Asian Journal of Chemistry Vol. 20, No. 3 (2008), 1859-1865

Synthesis and Physico-chemical investigation on Complexes of Ag(I), Zn(II), Cd(II), Hg(II), Pd(II), Co(II), Ni(II) and Pt(IV) with 3-Salicylideneamino-2-mercapto quinazoline(1*H*)-4-one

ABRAHAM JOSEPH* and B. NARAYANA†
Department of Chemistry, University of Calicut, Kerala-673 635, India
E-mail: drabrahamj@gmail.com

The complexes of Ag(I), Zn(II), Pd(II),Cd(II), Hg(II), Co(II), Ni(II) and Pt(IV) with 3-salicylideneamino-2-mercapto quinazoline(1*H*)-4-one (SMQ) have been synthesized and characterized on the basis of elemental analysis, spectral, magnetic susceptibility, conductance and thermal studies. Octahedral structures have been proposed for the Pt(IV), Co(II) and Ni(II) complexes, square-planar for the Pd(II) complex, tetrahedral for the Hg(II), Zn(II) and Cd(II) complexes and linear polymeric structures for the Ag(I) complex. The ligand coordinates to the metal ions through thiol sulfur after deprotonation and with azomethine nitrogen. Phenolic oxygen of the ligand is also involved in bonding after deprotonation in few of the complexes.

Key Words: Quinazoline, Metal complexes, Susceptibility.

INTRODUCTION

The thioamide heterocyclic systems and their transition metal complexes have numerous applications in biological fields. Metal chelates of certain multidentate Schiff bases have been used for the purification of metals because of their high volatility and solubility in non-polar solvents[1]. The metal complexes with Schiff bases find various industrial and biological applications[2-4]. The present paper discusses the synthesis and characterization of the complexes of Ag(I), Zn(II), Cd(II), Hg(II), Pd(II), Pt(IV), Co(II) and Ni(II) with 3-salicylideneamino-2-mercapto quinazoline(1*H*)-4-one (SMQ).

EXPERIMENTAL

The chemicals used were all of AnalaR or chemically pure grade. The ligand was synthesized[5] by condensing 2-mercapto quinazoline(1*H*)-4-one with salicylaldehyde. The product was recrystallized from ethanol and

---

†Department of Studies in Chemistry, Mangalore University, Mangalagangothri-574 199, India, E-mail: drabramj@gmail.com

characterized by various physico-chemical methods. The complexes were prepared by refluxing the respective metal chlorides/nitrates/acetates (0.01 mol) and the ligand (0.02 mol) in ethanol (75 mL) for 1-3 h. The separated solid was washed with hot water, warm ethanol and ether and dried at 120-130 ºC.

Sulfur and the metal contents were determined by the standard methods in the laboratory. C, H and N were analyzed at CDRI Lucknow. The magnetic susceptibility was determined with a Gouy balance at room temperature. Thermogravimetric analysis carried out on a Mettler TA 4000 thermal analyzer by heating the complexes in air at a rate of 10 ºC/min up to 800 ºC at Department of Chemistry CUSAT Kochi. The molar conductivity of the complexes (in 1×10^{3} mol dm^{-3} DMF solution) was measured using an Elico conductivity meter. Absorption spectrophotometric studies (Beckman DU-6) and infrared spectra (KBr/CsI) on a Perkin-Elmer 1330 spectrophotometer were carried out in the department.

RESULTS AND DISCUSSION

The analytical results (Table-1) show that Ag(I) form ML type complexes while Zn(II), Hg(II) and Cd(II) form ML_2 type complexes with SMQ. The Pd(II) complex contain a molecule of water and is of ML type. The Co(II) and Ni(II) complexes contain three molecules of water coordinated to the metal. The presence of coordinated water molecules in the Ni(II), Co(II) and Pd(II) complexes were further confirmed by TGA and spectral data. Even though octahedral structure is suggested for Pt(IV) complex, no coordinated water molecule is present in it as it is clearly evident from spectral and thermal studies. The magnetic susceptibility studies show that all the complexes, except of Ni(II) and Co(II) complexes are diamagnetic.

