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Synthesis, spectroscopic characterization, first order nonlinear optical properties and DFT calculations of novel Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes with 1,3-diphenyl-4-phenylazo-5-pyrazolone ligand

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PII:	S0022-2860(17)31333-9
DOI:	10.1016/j.molstruc.2017.10.002
Reference:	MOLSTR 24373
To appear in:	Journal of Molecular Structure
Received Date:	03 August 2017
Revised Date:	29 September 2017
Accepted Date:	01 October 2017

Please cite this article as: Samir A. Abdel-Latif, Adel A. Mohamed, Synthesis, spectroscopic characterization, first order nonlinear optical properties and DFT calculations of novel Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes with 1,3-diphenyl-4-phenylazo-5-pyrazolone ligand, *Journal of Molecular Structure* (2017), doi: 10.1016/j.molstruc.2017.10.002

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Highlights

- New azopyrazolone complexes were prepared and characterized.
- Spectroscopic, magnetic moments and molar conductance studies were carried out.
- Optimized geometry were computed by DFT theory and compared with experimental data.
- E_{HOMO} and E_{LUMO} and the energy gap were calculated.
- Nonlinear optical parameters are computed using B3LYP/GEN level of theory.

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Synthesis, spectroscopic characterization, first order nonlinear optical properties and DFT calculations of novel Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes with 1,3-diphenyl-4-phenylazo-5pyrazolone ligand

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ABSTRACT

Novel Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) metal ions with 1,3-diphenyl-4phenylazo-5-pyrazolone (L) have been prepared and characterized using different analytical and spectroscopic techniques. 1:1 Complexes of Mn(II), Co(II) and Zn(II) are distorted octahedral whereas Ni(II) complex is square planar and Cu(II) is distorted trigonal bipyramid. 1:2 Complexes of Mn(II), Co(II), Cu(II) and Zn(II) are distorted trigonal bipyramid whereas Ni(II) complex is distorted tetrahedral. All complexes behave as non-ionic in dimethyl formamide (DMF). The electronic structure and nonlinear optical parameters (NLO) of the complexes were investigated theoretically at the B3LYP/GEN level of theory. Molecular stability and bond strengths have been investigated by applying natural bond orbital (NBO) analysis. The geometries of the studied complexes are non-planner. DFT calculations have been also carried out to calculate the global properties; hardness (η) , global softness (S) and electronegativity $(\boldsymbol{\chi})$. The calculated small energy gap between HOMO and LUMO energies shows that the charge transfer occurs within the complexes. The total static dipole moment (μ_{tot}), the mean polarizability ($<\alpha>$), the anisotropy of the polarizability ($\Delta \alpha$) and the mean first-order hyperpolarizability ($\langle \beta \rangle$) were calculated and compared with urea as a reference material. The complexes show implying optical properties.

Keywords:

Pyrazolone, synthesis, complexes, spectroscopic studies, DFT calculations, nonlinear optics

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1. Introduction

Azole is the suffix used for five-membered ring containing two or more heteroatoms, at least one of which is nitrogen e.g. 3-methyl-1-phenylpyrazolone. This compound on methylation gives antipyrine (phenazone), which is exploited in medicine as a antipyretic compound [1,2]. The applicability of 5-pyrazolones as potential ligands for a large number of metal ions have gathered great attention in coordination compounds [3-6] due to their analytical and biological applications [7,8] of the formed metal complexes. 4-arylazo derivatives of 5-pyrazolones as well as their metal complexes were widely used in dye industry and as analytical reagents for micro determination of metals [9-13]. Electronic and IR spectra of some arylazopyrazolones were obtained [14,15] in organic solvents of differing polarities and buffer solutions and correlated to its molecular structure[16]. The studied absorption and fluorescence spectra of some arylazopyrazolone dyes indicated that the emission was appointed to their hydrazone form [17]. Nuclear magnetic resonance was utilized to determine the tautomeric forms of arylazo -3-, -4- and -5-pyrazolones and several related azo heterocycles in chloroform [18]. Mass spectra of the phenylazopyrazolones was found to occur primarily through rupture of the phenyl Nbond and less readily via rupture of the pyrazole-oxocyclic N bond [19] Kinetic studies of the thermal decomposition of metal chelates of substituted hydrazopyrazolone using TG, DTG and DTA were performed [20]. Structural studies of some transition metal complexes with some substituted-arylazo-5-pyrazolone compounds have been synthesized and characterized [21,22]. Spectroscopic, TG, DTG, DTA and molar conductivity studies have been carried out on chelates of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) with 3-methyl and 3-phenyl-4-nitroso-5pyrazolones [23]. Nonlinear optical (NLO) materials have variety of optical phenomena such as the generation of new light frequencies or the alteration of the materials optical properties. Nonlinear optical materials play a main role in nonlinear optics and with great effect on information technology and many industrial applications. The widespread range of applicability of single crystals is apparent in several fields such as solid state lasers, semiconductors, infrared detectors, non-linear optics, polarizers, piezoelectric, acousto-optics, photosensitive constituents and crystalline thin films for computer productions and microelectronics [24].

In this paper, the metal complexes were synthesized and their structures were elucidated by different analytical and spectroscopic techniques to get more information on the formed bonds and to elucidate their molecular structures. The geometrical parameters (bond lengths, bond angles and dihedral angles), NBO analysis (natural charges, natural population and natural configuration) and electrostatic potential of these complexes were computed using B3LYP/GEN level of theory. The electronic dipole moment (μ) and first order hyperpolarizability (β) values have been analyzed at the same level to study the NLO properties. Global reactivity descriptors; electronegativity (χ), hardness (η), global softness (S) were also estimated and analyzed.

2. Experimental

All chemicals used were of the highest degree of purity available from BDH chemicals and included manganese chloride ($MnCl_2.4H_2O$), cobalt chloride ($CoCl_2.6H_2O$), nickel chloride ($NiCl_2.6H_2O$), copper chloride ($CuCl_2.2H_2O$), zinc chloride ($ZnCl_2$), aniline, sodium hydroxide, ammonium hydroxide (30% NH₃), ammonium chloride, disodium salt of ethylenediamine tetraacetic acid dihydrate (EDTA), sodium chloride, silver nitrate ($AgNO_3$), sulphuric acid (H_2SO_4), hydrogen peroxide (H_2O_2 , 30%) and hydrochloric acid (37% HCl). The solvents used, ethanol, dimethylsulphoxide (DMSO) and dimethyl formamide (DMF), were purified by distillation [25]. The water used was doubly distilled.

