

Preparation and Identification of new azo-schiff base ligand (NASAR) and its divalent transition metal Complexes

Saad M Mahdi , Ali K Ismail

University of Babylon, College of Science – Chemistry Dept. /Iraq

Abstract

New azo - schiff base ligand (NASAR) was synthesized , via the coupling of the diazonium salt of the schiff base (NAS) with Resorcinol in a basic media .

The two organic compounds were identified with many techniques such (CHN,FTIR and H^1 NMR for SACAN), to ensure the ligand preparation , then a UV-Visible study was preformed for the ligand and their aqueous mixtures for three of divalent transition metal ions (Co, Ni and Cu) to determine the optimal concentration and λ_{max} for mole ratio solid complex preparation .

Solid complexes were prepared and diagnosed with the previous techniques and other complemetry techniques as (electrical coundictivity, magnatic suseptibility) were done to determine the complexes formula and suggestion the geometrical of the complexes.

Conclusion: From whole resulat , they can concude that the ionic complexes (cobalt , nickel and copper) have the geometries (tetrahedral , square planer and octaheral) respectively.

INTRODUCTION

Azo compounds (the $R-N=N-R$) compounds espically the aromatic type¹ regarded as an important organic compounds , due to thier multiple advantagous usage such (organic reagents², paints³ & food colorants⁴, LCD production as a color filter⁵). in addition, thier vital action & biological function toward many microorganisums (bactria & fungi)^{6,7}, that analogous antibiotic role aginst pathogenic microbiols, azo compounds and thier derevitives can also participate in the medical & pharmlological industry⁸ as(antitumer⁹, antioxidant¹⁰, drug delevary compounds and drug polymers¹¹).

Azo resorcenol dyes synthezied previously such (PAR,TAR)^{12,13} were famed previously as analytical tool for determination of many of (TME) ions,these orthohydroxy azo resorcenol dyes formed a tridentate chelating complexes¹⁴.

EXPERIMENTAL

All chemicals used in this work were of analytical grade from (Sigma, BDH and Fluka).

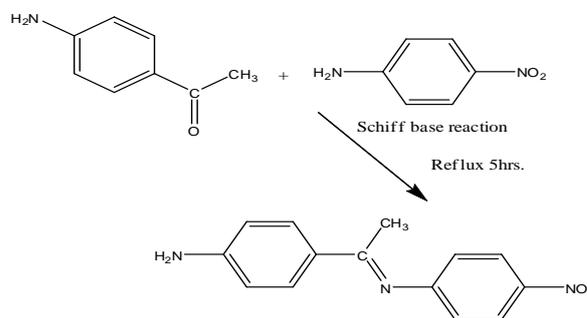
□□(C.H.N) % for the ligand and its complexes determined by (Micro Analytical unit, 1108 CHN Elemental analyzer).

- * Flame Atomic Absorption (Shimadzu AA) 6800.
- * Melting points with (Stuarts SPM300).
- * UV-Visible spectroscopic data by (Shimadzu 1650 PC).
- * H^1 NMR was done by (Burker 300MHz).
- * IR Data by using (Shimadzu 8400S FTIR test scan series).
- * Molar electrical conductivity measured by (Info lab terminal).
- * Balance magnetic Susceptibility Model MSB-MKI.

Procedures

Preparation of schiff base¹⁵ (NAS).

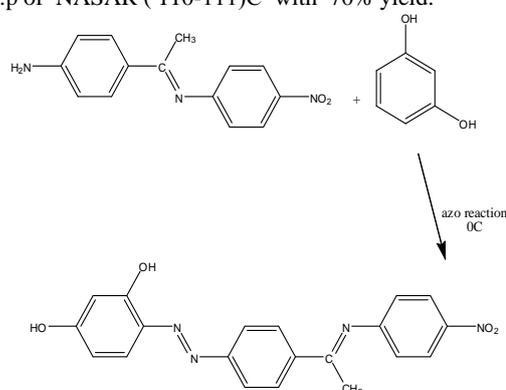
NAS was prepared via condinsation of eqimolal quantity (0.01mole) of the (p-aminoacetophenone and p-nitroaniline) using few drops of gly.acac as nucleophilic reaction activator on carbonyl group , the condinsation continuous for 5 hrs. With a monitering with TLC technique. The volume was reuded to minimum using boiling water bath , then the residual solution was cooled in iced crashed water to enhaced the schiff base precipitated , a pale yellow precipitant appeared , it was filtered, dried and recrystillized with a hot ethanol , the reaction yield 77% and the NAS m.p (99-101) $^{\circ}$ C.



