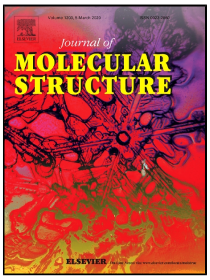

1H-Pyrazole- Azomethine Based Novel Diazo Derivative Chemosensor For The Detection Of Ni^{2+}

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PII: S0022-2860(20)30037-5
DOI: https://doi.org/10.1016/j.molstruc.2020.127713
Reference: MOLSTR 127713

To appear in: *Journal of Molecular Structure*

Received Date: 24 July 2019
Accepted Date: 08 January 2020

Please cite this article as: Gülnihal Erten, Fikret Karcı, Aykut Demirçalı, Sevil Söyleyici, 1H-Pyrazole- Azomethine Based Novel Diazo Derivative Chemosensor For The Detection Of Ni^{2+}, *Journal of Molecular Structure* (2020), https://doi.org/10.1016/j.molstruc.2020.127713

1H-Pyrazole- Azomethine Based Novel Diazo Derivative Chemosensor For The Detection Of Ni^{2+}

Gülnihal Erten[a], Fikret Karcı[a], Aykut Demirçalı[a], Sevil Söyleyici[a]*
Pamukkale University, Faculty of Science and Letters, Department of Chemistry, 20160, Denizli

* Corresponding Author. Ph: +902582963612, Email: szencir@pau.edu.tr

Abstract

In this study, 1H-pyrazole- azomethine based novel diazo derivative disperse azo dye was synthesized by a simple one-pot condensation reaction of 5-amino-3-methyl-4-phenylazo-1H-pyrazole (2) and salicylaldehyde in 1:1 ratio. This newly synthesized dye was characterized by elemental analysis and spectral techniques. The sensor properties of the SAG-1 was examined upon addition of the metal ions, such as Na^+, K^+,Mg^{2+}, Ca^{2+}, Sr^{2+} Al^{3+}, Cr^{3+}, Mn^{2+}, Cd^{2+}, Co^{2+}, Fe^{2+}, Fe^{3+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Hg^{2+} and Pb^{2+}. The interactions between receptor and ions were monitored by UV–Vis method. In addition, SAG-1-Ni^{2+} complex was investigated by UV-Vis spectroscopy with the detection of stoichiometry and binding constants of the complex.

Keywords: Disperse azo dye, Ni^{2+}, Organic sensor, Spectroscopic properties

1. Introduction

The synthesis of selective receptors for positively charged species began in 1978 with the first chromogenic compound synthesized by Vögtle et al. [1]. Recognition and detection of metal ions have become an active area due to their potential applications in various areas including environmental studies [2–4]. In sensor analysis, the use of organic ligand derivatives as sensor compounds in cations, anions or neutral metals is of great interest and many studies have been done [3].Ni^{2+} ion is a metal ion which is of secondary importance after Cu^{2+} metal ion in human life among various metal ions. Also, metallic nickel and its compounds are widely used in many fields in today's industry [5]. It is widely used in pigments, ceramics, electroplating and battery manufacturing. Detection of nickel is important because of its industrial applications and its toxicity at a certain level [6–9]. Among synthetic pigments, azo dyes are the most preferred dyes due to their dyeing quality. Particularly, the pyrazole group in their structure contributes to their useful properties[10]. The nitrogen groups and the unsaturated pyrazole ring in the structure can serve as a hard donor group and are of great interest as the coordination ligand for metal complex formation. In addition to the behavior of the pyrazole structure as a ligand, derivatives having different functional groups at the 4-position have also been shown to exhibit good antimicrobial properties[11,12]. Schiff bases are also important in sensor applications in modern coordination chemistry due to their well-known coordination capabilities [13]. The development of inexpensive, selective and simple sensors is particularly important for the environmental metal ions [14].

In this study, Schiff base derivative compound,2-[({3-methyl-4-phenyldiazenyl-1H-pyrazol-5-yl} imino) methyl] phenol (SAG-I), containing both pyrazole and the diazo group was synthesized and firstly the selectivity of the ligand to Ni^{2+} cation was determined and various spectrochemical properties were investigated.

2. Experimental

2.1. Materials and methods

All solvents and chemicals were obtained from Merck, Sigma and Carlo Erba and are of analytical purity. All reactions were performed at ambient conditions (no inert atmosphere). Metal cation solutions were prepared using metal nitrate salts and dissolved in DMSO. Aqueous Tris solution (0.01 mol L^{-1}) was used as a buffer solution to maintain pH (pH: 7.14) and ionic strength.^{1}H-NMR and ^{13}C-NMR spectra were obtained at NMR-Agilent 400/54 (400 mHz) in deuterated dimethylsulphoxide (DMSO-d_6) utilizing tetramethylsilane (TMS) as the internal reference and chemical shifts were reported in ppm. Absorption spectra were recorded on PG T80 + high-performance double beam spectrophotometer. IR spectra were measured with Perkin Elmer UATR two spectrophotometer in the range of 4000-400 cm^{-1} and direct analysis was performed with the ATR unit. Mass spectrum analysis was performed with LCMS/MS-Thermo TSQ Quantum Access mass spectrometer. Metal nitrate salts were used in the stock solutions of metal ions.

2.2. Synthesis of ligand

2.2.1 Preparation of 2-Phenylhydrazon-3-ketiminobutironitrile (1) and 5-amino-3-methyl-4-phenylazo-1H pyrazole (2)

The compounds, 2-phenylhydrazone-3-ketiminobutyronitrile (1) and 5-amino-3-methyl-4-phenylazo-1H-pyrazole (2) were synthesized in two reaction steps according to the literature [9]. In the first step, the diazonium salt of the aniline was reacted with 3-amino crotono nitrile. In the second step, the compound (1) purified by crystallization, followed by refluxing with hydrazine monohydrate in ethyl alcohol for 4 hours to give the product.

