or p-dimethylaminobenzaldehyde to form Schiffbase 6,6'-(-(1,2-phenylenebis(azaneylylidene))bis(methaneylylidene))bis(2,4-di-tert-butylphenol)(L1) and 4,4'-(1,2-phenylenebis(azaneylylidene))bis(methaneylylidene))bis(N,N-dimethylaniline) (L2) . L1 was react with one mole of Zinc acetate to form ZnL1(1) while L2 react with one mole of zinc acetate or cobalt chloride afforded {ZnL2(CH3COO)2}(2) and {ZnL2Cl2}(3). These complexes employed as colorant for finger print application the medium activity were achieved.

Keywords: *o-phenene, Schiffbase, Zinc acetate and cobalt chloride*

INTRODUCTION

One area of chemistry that is receiving growing attention from researchers worldwide is the schiff base compounds and their complexes. Hugu Schiff created primary amines for the first time in 1864[1], which are compounds that combine with aldehydes or ketones to produce condensation products[2-4].

Diamines schiff base and their metal complexes noticed is significantly increased attention[5, 6] owing to their metal-complexes biological activities such as antitumor[7], anticancer[8], antiviral ,and antimalarial activitie[9, 10]. Diamine coordinate with transition metals to form stable complexes due to they have contained multidonor NN features give the incidence of nitrogen atoms in their molecular backbone which shows high coordination usefulness.

Zinc complexes with cheap costs have recently been mentioned as potential new materials[11] for white organic light-emitting devices. In OLEDs, specific Zn(II) complexes of 2- (2-hydroxyphenyl)benzothiazolates ligands were employed as electron transporters, hosts, and materials that emit blue light also, used in other applications[12-14]. In terms of their device manufacturing, certain thermally activated high performance green Zn(II) complexes have also been described, and their great solubility in the majority of organic solvents is a key factor. Cobalt complexes also have catch more attention due to their applications in different fields[15, 16] for instant vitamin B12, which is a complex of triple-stranded cobalt octahedral Cobalt(III) is biologically important, As a catalyst for the oxidation of hydrozones in organic preparations[17], such as insecticides, cobalt and N,N-ethylenebis are combined to form salisaldimino[18]. Furthermore, numerous cobalt complexes have been investigated in combination with other pharmacological substances, including penicillin and ampicillin, as well as some amino acids[19].

EXPERIMENTAL

Materials

All reagents used in the present study were of the highest quality Analar grade , which includes both di-amine , 3,5-ditert-butylsalcyldehyde, 4-dimethylaminobenzaldehyde (Merck and Sigma chemicals). Methanol, ethanol and petroumether (Merck and Aldrich chemicals). $Zn(CH_3COO)_2$ acetate and $CoCl_2.6H_2O$ (Merck, BDH and Riedel company.

Preperation of the Schiff Base Ligand (L1)[20]

The ligand (L_1) was prepared by dissolving 3,5-di-tert-butylsalicylaldehyde (2.343 g, 0.01 mol) in a ethanolic solution and (0.540g, 0.005 mol) of benzen 1,2-diamine , 2-3 drops of glacial acetic acid were added to the mixture, the mixture was refluxed for 3 hours, then was cooled and the precipitate was filtered and dried it was recrystallized from absolute ethanol and then the precipitate was collected, giving a yield of (83 %), M.P(110-112). IR (Nujol mull, KBr): $\tilde{\nu}$ = 3550(s), 2460 (s), 2350 (s), 2240 (s), 1645 (s), 1480 (s), 1440 (s), 1320 (s), 1240 (m), 1196 (s), 1080 (s), 1040 (s), 760 (s), 640 (s), 540 (s) cm^{-1}.

Preperation of the Schiff Base complex (1)[21]

Dissolve (0.270 g, 0.0005 mol) of ligand (L_1) in 25 ml of methanol, to which (0.091 g, 0.0005 mol) of zinc acetate solution is added, the mixture was refluxed for (2h), then the mixture was cooled and the precipitate was collected, dried and recrystallized from absolute ethanol. IR (Nujol mull, KBr): $\tilde{\nu}$ = 3849 (s), 3833 (s), 3815 (s), 3798 (s), 3742 (s), 3707 (s), 3669 (s), 3058 (m), 2949 (s), 2864 (s), 2358 (s), 1609 (s), 1577 (s), 1522 (s), 1458 (s), 1433 (s), 1358 (s), 1253 (m), 1248 (s), 1196 (s), 1164 (s), 1024 (s), 927 (s), 872 (s), 828 (s), 805 (s), 745 (s), 640 (s), 512 (s)cm^{-1}. ^1H NMR (400 MHz, DMSO): δ = 9.034 (s, 1H, CH=N), 7.93-7.24 (m, 6 H, Ar-H), 1.64 (s, 18H, CH_3), 1.22 (s, 18H, CH_3C).

