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# Unreported Coordination Behavior of A Squaric Bis (Hydrazone) Ligand

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## Abstract

*A compartmental tetrabasic hexadentate ligand ($H_4L$) -has two symmetrical NNO sets of donor atoms- was synthesized by the condensation of squaric acid with a hydrazino triazine compound. The reaction of the ligand with Pd(II), Fe(III), Co(II), Ni(II), Cu(II), VO(II) and $UO_2$(II)- ions afforded mono- and binuclear as well as dimeric complexes. The ligational behavior of the ligand is highly affected by the type of the metal ion and its counter anion. The isolated complexes reflect the structural diversity (pentagonal bipyramid, octahedral, square pyramid and square planar) as well as the versatile coordination bonding modes. The size of the cation has proved to be of importance in directing the synthetic pathway. Structural elucidation of the isolated complexes was achieved via elemental and thermal analyses as well as spectral studies.*

**Key words:** *Squarichydrazones, coordination and bridging ability, transition metal complexes, magnetic properties.*

## Introduction

Squaric acid (3,4-dihydroxy-3-cyclobutene-1,2-dione) and its derivatives are important for synthesis of squaryl dyes, that absorb and emit light in the red and near infrared spectral regions. These dyes are widely used as fluorescent labels and probes for medical and biological research, in photo-electrochemical batteries and storage devices[1-3]. From the view point of crystal engineering, squaric acid is also a useful tool for constructing crystalline architectures, because of its rigid and flat four-membered ring framework, and its proton donating and accepting capabilities for hydrogen bonding[4]. From the view point of coordination chemistry, due to the presence of several potential donor oxygen atoms, increasing attention has been devoted to the study of the coordination chemistry of the squarate ligand by both inorganic and bioinorganic chemists for about two decades[5-7]. In our previous studies[8,9], squaric acid was used as a precursor to create symmetrical bis(carbazone or hydrazone) by condensation with thiosemicarbazide[8] or 2-(5,6-diphenyl -1,2,4-triazin-3-yl)hydrazide[9], respectively. Herein, the current study is planned to check the ligational behavior of the entitled ligand; 3,4-bis{[2-(5,6-diphenyl-1,2,4-triazin-3yl)hydrazono}cyclobut-1-ene-1,2-diol ($H_4L$; Scheme 1) towards the sulfates and/or chlorides of some transition metal ions.

## Material and Methods

Squaric acid, thiosemicarbazide, benzil, hydrazine hydrate, metal salts, EDTA and nitric acid were Aldrich, BDH or Merck products. Organic solvents were reagent grade chemicals and were used without further purification.

**Synthesis of Squaric bis(hydrazone); $H_4L$:** Squaric bis(hydrazone); ($H_4L$) was prepared as described in our previous study[9] by reacting squaric acid (1.14g; 10 mmol) with 2-(5,6-diphenyl-1,2,4-triazin-3-yl)hydrazide (5.27 g; 20 mmol) in 30 mL absolute ethanol. The reaction mixture was heated under reflux for 2h and the deep brown precipitate was filtered off, recrystallized from DMF; m.p. 200°C (yield: 85%).

**Synthesis of the Complexes:** A methanolic solution of metal salt was added gradually to a methanolic solution of the squaric hydrazone ($H_4L$) in the mole ratio 2 : 1 (M:L). Then, the reaction mixture was refluxed for 2 h. The solid complexes were precipitated, filtered off, washed with methanol and finally ether and then dried in *vacuo*. All the isolated complexes are stable at room temperature, non hygroscopic and insoluble in water and alcohols, soluble or partially soluble in DMSO and DMF. The melting points of the complexes were above 300°C. The molar conductance in DMF indicates a non-electrolytic nature for the soluble complexes. The results of elemental analyses are listed in table1.