Azo-schiff preparation¹⁶

NASAR was prepared via coupling of the diazonium salt of NAS (amin schiff base) with a basic solution of Resorcinol , a diazonium salt prepared by dissolution of the NAS amin (5 mmole , 1.275 g) in acidic mixture (15 ml 6M HCl) , cooling within 5 $^{\circ}$ C then the sodium nitrite solution (0.35 g in 10 ml D.W) was added slowly with stirring and cooling in (0-5) $^{\circ}$ C and left it for 15min for diazonium preparing , while the coupling component was prepared by dissolving eqi-molal quantity (5mmole , 0.55gm) Resorcinol in 10% basic olution and cooling with the same temp. When the diazonium salt prepared , it dropped with stirring and cooling to the coupling component , a red colour was observed (due to azo dye produced) , the pH value must adjusted to complete azo precipitation , the red solid was fitered , washed twice with deionzed water and dried , then they recrystallized with a hot ethanol .

The m.p of NASAR (110-111) $^{\circ}$ C with 70% yield.



Chemical Formula: $C_{21}H_{18}N_4O_4$
 Exact Mass: 376.12
 Molecular Weight: 376.37
 Elemental Analysis: C, 63.82; H, 4.28; N, 14.89; O, 17.00

Preparation of NASAR

Complexes preparation

Three type of transition metal ion complexes(Co II, Ni II and Cu II) was prepared for this new ligand (NASAR), by the condensation of 1mmole of the ligand with (1mmole of Co and Ni

chloride salts) and (0.5mmole of Cu chloride salt) for 90min., and cooling in iced water to produce there complexes , these precipitants were filtered , dried and the yield and milting points were calculated.

Physical properties with CHN data for NASAR and its complexes

Compounds	M.Wt g/mol	Color	m.p °C	Yield	Elementary analysis			
					C% Found (calculated)	H % Found (calculated)	N% Found (calculated)	M% Found (calculated)
NAS C ₁₄ H ₁₃ N ₃ O ₂	255	Yellow	99-101	77%	66.65 (65.78)	5.18 (5.13)	16.97 (16.46)	-----
NASAR C ₂₀ H ₁₆ N ₄ O ₄	376.12	Bloody-Red	110-111	70%	64.54 (63.82)	4.55 (4.28)	15.17 (14.89)	-----
[Co(NASAR)Cl(H ₂ O)] [CoC ₂₀ H ₁₇ ClN ₄ O ₅]	487.02	Deep red	158-160	77%	49.75 (49.25)	3.62 (3.51)	11.88 (11.49)	12.12 (12.08)
[Ni (NASAR) Cl (H ₂ O)] [NiC ₂₀ H ₁₇ ClN ₄ O ₅]	487.52	Deep orange	190-192	82%	49.53 (49.27)	3.64 (3.51)	11.52 (11.49)	12.22 (12.04)
[Cu(NASAR) ₂ (H ₂ O) ₂] [CuC ₄₀ H ₃₄ N ₈ O ₁₀]	850.29	Red-brawn	112-114	69%	57.41 (56.50)	4.05 (4.03)	13.87 (13.18)	7.75 (7.47)

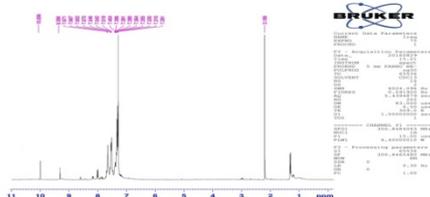
RESULTS

H¹ NMR data

NMR technique is more important spectroscopic tool than infrared to the organic chemist , that many nuclei may be studied reveals the type of the functional groups present in molecule , by giving the information about the number of magantically distinct atom of the type being studied ,indeed to the information of each type natue environment (espically with H¹ NMR)¹⁷.