Preperation of the Schiff Base Ligand (L2)

The ligand (L_2) was prepared by fellow the literature by dissolving compound 1,2-cyclohexene diamine in an amount (1.08g, 0.01 mol) and (2.9g, 0.02 mol) of P-(dimethylamino)benzaldehyde in (25 ml) of absolute ethanol a (2-3) drops of glacial acetic acid were added to the mixture, the mixture was refluxed for a period of (3 h), the mixture was cooled to form yellow powder, filtered and dried, then was recrystallized from absolute ethanol, giving a yield of (83%). IR (Nujol mull, KBr): $\tilde{\nu}$=3448 (s), 3335(s), 2955 (s), 2910 (s), 2870 (s), 2835 (m), 1645 (m), 1627 (m), 1579 (m), 1841 (m), 1425 (s), 1329(m), 1257 (s), 1209 (s) 1168 (s), 1122 (s), 1050 (s), 1018 (s), 966 (s), 920 (s), 829 (s), 744 (s), 705 (s), 572 (m), 516 (s), 511 (s) cm^{-1}.

Preperation of the Schiff Base complex (2)

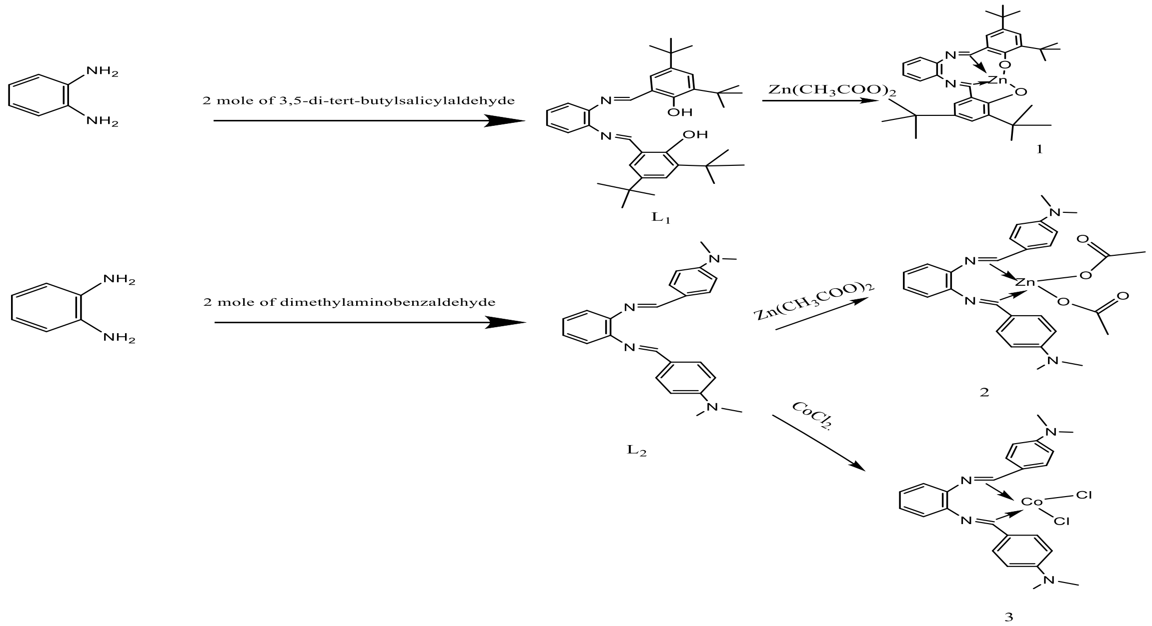
Dissolve (0.37 g, 0.001 mol) of ligand (L_2) in 25 ml of methanol in a (100 ml) round flask, to which (0.07 g, 0.001 mol) of zinc acetate solution is added. The mixture was refluxed for(2h), the mixture was cooled to form precepitate, which was dried and recrystallized from absolute ethanol. IR (Nujol mull, KBr): $\tilde{\nu}$ = 3850 (m), 3741 (s), 3672 (s), 3647 (s), 3616 (s), 2921 (m), 2360 (s), 2328 (s), 1737 (s), 1698 (s), 1532 (s), 1392 (s), 1311 (s), 1237 (s), 1199 (s), 1136 (s), 1030 (s), 878 (s), 824 (s), 781 (s), 745 (s), 669 (m), 622 (s), 460 (s)cm^{-1}.. ^1H NMR (400 MHz, DMSO): δ = 7.96 (s, 2H, CH=N), 7.46-6.89 (m, 6 H, Ar-H), 1.25 (s, 6H, CH_3), 0.83 (s, 6H, CH_3).