**Physical Measurements:** Microanalyses were carried out on a Perkin- Elmer 2400 CHN elemental analyzer. The complexes were analyzed for their metal content by EDTA titration. Analyses of the metal ions followed decomposition of their complexes with concentrated nitric acid. The resultant solution was diluted with doubly distilled water and filtered off. The solution was then neutralized with aqueous ammonia solution and the metal ions were titrated with EDTA. Thermal analyses (TG-DSC) were carried out on a Shimadzu-50 thermal analyzer in nitrogen atmosphere (30 mL/min) and heating rates of 10°C/min. Electronic spectra were recorded on a Jasco V-550 UV/VIS spectrophotometer. IR spectra were recorded on a Bruker Vector 22 spectrometer using KBr pellets. ESR spectra were recorded on a Bruker Elexsys, E 500 operated at X- band frequency. Mass spectra were recorded at 70 eV on a gas chromatographic GCMSQP 1000-EX Shimadzu mass spectrometer. Molar conductivity was measured as DMF solutions on the Corning conductivity meter NY 14831 model 441. Magnetic susceptibility of the complexes was measured at room temperature using a Johnson Matthey, MKI magnetic susceptibility balance. Melting points were determined using a Stuart melting point apparatus.

## Results and Discussion

**On the Coordination Ability of the Ligand ($H_4L$):** The bi-functionality of squaric acid was used to create a tetrabasic hexadentate compartmental ligand. The most motivating feature of the ligand ($H_4L$) is that it has two symmetrical NNO sets of donor atoms, in addition to its flat four- membered cyclobutene ring backbone bearing two adjacent triazinyl hydrazone arms. The ligand was chosen due to its novelty as well as its versatile coordination bonding modes. The ligand can bind one or two metal ions in various ways supporting its ambidentate and flexidentate characters. The ligand was allowed to react with the metal ions as chlorides or sulfates at the mole ratio 2:1 (M:L). Depending on the type of the metal ion and its counter anion, these reactions afforded mono- and binuclear as well as dimeric complexes (schemes 2, 3). The ligand showed a variety of modes of bonding *viz.* $(NNNN)^{2-}$, $(NN)^0$, $(NO)^-$ or $(OO)^{2-}$ per each metal ion. Structural elucidation of the isolated complexes was achieved *via* elemental and thermal analyses as well as electronic, vibration, ESR and mass spectra in addition to conductivity and magnetic susceptibility measurements. The proposed structures of the complexes are in good agreement with their analytical data (Table 1). Complex 8 has a unique mode of bonding and is even more stable since it contains a system of alternate double and single bonds (conjugate system). The $\pi$ electron density is delocalized and spread over the system, which is said to be stabilized by resonance. The basal equatorial plane is occupied by four N-atoms in which the copper(II)-ion is encapsulated in a macro system like. By such mode the ligand squeezes its two triazinyl arms to create a cavity of the right size to accommodate one Cu(II)- ion. This mode reflects the high affinity of Cu(II)- ions for N-donors[8]. The size of the metal ion has proved to be of importance in directing the synthetic pathway. Another unique mode of bonding was obtained in case of the Fe(III)- and $UO_2$(II)- complexes (complexes **2** and **10**) in which $H_4L$ acts as a dibasic bidentate; $(OO)^{2-}$ using its two squarate oxygens after releasing the hydrogen ions. This mode reflects the high affinity of Fe(III)- and $UO_2$(II)- for O-donors as expected. Arguments supporting the bonding mode in complex (**7**) begin with the observation that a pronounced decrease in its $\mu_{eff}$ value was obtained which was taken as a good evidence for its dimeric structure with two adjacent copper(II)- ions. Also, for the square pyramid complexes (5, 7), the apical position is occupied by a water molecule. On the other side, complexes 4, 6, 7 and 9 summarize for the polymeric nature of squaryl complexes[2,5]. Finally, the extra stability of all complexes was achieved *via* H- bonding (schemes 2, 3).