2.1. Synthesis of 1,3-diphenyl-5-pyrazolone

A mixture of ethylbenzoyl acetate (9.6g; 0.05mol) and phenyl hydrazine (5.4g; 0.05mol) was heated at 100°C in water bath for one hour. The resulting oil was cooled and stirred with ether (50 ml) until solidification occurred. The crude product was then filtered off. The final product was crystallized from 50% aqueous ethanol and collected as white powder [26].

2.2. Synthesis of 1,3-diphenyl-4-phenylazo-5-pyrazolone (L)

A well-stirred solution of aniline 0.01mole in 40 mL ethanol and 20 mL of 2 M HCl was cooled in an ice salt bath and diazotized with aqueous sodium nitrite solution (20 mL, 0.01 mol). The cooled (0-5 °C) diazonium solution was added slowly to a well-stirred solution of 0.01 mole 1,3-diphenyl-5-pyrazolone in 100 mL ethanol containing sodium hydroxide (10 g). The reaction mixture was stirred for one hour at room temperature and then acidified with diluted HCl (100 mL, 2.5 M) to neutralize the reaction mixture and precipitate the ligand [25]. The product was recrystallized from ethanol and subjected to elemental analyses as shown in Table 1; the structural formula is presented in Scheme 1.

2.3. Synthesis of solid complexes

The solid complexes were synthesized by mixing 0.001 mole of metal ion dissolved in hot ethanol with the required amount of the ligand to form 1:1 or 1:2 (M:L) complexes. The pH of the solution was then maintained at a value of 6.5-7.5 by addition of dilute (10% v/v) 30% ammonia solution [27]. The reaction mixture was heated on a steam bath with continuous stirring for 4 hours and evaporated until dryness. The produced complexes were then dissolved in ethanol to remove unreacted species. It was then filtered off by suction and rewashed with ethanol until a colorless filtrate was obtained, filtered and then finally kept in a vacuum desiccator. The prepared complexes were subjected to elemental analyses of their C, H, N and the results are shown in Table 1. The metal ions of the prepared solid complexes were determined by titration with EDTA using recommended indicators and also the metal content of the complexes were determined [28].

2.4. Physical measurements

The FTIR spectra were performed on Shimadzu FTIR-8201 PC spectrophotometer applying the KBr disc technique in the range 400-4000 cm⁻¹. ¹H NMR spectra were acquired by using a Varian Gemini 200 MHz NMR spectrometer using deutrated DMSO (d⁶-DMSO) as solvent. The spectra were extended from 0-14 ppm using TMS

as internal standard. Mass spectra were done on GC-Mass 2b 1000 Ex mass spectrophotometer at 70 eV and MA energy using a direct insertion probe at temperature 220 °C. Thermal studies were determined using Shimadzu, Type TG-50 and DTA-50 derivatograph thermal analyzer (Japan). The TG curves were obtained by the weight loss percent from ambient temperature up to 800 °C with a heating rate of 10 °C per minute. Molar conductance of the solid complexes in DMF was measured using a conductivity meter type (Philips, PW 9526 digital conductivity meter). Magnetic susceptibility measurements were obtained at room temperature (25°) using Faraday's method with a model MKI, MSBI/24093/6232 Sherwood Scientific, Magnetic Susceptibility Balance (Cambridge, U.K.). The electron spin resonance (ESR) spectra of copper complexes were recorded by means of EMS ESR spectrometer (Bruker) 1998 Y.

3. Computational details

Due to the absence of a crystal structure and to get the molecular conformation of the ligand and its complexes, energy minimization studies were carried out using Gaussian 09W software package [29]. The ground state geometrical structures were optimized using the DFT [30] method with the B3LYP exchange correlation functional [31] approach. The 6-311G(d,p) and LANL2DZ were used as the basis set for C, N, O, H atoms and metal ions [32-34], respectively.

The geometry of the studied systems was fully optimized in gas phase without any symmetry constraints. The vibrational frequency calculations were performed to ensure that the obtained optimized geometries represent local minima. The spin density difference map calculations were also performed to explain their optical properties. The Gauss View 5 software [35] was used to prepare figures of MOs. Natural bond orbital (NBO) calculations were performed with the NBO code included in Gaussian 09 to understand different second order interaction between the filled orbital of one subsystem and empty orbital of another subsystem which is measure of the molecular delocalization or hyperconjugation. The total static dipole moment (μ), the mean polarizability $<\alpha>$, the anisotropy of the polarizability $\Delta\alpha$ and the mean first-order hyperpolarizability $<\beta>$ using the x, y, z components were determined by using the B3LYP method of theory [36-38] in order to estimate the nonlinear optical properties.

4. Results and discussion

The solid complexes of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) with the investigated ligand 1,3-diphenyl-4-phenylazo-5-pyrazolone (L) were prepared as described under the experimental section. The resulting complexes were subjected to elemental analyses for their C, H, N, Cl and metal content [28], infrared spectral studies (FTIR), nuclear magnetic resonance (¹H NMR), magnetic susceptibility, thermogravimetric analyses (TG and DTA), electron spin resonance (ESR) and molar conductance. The results of elemental analyses listed in Table 1 are in good agreement with those postulated by the proposed formula where 1:1 and 1:2 (M:L) solid complexes are formed.

4.1. Spectroscopic results

4.1.1. Infrared spectra of the free ligand and its solid complexes

The infrared absorption spectrum of the free ligand (L) presented in Table 2 and Figure 1 shows the presence of a broad band at 3429 cm⁻¹ which corresponds to the stretching vibration of the OH group results from the azo-hydrazo tautomerism (CH-N=N to C=N-NH) followed by hydrogen bonding with C=O group of the pyrazolone ring. The appearance as well as the broadness and the low frequency of the band denote the presence of intramolecular hydrogen bonding [39]. The vNH band appears as a medium broad one at 3294 cm⁻¹. The vC=C band appeared at 1550 cm⁻¹ while the vN=N band is observed at 1496 cm⁻¹. The band observed at 1654 cm⁻¹ is assigned to vC=O stretching for the carbonyl group [40,41]. The infrared spectra of the solid complexes display interesting changes which may give a sufficient idea about the structure of these complexes as shown in Table 2 and Figure 1. The IR spectra of the metal complexes showed that the vN=N are shifted to lower or higher wavenumber compared to that of the free ligand suggesting a center of chelation. The vC=O band disappeared indicating that it is a center of chelation as it loses its double bond

character (-C-O-M-) which is confirmed by the appearance of a new band corresponding to vC-O in the range 1211-1265 cm⁻¹ for all the complexes. For 1:1 and 1:2 complexes, the OH stretching frequency appears in the spectra of the complexes as a broad band in the range 3355-3494 cm⁻¹ which is ascribed to coordinated water molecules and chelated OH⁻ ion neutralizing the charge on the metal ion. The spectra of the metal complexes exhibits bands in the ranges 510-590 and 416-489 cm⁻¹ which may assign to (M \leftarrow N) and (M \leftarrow O) stretching frequencies [42], respectively. These bands are possibly due to the formation of coordination bonds between the donor atoms (O and N) and the central metal ion.