Preperation of the Schiff Base complex (3)

As in (L_1C_1) but using (0.36 g, 0.0004 mol) of ligand (L_1) to which (0.07 g, 0.0004 mol) of cobalt chloride. the mixture was refluxed for (2h), then was cooled, to form precipitate , which was dried and recrystallized from absolute ethanol.). IR (Nujol mull, KBr): $\tilde{\nu}$=3743 (m), 3448(s), 3335 (s), 3105 (s) 1627 (s), 1579 (m), 1506 (s), 1494 (s), 1423 (s), 1332 (s), 1261 (m), 1168 (m), 1122 (s), 1058 (s), 1012 (s), 918 (s), 831 (s), 748 (s), 704 (s), 630 (s), 572 (m), 513 (s), 416 (s) cm^{-1}. ^1H NMR (400 MHz, DMSO): δ = 9.18 (s, 1H, CH=N), 7.13-6.89 (m, 8 H, Ar-H), 1.62 (s, 6H, $(CH_3)_2N$), 1.25 (s, 6H, $(CH_3)_2N$).

RESULT AND DISSCUTION

Charactrization of the compounds



SCHEME 1: Ligands and their complexes in this study

The preparation of L_1 involving a mixture of 2 mole of 3,5-di-tert-butylsalicylaldehyde, one mole of benzene-1,2-diamine to form Schiff base(L_1). It was employed to prepare(3,5-di-tert-butylsalicylaldehyde)cyclohexyl-1,2-diamino zinc(II) (1) Scheme 1.

It is clear from the ^{1}HNMR spectrum of both complexes Figure 1 and Figure2 showed a singlet peak at δ = 9.03 ppm for to two protons of the azomethine group in CH=N. The proton for the aromatic ring also appear between (7.24 to 7.90 ppm) as multiple signals while the signals around 5 are attributed to the protons of hydroxyl group, a single signals peak is belong to the methyl group of tert-butyl proton as shown in the selected figure. 1 below.

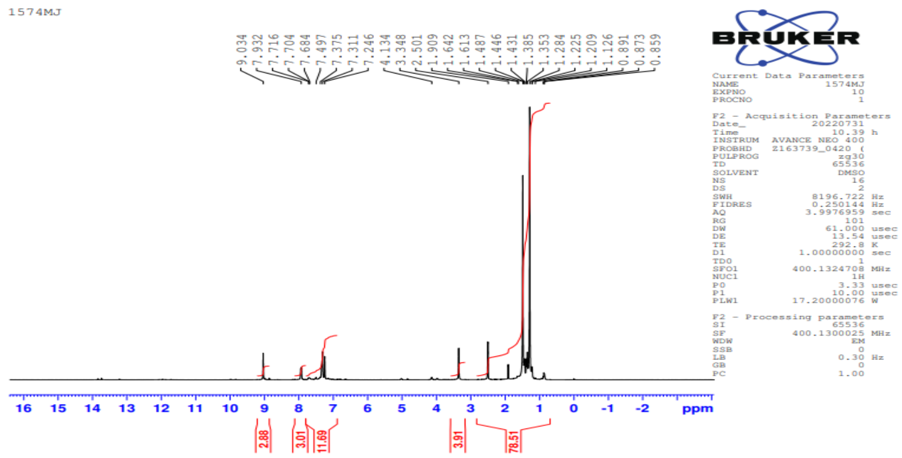


FIGURE 1: ^{1}HNMR of the complex(1)

Also (L_2) Schiff base was prepared by reacting 2mole of p-dimethylamino benzaldehyde and one mole of benzene 1,2-diamine, same for L_1 ligand $L_2$was used for the production of bis(p-dimethylamino benzaldehyd)benzene 1,2-diamino zinc(II) and cobalt azomethine complexes (2) and (3). The important peaks clear in the figures(2 and 3) below.