2.2.2. Preparation of 3-methyl-4-phenylazo-5-(2'-hydroxybenzylidene)-1H-pyrazole (SAG-I)

In a 100 mL round-bottom flask, 0.5 g (2.5 mmol) of the pyrazole-diazonium compound (2) refluxed with 0.3 mL of salicylaldehyde in 30 mL of ethyl alcohol. The reaction was monitoredwith CH_2Cl_2: MeOH (1:1) solvent system. At the end of the reaction period, the solvent was evaporated and the resulting bright yellow product (SAG-1) was used without purification.

SAG -1 : Yield: % 82; Melting point: 230°C ; ^{1}H-NMR (400 MHz, DMSO-d_6) δ: 2.66 (s, 3H, CH_3), 6.93-7.49 (Ar–H), 7.89 (s, 1H, CH=N) 9.26 (br, 1H, OH), 13.54 (br, 1H, NH), ^{13}C-NMR (xxx MHz, DMSO-d_6 , 25 ◦C, ppm): δ 164.422 (C=N), 119.560, 119.787, 133.201, 130.485, 62.266 (Ar-OH), 129.005, 129.415, 129.734, 122.003, 153.398 (Ar-N=N-), 147.260, 134.157, 117.397 (pyrazole moiety), 58.21 (pyr-CH_2), 11.76 (pyr- CH_3), IR ν (cm^{-1}): 3422 (-OH), 3164 (-NH (pyrazole)), 3056, 3033 cm^{-1} (Ar-H), 2922, 2852 cm^{-1} (Aliphatic C-H), 1610 (CH=N), 1573 (C=N (pyrazole)), 1503 (N=N), 1469 (C=C (pyrazole)).

2.2.2. UV- Vis selectivity experiment

The change in the absorption properties of the SAG-1 receptor was investigated after the addition of different metal cation nitrate salts (Na^+, K^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Al^{3+}, Cr^{3+}, Mn^{2+}, Cd^{2+}, Co^{2+}, Fe^{2+}, Fe^{3+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, $Hg^{2+}$and Pb^{2+}).SAG-1 (0.01 mmol) was dissolved in DMSO (1 mL) and 0.012 mL of the SAG-1 (10^{-3} M) were diluted with 2.988 mL tris buffer (10 mM, pH 7.14) to a final concentration of 4.10^{-5} M. The metal cations were dissolved in tris buffer and were added to the receptor compound as 1 equivalent separately and the absorption values were recorded after 10 minutes at room temperature[15].

2.2.3. UV-Vis titration measurement of Ni^{2+} and pH effect

UV-Vis titration measurements were also measured by adding (0-5 eq) $Ni(NO_3)_2.6H_2O$ at increasing concentrations to the receptor solutions prepared at the above concentrations. The effect of pH on SAG-1 and SAG-1-Ni^{2+} was investigated in the range of pH 2-12 and monitored by the absorption spectrum. The pH of the solutions was adjusted using concentrated NaOH and HCl solutions and the pH was measured with a pH meter.

2.2.4. Job's plot measurement

The stoichiometry of the SAG-1-Ni^{2+} complex was determined by the Job Method. SAG-1 (0.01 mmol) and $Ni(NO_3)_2$ (0.01 mmol) were dissolved separately in DMSO and trisbuffer (1 mL). 0.15 mL of SAG-1 solution was diluted with 29.85 mL of tris buffer (10 mM, pH 7.14) to form a concentration of 10^{-4} M. The $Ni(NO_3)_2$ solution was diluted in the same manner. 5, 4.5, 4, 3.5, 3, 2.5, 2, 1.5, 1, 0.5 and 0 mL of SAG-1 solution were taken and transferred to test tubes. 0, 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5 and 5 mL of Nickel solution were added to each solution separately. The total volume of each solution is 5 mL. After shaking the solutions in test tubes for a few minutes, UV-Vis spectra were taken at room temperature. The possible structure of the SAG-1-Ni^{2+} complex was also determined by mass spectroscopy. The possible structure of the metal complex is given in Scheme 2.

2.2.5. Recognition reversibility test

Recognition reversibility is an important requirement in sensor compounds. In our study, the reversibility between SAG-1 and Ni^{2+} was tested. For this purpose, wavelength scans of SAG-1 (6.10^{-5} M), SAG-1-Ni^{2+} (1 equiv.) and SAG-1-Ni^{2+}-EDTA (1 equiv.) solutions were prepared and comparative UV-Vis spectrums were obtained respectively (Figure 4) [16].

2.2.6. Binding studies

Determination of the binding constant spectrophotometrically is possible with the Job method[17–19]. In this method, SAG-1 (0.01 mmol) and $Ni(NO_3)_{2.}6H_2O$ (0.02 mmol) were dissolved separately in DMSO and tris buffer (1 mL, 10 mM, pH: 7.14). 0.15 mL of SAG-1 solution was diluted to 10 mL with tris buffer to a final concentration of 10^{-4} M. The same dilution was applied to the metal salt. Mole fractions of SAG-1 and nickel concentrations were changed but the total concentrations were kept constant and then the absorption spectrum of the fractions was collected. The receptor and metal salt solution were mixed in the test tubes at a total volume of 5 mL and then measured at room temperature after 10 minutes. It is difficult to get an exact equation for many binding mechanisms other than 1:1 complex. The binding constant of the metal complex at 2: 1 was calculated using the equation given below.[20]

Ni^{2+} + SAG-1 $\rightarrow$(SAG-1)$_2$Ni (1)

Binding constant equation and fraction of the ligand that participates in the complex are shown Eqs (2) and (3).

$$K = \frac{[(SAG-1)_2]_e}{[Ni]e[(SAG-1)]_e^2} \tag{2}$$

The subscript e is used for the expression of equilibrium concentrations of the components in the equation. The equilibrium ratio between complex and the initial concentration of SAG-1 can be derived from the absorbance of the receptors at a selected wavelength when the system is in equilibrium. Au, Am and Ac are the absorbance values of Ni^{2+} solutions (Au: before adding Ni^{2+}, Am: During titration, Ac: At saturation). The obtained derivation equation is given in Eq. (3) and (4).

$$\mathrm{Fc}=\frac{Au-Am}{2Au-2Ac} \tag{3}$$

$$\mathrm{K}=\frac{Fc}{2[SAG-1]_0[Ni^{2+}](1-Fc)^2} \tag{4}$$

3. Results and discussion

3.1. Synthesis of receptor

In this study, the receptor compound SAG-1 which is containing N and O donor groups as a coordination site was synthesized by the one-step condensation reaction of 2-phenylhydrazone-3-ketiminobutyronitrile (1) and 5-amino-3-methyl-4-phenylazo-1H pyrazole (2) and salicylaldehyde in ethyl alcohol. The synthesis reaction is given in Scheme 1. The synthesized compound (SAG-1) was characterized by spectroscopic methods such as IR, ^{1}H-NMR,^{13}C-NMR.