Nickel(II) complexes in octahedral field contain two unpaired electrons and hence shows paramagnetism. Their magnetic moment are in general slightly higher than the spin-only value of 2.83 BM. This difference may be due to either the ferromagnetic interaction in the clusters[5] or to Jahn-Teller distortion or both. The magnetic moments of the Ni(II) complex (3.11 BM) is in good agreement with those reported for octahedral nickel(II) complexes[5,6]. The expected range of spin only magnetic moment for d^8 system is 2.50-3.50 BM. Generally the magnetic moments of nickel(II) complexes show 10-15 % above the spin only value of 2.83 BM. The reason for the higher observed value than the expected one may be due to the above mentioned reasons. Since the T_d symmetry which gives triplet[5,6] state as the ground state, the orbital contributions would have been much more than that are actually observed. A distorted O_h symmetry for the Ni(II) complexes seems to be more appropriate than a perfectly symmetric one. This observation is further supported by the different spectral results.

TABLE-1
ANALYTICAL DATA OF METAL COMPLEXES OF SMQ

Complex	Elemental analysis %: Found (Calcd.)				
	C	H	N	S	M
$[Pt(C_{15}H_{10}N_3O_2S)_2]$	46.05 (46.07)	2.34 (2.35)	10.74 (10.75)	8.19 (8.21)	24.93 (24.96)
$[Ag(C_{15}H_{10}N_3O_2S)]$	33.10 (33.09)	2.97 (2.98)	11.04 (11.03)	6.30 (6.32)	40.25 (40.27)
$[Cd(C_{15}H_{10}N_3O_2S)_2]$	46.73 (46.74)	4.20 (4.21)	15.56 (15.58)	8.90 (8.92)	15.61 15.64)
$[Zn(C_{15}H_{10}N_3O_2S)_2]$	50.00 (50.02)	4.51 (4.50)	16.66 (16.67)	9.53 (9.55)	9.76 (9.73)
$[Hg(C_{15}H_{10}N_3O_2S)_2]$	41.61 (41.64)	3.74 (3.75)	13.87 (13.88)	7.94 (7.95)	24.87 (24.86)
$[Co(C_{15}H_{10}N_3O_2S)\cdot 3H_2O]$	40.45 (40.46)	4.85 (4.86)	13.46 (13.48)	7.70 (7.72)	14.18 (14.19)
$[Ni(C_{15}H_{10}N_3O_2S)\cdot 3H_2O]$	40.47 (40.49)	4.87 (4.86)	13.48 (13.49)	7.71 (7.73)	14.12 (14.14)
$[Pd(C_{15}H_{10}N_3O_2S)\cdot H_2O]$	39.38 (39.40)	3.77 (3.78)	13.12 (13.13)	7.48 (7.52)	24.88 (24.89)
$(C_{15}H_{10}N_3O_2S)$ (ligand)	60.56 (60.57)	3.74 (3.73)	14.15 (14.13)	10.76 (10.79)	–

The Co(II) has a d^7 system and its complexes show paramagnetism either equivalent to three unpaired electrons (octahedral or tetrahedral) or equivalent to one unpaired electron (square-planar). The magnetic moment of the complex is 4.72 BM. Since the orbital contribution of tetrahedral Co(II) is much less than that of octahedral complexes, tetrahedral Co(II) complexes have generally lower values of magnetic moments as compared to that of octahedral complexes[5]. This high degree of orbital contribution for octahedral complexes is due to the three-fold degeneracy of $^4T_{1g}$ ground state. The value of magnetic moment of Co(II)-SMQ complex lies well within the range of high-spin octahedral complexes[6,7].