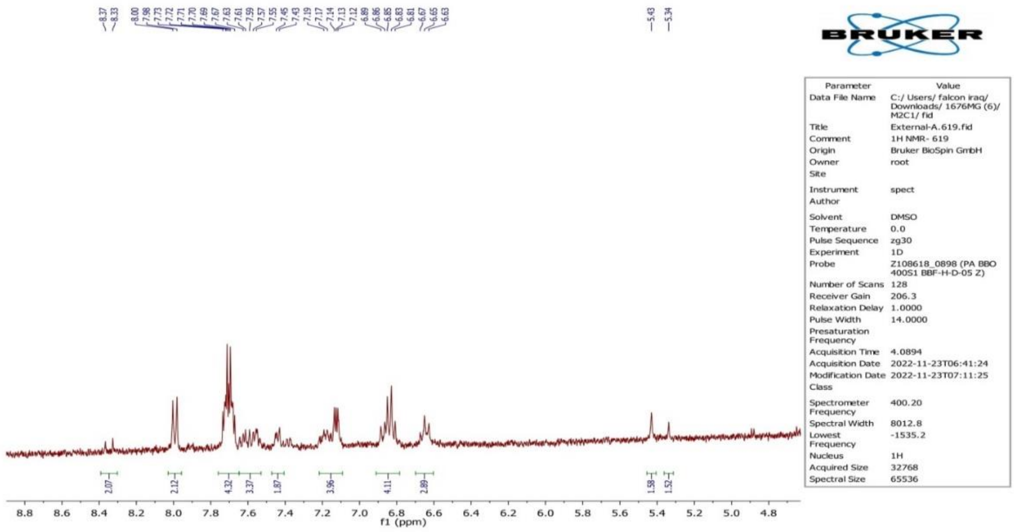


FIGURE 2: ^{1}HNMR of the complex(2)

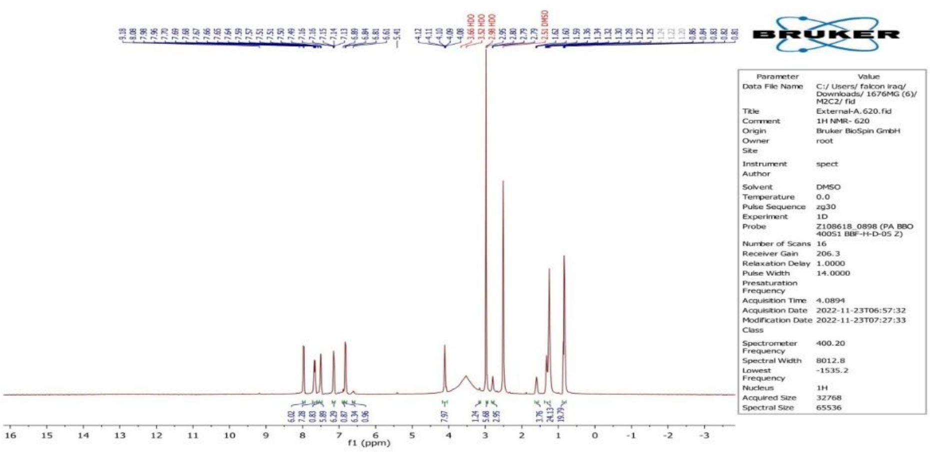


FIGURE 3: ^{1}HNMR of the complex (3)

The IR spectrum of the (1), (2) and (3) complexes show clear bands around 1616-1650 cm^{-1} for azomethine which is shifted to higher energy in the complexes as it clear in the figures.4, 5 and 6.

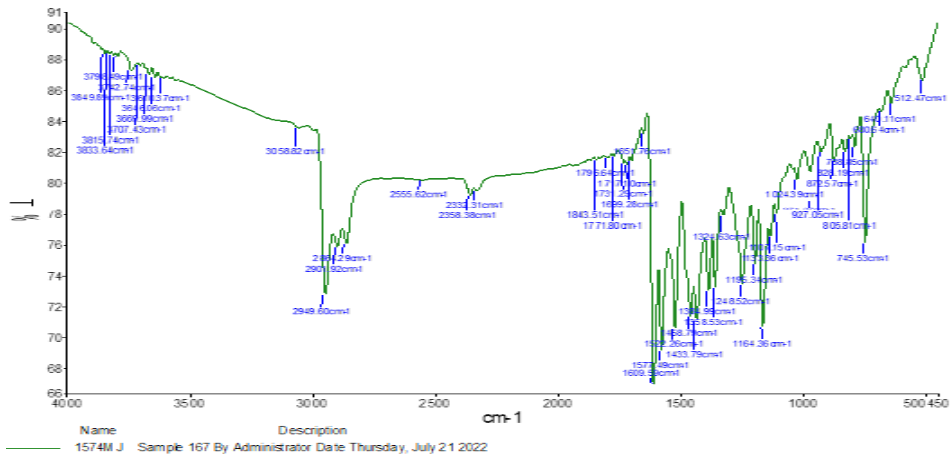


FIGURE 4: Infra-red spectrum of the complex(1).