3.2. Spectroscopic and selectivity studies

As mentioned above, the SAG-1 receptor comprises an aniline-type donor moiety which is a pyrazole heterocyclic group and is attached to the azo linker, exhibiting π-electron delocalization on the chromophoric system. The FT-IR spectrum of the ligand showed -OH peak at 3422 cm^{-1} and pyrazole-NH peak at 3164 cm^{-1} (1573 cm^{-1} pyrazole C=N, 1469 cm^{-1} pyrazole C=C), Schiff base imine (CH=N) peak at 1610 cm^{-1} and diazo group -N=N- at 1503 cm^{-1}. In the spectrum of the complex, significant changes and shifts were observed in the peaks of the ligand OH, pyrazole NH and imine groups. This result gives us an idea about the possible binding region of Ni^{2+}. The overlapping IR spectrum of the ligand and complex is shown in Figure 7. When the Ni^{2+} metal sensor ligands in the literature are examined, it is emphasized that the selectivity in derivatives carrying imine, pyridyl and hydroxyl groups increases for Ni^{2+} ion [21]. The solution of light yellow SAG-1 (4.10^{-5} M) in DMSO was found to absorb maximal absorbance at 365 and 334 nm, which corresponds to the $\pi - \pi^*$ transition (Figure 1a). The spectroscopic measurement after the addition of the metal salts (Na^+, K^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, $Al^{3+,}$ Cr^{3+}, Mn^{2+}, Cd^{2+}, Co^{2+}, Fe^{2+}, Fe^{3+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Hg^{2+} and Pb^{2+})was showed a new band at 472 nm that belonged metal complex between the receptor and Ni^{2+}. This new band at 472 nm has a molar coefficient (ε) of $3{,}9.10^3$ $M^{-1}cm^{-1}$. This value is very large for Ni-based d-d transitions, so it can be argued that the new peak belongs to a ligand-metal charge transfer complex (LMCT) [15,22]. The binding property of SAG-1 with Ni^{2+} was also studied by the UV-Vis titration experiment. It was observed that the maximum absorbance value at 472 nm increased gradually as a result of the addition of Ni^{2+} solution at increasing concentrations on the receptor (Fig. 1b). The result shows that a stable complex was formed between SAG-1 and Ni^{2+}. The graph of the Job method for determining the complex stoichiometry was shown in Figure 2. Job's graph shows us that the molar fraction between SAG-1 and Ni^{2+} is 2:1 ratio[20,23]. The resulting complex structure was also accurately determined by mass spectroscopy. According to the peak value of LCMS/MS m/z = 689.02, the possible structure was found to be $[(2SAG\text{-}1\text{-}Ni^{2+})+Na]^+$(calculated m / z = 689.71) (Fig. 3).

In order to investigate the reversibility of complexation with Ni^{2+} ion, EDTA titration experiments were performed. Absorbance was significantly reduced when EDTA is added to the SAG-1-Ni^{2+} solution (v:v 1:1, pH: 7.14) in DMSO containing SAG-1 and Ni^{2+}, while re-addition of Ni^{2+}ion may recover the absorbance signal (Fig. 4).

In this study, the effect of pH on the absorption of SAG-1 and SAG-1-Ni^{2+} was investigated with a series of solutions between 2-12 and the graph in Figure 5 was obtained. It can be thought that this result may be due to the fact that the compound may show different tautomeric structures [24]. A colorimetric detection study was also performed for the SAG-1-Ni^{2+} compound. When the Ni^{2+} solution was added to the yellow SAG-1 receptor, the color change showed us that the compound responded with chromogenic and the metal could be detected with the naked eye (Fig. 1c). It was examined whether the response of SAG-1 ligand to Ni^{2+} underwent any changes in the presence of other metal ions. As a result, SAG-1-Ni^{2+} absorption was not significantly affected by the presence of any of the other metal ions.

Numerous conventional methods are used to calculate the binding constants. These methods are based on experimental measurements by analytical signals from the metal complex system and graphical representation of signal data. Since the evaluation of the curves obtained in these graphs depends on many components, the accuracy of the results cannot be guaranteed statistically. In this section, the binding properties of the reversible complex formed by Ni^{2+} ion with SAG-1 were investigated. For this purpose, the absorbance values at 472 nm versus the concentration ratio of Ni^{2+}/SAG-1 were plotted. The absorbance curve showed a sigmoidal curve at a concentration at 0,5 (Figure 1b inset). The Ni^{2+} titration indicated that a 2: 1 complex formed between SAG-1 and Ni^{2+}. The binding constant of this complex was calculated by using the absorbance at 472 nm with the equations described in the experimental section and was found to be 5.1.109 M^{-2} [25–27].

4. Conclusions

Heterocyclic benzothiazole containing a diazo unit at its side chain was synthesized and evaluated as chemosensor based on imine core for a series of transition metal cations (Na^{+}, K^{+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Al^{3+}, Cr^{3+}, Mn^{2+}, Cd^{2+}, Co^{2+}, Fe^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Hg^{2+}, and Pb^{2+}). From the spectroscopic titrations in the DMSO-Buffer solution, it was found that the tested compound could sense the presence of Ni^{2+}. The spectroscopic results obtained suggest that this synthesized compound can be used for the detection of Ni^{2+} in the DMSO solution.