4.1.2. ¹H NMR spectra of the free ligand and its Zn complexes

¹H NMR technique is used for the purpose of establishing the possible azohydrazo [43] or keto-enol tautomerism. The signals observed at 8.19-7.23 ppm are assigned to the protons of the aromatic ring [41] while the signal observed at 13.7 ppm is assigned to the NH proton as shown in Table 3 and Figure 2. The appearance of this signal indicates the involvement of this ligand in azo-hydrazo tautomerism followed by hydrogen bonding as shown in Scheme 2.

For Zn-L (1:1) complex, the signal observed at 16.6 ppm is assigned to the proton of the coordinated OH⁻. The signals observed within the range 8.19-6.71 ppm are assigned to the protons of the aromatic ring. For Zn-L (1:2) complex, the signals observed within the range 8.18-7.05 ppm are assigned to the protons of the aromatic ring. The upfield shift of these signals may be due to complexation. For 1:1 and 1:2 complexes, the signal observed at 3.32 and 3.37 ppm is assigned to protons of coordinated H₂O molecules.

4.1.3. Mass spectrum of the investigated ligand

The mass spectrum of the investigated ligand as indicated in Figure 3 was in good agreement with the proposed structure and shows a molecular ion peak at m/z = 339 (Calc. M. wt. = 340) with a relative intensity near to 75% which is equal to its molecular mass. The other peaks appeared in the mass spectrum (abundance range 1–

100%) are assigned to the fragmentation of the ligand molecule obtained from the rupture of different bonds in the molecule. In addition, fragment peaks observed at m/z 311, 263, 234,194 and 105 are attributed to cleavage of $C_{20}H_{15}N_4$, $C_{15}H_{11}N_4O$, $C_{14}H_{10}N_4$, $C_{13}H_{10}N_2$ and $C_6H_5N_2$, respectively.

4.1.4. Thermogravimetric analysis (TG and DTA)

To estimate the stability of the complexes, thermogravimetric measurements for Mn (1:1 and 1:2) complexes were carried out at the atmosphere of nitrogen in the temperature range 25-800 °C. The TG curve of 1:1 shows a weight loss of 11.51% (Calc. 11.61%) from 150-378 °C, corresponding to the removal of three coordinated water molecules. In the temperature range 378-400 °C a weight loss of 3.23% (Calc. 3.60%) is observed corresponding to the loss of OH⁻. Then the decomposition of the ligand anion was followed in the temperature range 400-550 °C with a weight loss of 72.32% (Calc. 72.91%) corresponding to the departure of $C_{21}H_{15}N_4O$ (ligand). Constant weight is attained at around 550 °C. The end product, estimated as MnO, has an observed mass of 15.88% (Calc. 15.26%) which is in good agreement with the calculated values obtained by determination of the metal content after decomposition of the complex applying the method described by Macdonald [28] and with the results of elemental analysis (Table 1). 1:2 Complex exhibits a continuous weight loss in the temperature range of 223-800°C. The first weight loss (2.26%) in the range of 223-319 °C corresponds to the departure of one water molecule. The weight loss is consistent with the calculated value (2.39%). The decomposition of the ligand anions was followed in the temperature range of 319-557 °C. The observed mass loss (90.66) agrees with the calculated value (90.29%) due to the loss of the two ligands. The final residue is qualitatively proved to be MnO, the observed mass of 9.62% as compared to the calculated value of 9.45%. Differential thermal analysis curves (DTA) are characterized by the presence of a large and sharp exothermic peak on the DTA curves at the temperature range 437-438 for Mn-L1 (1:1 and 1:2) complexes. At these temperatures a phase change is occur due to the change in crystal structure of the complex, i.e. crystallographic phase transition. By increasing the temperature above these values the metallic oxide residue is formed.

4.1.5. Molar conductance measurements

The molar conductance values of the complexes in DMF (10⁻³ mol L⁻¹ solution at 25 °C) are found in the range 4.78-7.73 ohm⁻¹ cm² mol⁻¹. These values were small for the ionic complexes of the divalent metal ions [44,45]. These low conductivity ascribed to the absence of chloride ions rather than ionic association to the metal ions during complex formation indicating that the complexes are non-electrolytes in nature [46,47]. The conductivity values for all of the complexes are listed in Table 1.

4.1.6. Magnetic susceptibility measurements

The calculated magnetic moments of 1:1 and 1:2 (M:L) complexes for Mn(II) metal ion are 5.89 and 5.90 B.M., respectively. It indicates the presence of 5 unpaired electrons in its d-orbital ($\mu_{eff} = 5.92$ B.M) and shows a high spin d⁵ configuration $(t_{2a}^3 - e_a^2)$ [48] and supports the octahedral geometries of these complexes [49]. For Co(II) 1:1 and 1:2 complexes, the calculated magnetic moments of the complexes are 3.89 and 3.85 B.M., respectively. It shows the presence of three unpaired electrons per metal ion (μ_{eff} = 3.87 B.M.) which supports the octahedral geometries of these complexes [49], Table 1. For Ni(II) 1:1 and 1:2 complexes, the μ_{eff} are 0.32 and 0.45 B.M. representing no unpaired electrons ($\mu_{eff} = 2.83$ BM for paramagnetic) and showing diamagnetic properties and supports a low spin Ni(II) ion in square planar geometry [48]. The room temperature magnetic moment of Cu(II) complexes (1:1 and 1:2) are 1.77 and 1.78 BM, respectively, which is close to one electron paramagnetism ($\mu_{eff} = 1.73$ BM) of a mononuclear Cu(II) ion [50]. The Cu(II) ion center is five-coordinated [51] and this is typical for square pyramid or distorted square pyramid geometries. Thus, the geometry about the Cu(II) center in the complexes is closer to square pyramid. The data obtained are consistent with the reported literature for distorted square pyramidal Cu(II) complexes [52] For Zn 1:1 and 1:2 complexes, the calculated magnetic moment are 0.44 and 0.54 B.M. indicating the absence of unpaired electrons and Zn(II) complexes has a diamagnetic properties and Zn(II) ion centers are six-coordinated [51]

