

SPECTROSCOPIC AND ELECTRICAL PROPERTIES OF PHTHALOCYANINATO COBALT (II)

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ABSTRACT

Phthalocyaninato Cobalt (II), PcCo (II), was synthesized and characterized by CHN, and spectroscopic methods. The complex was doped with Iodine and DDQ. Electronic spectroscopy shows the increase of height of Q and Soret bands with concentration. And the shift of the Q band of the doped complex (for both Iodine and DDQ Doping). The x-ray shows its crystalline structure, with a characteristic d-spacings. The mass spectrum of electron impact didn't show the molecular ion, but the other mass fragments show the suggested fragmentation of the molecular ion. The DC electrical properties of the undoped complex Iodine and DDQ doped was studied and show that, Iodine doping gives higher electrical conductivity than both undoped and DDQ doped. The doping suggests the formation of charge transfer complexes, from donor and acceptors.

KEYWORDS: Phthalocyaninato Cobalt (II), Iodine and DDQ Doping, Spectroscopic Study of X-Ray and Mass Spectra

INTRODUCTION

The porphrazines are cyclic tetrapyrrole linked by nitrogen atoms, from which two types of compounds are derived: 1) Phthalocyanines and 2) Semiphthalocyanines (Azaphthalocyanines), in which the benzene rings are substituted by pyrazine rings⁽¹⁾. Both types of compounds were first prepared by Lindsey⁽²⁾. There are many methods to synthesize such compounds⁽³⁾. Both types of compounds have many applications such as in the electrical instruments as semiconductors, solar cells, information transportations, as a sensitizer in Photodynamic therapy (PDT)⁽⁴⁾ in addition to their applications as dyes. Their importance is due to their chemical and thermal stability, their thermal and electrical conduction and their variable optical properties. They are mostly stable till 300 °C under atmospheric pressure⁽⁵⁾.

Due to the thermal and chemical stability and interesting electronic properties of phthalocyanines, it has attracted a considerable interest and studies. It usually acts as an electron acceptor in the presence of oxygen and other oxidizing agent, while it acts as a donor in the presence of acceptors so it act either p-type or n-type semiconductors⁽⁶⁾.

The DC electrical properties have received great attentions and most of the work focused on metal phthalocyanines. Cobalt phthalocyanine got less attention^(3,7).

In this work a DC electrical conductivity of PcCo (II) was studied, before and after doping with Iodine and DDQ, as oxidants over the temperature range 298- 393K, in addition to spectroscopic, x-ray and mass study.

Synthesis of Phthalocyaninato Cobalt (II), PcCo (II)⁽⁸⁾

2.795 gram (0.02 mole) of phthalic anhydride, 1.19 gram (0.005 mole) of hydrated Cobalt chloride (CoCl₂.6H₂O), 5 gram of urea and 0.01 gram of ammonium molybdate were dissolved in 25 ml of nitrobenzene and refluxed for 6 hours with mechanical stirring. The reaction mixture then cooled and filtered. Because the blue solid product is not soluble by the

known solvents, it is refluxed with water for 10 minutes, cooled and filtered. Same process where repeated with acetone, Hexane, chloroform and carbon tetrachloride respectively to remove the other impurities. The solid product then is dried less than 110°C. The final product is blue solid. It decomposes above 2270°C. The yield is 74.2%. CHN ($C_{32}H_{16}N_8Co$): Calculated C: 73.33, H: 3.30, N: 18.50; Found; C: 72.50, H: 3.18, N: 19.90. Figure 1 shows the reaction equation.