Acknowledgment

This study was supported by the Scientific Research Projects Coordinatorshipof Pamukkale University (Project Number: 2016FEBE035).

5. REFERENCES

[1] T. Ábalos, M. Moragues, S. Royo, D. Jiménez, Dyes That Bear Thiazolylazo Groups as Chromogenic Chemosensors for Metal, Eur. J. Inorg. Chem. (2012) 76–84. doi:10.1002/ejic.201100834.

[2] S. Biswas, S. Acharyya, D. Sarkar, S. Gharami, T.K. Mondal, Novel pyridyl based azo-derivative for the selective and colorimetric detection of nickel(II), Spectrochim. Acta Part A Mol. Biomol. Spectrosc. 159 (2016) 157–162. doi:10.1016/J.SAA.2016.01.046.

[3] G.G. Vinoth Kumar, R.S. Kannan, T. Chung-Kuang Yang, J. Rajesh, G. Sivaraman, An efficient “ratiometric” fluorescent chemosensor for the selective detection of Hg 2+ ions based on phosphonates: Its live cell imaging and molecular keypad lock applications, Anal. Methods. 11 (2019) 901–916. doi:10.1039/c8ay02483a.

[4] G.G. Vinoth Kumar, M.P. Kesavan, M. Sankarganesh, K. Sakthipandi, J. Rajesh, G. Sivaraman, A Schiff base receptor as a fluorescence turn-on sensor for Ni2+ ions in living cells and logic gate application, New J. Chem. 42 (2018) 2865–2873. doi:10.1039/c7nj03784h.

[5] M. Dhanushkodi, G.G. Vinoth Kumar, B.K. Balachandar, S. Sarveswari, S. Gandhi, J. Rajesh, A simple pyrazine based ratiometric fluorescent sensor for Ni2+ ion detection, Dye. Pigment. 173 (2020) 107897. doi:10.1016/j.dyepig.2019.107897.

[6] F.A.G. Elsaid, S. Hamza, N. Rizk, H.A.B. Matter, E.A.S. Amerah, Ni2+ Selective Membrane Sensors Based on Sulfamethoxazole Diazonium Resorcinol in Poly (Vinyl Chloride) (PVC) Matrix, Arab. J. Sci. Eng. 38 (2013) 1681–1689. doi:10.1007/s13369-012-0383-2.

[7] G.G. Vinoth Kumar, M.P. Kesavan, A. Tamilselvi, G. Rajagopal, J.D. Raja, K. Sakthipandi, J. Rajesh, G. Sivaraman, A reversible fluorescent chemosensor for the rapid detection of Hg2+ in an aqueous solution: Its logic gates behavior, Sensors Actuators B Chem. 273 (2018) 305–315. doi:10.1016/J.SNB.2018.06.067.

[8] G.G.V. Kumar, M.P. Kesavan, G. Sivaraman, J. Rajesh, Colorimetric and NIR fluorescence receptors for F− ion detection in aqueous condition and its Live cell imaging, Sensors Actuators B Chem. 255 (2018) 3194–3206. doi:10.1016/J.SNB.2017.09.145.

[9] V.K. Gujuluva Gangatharan, K. Mookkandi Palsamy, S. Gandhi, A. Jamespandi, A. Kandasamy, T. Arunachalam, A. Shenmuganarayanan, S. Balasubramaniyam, R. Jegathalaprathaban, Reversible NIR fluorescent probes for Cu2+ ions detection and its living cell imaging, Sensors Actuators, B Chem. 255 (2018) 3235–3247. doi:10.1016/j.snb.2017.09.150.

[10] E. Bakan, The synthesis , characterization and investigation of absorption properties of disperse disazo dyes containing pyrazole and isoxazole, J. Mol. Struct. 1181 (2019) 8–13. doi:10.1016/j.molstruc.2018.12.033.

[11] S. Özkınalı, M. Gür, N. Şener, S. Alkın, M.S. Çavuş, Synthesis of new azo schiff bases of pyrazole derivatives and their spectroscopic and theoretical investigations, J. Mol. Struct. 1174 (2018) 74–83. doi:10.1016/j.molstruc.2018.06.070.

[12] S. Malladi, A.M. Isloor, S. Isloor, D.S. Akhila, H.-K. Fun, Synthesis, characterization and antibacterial activity of some new pyrazole based Schiff bases, Arab. J. Chem. 6 (2013) 335–340. doi:10.1016/J.ARABJC.2011.10.009.

[13] Ö. Özdemir, Novel symmetric diimine-Schiff bases and asymmetric triimine-Schiff bases as chemosensors for the detection of various metal ions, J. Mol. Struct. 1125 (2016) 260–271. doi:10.1016/j.molstruc.2016.06.074.

[14] B. Dolai, A. Bhaumik, N. Pramanik, K.S. Ghosh, A.K. Atta, Naphthaldimine-based simple glucose derivative as a highly selective sensor for colorimetric detection of Cu2+ ion in aqueous media, J. Mol. Struct. 1164 (2018) 370–377. doi:10.1016/j.molstruc.2018.03.066.

[15] Y.J. Na, Y.W. Choi, G.R. You, C. Kim, A novel selective colorimetric chemosensor for cobalt ions in a near perfect aqueous solution, Sensors Actuators, B Chem. 223 (2016) 234–240. doi:10.1016/j.snb.2015.09.098.

[16] N. Mergu, A.K. Singh, V.K. Gupta, Highly sensitive and selective colorimetric and off-on fluorescent reversible chemosensors for Al^{3+} based on the rhodamine fluorophore, Sensors (Switzerland). 15 (2015) 9097–9111. doi:10.3390/s150409097.

[17] K. Hirose, A practical guide for the determination of binding constants, J. Incl. Phenom. 39 (2001) 193–209. doi:10.1023/A:1011117412693.