4.1.7. Electron spin resonance (ESR)

The solution spectra were carried out in DMF solution in capillary tube and recorded to confirm that the complexes do not undergo structural change in solution. The solution ESR spectra of Cu(II) complexes as illustrated in Figure 4 were studied and Hamiltonian parameters $g_{//}$, g_{\perp} were also calculated. The X-band ESR spectra of 1:1 Cu complexes at room temperature generally show two broad signals ($g_{//}$ and g_{\perp}) at 2.0559 and 2.0678. For 1:2 complexes, the signals appear at 2.0381 and 2.0714, respectively. For Cu(II) complexes, g_{ll} indicates covalence with $g_{ll} < 2.3$ for covalent and $g_{ll} \ge 2.3$ for ionic complexes [53,54]. The nature of ligand is calculated from G which is the gauss value. The parameter G measures the exchange interaction between the metal centers in a polycrystalline solid [55] and can be measured using the equation $G = (g_{//} - 2)/(g_{\perp} - 2)$. According to Hathaway et al. [56] if G > 4, the exchange interaction is negligible, while for G < 4 indicates considerable exchange interaction in the solid complexes. For G < 4.0, the ligand forming the complex is regarded as a strong field ligand in copper complexes [53] which can be attributed to trigonal bipyramid or distorted square pyramid around the Cu(II) ions. Moreover, the apparent broadening of the ESR signals may be due to an interaction between Cu(II) ions which are probably present in nonequivalent lattice position. The positive shift of g values from that of the free electron (2.0023) indicates a high covalent character of the bonding between the Cu(II) ions and the ligands [57,58], indicating a $d_x 2 - v^2$ ground state which is consistent with the electronic absorption spectroscopic assignments [59].

Based on the above results the structures of the complexes are formulated as seen below in Scheme 3. The proposed geometrical structures for the investigated metal complexes (1:1) suggest octahedral geometry for Mn, Co and Zn; square planar for Ni and square pyramidal structure for Cu. The proposed stereochemical structures for 1:2 complexes suggest square pyramidal structures and tetrahedral for Ni complex.

4.2. Molecular orbital treatment

4.2.1. Geometry of the Ligand

Geometry structures of the ligand L was optimized at the B3LYP/6-311G(d,p) level and the results are given in Table 4. The ketoamine H-N structure of L was

found to be the most stable tautomer while H-O and H-C tautomers have 23.31 and 34.04 kcal/mol higher than H-N structure, which is explained by the hydrogen bond O--H-N stabilizing H-N tautomer as seen in Figure 5. Experimental and computational data for similar ligand revealed that ketoamine H-N tautomeric form predominates for the azomethines of 1-phenyl-3-methyl-4-formylpyrazole-5-one both in solutions and in the solid state [60,61].

Our obtained results show that the ligand L has a complete coplanar structure as indicated by the dihedral angles of the phenyl rings attached to the pyrazolone ring. On complexation, L loses the hydrogen atom converting to the anion form L⁻. The calculated natural charges of the expected chelating centers of L are given in Table 5. It is clear from this presented data that the natural charge on O6 atom is -0.641, while on N7 is -0.245 and on N8 is -0.297 which indicates the suitability of O6 and N8 atoms as chelating centers for coordination to the positively charged metal ions.

4.2.2. Geometry of the complexes

As mentioned before, the ligand is coordinated to the metal ions as a bidentate one through pyrazolonic-oxygen O6, and azo-nitrogen N8, forming a six membered ring. The coordination number of each metal ion is completed by hydroxyl group and oxygen of the water molecules. This perception was experimentally confirmed by the results of the IR spectra of both free ligand and the complexes, Table 2, as indicated by the shift of vN=N band, the disappearance of vC=O band and appearance of a new band corresponding to vC-O on complex formation. Also, the presence of broad band in the range 3355-3494 cm⁻¹ corresponding to coordinated water molecules and coordinated OH^{-} ion as well as new bands which may assigned to (M \leftarrow N) and $(M \leftarrow O)$ stretching frequencies [42] confirming that they are center of chelation. The thermodynamic stability of the various chelated structures of 1:1 M:L (OH)(OH₂)_n, n=1,2 or 3, and 1:2 complexes were calculated using the B3LYP method and the mixed basis sets 6-311G(d,p) and LANL2DZ. The calculated results showed that, the best optimized geometry located of the Zn-L (OH)(OH₂) complex is the tetrahedral structure and the octahedral one, Zn-L (OH)(OH₂)₃. Nevertheless the trigonal bipyramid or square pyramid structures were not located as local minima.

The tetrahedral form was obtained with the second water molecule existing in the

hydration sphere, the distance $H_2O...Zn = 3.187$ Å. The two structures, tetrahedral and octahedral, are energetically stable i.e. as two minima at this level but the latter one formed, isolated and has the highest negative ΔG_{f} , therefore it will be considered as the lonely complex in this study. The same results were also found in case of Mn-L (OH)(OH₂)₃ and Co-L(OH)(OH₂)₃ complexes. On the other hand the calculations at the same level showed that the most stable structure of copper complex, Cu-L $(OH)(OH_2)_2$, is the trigonal bipyramid one while the distorted square planar structure was obtained for nickel complex, Ni-L(OH)(OH₂). In the latter two cases the distance between the third water molecule and Cu ion is 3.191 Å and in case of Ni the distances are 3.308 and 3.644 Å, respectively, implying that these water molecules subsist in the hydration sphere. The above obtained complexes are stabilized by the formation of six membered rings and existence of hydrogen bonds of different strengths with the coordinated OH⁻ and H₂O; 1.704 Å and 1.821 Å, respectively. The geometrical parameters of the most stable structures of the ligand and the investigated 1:1 and 1:2 complexes are quoted in Table 4. For all complexes the C=O6 bond distance does not appreciably affected while the calculated N7-N8 bond distance for Zn, Co and Mn complexes elongates by 0.01 Å while for Cu and Ni complexes it shortens comparing with the free ligand. In our calculations, the computed M-N8 and M-O6 bond lengths are predicted near 2.24 and 1.91 Å, respectively, which are in good agreement with the available experimental values [51,62,63], Table 4. One also notices that, the ligand moiety became non-planar where the phenyl groups rotate out of the pyrazolone moiety plane.

In case of 1:1 octahedral structure, Mn, Co and Zn metal ions are coordinated in the equatorial plane to the O6, azo-nitrogen N8, O28 of the hydroxyl group and oxygen of the water molecule, O30, while the oxygen of the other two water molecules O29 and O31 are positioned in the apical site, Figure 5. Also, it can be noted that metal ion deviates out of the equatorial plane by the angle \angle C1N7N8M \approx 6.7-8.7° and \angle C1C5O6M \approx 11.7–16.5° leading to a distorted octahedral structure. The same finding is also confirmed by the angle value of \angle O30MO29 which has a value of 76.46°. The effect of metal ion size on the geometrical parameters of the chelation is well noticed by the variation of the values of M-X bond distances. Zn complex has the longest distances. The presence of H-bond interactions of different strengths with the O28 atom of the hydroxyl group influences the bond lengths around

the metal ion. In the case of the trigonal bipyramid structure of copper complex, [Cu- $L(OH)(OH_2)_2$], the calculated results showed that the basal plane is occupied by the O6, azo-nitrogen N8, and O28 of hydroxyl group coordinated to copper ion while the two oxygen of the water molecules O29 and O31 are located in the apical site. Finally, the bond lengths of the distorted square planar structure obtained for nickel complex are shorter than those of the other complexes.