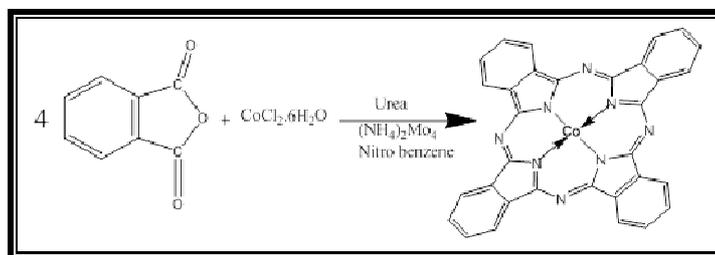


Figure 1: Synthesis of PzCo (II)

IDENTIFICATION OF THE COMPOUNDS

IR Spectrum

Figure 2 shows the IR spectrum of PcCo (II). The main characteristic features are the disappearance of the anhydride group peak at about 1810 cm^{-1} . The aromatic C-H is stretching at 3016 cm^{-1} and 3120 cm^{-1} . The peak at 3410 cm^{-1} might be due to bonded water (it might be bonded inside the structure even it is dried at 110°C). The peak at 1053 cm^{-1} is due to C-H bending⁽⁹⁾. Figure 2 shows the IR spectrum of PcCo (II).

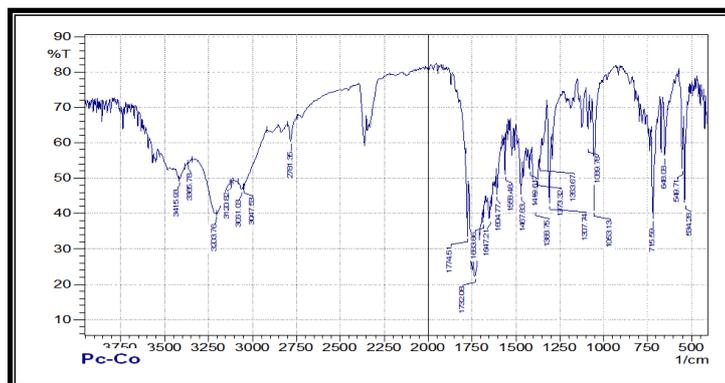


Figure 2: IR Spectrum of PcCo(II)

THE ELECTRONIC SPECTRUM^(3, 9, 10)

Figure 3 shows the electronic spectrum for PcCo (II) in DMF as solvent. It shows the phthalocyanine characteristic two main bands, the Q-band, at 665 nm (extinction coefficient, $5.4 \times 10^3\text{ L. Mol}^{-1}.\text{cm}^{-1}$) which is due to $\pi\text{-}\pi^*$ as a result to the excitation of the macro ring's and $n\text{-}\pi^*$ as a result to the excitation of the electrons of the nitrogen, in addition to the d-d transition which is weak and it is hidden within the Q-band. The other band is B-band at 329.5 nm which is due to $\pi\text{-}\pi^*$ and $n\text{-}\pi^*$ also.

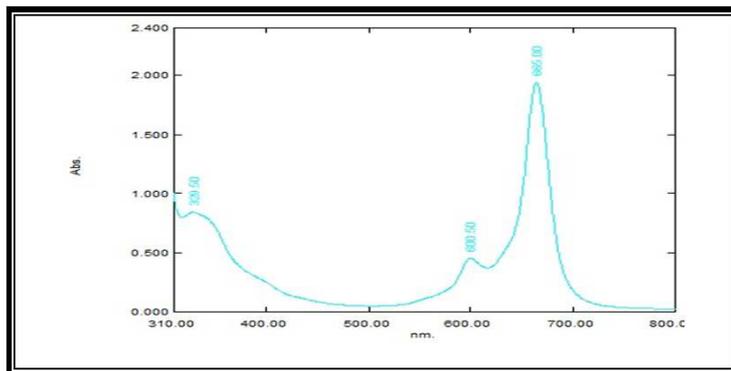


Figure 3: The Electronic Spectrum of PcCo (II) in DMF

Figure 4 shows the variation of Absorption intensity with the concentration of the complex, PcCo (II) and table 1 shows the variation of the absorption intensity of the peaks.