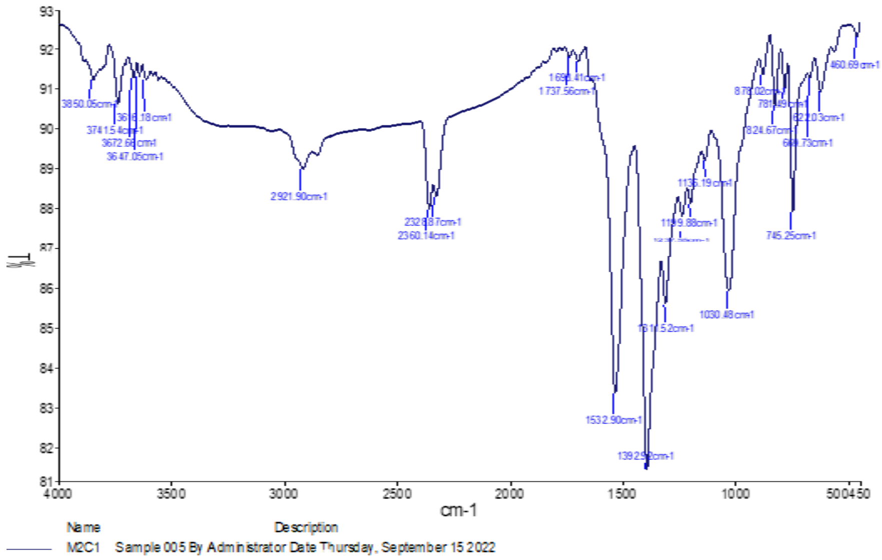


FIGURE 5: Infra-red spectrum of the (2)

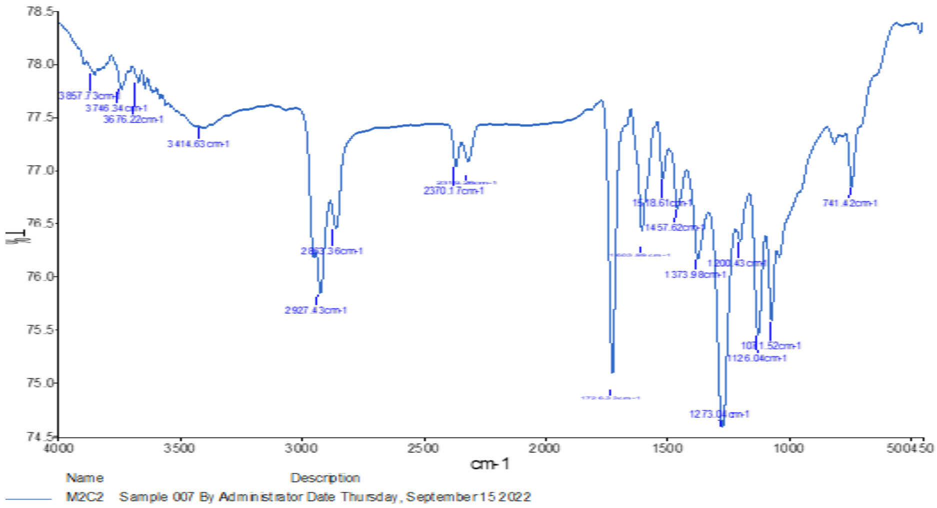


FIGURE 6: Infra-red spectrum of the (3)

The ν(Zn-N) in both complexes (1 and 2) were noted at 601 cm^{-1} and 622 cm^{-1} respectively[22], while the peak at 715 cm^{-1} was appear for (Zn–O), while the ν(Co-N) stretching clear at 450 cm^{-1} and azomethine (-C=N-) group stretched shifted to different position than the ligand due to the coordinate between ligand and the metals.

Scanning Electron Microscopy

One of the important technique use to characterize surface morphology is scanning electron microscopy also use to predict the properties of the compounds. SEM was employed to analyzed the surface morphology of the complexes **1** and 2, it is clear from the figures of the SEM that broken stone like structure for **1** (size 27 to 80 µm), while the complex 2 was botryoidal structure (36 to 280µm length). According to the earlier report shown that complexes with rod or rock shape structure could be have photoluminescence possessions. The element composition(zinc, oxygen and carbon) atoms, also proved by The EDAX spectrum (Figure 7 and 8), which gave more evidence to form the metals complexes.