**IR spectra of the Metal Complexes:** The IR spectra of the metal complexes exhibit the characteristic bands of both squaric and triazine rings. All complexes showed strong broad bands around 3483-3380 $cm^{-1}$ due to ν(OH) stretches. Also, the band at 1510 $cm^{-1}$ in the free ligand, belonging to the combination of C-O (squarate) and C = N (triazine) was shifted to higher wave numbers (1527- 1519 $cm^{-1}$) in most metal complexes, as a result of complexation. For complexes 9 and 10, the ν(V=O) and ν(U=O) were observed at 932 and 922 $cm^{-1}$. The υ value was used to calculate the force constant (F) of (U=O) bond by the relation[10]:

$(\upsilon)^2 = (1307)^2 (F_{U\text{-}O}) / 14.103$

which was then substituted into the Jones relation[11] to calculate its bond length (R):

$R_{U\text{-}O} = 1.08 (F_{U\text{-}O})^{-1/3} + 1.17$ The calculated $F_{U\text{-}O}$ and $R_{U\text{-}O}$ are 7.018 m dynes / A$^o$ and 1.7378 A$^o$, respectively, falling within the usual range for uranyl complexes[12].

**Magneto Chemistry:** The magnetic properties of the complexes provide valuable information for distinguishing their stereochemistry. The effective magnetic moment ($\mu_{eff}$) of the iron(III)- complex (2) has the value 6.08 B.M. (table 1) which is consistent with five unpaired electrons suggesting an $sp^3d^2$ hybridization, and falls within the range reported for high spin $O_h$- geometry[13]. In addition, the cobalt(II)- complexes (3 and 4); $3d^7$-system showed effective magnetic moments of 4.11 and 3.99 B.M., respectively, confirming their octahedral geometry which is related to three unpaired electrons. The copper(II)- complexes (7 and 8), $3d^9$-system and oxovanadium (IV) complex (9); $3d^1$-system exhibit $\mu_{eff}$ values of 1.43, 1.89 and 1.97 B.M., respectively, (table 1) indicating the presence of one unpaired electron. The value of 1.43 B.M. confirms the binuclear nature of complex 7 with two adjacent copper(II) ions. The subnormal $\mu_{eff}$ values, suggest anti- ferromagnetic exchange between the two adjacent metal ions; the smallest the $\mu_{eff}$ values, the strongest is the exchange[13-15]. The anti-ferromagnetic exchange coupling is mediated through the μ- chlorides. The structure of complex 8 has some interesting features; the Cu(II)- ion is encapsulated at a center of a square plane of the chromophore $N_4$ with a unique mode. In contrast, the diamagnetism of the palladium(II) and nickel(II)- complexes (1 and 6) confirms their square planar geometry[15]. In general, square planar complexes rather than tetrahedral complexes usually arise from strong field ligands. Furthermore, the nickel(II)- complex (5); $3d^8$- system showed $\mu_{eff}$ value of 2.96 B.M. which is consistent with two unpaired electrons confirming its square pyramid geometry. Also, room temperature magnetic moment data (table 1) showed the diamagnetism of the dioxouranium(VI)- complex (10) as expected[10].

**Mass and Electronic Spectra:** The mass spectra of complexes 2; $[Fe(H_2L)(H_2O)_3Cl]$, (747.97) and 8; $[Cu(H_2L)(H_2O)]$, (684.2) -as representative examples- showed their molecular ion peaks at *m/z* = 745 and 686, respectively, confirming their suggested structures. Also, the base peaks were observed at *m/z* = 103 for both complexes, supporting that the most abundant ion is the same for both complexes. On the other side, the electronic spectra of the ligand as Nujol mulls showed a charge transfer broad band centered at 625 nm which impacts the ligand its dark brown color. However, the electronic spectra of the complexes (dark brown or dark violet) as Nujol mulls showed this band in the range 600-660 nm confirming its charge transfer nature. The observed bands are nearly similar in terms of the position, intensity and their shapes.

Therefore, the color of all complexes is dominated by a CT transition which obscured the weak d-d transitions occurring in the same region. In general, it was not possible to identify the type of d-d transitions due to the strong charge transfer bands tailing from UV- region to the visible region[8,16].