H¹ NMR data(CDCl₃ , δ, ppm) for (NASAR) is ; 2.19 (3H,CH₃, s) , 7.29 – 7.67

(11H, aromatic ,m) , 9.36 (1H, o-OH ,s) and 10.05 (1H, p-OH , s) as shows in fig.



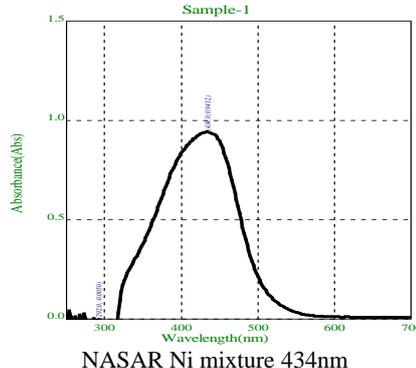
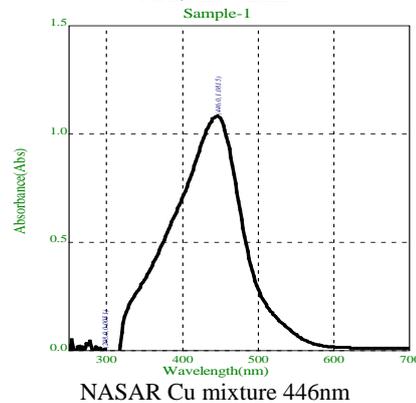
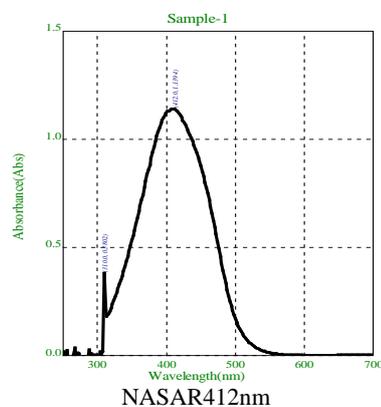
UV-Visible spectroscopic data

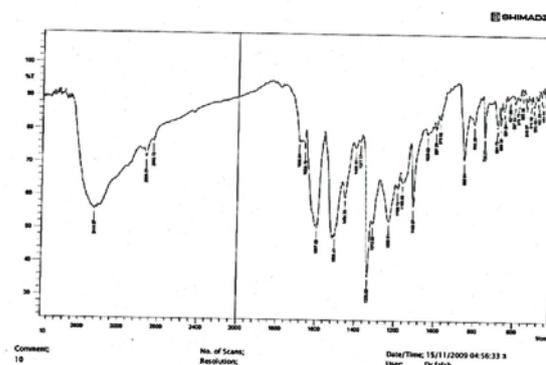
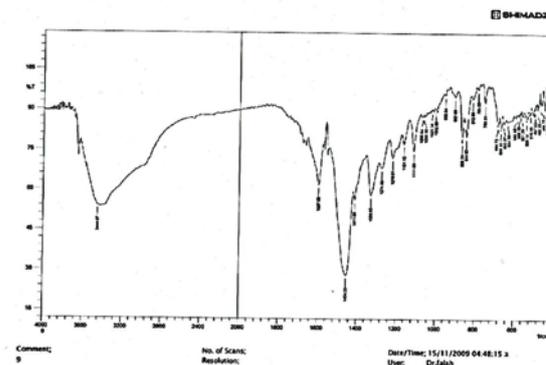
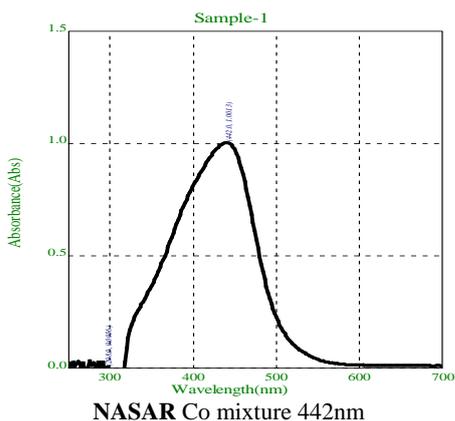
The ultraviolet-visible spectroscopy was one of the important techniques used for azo compound and thier complexes charecterization via the determination of the (λ_{max}) and thier concentration utilizing beer's law, and thier electronic transition within these region¹⁸.