In case of 1:2 [M-L(OH₂)_n, n=0,1], the B3LYP results show that also the metal ions coordinated with each L⁻ via oxygen atoms of the carbonyl groups, O6 and O28, and α -N atoms of the azo groups, N8 and N29, Figure 5. The thermodynamical findings indicated that, the best optimized geometry located of the Ni-2L complex is the distorted tetrahedral structure while the other studied metal complexes behave as distorted trigonal bipyramid M-2L(OH₂). In each case two six membered rings stabilize the complexes and the phenyl group substituents rotate out to avoid the steric hindrance. Table 4 displays the geometrical parameters of these complexes. In comparison of 1:1 with 1:2 complexes, one notices that the maximum difference between the corresponding parameters of the coordination sphere, Δr is 0.04Å. The basal plane of the trigonal bipyramid M-2L(OH₂) is occupied by the O6, azonitrogens N8, and N28 coordinated to metal ion while O28 and oxygen of water molecule O54 are positioned in the apical site. Our computed values are in very good agreement with the available experimental values [51,62-63].

It is well known that the study of the molecular orbital compositions and energy levels of the molecule is very important in describing the electronic characteristics of molecular systems. E_{HOMO} characterizes its electron donating ability, while E_{LUMO} energy characterizes the electron withdrawing ability. Moreover, the difference between E_{HOMO} and E_{LUMO} , Energy gap E_g , depicts the molecular chemical stability and electron conductivity thus it is an essential factor in determining molecular electrical transport. The spatial distribution of frontier MOs, HOMO and LUMO acidic L form of the ligand is given in Figure 6. The calculated values of E_{HOMO} and E_{LUMO} of L are respectively, -0.21806 and -0.10758 au, thus the corresponding energy gap value E_g is 3.01 eV. The HOMO of L resides on pyrazolone moiety and the two attached phenyl groups while the LUMO is mainly localized on pyrazolone and the phenyl azo moiety. Table 6, Figures 7 and 8 list the partial frontier molecular orbital compositions and energy levels of the investigated complexes in the ground state.

These results show that the HOMO of the 1:1 complexes is lying within the range 5.55-5.94 eV. Comparing with the values corresponding to the acidic form of ligand, it can be noted that the chelation process does not appreciably affect E_{HOMO} but leads to destabilization of the LUMO except of Zn case. Cu and Zn complexes have the most stable HOMO whereas Mn complex is the lowest stable. On the other hand, the LUMO values are 2.27-3.35 eV whereas Zn complex has the most stable LUMO and the lowest stable one is found for Mn complex. The ionization potential of the investigated complexes can be explicated as IP \sim -E_{HOMO}, and the electron affinity as, $EA \sim -E_{LUMO}$. The computed ionization potential values of the free ligand and its complexes can be arranged as: Mn <Co < Ni < L ~ Zn ~Cu, whereas the electron affinity values have the order: Mn< Ni < Cu < Co < L< Zn. The electron density in the HOMO of Co complexes is nearly extended overall the molecule except of water molecule. In case of Ni, Cu and Zn complexes, the electron density in the HOMO is mainly localized on pyrazolone and the two attached phenyl groups, azo moiety as well as the metal ion. While the electron density in the LUMO is mainly localized on the pyrazolone ring and phenyl group attached to the N=N bond along with some metal d orbital.

4.2.3. Global reactivity descriptors

The energy difference between the HOMO and LUMO, E_g , of the studied complexes occurs in the range 3.54-2.60 eV. The energy gap for Cu complex is the maximum (3.54 eV) while Zn complex has the minimum (2.59 eV) value. It is also worth noting that E_g values of Mn and Co complexes are of the same magnitude. Similar observation is also noticed for Cu and Ni complexes. As a result, charge transfer and polarization can easily occur within the Zn complex than other complexes with more reactivity. The chemical hardness, η , electronegativity, χ , chemical potential, μ , and global softness, S, were calculated using HOMO and LUMO energies and listed in Table 6. Zn complex has the lowest η and maximum S values which means that the charge transfer occurs easily in this complex and has a lower chemical hardness. It can be concluded that the large E_g gap indicates a hardness of the molecule, while smaller E_g gap is a characteristic for a soft and reactive molecule. The collected data in Table 6 show that the HOMO of the 1:2 complexes are less stable than that of the 1:1 complexes and the acidic form of ligand which is reflected on their IP values. Thus, the ionization potential values of the 1:2 complexes are less than those of 1:1 complexes, except for Mn. On the other hand, LUMO of 1:2 complexes of Co, Cu and Zn are destabilized while that of Mn and Ni are stabilized comparing with the values of the 1:1 complexes. Therefore, their electron affinity values have the order: Co < Cu < Zn < Mn < Ni. Consequently, the obtained energy gap E_g, for 1:2 Co complex has the maximum value (3.48 eV) while that of Ni complex is the minimum (2.83 eV). Therefore, charge transfer and polarization can easily occur within the Ni complex than the other complexes due to its higher reactivity. The computed reactivity parameters shown in Table 6 reveals that Ni complex has the lowest η and maximum S values which means that the charge transfer occurs in this complex and has lower chemical hardness.

4.2.4. Natural charges and natural population

The calculation of atomic charges is a very important in describing the electronic characteristics of the molecular systems. Natural atomic charges of the metal ions and those atoms where coordinated to them for the studied complexes are collected in Table 7. It can be noticed that the calculated charge on the metal ion is considerably lower than its formal charge of +2. This is due to significant charge donation from the O6, N7, N8 and the pyrazolone ring. The charge on the N8-donor center is significantly smaller and less negative than the charge on the oxygen atom of C=O6 group, indicating that there is higher electron density delocalization from the N-donor center to the metal ion. The highest observed natural positive charge (1.252) of Zn ion is attributed to the completely filled d¹⁰ orbital, while the lowest natural positive charge (0.684) is observed in case of Mn ion. It is evident from Table 7, the central metal ion coordinates with the coordinating atoms via mostly the 3d, 4s and 4p orbitals, e.g. the electronic arrangement of Mn ion is [core]4s^{0.11}3d^{3.34}4p^{0.20}4d^{0.01}. The contribution of 4d and 5p orbitals is negligible except of Zn ion where the electron number of 5p orbital is 0.50. Both oxygen and nitrogen atoms of the ligands are bonded through 2s and 2p orbitals. The natural charge distribution of metal ion and the donating atoms of 1:2 complexes are similar as in case of 1:1 complexes. The calculated natural positive charge on each metal ion observed in case of 1:1

complexes is lower than that of 1:2 complexes suggesting that lower donation in case of the later. This variation in natural charges distribution on the different centers of the two types of complexes is reflected on their dipole moments. 1:2 complexes have higher values of dipole moment except of Ni one.