[18] A.A.Ra. andM. R.C. Gonzalez, D V, A new graphic method for differentiating monoonüclear and polynüclear complexes and for determining their stability constants., Talanta. 26 (1979) 215–218.

[19] M.R.C. T. Roman Galan, A.Areebola Ramirez, A new spectrophotometric method for differentiating mononüclear and polynüclear complexes and for determining their extraction constants., Talanta. (1979) 545–547.

[20] Z. Aydin, M. Keleş, Highly selective Schiff base derivatives for colorimetric detection of Al3+, Turkish J. Chem. 41 (2017) 89–98. doi:10.3906/kim-1603-127.

[21] S. Upadhyay, A. Singh, R. Sinha, S. Omer, K. Negi, Colorimetric chemosensors for d-metal ions: A review in the past, present and future prospect, J. Mol. Struct. 1193 (2019) 89–102. doi:10.1016/J.MOLSTRUC.2019.05.007.

[22] E.J. Song, J. Kang, G.R. You, G.J. Park, Y. Kim, S.J. Kim, C. Kim, R.G. Harrison, A single molecule that acts as a fluorescence sensor for zinc and cadmium and a colorimetric sensor for cobalt, Dalt. Trans. 42 (2013) 15514–15520. doi:10.1039/c3dt51635k.

[23] Y.W. Choi, G.J. Park, Y.J. Na, H.Y. Jo, S.A. Lee, G.R. You, C. Kim, A single schiff base molecule for recognizing multiple metal ions: A fluorescence sensor for Zn(II) and Al(III) and colorimetric sensor for Fe(II) and Fe(III), Sensors Actuators B Chem. 194 (2014) 343–352. doi:10.1016/J.SNB.2013.12.114.

[24] F. Karci, A. Demirçali, F. Karci, I. Kara, F. Ucun, The synthesis, spectroscopic properties and theoretical calculation of some novel disperse disazo dyes derived from 3-amino-5-hydroxy-1-phenylpyrazole, J. Mol. Struct. 935 (2009) 19–26. doi:10.1016/j.molstruc.2009.06.040.

[25] J.M. Bosque-Sendra, A.M.G.-C. Eva Almansa-Lopez, L. Cuadros-Rodriguez, Data Analysis in the Determination of Stoichiometries and Stability Constants of Complexes, Anal. Sci. 19 (2004) 1431–1439. doi:10.2116/analsci.19.1431.

[26] C.A. Perez, Y. Wei, M. Guo, Iron-binding and anti-Fenton properties of baicalein and baicalin, J. Inorg. Biochem. 103 (2009) 326–332. doi:10.1016/J.JINORGBIO.2008.11.003.

[27] N. Pekel, O. Güven, Investigation of complex formation between poly(N-vinyl imidazole) and various metal ions using the molar ratio method, Colloid Polym. Sci. 277 (1999) 570–573. doi:10.1007/s003960050426.

Scheme and Figure Captions

Scheme 1: Synthesis of SAG-1

Scheme 2: Proposal SAG-1-Ni^{2+} complex structure.

Figure 1: a) Absorption change in the presence of various metal ions in tris buffer (4.10^{-5} M, pH 7.14) of SAG-1 **b)** Uv-Vis spectra of SAG-1 absorption due to increased Ni^{2+} concentration (0-5 eq.) c) Color change of SAG-1 (40 μM) upon addition of various metal ions (1equiv.) in tris buffer (10 mM, pH 7,14)

Figure 2: Job plot of SAG-1 and Ni^{2+}. The total concentration of Ni^{2+} with SAG-1 was kept at 1.10^{-4} M. Absorbance at 472 nm was plotted as a function of the mole fraction of Ni^{2+}.

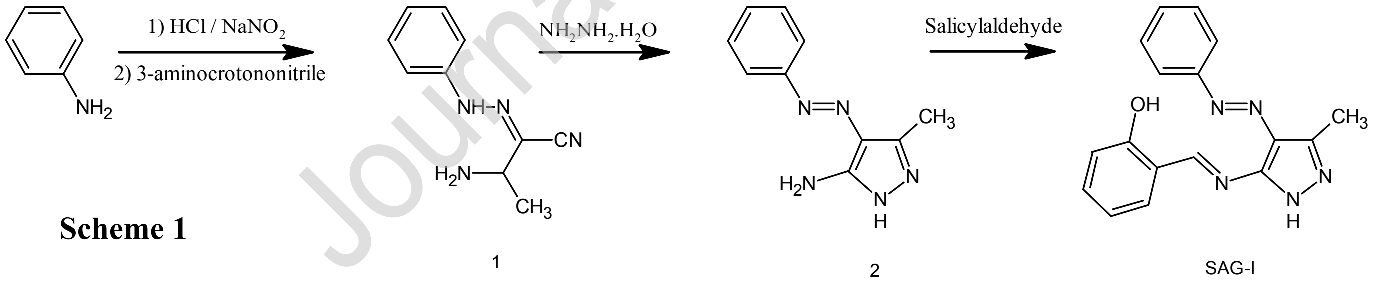
Figure 3: Mass spectrum of ([SAG-1]+[Ni^{2+}])

Figure 4: The variation in UV-Vis spectra of ([SAG-1]+[Ni^{2+}]) upon addition of EDTA