The Uv-visible data revealed that the new azo ligand (NASAR) has a maximum absorption at 412nm related to the ($n \rightarrow \pi^*$) in the visible region while a small peak appear in the ultraviolet region related to the ($\pi \rightarrow \pi^*$) transition.

A red shifting were observed in the spectrums of the ligand – transition metal ions mixture solutions with different colors , that may be due to the coordination between the ligand lone pairs with the vacant metal orbitals and formation of complexes¹⁹.

To prepare the solid complexes, a mole ratio method was achieved and the most proper (M:L) ratio was (1:1) for coblet & nickel ions , while the copper ion ratio was (1:2).

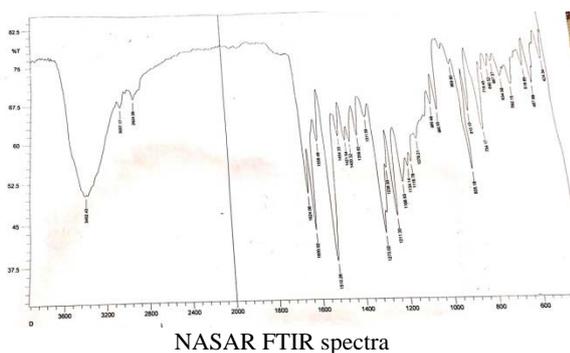




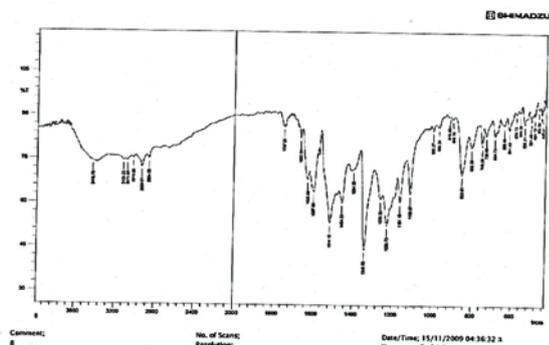
FTIR data

FTIR data was utilized for the determination of the functional groups in molecules (organics especially)²⁰, indeed it can give a hints for complexes formation in somewhat, when coordination takeplace via the variation of the functional group freuqances (that have the donating atom).²¹

NASAR ligand spectra shows clearly an important absorbtion bands as : the resorcenol hydroxyl groups at 3400 Cm⁻¹, in addition to the schiff base azomethene (C=N) group that absorbed at 1624 Cm⁻¹ and the azo group at 1454Cm⁻¹, as a good indication for ligand synthesis.



While in their complexes spectra, azo group was shifted toward lower freuqances and the aqua hydroxyl group was appeared within 3440 Cm⁻¹ region, and disappearance of resorcinol hydroxyl group, these can suggested that the participation of resorcinol hydroxyl group & azo- nitrogen in coordination with the metallic ions²¹ and these observed in complexes spe ctras.



Electrical molar conductivity & magnetic suceptibility

The ionic charecteristic for the complexes can determine from the conductivity data, that the conductivity values propotional with the ionic species in solutions²², within the work in room temperature and (1X10⁻³M) concentration using ethyl alcohol as a solvent.

The depression in the complexes conductivity values indicate the non-ionic charecter of all prepared complexes, this indicate the attachment of chlorine atom directly with the metallic ions for the (cobalt & nickel) complexes.

In another hand the magnatic suceptibility data give us the number of odd electron(s) and the oxidation state of the metal ions, indedd to enhanced us for geometrical suggestion for the complexes²³.