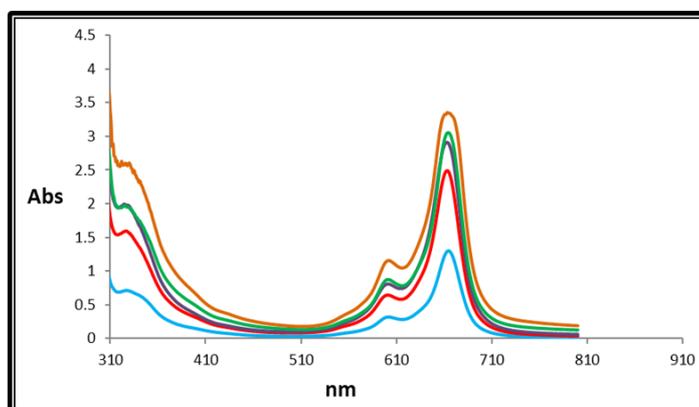


Figure 4: Variation of Absorbance with Concentration of the Complex PcCo (II). Blue Line (Lower Line) is of Lower Concentration and the Brown Line (Upper Line) is of the Higher Concentration

Table 1: Variation of Absorbance Intensity with the Concentration

No. of Peak	Concentration(mole/l)	Absorbance
1(blue)	2.8×10^{-4}	1.305
2(red)	5.6×10^{-4}	2.493
3(black)	8.4×10^{-4}	2.913
4(green)	1.1×10^{-3}	3.053
5(brown)	1.4×10^{-3}	3.357

SPECTROSCOPIC STUDY

Three solutions of the complex PcCo (II), were of the same concentrations (3.5×10^{-4} molar) in DMF. 1.0×10^{-5} mol of each of solid Iodine and solid DDQ were added to the two complex solutions 2 and 3 and shaken to form a solution of the mixtures of the complex and both Iodine and DDQ with the complex, PcCo (II).

Figure 5 shows the shift of λ_{\max} for both Iodine-complex and DDQ-complex solutions. The shift could be attributed to the interaction between Iodine and DDQ with the complex, PcCo (II). Iodine is known to act as oxidant to the phthalocyanine complexes to form I^{-3} and I^{-5} species⁽³⁾. And DDQ may act as charge transfer complex with the complex PcCo (II)

Figure 6 shows the close view to the Q band of the electronic spectra. The figure shows the longer red shift of DDQ mixture in compared to the Iodine –complex mixture. λ_{\max} for PcCo, Iodine doped PcCo and DDQ doped PcCo respectively, 661.5 nm, 665.5 nm and 669.5 nm^(3, 9, 11).

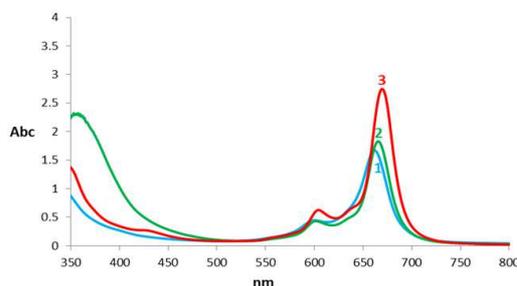


Figure 5: The Shift of λ_{\max} for both Iodine-Complex and DDQ-Complex Solutions in DMF

Blue (1): PcCo (II) complex, Green (2): Iodine doped PcCo, red (1): DDQ doped PcCo

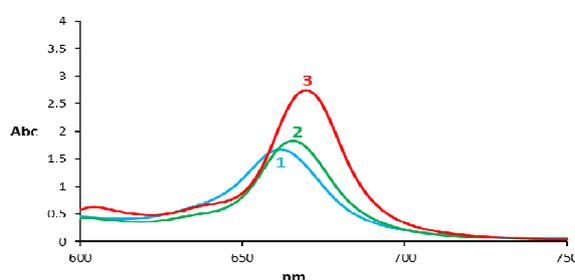


Figure 6: A Close View to the Q Band of the Electronic Spectra in DMF. 1. For the Complex PcCo (II), 2. For the Iodine- Complex Mixture Solution, 3. For the DDQ - Complex Mixture Solution

¹³C SPECTRUM

The ¹³C spectrum of the solution of the complex in DMSO shows the characteristic peaks of the phthalocyanine carbon atoms in addition to the DMSO main peak in around 40 ppm. The benzene carbons of the Phthalocyanine ring are 3 peaks averaged as 134.8, 123.5 and 123.2 ppm while the the carbons linked to the internal nitrogen atoms is at 169.5 ppm⁽⁹⁾, as shown in the figure 7.