Thermogravimetric analysis of the metal complexes of SMQ indicates the presence of water molecules in the Ni(II), Co(II) and Pd(II) complexes. The loss in weight of these complexes occurs in the temperature range 110-225 ºC, which indicates the loss of coordinated water molecules. The thermogram of Ni(II) and Co(II) complexes with SMQ indicates a loss in weight corresponds to the loss of three water molecules, when heated from 110 to 225 ºC and which corresponds to the loss of one molecule of water in the case of Pd(II)-SMQ complex. A steep decrease in weight is observed in the thermograms of the complexes at a temperature range 250-550 ºC. This may be due to the oxidation of the organic matter and formation of the metal oxides. All the other complexes are stable up to 200 ºC and suffer a two stage decomposition. The final products at 600-800 ºC are mainly metal oxides.

The molar conductance values of all the complexes are in the range 5.0-57.8 Ω^{-1} mol^{-1} cm^2. The relatively low values of molar conductance indicate that the complexes are non-electrolytes and neutral in nature.

Electronic spectral band positions and assignments in respect of Co(II), Ni(II) and Pd(II) complexes of SMQ are given below.

For high spin octahedral complexes of Co(II), three transitions are expected in the electronic spectra at $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and $^4T_{1g}(P)$ in the order of increasing energies. The first transition was not recorded but its position was calculated from the second transition. The values of the crystal field stabilization energy (10 Dq), Racah parameter (B) and the covalency factor (β) have been evaluated[8]. In case of six-coordinate octahedral and pseudo-octahedral nickel(II) complexes, the three spin-allowed transitions from $^3A_{2g}(F)$ to $^3T_{2g}(F)$, $^3T_{1g}(F)$ and $^3T_{2g}(P)$ generally fall within the range 7000-13000, 11000-22000 and 19000-27000, respectively[6]. The ratio of the frequencies of the second to the first transition would be around 1.8[4,7]. The first transition corresponding to $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ is not recorded in the electronic spectra. The assignment of the transition and ligand field parameters are calculated and presented. The calculated B values are lower than the free-ion value of 1080 cm^{-1}.

In the case of Pd(II), which generally forms square-planar complexes has D_{4h} symmetry of the ligand field around the central metal ion[5]. The metal orbitals, namely, *s, p* and *d*, span (i) a_{1g}, (ii) e_u and a_{2u} and (iii) b_{1g}, b_{2g}, a_{1g} and e_g representations, respectively. Similarly, the ligand orbitals transform as b_{1g}, a_{1g} and e_u. The σ bond formation between the metal ion and the ligand units would use one *d*-orbital (b_{1g}), one *s*-orbital (a_{1g}) and two *p*-orbital (e_u) of the metal ion. The ground state for the low spin d^8 system is therefore $^1A_{1g}$. Assuming D_{4h} symmetry of the field around the central metal ion, one should expect three spin-allowed and three spin-forbidden bands in the electronic spectra of the complexes[9] corresponding to the transitions $^1A_{1g} \rightarrow {}^3A_{2g}$, $^1A_{1g} \rightarrow {}^1A_{2g}$, $^1A_{1g} \rightarrow {}^3E_g$, $^1A_{1g} \rightarrow {}^1E_g$, $^1A_{1g} \rightarrow {}^3B_{1g}$. However, not all the possible transitions can really be observed because some of them are masked either due to charge transfer or due to inter-ligand interactions.

The ground state of the metal ion Pt(IV) in an octahedral field is $^1A_{1g}$. The excited state corresponding to t_{2g} and e_g configuration are $^3T_{1g}$, $^3T_{2g}$, $^1T_{1g}$ and $^1T_{2g}$ in the increasing order of energy. Thus four transitions can be expected as

$$^1A_{1g} \rightarrow {}^3T_{1g},\ {}^1A_1 \rightarrow {}^3T_{2g},\ {}^1A_{1g} \rightarrow {}^1T_{1g} \text{ and } {}^1A_{1g} \rightarrow {}^1T_{2g}$$