**ESR Spectra:** The X- band ESR spectra at room temperature of a powdered sample of complexes 7 and 9 are depicted in Fig. 1. The X- band ESR spectrum of complex 7 consists of a broad signal with a g- value of 2.14. Upon the existence of two copper(II)- ions, the two electron spins may combine to a nonmagnetic spin singlet state (S = 0) or a paramagnetic spin triplet state (S = 1); only the latter is an ESR detectable. The super-exchange interaction between the two copper(II)- ions lead to the lack of the hyperfine structure which agree well with the subnormal magnetic moment value (1.43 B.M.) and confirms the dimeric nature of complex (7). Also, The X- band ESR spectrum of complex (9) showed a symmetrical broad band centered on g=2.02 without resolved hyperfine structure. In general, the positive contribution in the $g_{eff}$ value over the free electron (2.0023) indicates an increase in the covalent nature of the bonding between the metal ion and the ligand[8]. The absence of vanadium's hyperfine coupling is common in the solid state and is attributed to the simultaneous flipping of neighboring electron spin or strong exchange interactions, which average out the interaction with the nuclei[17].

**Thermal analyses (TG-DSC):** TG-DSC studies were carried out at a heating rate 10°C/min in nitrogen atmosphere (30 mL/min) over a temperature range 30-800°C. The results showed a good agreement with the theoretical formulae as suggested from the elemental analyses. The TG-DSC thermogram of complex (3) showed three decomposition stages; the liberation of the crystal water molecules forms the first decomposition stage in the temperature range 33-122°C; (found: 7.40% , calcd: 7.64%). Also, the liberation of four coordinated water molecules forms the second decomposition stage in the temperature range 122-230°C; (found: 7.63% , calcd: 7.40%). This stage fulfill the transformation; octahedral to square planar geometry. Furthermore, the third stage which extends up to 800°C constitutes the removal of two water molecules and two HCl molecules, together with the degradation of the organic part and the formation of $Co_2O_3$ as the end product (found: 17.98% , calcd: 17.05%). On the other hand, the TG-DSC thermogram of complex (8) showed a sharp sudden inflection at 482°C with a mass loss; 81.30% via a strong endothermic process ($\Delta H$ = 494.2 J/g); supporting its unique mode. The residue is $Cu_2O$ (found: 18.70%, calcd: 20.91%).

## Conclusion

Depending on the type of the metal ion and its counter anion, the obtained complexes reflect the structural diversity [pentagonal bipyramid (10), octahedral (2-4, 9), square pyramid (5, 7, 8) and square planar (1, 6)]. Also, the ligand showed a variety of modes of bonding *viz.* $(NNNN)^{2-}$, $(NN)^{0}$, $(NO)^{-}$ or $(OO)^{2-}$ per each metal ion. For complex 8, the ligand squeezes its NNNN compartment to generate a cavity of the right size in which the copper(II)-ion is encapsulated. Complexes (1, 8) reflect the preference of palladium(II) and copper(II)- ions for N-donors and the former to form chains. In contrast, complexes (2, 10) reflect the preference of iron(III) and dioxouranium(VI)- ions for O-donors. For complex 7, the pronounced decrease in the $\mu_{eff}$ value was taken as a good evidence for its dimeric nature. Furthermore, complexes (4, 6, 8-10) point out to senseless of the coordinating ability of the sulfate anion. In general, the synthetic pathway of the ligand is highly affected by the type and size of the metal ion as well as its counter anion. For clarifying their proposed structures, the complexes were subjected to elemental and thermal analyses as well as spectral studies.