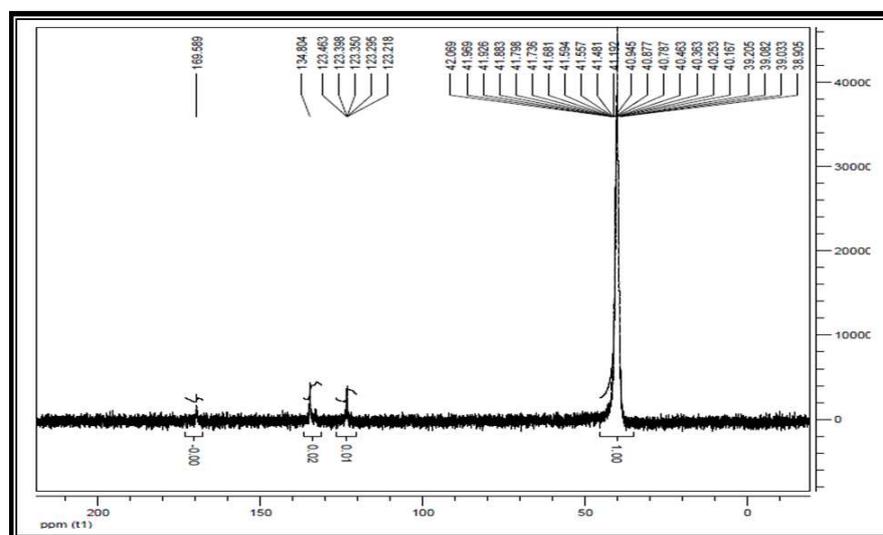


Figure 7: The ¹³C Spectrum of PcCo(II)

ELECTRICAL PROPERTIES

A sandwich cells from the undoped and doped with Iodine and DDQ complex were prepared by casting a thick solution, from each sample, on a fluorine tin oxide (FTO) glass substrate which is conducting from one side with 1 cm^2 surface area. The thickness of the casted film was 0.5 mm making the cell constant of $10^{-2} \text{ cm}^{-1} \text{ mm}$. The sample was put in cryostat which is connected to voltmeter and ammeter to measure the voltage and the current. The temperature is measured using copper constantan thermocouple placed near the sample^(8, 12). The DC electrical conductivity is measured in the temperature range (303-393) K.

The I/V characteristic curve study for the complex (PcCo (II)), in the voltage range 0-10 volts and at 30°C shows an ohmic relation at lower voltages where there is no space charge limited current as it shown in figure 8.

Figure 9 shows the relation between $\ln \sigma$ and the reciprocal temperatures at $(1/T)$ at 3 volts for the undoped complex and doped with Iodine and DDQ. The graph shows a higher dc conductivity of the Iodine doped in compared to the both DDQ doped and undoped complex which could be attributed to the oxidation of the complex by the electron acceptor, I_2 , (Iodine is oxidizing agent). The DDQ oxidation is of the lower extent in compared to the Iodine. The oxidation-reduction process may form a charge transfer complex between the PcCo (Donar) and I_2 and DDQ as accepters, as follows:



The donating process could be either from the electrons of the phthalocyanine ring or from the central metal atom, while the acceptor is either I_2 to form iodine complexes (I^3 or I^5)⁽⁷⁾, in the case of iodine doping or oxidation of the Quinone ring in the case of DDQ doping to form Hydroquinone cation radical^(12, 13).