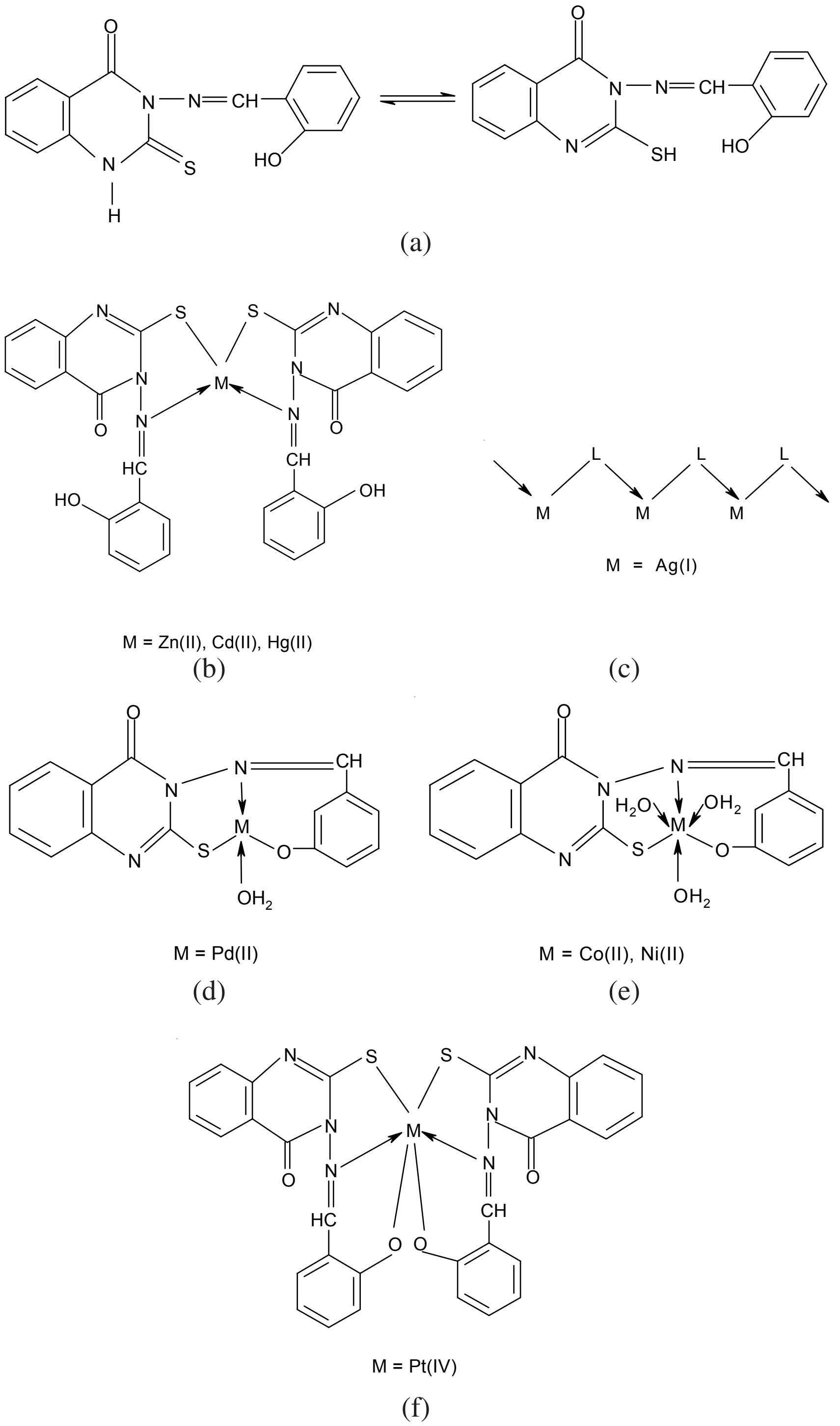
The positions of the bands observed and the probable assignments are given in Table-2 along with the values of 10 Dq, B and β. The positions of the bands and the values of 10 Dq, B and β are in conformity with that of other Pt(IV) complexes with similar donors.