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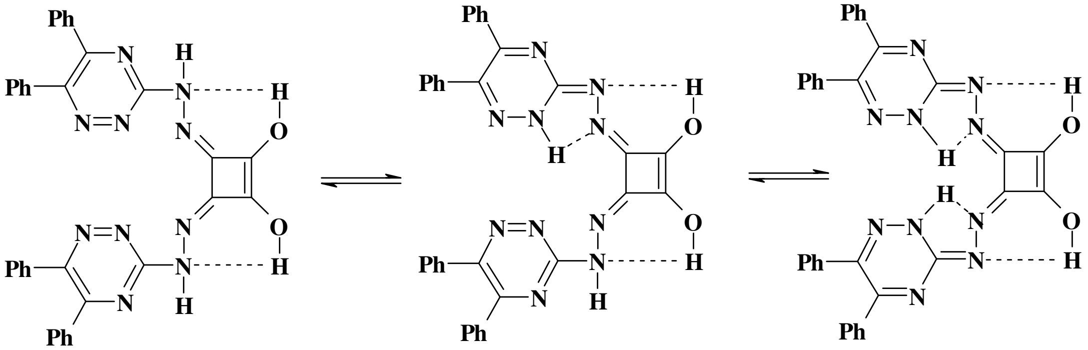
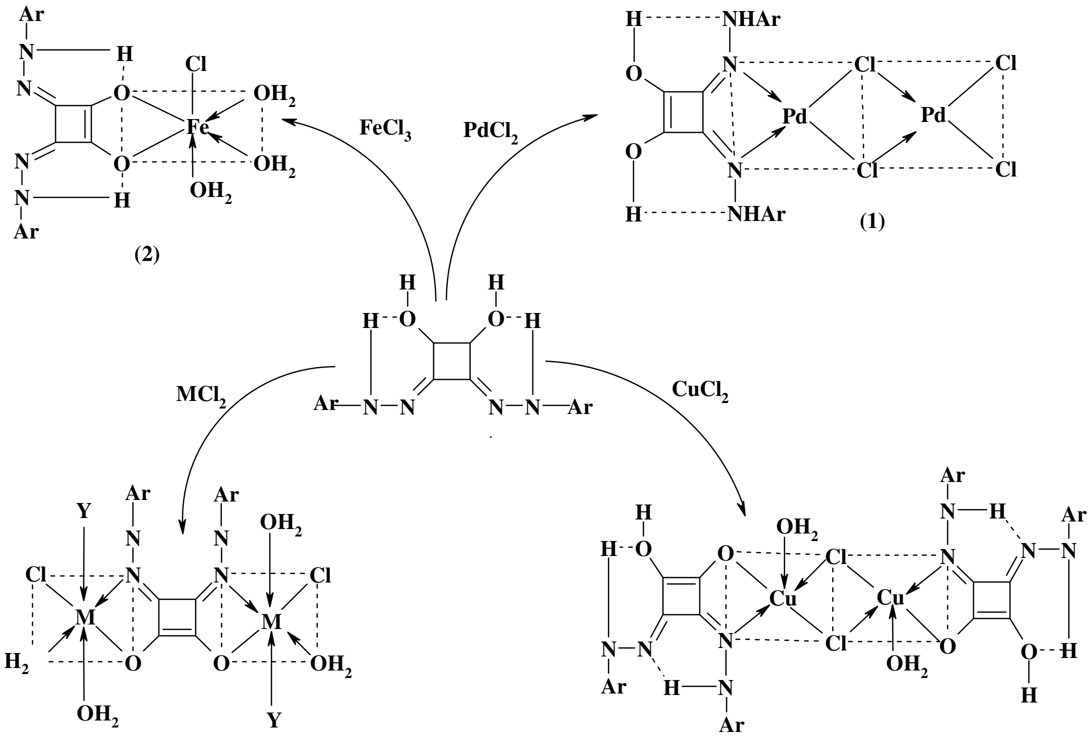