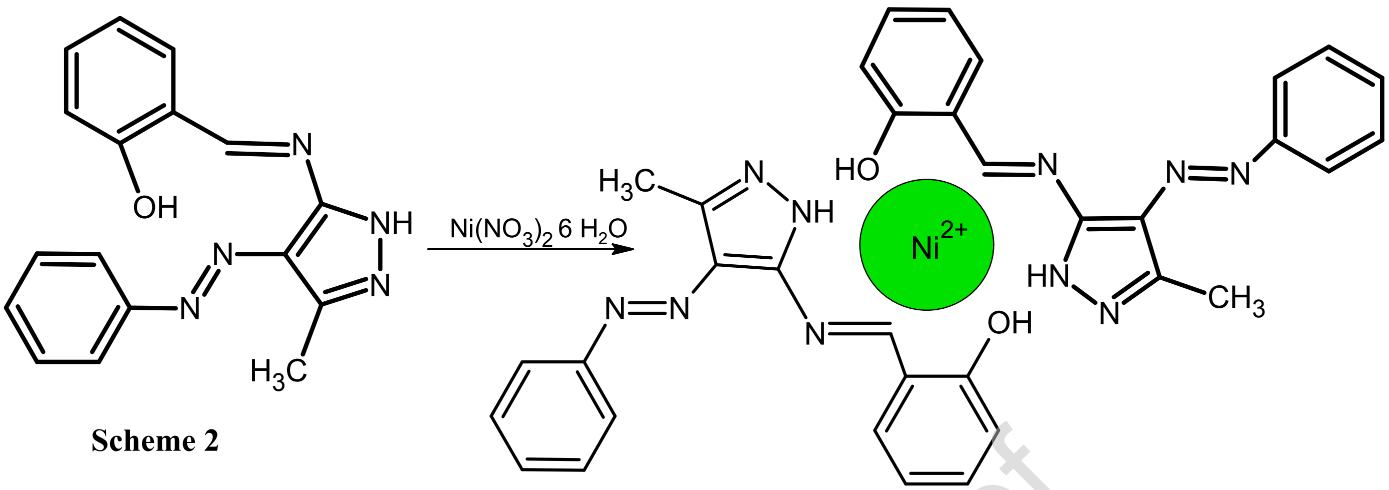
Figure 5: Variation in absorption (472 nm) of SAG-1 and SAG-1-Ni^{2+} at various pH values in the DMSO solution.

Figure 6: a) Interference responses of SAG-1 with Ni^{2+} (40 μM) and other metal ions (80 μM) in tris buffer (10 mM, pH 7,14) b) Absorption spectral change of SAG-1 in the presence of other metal ions.

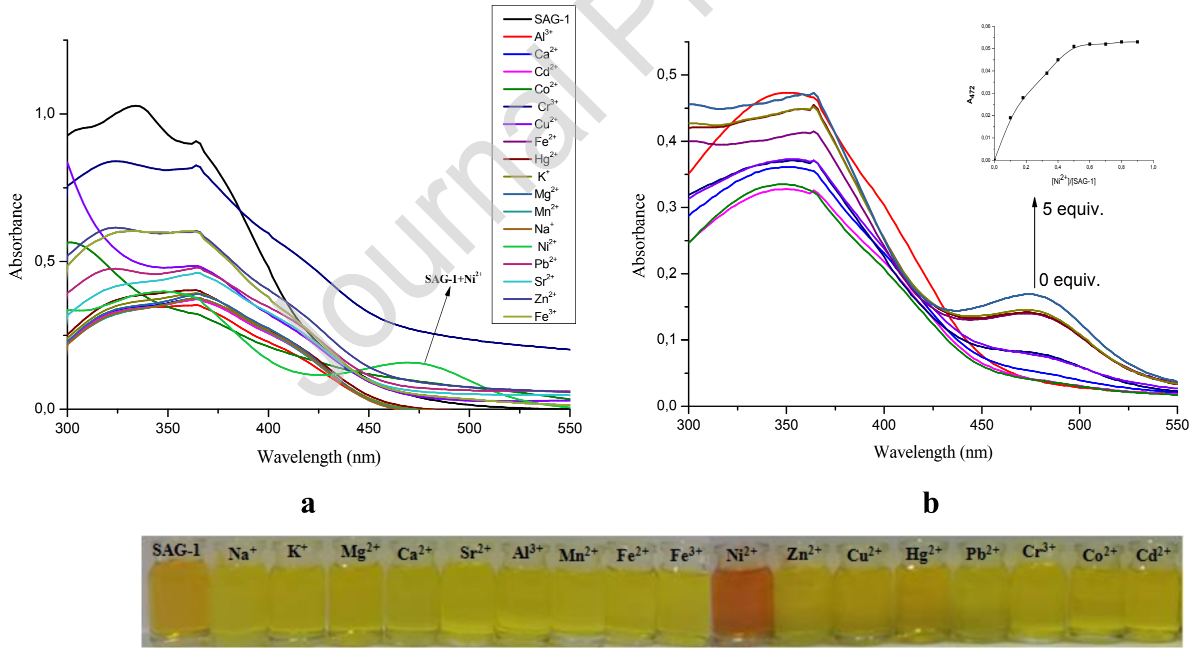
Figure 7: The overlapping FT-IR spectrum of the SAG-1 and SAG-1-Ni^{2+}complex.



Scheme 1



Scheme 2



a **b**

c

Fig. 1

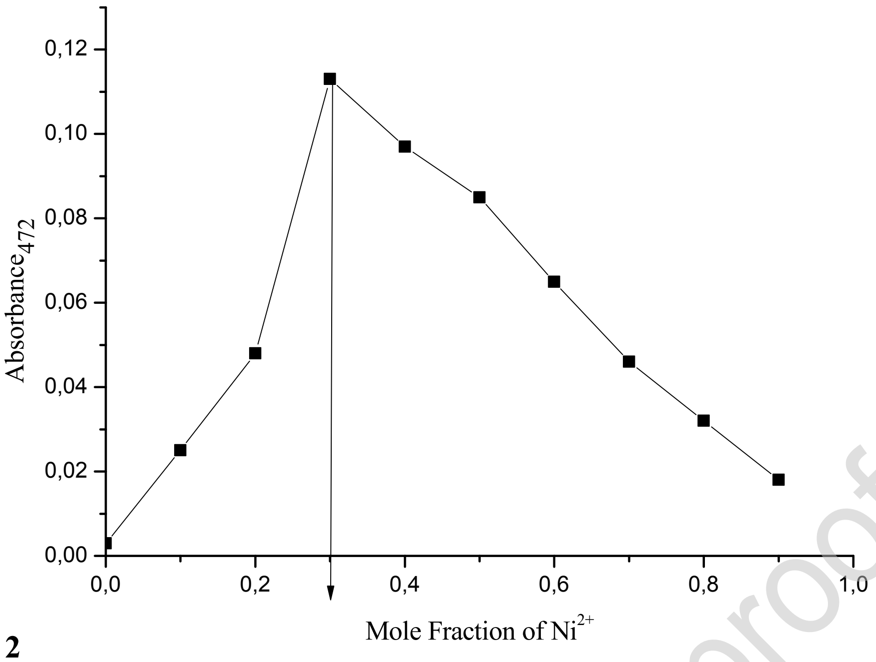

Absorbance$_{472}$
0,12
0,10
0,08
0,06
0,04
0,02
0,00
0,0
0,2
0,4
0,6
0,8
1,0
Mole Fraction of Ni^{2+}