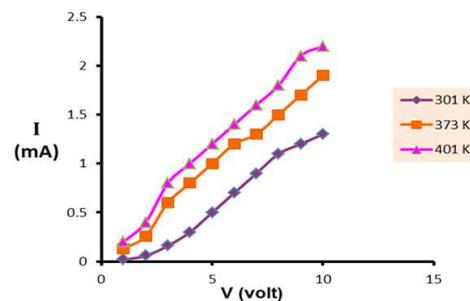


Figure 8: I/V Characteristic Curve in the Temperature Range (28-120) $^\circ \text{C}$ and Voltage Range of (1-10) Volts

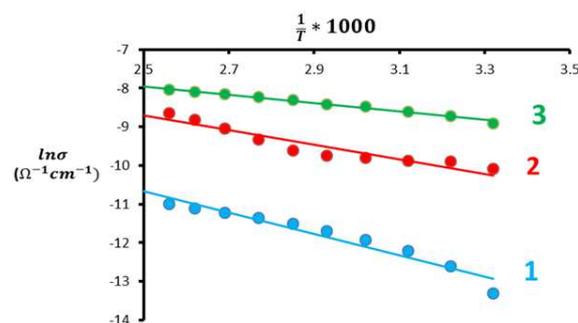


Figure 9: The Relation between $\ln \sigma$ and Reciprocal Temperature for the Complex(1), the Complex Doped with DDQ(2) and Iodine Doped(3)

X-RAY DIFFRACTION

Figure 9 Shows the X-ray diffraction spectrum of the powder of PcCo (II). It shows a crystalline parts with interplaner spacing, d- values, with 2θ values (table 2).

The d-spacing where calculated using Bragg law, and using $\text{CuK}\alpha 1$ (1.5406 \AA)^(10, 14).

Table 2: The Most Important Interplanar Spacing, d-Value Taken from X-Ray Spectrum of PcCo (II)

$[\text{ }^\circ 2\theta]$	Hight(Count/s)	D-Spacing(\AA)	Relative Intensity(%)
12.804	35.56	6.91	100.00
17.8954	27.39	4.96	77.01
19.4091	29.41	4.57	82.70
26.0614	30.63	3.42	86.13
29.3676	31.59	3.04	88.84