**(I)** **(II)** **(III)**

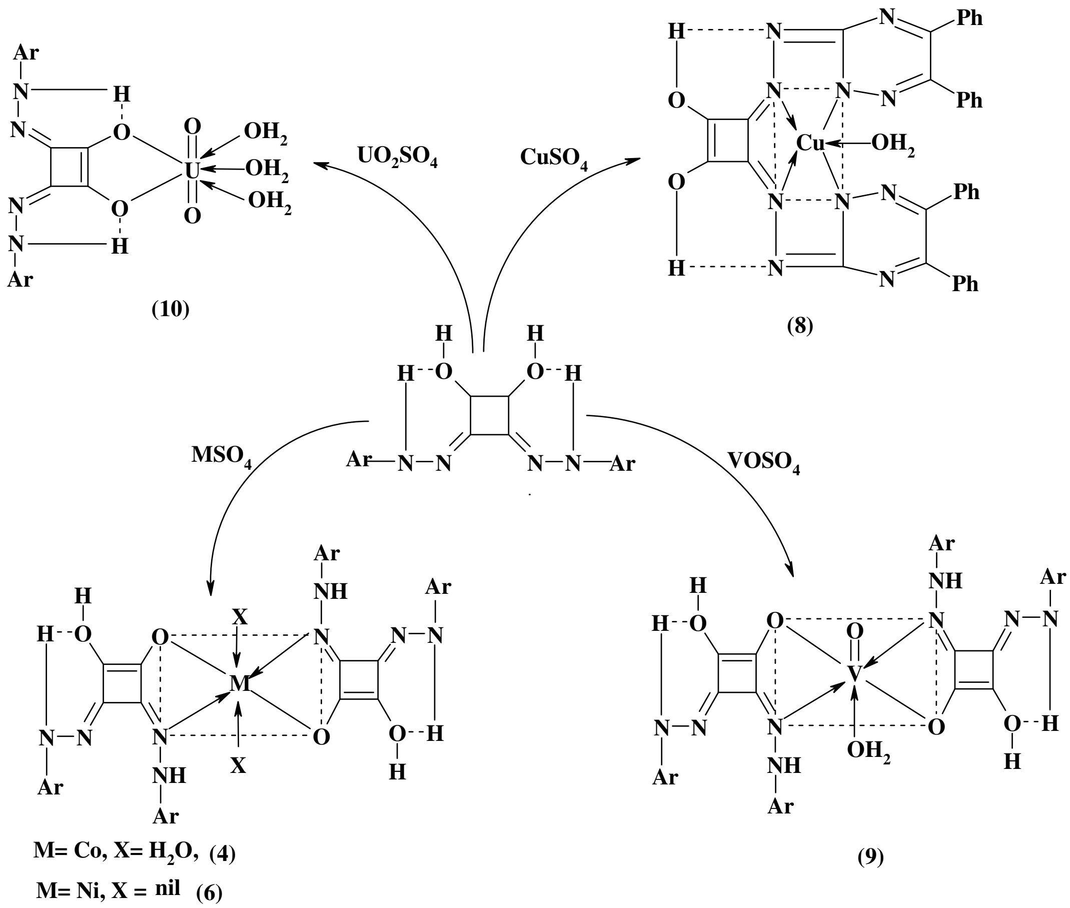
**Scheme-1: Tautomeric forms of the ligand**