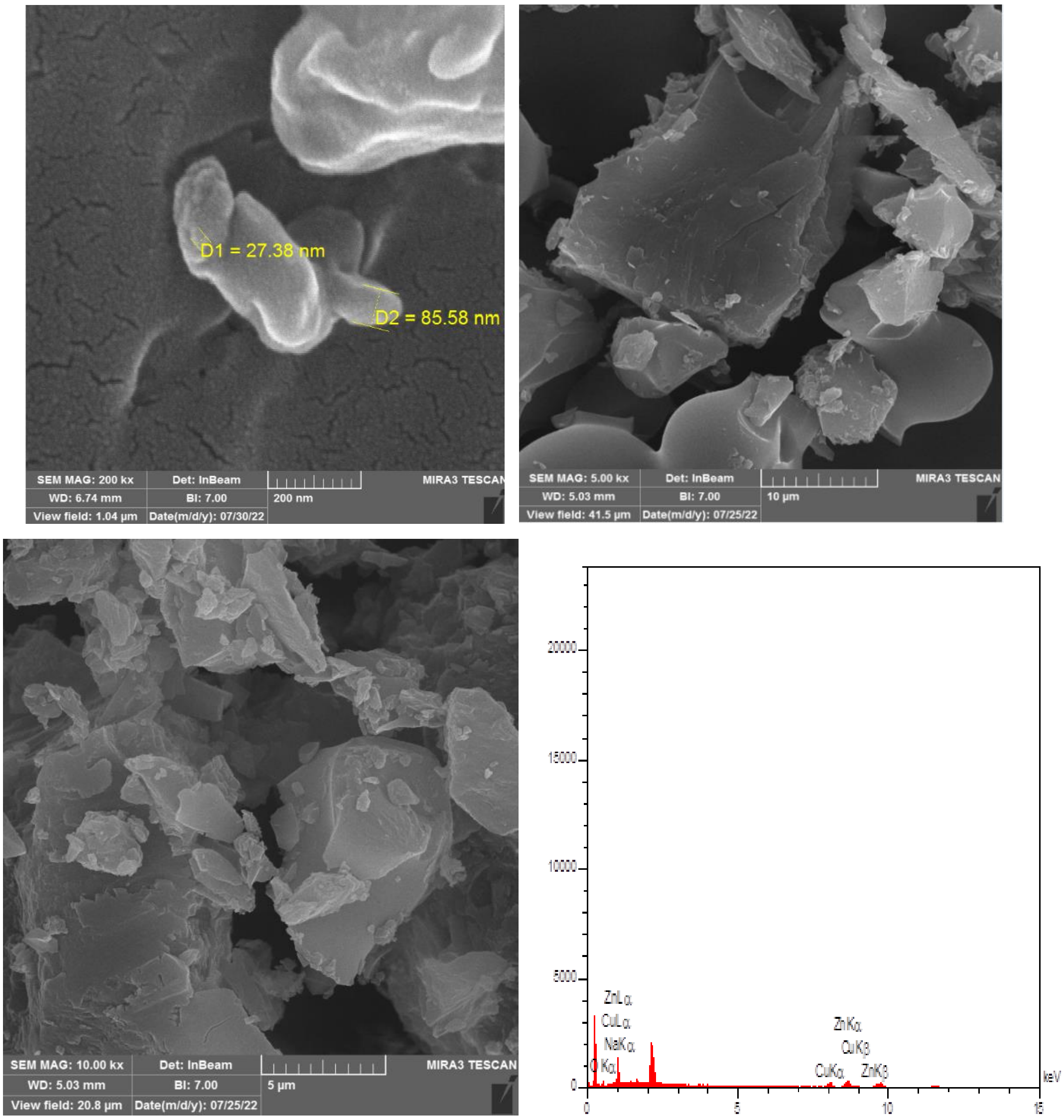
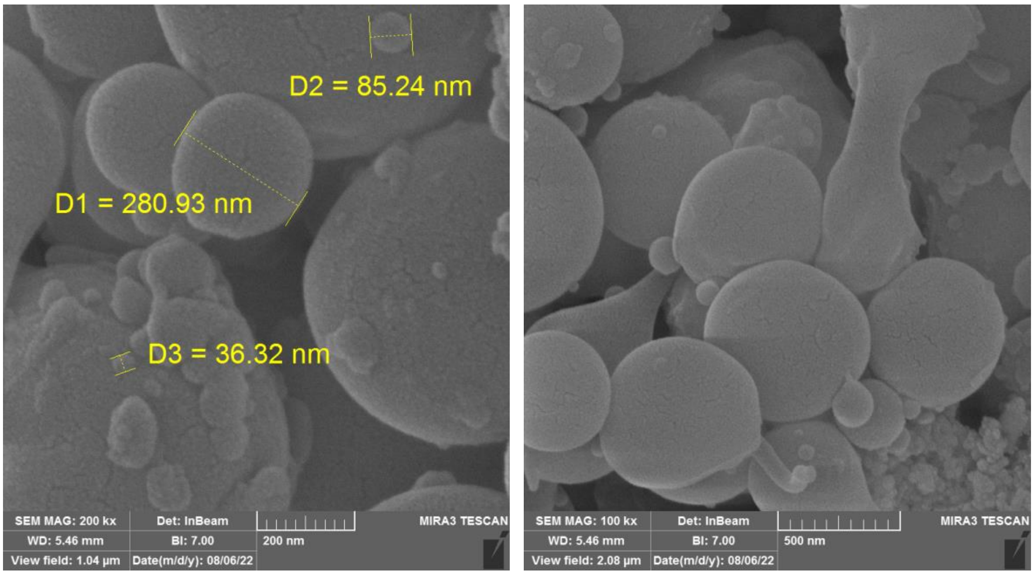