Fig. 2

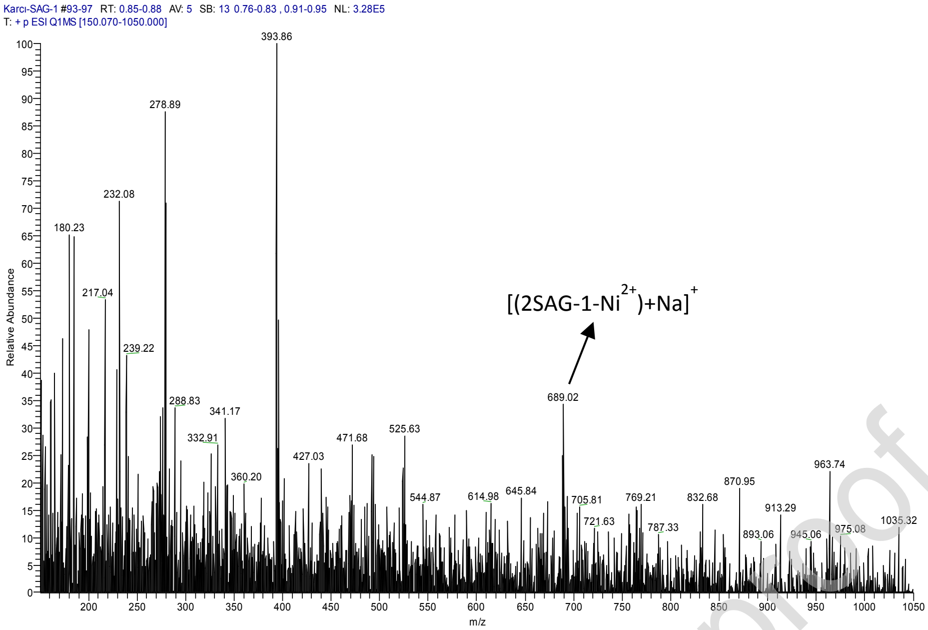

Karcı-SAG-1 #93-97 RT: 0.85-0.88 AV: 5 SB: 13 0.76-0.83 , 0.91-0.95 NL: 3.28E5
T: + p ESI Q1MS [150.070-1050.000]
Relative Abundance
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
393.86
278.89
232.08
180.23
217.04
239.22
288.83
341.17
332.91
360.20
427.03
471.68
525.63
544.87
614.98
645.84
689.02
705.81
721.63
769.21
787.33
832.68
870.95
893.06
913.29
945.06
963.74
975.08
1035.32
[(2SAG-1-Ni^{2+})+Na]$^+$
200
250
300
350
400
450
500
550
600
650
700
750
800
850
900
950
1000
1050
m/z

Fig.3

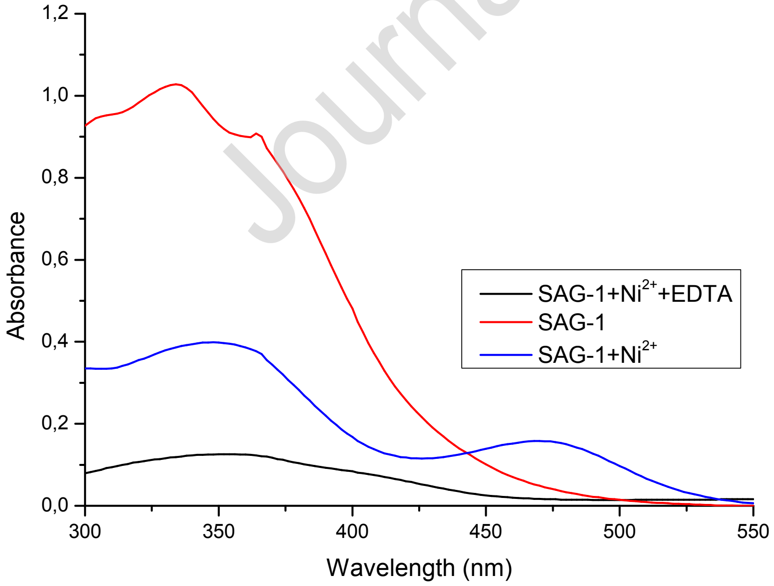

1,2
1,0
0,8
0,6
0,4
0,2
0,0
Absorbance
300
350
400
450
500
550
Wavelength (nm)
SAG-1+Ni^{2+}+EDTA
SAG-1
SAG-1+Ni^{2+}