4.2.5. Nonlinear optical properties (NLO)

The distribution of the atomic charges in the complexes is also valuable in the determination of the magnitude and direction of its moment vector which depends on the centers of negative and positive charges. The dipole moment, the mean polarizability, the anisotropy of the polarizibility and the first-order hyperpolarizibility for the studied free ligand and all complexes as well as urea was calculated using the same level and the obtained values are tabulated in Table 8. The table also contains the experimental values of urea. Our calculated dipole moment value of the free ligand in the gas phase is 2.52 D. The three complexes Mn, Co and Zn in the octahedral form have higher dipole moment values than L while those of Cu and Ni complexes are lower which is attributed to that the dipole moment vectors of different moieties of the first complexes are of the same direction. Table 8 also shows that 1:2 complexes have higher dipole moment values than the corresponding 1:1 complexes except of Ni. On the other hand the calculated values of the polarizability of 1:1 complexes have the range 24.10-26.63x10⁻²⁴ (esu). Ni complex has the lowest calculated value and Mn complex has the highest value. In case of 1:2 complexes the values are lower than that of 1:1 complexes. Compared with urea [64] as a reference compound, all the studied complexes have higher polarizability and first-order hyperpolarizability values indicating that they are expected to be an effective candidate for NLO materials.

5. Conclusion

From the experimental data obtained for the ligand and its complexes, 1:1 and 1:2 complexes are isolated and characterized. The metal complexes of the ligand were prepared and subjected to different analytical and spectroscopic techniques such as elemental analysis, IR, ¹H NMR, mass spectra, Thermal analysis (TG and DTA),

magnetic susceptibility, molar conductance, electron spin resonance and Density Function Theory (DFT). 1:1 complexes of Mn(II), Co(II) and Zn(II) are distorted octahedral whereas Ni(II) complex is square planar and Cu(II) is distorted trigonal bipyramid stryctures. 1:2 complexes of Mn(II), Co(II), Cu(II) and Zn are distorted trigonal bipyramid whereas Ni(II) complex is distorted tetrahedral. All complexes behave as non-ionic in dimethyl formamide (DMF). The molecular geometry of the studied 1:1 and 1:2 complexes in the ground state have been calculated by using DFT-B3LYP/GEN level of theory. The optimized structures of the studied complexes are nonlinear with the metal ion and are not in the same plane as the donating sites. The HOMO-LUMO energy gap helped in analyzing the chemical reactivity, hardness, global softness, chemical potential and electronegativity. The computed ionization potential values of the free ligand and its complexes are arranged as: Mn <Co < Ni < $L \sim Zn \sim Cu$, whereas the electron affinity values have the order: Mn < Ni < Cu < Co < L< Zn. The electron affinity values have the order: Co < Cu < Zn < Mn < Ni. Consequently, the obtained energy gap E_g , for 1:2, Co complex has the maximum value (3.48 eV) while that of Ni complex is the minimum (2.83 eV). Natural charge distribution of the studied complexes was studied which indicated the electronic charge distribution in the complexes. The calculated dipole moment and first-order hyperpolarizability results indicate that the complexes have acceptable good nonlinear optical behavior.

Acknowledgement

The authors are grateful to thank Chemistry Department, Faculty of Science, Helwan University which supporting this study.

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Fig. 1. FT-IR spectra of L and its Mn complexes.





Fig. 2. NMR spectra of L and its Zn complexes.





Fig. 3. Mass spectrum of the investigated ligand (L).



Fig. 4. ESR spectra of Cu-L (1:1 and 1:2) complexes.



Fig. 5. The optimized structures, the vector of the dipole moment and numbering system of L using B3LYP/6-311G** and its 1:1 and 1:2 complexes using B3LYP/GEN level.



Fig. 6. HOMO and LUMO charge density maps of of the investigated ligand (L) using B3LYP/6-311G** level.

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Fig. 7. HOMO and LUMO charge density maps of 1:1 complexes using B3LYP/GEN level.



Fig. 8. HOMO and LUMO charge density maps of 1:2 complexes using B3LYP/GEN level.



Scheme 1. Structural formula of the investigated ligand (L)



Scheme 2. Azo-hydrazo tautomerism of the investigated ligand



Elemental analysis, molar conductance (Λ m) and magnetic moment (μ_{eff}) of the ligand and its studied complexes

				С%	Н%	N%	M%		
Ligand/ Complexes	M:L	Empirical formula	M. Wt.	(Calcd.)	(Calcd.)	(Calcd.)	(Calcd.)	$\Lambda_{\rm m}$	$\mu_{\rm eff}$
		-		Found	found	found	found		
(L)	-	$C_{21}H_{16}N_4O$	340	(74.12)	(4.71)	(16.47)			
				74.44	5.03	16.64			
$[Mn(L).OH.3H_2O]$	1:1	$C_{21}H_{22}MnN_4O_5$	464.94	(54.20)	(4.73)	(12.04)	(11.82)	6.66	5.89
				54.37	4.89	12.24	11.41		
$[Mn(L)_2.H_2O]$	1:2	$C_{42}H_{32}MnN_8O_3$	750.94	(67.12)	(4.26)	(14.91)	(7.32)	4.78	5.90
				67.03	4.01	14.55	7.43		
$[Co(L).OH.3H_2O]$	1:1	$C_{21}H_{22}CoN_4O_5$	468.93	(53.74)	(4.69)	(11.94)	(12.57)	7.08	3.89
				53.78	4.76	11.68	12.42		
$[Co(L)_2.H_2O]$	1:2	$C_{42}H_{32}CoN_8O_3$	754.93	(66.76)	(4.24)	(14.84)	(7.28)	5.10	3.85
				66.99	4.38	14.48	7.28		
[Ni(L).OH.H ₂ O]	1:1	$C_{21}H_{18}NiN_4O_3$	432.69	(58.24)	(4.16)	(12.94)	(13.56)	7.06	0.32
			\sim	58.35	4.36	12.78	13.18		
$[Ni(L)_2.H_2O]$	1:2	C ₄₂ H ₃₂ NiN ₈ O ₃	754.69	(66.78)	(4.24)	(14.84)	(7.78)	5.03	2.91
				66.46	4.20	14.59	7.62		
$[Cu(L).OH.2H_2O]$	1:1	$C_{21}H_{20}CuN_4O_4$	455.55	(55.32)	(4.39)	(12.29)	(13.95)	7.55	1.77
				55.13	4.41	12.46	13.76		
$[Cu(L)_2.H_2O]$	1:2	$C_{42}H_{32}CuN_8O_3$	759.55	(66.36)	(4.21)	(14.75)	(8.37)	5.37	1.78
				66.13	4.08	14.53	8.54		
$[Zn(L).OH.3H_2O]$	1:1	$C_{21}H_{22}ZnN_4O_5$	475.39	(53.01)	(4.63)	(11.78)	(13.76)	7.73	0.44
				53.10	4.57	11.66	13.44		
$[Zn(L)_2.H_2O]$	1:2	$C_{42}H_{32}ZnN_8O_3$	761.39	(66.91)	(4.20)	(14.71)	(8.59)	5.51	0.54
				66.76	4.07	14.50	8.38		
		7							