FIGURE 7: FESEM and EDX for the complex(1)



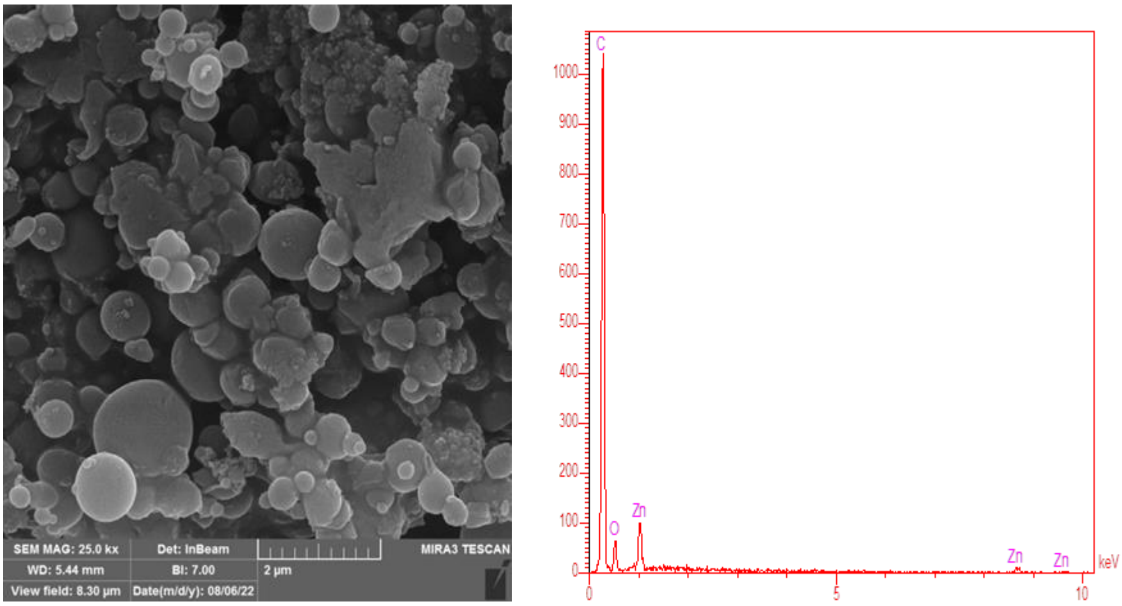


FIGURE 8: FESEM for the complex(2)

Fingerprint application

The metal complexes have been employed as colorant latent finger print which were carry through for the prepared complexes by choosing glass as surface. In this study, we exploted how these complex can be colorate latent finger prints under ultraviolet light to observe their possibility to detect in forensic fingerprints.

All complexes was tested as colorant and from the results noticed that the powder of the complex (2) was better than standard powder(black and white) used in this purpose. Figure 9 represented used (1) while Figure 10 employed (2) powder.