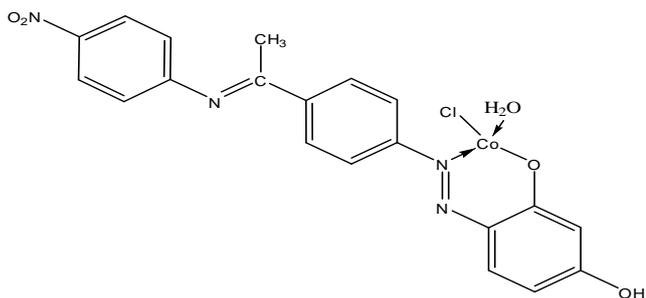
Data indicated the cobalt complex has 4.2 B.M thisvalue related to the present of three odd high spin electrons in cobalt tetrahedral complexes²⁴.

The diamagnatsum property of the nickel complex give no data (zero value) and this indicated with sequare planer nickel complexes.

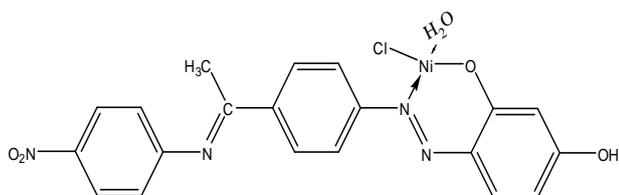
A 1.83 B.M value of copper complex indicated to the uniqe odd electron of the octahedral copper complexes.²⁵

No.	Complex	Molar conductivity /S.mol ⁻¹ cm ²	Magnatic suceptibility B.M /
1	[Co(NASAR)Cl(H ₂ O)]	13	4.2
2	[Ni(NASAR)Cl(H ₂ O)]	15	Zero
3	[Cu(NASAR) ₂ (H ₂ O) ₂]	6	1.83

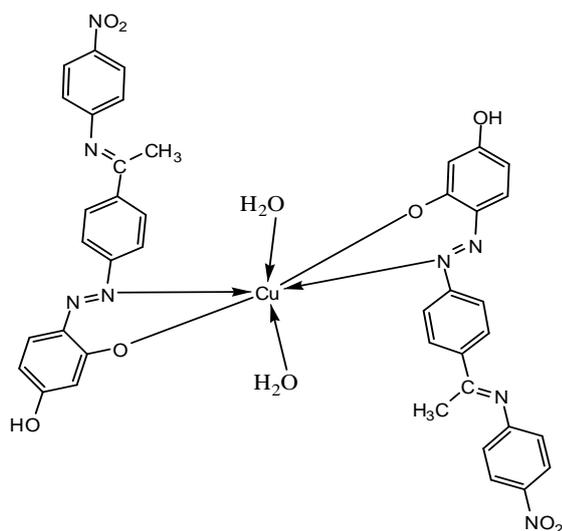
From the data of the results of this work , we can conclude the suggested geometries of the ionic (NASAR) complexes , as follow :-



Cobalt tetrahedral complex



Nickle Square planer complex



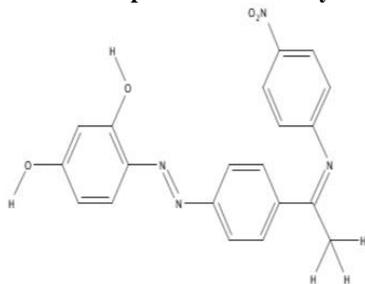
Copper octahedral complex

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REFERENCE:

- H.Zollinger "Diazo chemistry"Vol.1(Aromatic and Heteroaromatic compounds), VCH Verlagsgesellschaft mbH publisher , Germany.pp: 1-5, 1994
- Z.Marczenko and M.Balcerzak"Separation,preconcentration and Spectrophotometry in inorganic analysis", Elsevier. pp: 87,110,118. 2000
- Smith. T. P., Malcomber, D.W., and Almasry. M. A. US Patent.5.166.326, 1992
- S. Carmen"Food colorants chemical and functional properties". CRC Press, pp : 5. 2008
- Woo-Geun Choi and Y.T.Jeong.,(Synthesis and Characterization of Hybrid Azo Colorants for LCD Color Filter) *J.KIEEME.*, 26(7) .pp: 528-533 (2013) .
- J. Tamokou, J. Kuate, J. Tsemeugne, A.N.Djintchui, E.S. Fondjo, B.L. Sondengam, P. Sarkar and P.K. Bag (Antibacterial and Cytotoxic Activities and SAR of Some Azo Compounds Containing Thiophene Backbone), *Parmaecologia*,7(4), pp;182-192 .2016
- B.K.Patal and S.D.Patal (Synthesis and antifungal activity of novel metal chelates containing heterocyclic azo dyes) *Der.Pharm.Chem.* 7(9), pp:165-169 . 2015
- E. W.Tomczak and L. Gorecki, (Azo dyes – biological activity and synthetic strategy) *CHEMIK*,66(12) , pp ; 1298-1307 . 2012
- M. A.Gouda , H. Fakhr Eldien , M. M. Girges and M. A. Barghot. (Synthesis and antitumor evaluation of thiophene based azo dyes incorporating pyrazolone moiety) *J. Saudi Chem.Soc.* , 20(2) , pp ; 151-157, 2016
- C.T.Kumar, J. Keshavayya, T.N.Rajesh, S.K.Peethamber and A.R.Ali (Synthesis, Characterization, and Biological Activity of 5-Phenyl-1,3,4-thiadiazole-2-amine Incorporated Azo Dye Derivatives)*Org.Chem.Int.*, Volume 2013, Article ID 370626,pp;7 , 2013
- M.Roldo, E.Barbu, J.F.Brown, D.W. Laight, J.D.Smart and J.Tsibouklis, (Azo compounds in colon-specific drug delivery) *Exp. Opin. Drug Del.* 4(5) , pp; 547-560 (2007)
- H.Kristiansen and F.J.Langmyer (composition ans stability constant of the complex between lead II and 4-(2-pyridyl azo) resorcenol PAR) *Acta.Chem.Scand.*, 13(7) , pp1473, (1959)
- C.H.Lee, J.S.Kim, M.Y.Suh and W.Lee (A chelating resin containing 4-(2-thiazolylazo)resorcinol as the functional group Synthesis and sorption behaviour for trace metal ions) *Anal.Chem.Acta.* 339(3), pp;303-312, 1997
- A.Corsini (Metal Complexes of PAR, TAR and PAN) *Talanta*, 15,pp; 993-995, (1968)
- U. K. Singh, S. N. Pandeya, S. K. Sethia, M. Pandey, A. Singh, A. Garg and P. Kumar, (Synthesis and Biological Evaluation of Some Sulfonamide Schiff's Bases) *Int. J. Pharma. Sci. Drug Res.*, 2(3), pp; 216- 218, (2010)
- S.Shibata, M.Furuawa and k.toei " synthesis and spectrophotometric studies of azo dyes contianing m-dimethylaminophenol as analytical reagents" *Anal.Chem. Acta.* Vol. 66,pp; 397- 409, (1973)
- D.L.Pavia, G.M.Lampman, G.Z.Kriz"Introduction of spectroscopy" 5th ed , Cengage learning,pp:215, (2015)
- Z. Marczenko"Separation and Spectrophotometric determination of elements" 2nd ed , Ellis Harwood Ltd., England, pp;100 (1986)
- B.K.Reddy, J.R.Kumar, K.J. Reddy and A.V. Reddy,(A Rapid and Sensitive Extractive Spectrophotometric Determination of Copper(II) in Pharmaceutical and Environmental Samples Using Benzildithiosemicarbazone) *Anal.Sci.*19(3);pp423. (2003).
- B.D.Mistry,"A handbook of spectroscopic data Chemistry", Oxford Book Company,pp; 28 (2009)
- K.Nakamoto " Infrared and Raman Spectra of Inorganic and Coordination compounds". 6th Ed, John Wiley& Sons, Inc. Publication. pp; 55,57, 2009
- D. A. Skooge,"Fundamentals Analytical Chemistry", 5th. Ed. New York . pp; 411, (1998) .
- R.S.Nyholm, (Manuscript titel) *Quart Rev.*7, 377, (1953)
- B.N.Figgis, "Introduction to ligand field", Inter science, New York , (1967)
- J.Kotz , P.Treichel , J.Townsend and D.Treichel "Chemistry &Chemical Reactivity " 9th ed. Cengage learning publisher , USA,pp; 887, (2015)