IR spectral bands of L and its complexes with Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) metal ions

Ligand/Complexes		Band Assignment							
	M:L	ν_{OH}	$\nu_{C=N}$	$\nu_{C=C}$	$\nu_{N=N}$	ν_{C-O}	ν_{M-N}	v _{M-O}	
L		3429	1594	1550	1496	-	Ò	-	
Mn-L	1:1	3413	1596	1550	1488	1265	590	489	
Mn-L	1:2	3444	1596	1550	1488	1265	590	489	
Co-L	1:1	3448	1593	1550	1492	1218	520	416	
Co-L	1:2	3494	1554	1554	1492	1218	513	474	
Ni-L	1:1	3425	1658	1550	1488	1265	510	424	
Ni-L	1:2	3363	1658	1581	1488	1211	528	416	
Cu-L	1:1	3355	1654	1558	1488	1222	567	428	
Cu-L	1:2	3440	1654	1558	1488	1218	509	424	
Zn-L	1:1	3386	1666	1596	1485	1242	532	424	
Zn-L	1:2	3388	1666	1594	1488	1247	535	429	

¹H NMR spectral bands of the investigated ligand (L) and its Zn complexes

Ligand and complexes	Chemical Shift	Assignment
L	13.7 8.19-7.23	NH hydrazone Aromatic C-H protons
Zn-L (1:1)	16.6 8.19-6.71 3.32	Coordinated OH- Aromatic C-H protons Coordinated H ₂ O molecules
Zn-L (1:2)	8.18-7.05 3.37	Aromatic C-H protons Coordinated H ₂ O molecules

Some selected geometrical parameters for the investigated ligand (L) and its 1:1 and 1:2

	M:L	L	Mn	Со	Ni	Cu	Zn
Bond lengths (Å)							
C5=O6	1:1	1.264	1.268	1.262	1.276	1.26 7	1.263
	1:2	$(1.239)^{a}$	1.278	1.263	1.274	1.268	1.273
N=N	1:1	1.345	1.296	1.287	1.279	1.280	1.288
	1:2	$(1.309)^{a}$	1.295	1.281	1.288	1.286	1.290
M-O	1:1	-	1.973	1.947	1.912	1.997	2.049
			(1.922) ^b	(1.967) ^c	(1.995) ^d	$(1.930)^{d}$	$(2.026)^{d}$
	1:2		1.956	1.953	1.922	2.058	2.013
M-N	1:1	-	2.067	2.065	1.922	2.042	2.241
			(2.014) ^b	(1.997)°	$(2.005)^{d}$	$(2.012)^{d}$	$(2.226)^{d}$
	1:2		2.063	1.997	1.964	2.064	2.191
M-OH	1:1	-	1.985	1.944	1.840	1.911	2.034
M-OH ₂	1:1	-	2.153	2.299	1.963	2.436	2.227
	1:2		2.134	2.134	-	2.324	2.224
HOH ₂	1:1	-	1.773	1.803	1.821	1.763	1.831
Bond angles/°							
<o6mn8< td=""><td>1:1</td><td></td><td>92.85</td><td>45.46</td><td>95.79</td><td>92.75</td><td>87.65</td></o6mn8<>	1:1		92.85	45.46	95.79	92.75	87.65
	1:2		45.95	92.82	43.50	44.78	47.65
<o6mo31< td=""><td>1:1</td><td></td><td>86.91</td><td>87.75</td><td>87.68</td><td>90.29</td><td>86.43</td></o6mo31<>	1:1		86.91	87.75	87.68	90.29	86.43
<o6mn29< td=""><td>1:2</td><td></td><td>47.35</td><td>87.66</td><td>47.24</td><td>46.90</td><td>46.80</td></o6mn29<>	1:2		47.35	87.66	47.24	46.90	46.80
<o6mo30< td=""><td>1:1</td><td></td><td>85.28</td><td>85.98</td><td>31.43</td><td>95.84</td><td>85.43</td></o6mo30<>	1:1		85.28	85.98	31.43	95.84	85.43
<o6mo54< td=""><td>1:2</td><td>\frown</td><td>13.32</td><td>154.04</td><td>-</td><td>49.53</td><td>24.80</td></o6mo54<>	1:2	\frown	13.32	154.04	-	49.53	24.80
Dihedral angles/°							
C1C5O6M27	1:1		11.66	16.54	0.55	10.40	16.22
	1:2		0.72	1.28	-10.99	4.30	-0.26
C5O6M27O29	1:1		-119.19	-128.68	3.31	-116.34	-117.92
	1:2		26.20	13.36	179.21	1.22	47.00
C1N7N8M 27	1:1		-8.10	6.74	-5.55	-9.50	-8.73
C5O6M27N8	1:2		0.17	-174.94	14.76	6.06	-0.92

complexes using B3LYP level

a, b, c, d The experimental data from references 61, 51, 62 and 63

	L	Mn	Со	Ni	Cu	Zn
1:1						
06	-0.667	-0.684	-0.600	-0.659	-0.706	-0.724
N8	-0.322	-0.287	-0.284	-0.280	-0.323	-0.436
М		0.684	0.630	0.692	0.884	1.252
N7	-0.183	-0.203	-0.310	-0.149	-0.153	-0.263
OH	-	-1.042	-0.984	-0.935	-1.007	-1.154
OH_2		-0.832	-0.833	-0.834	-0.882	-0.938
OH_2	-	-0.847	-0.870	-	-0.892	-0.956
OH_2	-	-0.829	-0.840	-	-	-0.904
1:2						
O6		-0.631	-0.628	-0.634	-0.664	-0.755
(O28)		(-0.636)*	(-0.660)	(-0.657)	(-0692)	(-0.778)
N8		-0.294	-0.283	-0.288	-0.316	-0.389
(N29)		(-0.272)	(-0.267)	(-0.276)	(-0.328)	(-0.405)
Μ		0.702	0.713	0.700	0.864	1.309
N7		-0.177	-0.152	-0.154	-0.151	-0.167
(N30)		(-0.181)	(-0.160)	(-0.147)	(-0.148)	(-0.152)
OH ₂		-0.847	-0.899		-0.925	-0.951

NBO charges calculated for 1:1 and 1:2 complexes using B3LYP level

*Values between brackets correspond to 2nd ligand

 E_{HOMO} and E_{LUMO} , ionization energy, I, electron affinity, A, energy gap, E_g , electronegativity, χ , global softness, S, hardness η , and chemical potential, μ , of the studied 1:1 and 1:2 complexes using B3LYP level.