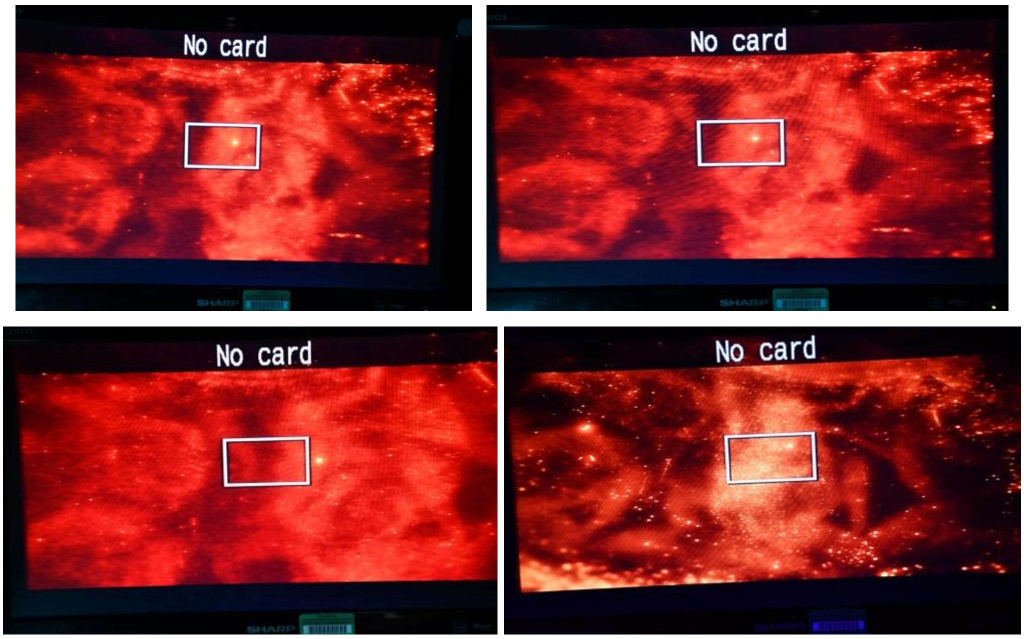


FIGURE 9: Test complex (1) under UV light

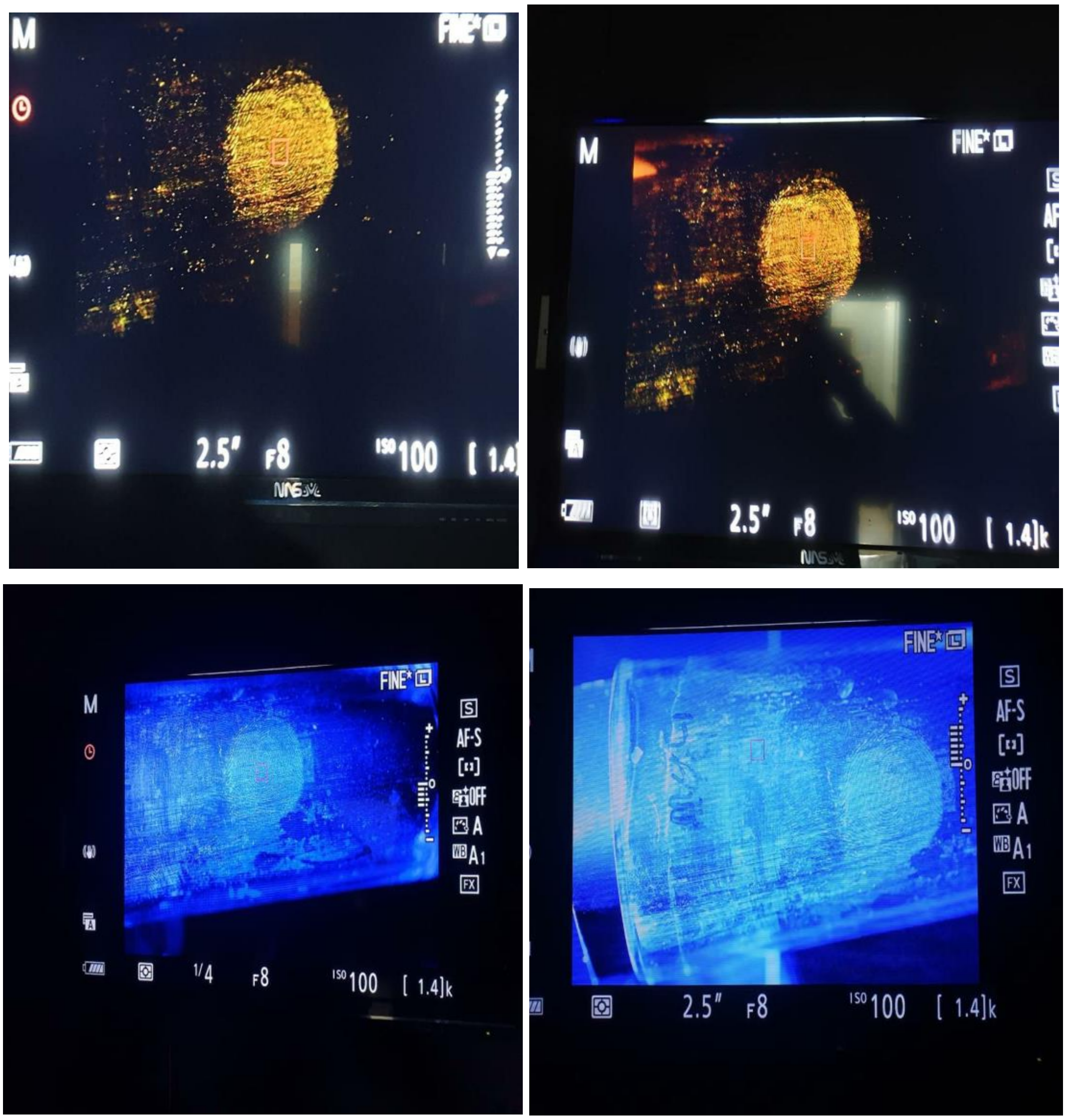


FIGURE 10: Test complex (2) under UV light

CONCLUSION

In summary, synthesis of complexes of zinc and cobalt with nno group containing diamine (aromatic and aliphatic) schiff base ligands these complexes are characterized by different technique**.** In term of structure according to the literature some of these complexes could be used in finger print application.

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