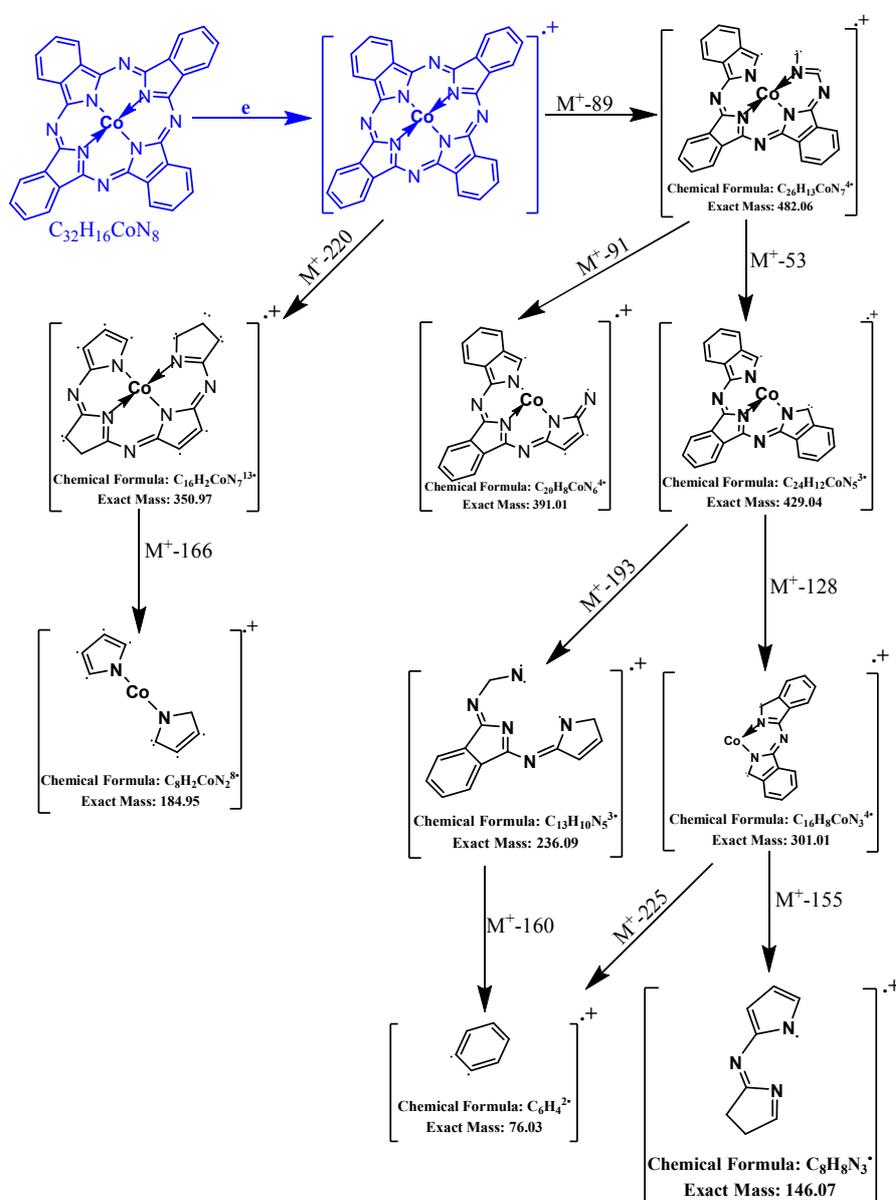


Figure 9: The X-Ray Powder Diffraction Spectrum for PcCo (II)

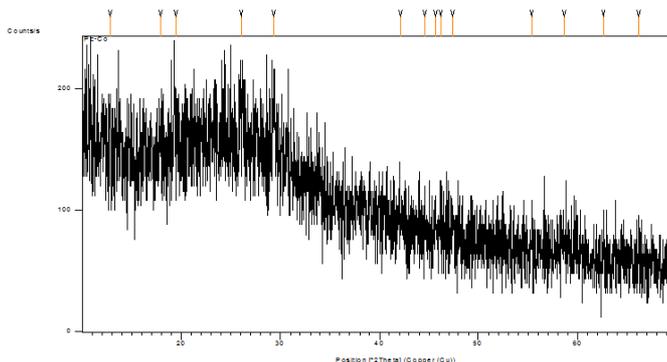


Figure 10: The X-Ray Diffraction Spectrum of PcCo (II)

Mass Spectrum

Figure 10 shows the electron impact mass spectrum of the complex PcCo (II), it shows the registered fragments of the a complex. The molecular ion is not apperead, which could be attributed to the high molecular weight of the complex (571.47 gram/mol). Such molecular weight might required FAB(fast atm bombardment) technique^(10,15,16).

Figure 11, shows the suggested structure of the fragments according to the fragment weights taken from the mass spectrum figure 10.

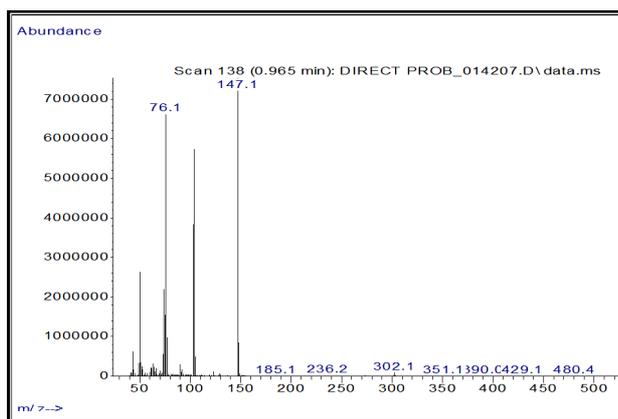


Figure 10: The Mas Spectrum of PcCo (II)