Fig. 4

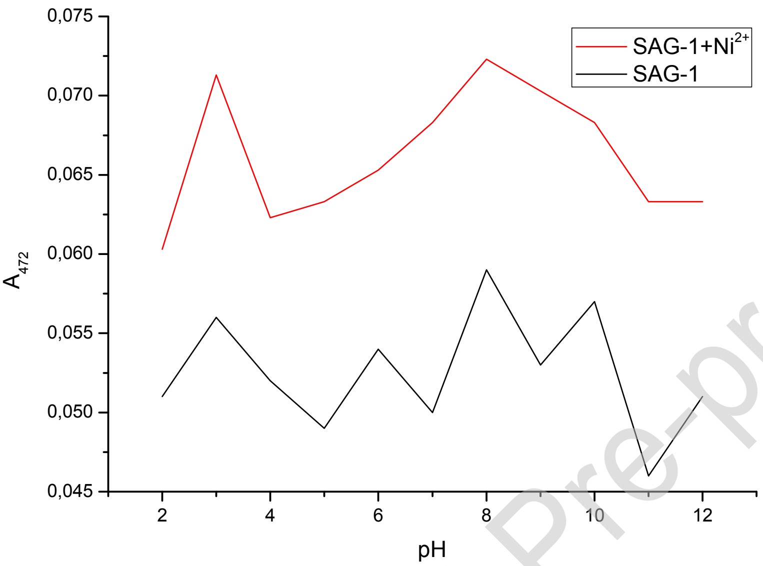
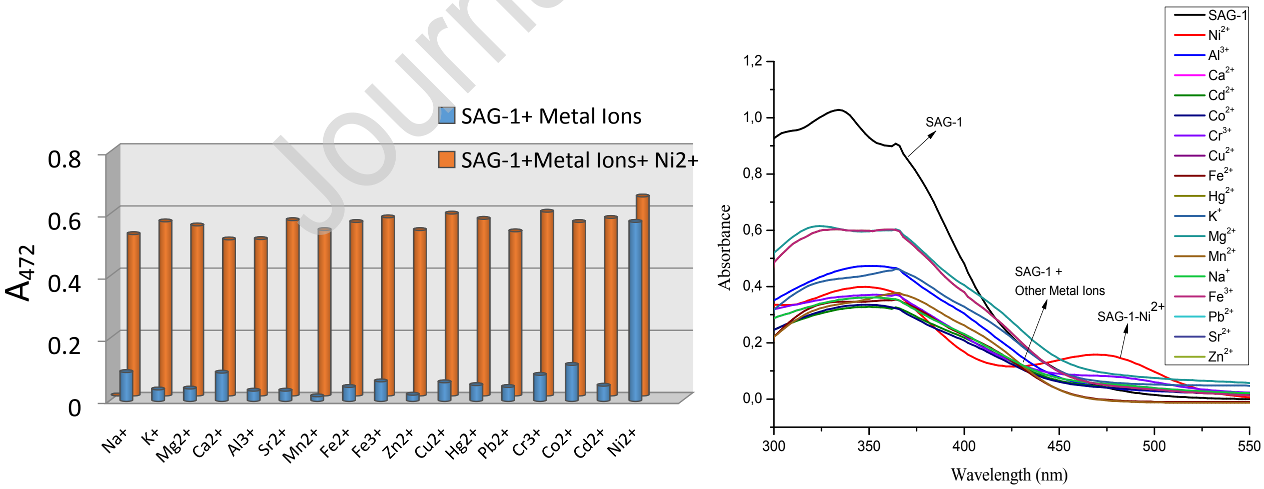

0,075
0,070
0,065
0,060
0,055
0,050
0,045
A472
2
4
6
8
10
12
pH
SAG-1+Ni2+
SAG-1

Fig. 5


SAG-1+ Metal Ions
SAG-1+Metal Ions+ Ni2+
0.8
0.6
0.4
0.2
0
A472
Na+
K+
Mg2+
Ca2+
Al3+
Sr2+
Mn2+
Fe2+
Fe3+
Zn2+
Cu2+
Hg2+
Pb2+
Cr3+
Co2+
Cd2+
Ni2+
1,2
1,0
0,8
0,6
0,4
0,2
0,0
Absorbance
300
350
400
450
500
550
Wavelength (nm)
SAG-1
SAG-1 + Other Metal Ions
SAG-1-Ni2+
SAG-1
Ni2+
Al3+
Ca2+
Cd2+
Co2+
Cr3+
Cu2+
Fe2+
Hg2+
K+
Mg2+
Mn2+
Na+
Fe3+
Pb2+
Sr2+
Zn2+

a

b

Fig. 6

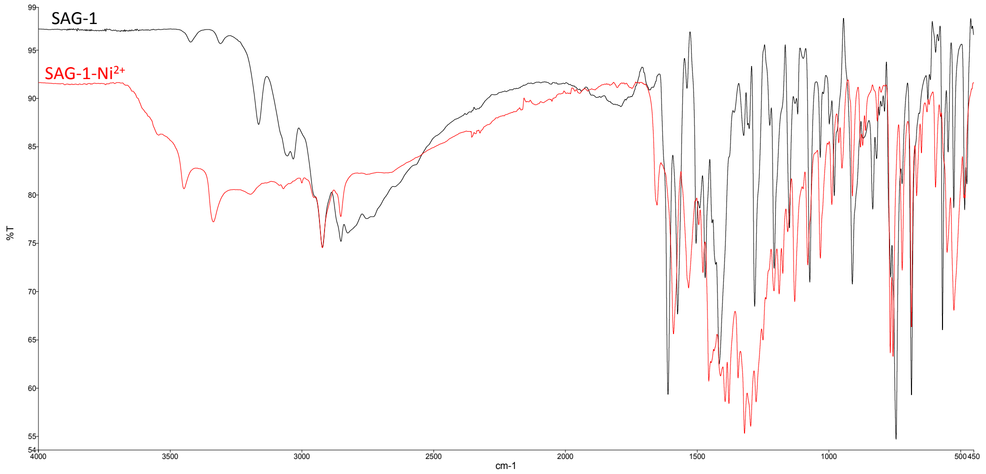


Fig.7

Research highlights:

- Preparation of 3-methyl-4-phenylazo-5-(2'-hydroxybenzylidene)-1H-pyrazole (SAG-I) has been synthesized.
- Chemosensor (SAG-1) shows selectivity and can be used for the detection of Ni^{2+} in the DMSO solution.
- The binding constant of the complex has been calculated via Job plot graphic.

Credit Author Statement

Gülnihal Erten: Conceptualization, Methodology, Investigation

Fikret Karcı: Supervision

Aykut Demirçalı: Conceptualization, Investigation

Sevil Söyleyici: Conceptualization, Methodology, Investigation, Writing - Original Draft,