**(2)** **(1)** **(7)**

**M= Co, Y= $H_2O$, (3)**
**M= Ni, Y = nil (5)**

**Scheme-2: Proposed structures of the chloro-complexes**



**Scheme-3: Proposed structures of the squaric complexes derived from the sulfate salts**

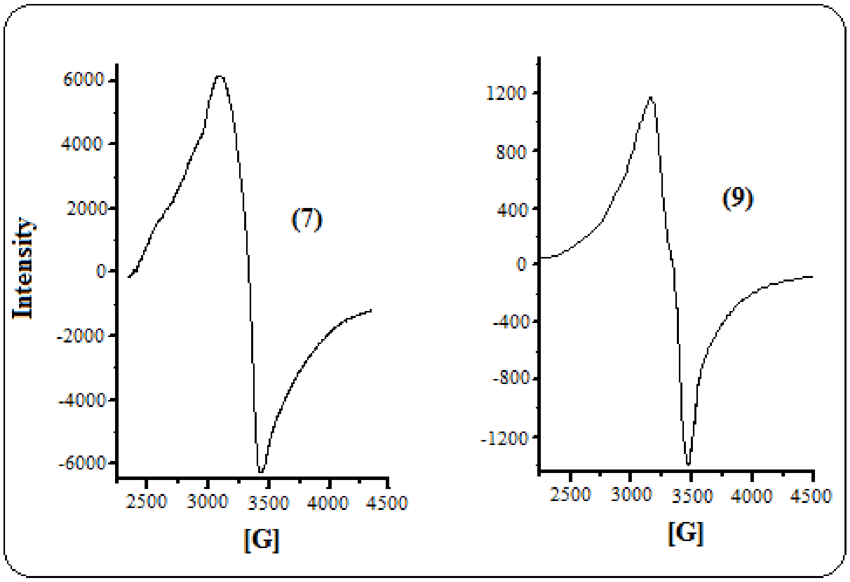


**Figure-1: X-band ESR spectra of complexes 7 and 9**

## Table-1: Analytical and Physical Data of the Complexes

| | **Reactants ($H_4L$+ Metal salt)** | **Complex** | **F.W.** | **Color** | **Yield (%)** | **$\mu_{eff}$ (B.M.)** | **Elemental Analysis; % found/(calcd.)** | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | **C** | **H** | **N** | **M** |
| 1 | $PdCl_2$ | $[Pd_2(H_4L)Cl_4]$ | 959.23 | Dark violet | 75 | ----- | 42.27<br>(42.57) | 2.71<br>(2.52) | 14.71<br>(14.60) | ---- |
| 2 | $FeCl_3.6H_2O$ | $[Fe(H_2L)\ (H_2O)_3Cl]$ | 747.97 | Dark violet | 60 | 6.08 | 54.70<br>(54.60) | 3.50<br>(3.77) | 18.90<br>(18.73) | 7.22<br>(7.47) |
| 3 | $CoCl_2.6H_2O$ | $[Co_2(H_2L)(H_2O)_6Cl_2].4\frac{1}{8}H_2O$ | 973.80 | Dark violet | 45 | 4.11 | 41.90<br>(41.94) | 4.60<br>(4.37) | 14.05<br>(14.37) | 11.87<br>(12.10) |
| 4 | $CoSO_4.7H_2O$ | $[Co(H_3L)_2(H_2O)_2]$ | 1302.22 | Dark violet | 53 | 3.99 | 62.71<br>(62.72) | 4.00<br>(3.87) | 21.70<br>(21.51) | 4.12<br>(4.53) |
| 5 | $NiCl_2.6H_2O$ | $[Ni_2(H_2L)(H_2O)_4Cl_2].\frac{1}{2}H_2O$ | 871.99 | Brownish gray | 42 | 2.96 | 46.86<br>(46.83) | 3.56<br>(3.58) | 15.99<br>(16.06) | 13.30<br>(13.46) |
| 6 | $NiSO_4.6H_2O$ | $[Ni(H_3L)_2]$ | 1265.95 | Dark brown | 80 | ---- | 64.40<br>(64.52) | 3.30<br>(3.66) | 21.95<br>(22.13) | 4.45<br>(4.64) |
| 7 | $CuCl_2.2H_2O$ | $[Cu(H_3L)(H_2O)Cl]_2.\ \frac{3}{4}H_2O$ | 1454.79 | Dark violet | 40 | 1.43 | 56.00<br>(56.14) | 3.50<br>(3.57) | 19.52<br>(19.26) | 8.40<br>(8.74) |
| 8 | $CuSO_4.5H_2O$ | $[Cu(H_2L)(H_2O)]$ | 684.2 | Dark violet | 67 | 1.89 | 59.60<br>(59.69) | 3.50<br>(3.53) | 20.71<br>(20.47) | 9.17<br>(9.30) |
| 9 | $VOSO_4.H_2O$ | $[VO(H_3L\underline{)_2}(H_2O)].\frac{1}{4}H_2O$ | 1296.71 | Dark brown | 75 | 1.97 | 62.92<br>(62.99) | 3.50<br>(3.77) | 21.83<br>(21.6) | ---- |
| 10 | $UO_2SO_4.\ 3\frac{1}{2}H_2O$ | $[UO_2\ (H_2L)(H_2O)_3].2H_2O$ | 962.72 | Dark brown | 47 | ----- | 42.30<br>(42.42) | 3.00<br>(3.35) | 14.70<br>(14.55) | ---- |