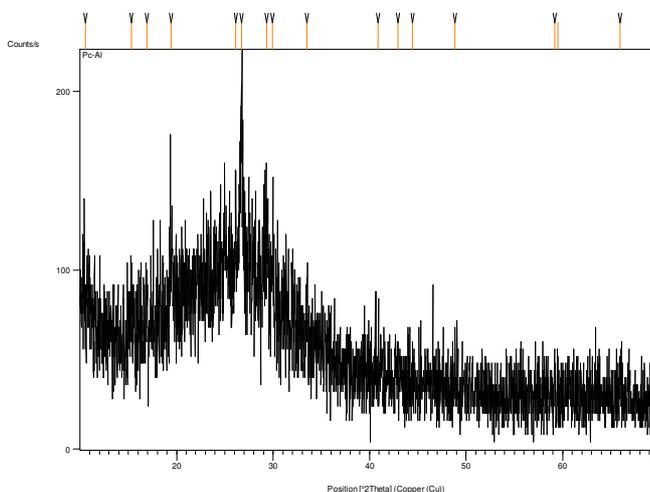


Figure 11: The Suggested Structures of the Fragments taken from the Mass Spectrum

CONCLUSIONS

The PcCo (II) complex was synthesized and characterized, and doped with iodine and DDQ. The DC electrical conductivity shows a higher conductivity of Iodine doped and DDQ doped.

REFERENCES

1. M. P. Donzello, C. Ercolani and P. A. Stuzhin; *Coordination Chemistry Review*, 250, 1530(2006).
2. R. P. Linstead, *J. Chem. Soc.*; 1016, 1934.
3. J. Simon and J. J. Andre; *Molecular Semiconductors*, Springer-Verlag, Berlin, 1985. *International Journal of U. H. Ramadhan*¹, N. A. Hussein, and H. S. Aboud; *Pharmaceutical Sciences and Nanotechnology*; 5(3), 1(2012).
4. Lenzno□, A. Lever, *Phthalocyanines, properties and applications*, Vol. 3, VCH, New York(1993).
5. H.S. Soliman¹, A.M.A. El-Barry, N.M. Khosifan, and M.M. El Nahass; *Eur. Phys. J. Appl. Phys.* 37, 1 (2007).
6. T. P. Linisky, T. R. Paul. R. S. Nohr and M. R. Kenny; *Inorg. Chem*, 19, 3131(1980).
7. Ayat Jawdat Khadim, MSc Thesis, Basrah University, Iraq (2017).
8. R. M. Silverstein and F.X-Webster, "Spectroscopic Identification of Organic Compounds", 6th Ed, John Wiley and Sons, Inc New York (1996)
9. N. A. Hussein, PhD Thesis, Nottingham University, UK (1990).
10. T. P. Linisky, T. R. Paul, R. S. Nohr and M. R. Kenny; *Inorg. Chem*, 19,3131 (1980).
11. Nazar A. Hussein; *International Journal of Management Information Technology and Engineering (Best, IJMITE)* s5(8)133(2017).
12. N. Rahman, S. Sameen and M. Kashif; *Journals of Molecular Liquids*, 222, 944(1916).
13. G. G. Mohamed, M. M. Hamed, N. G. Zaki, M. M. Abdou, M. El Badry Mohamed, A. M. Abdullah; *Spectra chemical Acta Part A: Molecular and Biomolecular Spectroscopy*, 182,143 (2017).
14. J. D. Wright."Molecular crystals" Cambridge Universit press, Cambridge, 1987.
15. M. Barber, R. S. Bardoll, G. J. Elliot, A. N. Tyler: *Anal. Chem.*, 56, 645A (1982)
16. R. B. Freas and J. E. Campana; *Inorg.Chem.*,23, 4654(1984).