Parameter	L	Mn	Со	Ni	Cu	Zn
E _{HOMO} , a.u.	-0.2181	-0.2041	-0.2137	-0.2156	-0.2185	-0.2182
		(-0.2103)*	(-0.2026)	(-0.2157)	(-0.2046)	(-0.2041)
E _{LUMO} , a.u.	-0.1076	-0.0835	-0.0889	-0.0876	-0.0882	-0.1231
		(-0.0881)	(-0.0748)	(-0.1116)	(-0.0813)	(-0.0797)
Eg, eV	3.0100	3.280	3.395	3.482	3.544	2.587
0		(3.324)	(3.476)	(2.832)	(3.354)	(3.384)
I, eV	5.9323	5.554	5.813	5.864	5.943	5.935
		(5.720)	(5.513)	(5.867)	(5.567)	(5.554)
A, eV	2.9267	2.271	2.418	2.383	2.399	3.348
		(2.396)	(2.035)	(3.036)	(2.211)	(2.168)
χ, eV	4.4295	3.911	3.915	4.124	4.171	4.642
		(4.058)	(3.773)	(4.451)	(3.888)	(3.860)
η, eV	1.5030	1.640	1.697	1.741	1.772	1.293
		(1.662)	(1.738)	(1.416)	(1.677)	(1.692)
S, eV ⁻¹	0.3322	0.305	0.295	0.287	0.282	0.387
		(0.301)	(0.288)	(0.420)	(0.298)	(0.296)
μ, eV	-4.4295	-3.911	-3.915	-4.124	-4.171	-4.642
• -		(-4.058)	(-3.773)	(-4.124)	(-3.888)	(-3.860)

*Values between brackets correspond to 1:2 Complexes

5

Calculated natural charge, natural population and natural electronic configuration of metal in the studied complexes using B3LYP level

Complex	M:L	Natural charge	Core	Natura Valence	l population Rydberg	Total	Natural electronic configuration
Mn	1:1	0.6843	17.9948	6.2941	0.02675	24.3157	[core]4s ^{0.22} 3d ^{5.68} 4p ^{0.39} 4d ^{0.02} 5p ^{0.01}
	1:2	0.7019	17.9897	6.2844	0.02388	24.2980	$[\text{core}]4\text{s}^{0.21}3\text{d}^{5.71}4\text{p}^{0.36}4\text{d}^{0.02}$
Со	1:1	0.771	17.9964	8.2156	0.0173	26.2293	$[core]4s^{0.25}3d^{7.54}4p^{0.42}4d^{0.01}5p^{0.01}$
	1:2	0.7133	17.9937	8.2788	0.0142	26.2867	$[core]4s^{0.25}3d^{7.62}4p^{0.41}4d^{0.01}5p^{0.01}$
Ni	1:1	0.6917	17.9956	9.2985	0.0141	27.3083	[core]4s ^{0.33} 3d ^{8.67} 4p ^{0.30}
	1:2	0.6999	17.9937	9.2983	0.0081	27.3001	$[core]4s^{0.29}3d^{8.69}4p^{0.32}$
Cu	1:1	0.8844	17.9971	10.1044	0.0141	28.1156	$[core]4s^{0.31}3d^{9.41}4p^{0.39}5p^{0.01}$
	1:2	0.8636	17.9969	10.1307	0.0089	28.1364	$[core]4s^{0.29}3d^{9.42}4p^{0.42}5p^{0.01}$
Zn	1:1	1.2522	18.0000	10.7294	0.0183	28.7478	$[core]4s^{0.26}3d^{9.97}4p^{0.02}5p^{0.50}$
	1:2	1.3086	18.0000	10.6845	0.0069	28.6913	[core]4s ^{0.33} 3d ^{9.98} 4p ^{0.37}

Calculated total static dipole moment (μ), the mean polarizibility $\langle \alpha \rangle$, the anisotropy of the polarizibility $\Delta \alpha$ and the first-order hyperpolarizibility $\langle \beta \rangle$ for the studied 1:1and 1:2 complexes using B3LYP level

Property	Urea	L	Mn	Со	Ni	Cu	Zn
1:1					6		
μ, D	1.3197	2.5200	3.1231	3.9706	1.7275	1.4304	4.3957
<α>, esu	-	2.074x10 ⁻²³	26.635x10 ⁻²⁴	26.493x10 ⁻²⁴	24.136x10-24	25.305x10 ⁻²⁴	26.167x10 ⁻²⁴
$\Delta \alpha$, esu	-	2.9917x10 ⁻²⁴	1.2496x10 ⁻²⁴	1.5951x10 ⁻²⁴	2.9534x10 ⁻²⁴	3.0350x10 ⁻²⁴	1.9210x10 ⁻²⁴
<β>, esu	0.1947 x 10 ⁻³⁰	0.53821x10 ⁻³⁰	1.6264x10 ⁻³⁰	1.6595x10 ⁻³⁰	1.8379x10 ⁻³⁰	1.9541x10 ⁻³⁰	2.4292x10 ⁻³⁰
1:2							
μ, D	-	-	5.1861	4.8583	1.6918	3.9080	4.8089
<α>, esu	-	-	4.4653x10 ⁻²³	4.3648x10 ⁻²³	4.3402x10 ⁻²³	4.3593x10 ⁻²³	4.3612x10 ⁻²³
$\Delta \alpha$, esu	-	-	5.9059x10 ⁻²⁴	3.5661x10 ⁻²⁴	4.2502x10 ⁻²⁴	3.5780x10 ⁻²⁴	3.3846x10 ⁻²⁴
<β>, esu	-	-	1.5684x10 ⁻³⁰	0.46318x10 ⁻³⁰	0.59808x10 ⁻³⁰	0.98783x10 ⁻³⁰	1.1839x10 ⁻³⁰