TABLE-2
INFRARED BANDS (cm^{-1}) OF SMQ AND ITS COMPLEXES

Ligand	Ag(I), Zn(II), Cd(II), Hg(II) Complexes	Co(II), Ni(II), Pd(II) Complexes	Pt(IV)	Assignment
–	–	3500 br	–	ν(OH) water
3100-3000 br	2990 ± 10 s	2970 ± 5 s	2900 ± 5 s	ν(N-H)
2900 m	2890 ± 10 m	2880 ± 10 m	2860 ± 10 m	ν(C-H)
1670 m	1670 ± 5 s	1650 ± 5 s	1650 ± 10 s	ν(C=O)
1630 m	1610 ± 5 s	1610 m	1600 ± 10 s	ν(C=N)
1550 s	1540 m	1540 ± 5 w	1550 ± 10 m	Thioamide band I
1420 s	1470 ± 5 s	1450 s	1480 ± 10 s	Thioamide band II
1310 s	1310 ± 5 s	1350 s	1320 ± 10 s	ν(C-O)
1190 m	1190 ± 10 m	1200 ± 10 m	1200 ± 10 m	Thioamide band III
1050 m	1050 ± 10 m	1050 ± 5 m	1050 ± 5 m	ν(N-N) triazine ring
–	–	890 ± 10 m	–	Characteristic of coordinated water
760 s	710 ± 5 m	710 ± 5 m	700 ± 10 m	Thioamide band IV and Ph. gp. with 5 adj. H-atoms
680 m	680 ± 5 w	680 ± 5 w	670 ± 10 w	Aromatic ring
–	480 ± 10 w	470 ± 10 w	470 ± 10 w	ν(M-N)
–	–	460 ± 5 s	460 ± 5 s	ν(M-O)

The infrared spectrum of the ligand has bands at 3100-3000 ν(NH) and 2900 cm^{-1} ν(C-H). The band at 1650 cm^{-1} ν(C=O) of the ligand is also observed in the spectra of the complexes. This shows the non-participation of the carbonyl group in bonding. The ligand bands at 1630 and 1590 cm^{-1} is assigned to ν(C=N) of the azomethine linkage[10]. The slight shift of the band to lower wave number side in the complexes indicates the coordination of this nitrogen with the metal ions.

The ligand molecule containing thioamide moiety is expected to exist in tautomeric thiol and thione forms (Fig. 1). Due to the presence of thioamide moiety, four characteristic thioamide bands can be expected in the spectra of the ligands. The position of the thioamide band I (1560-1530 cm^{-1}) in the spectrum of the ligand is not shifted appreciably in the spectra of the complexes. But the position of thio amide band II of the ligand (1420 cm^{-1}) suffered a considerable shift towards higher wave number side in the complexes (1460-70 cm^{-1}). The ligand band at 1320-1290 cm^{-1} (C-O)[11,12] shifted to higher wave number side in some complexes, indicating



(a)

M = Zn(II), Cd(II), Hg(II)

(b)

M = Ag(I)

(c)

M = Pd(II)

(d)

M = Co(II), Ni(II)

(e)

M = Pt(IV)

(f)

Fig. 1.

coordination through oxygen of the phenolic group, while in some complexes this shift was not observed and hence the phenolic oxygen is not involved in bonding. The thio amide band IV (790-760 cm^{-1}) in the spectra of the ligand is shifted to lower wave number side in their complexes[11,12]. The increased intensity of the thioamide band IV in the spectra of the ligands may be due to the mixing of thio amide band IV and the band characteristic of phenyl ring. In the complexes the band around 790 cm^{-1} is due to the presence of phenyl group. The band around 690 cm^{-1} (aromatic ring) is observed in the spectra of the ligand and the complexes.

New bands are also observed in the spectra of the complexes due to ν(M-N), ν(M-O) and ν(M-S) coupled with other modes of vibrations of the ligand molecules. Bands due to coordinated water molecule are also observed in the spectra of the Co(II), Ni(II) and Pd(II) complexes around 3500 and 890 cm^{-1} due to ν(OH) and characteristics of coordinated water molecules, respectively.

All these observations provide an insight into the bonding scheme. These results clearly establish that the ligand chelate with the metal ions through the deprotonated sulfur and the nitrogen atom of the azomethine linkage. The chelating ability of the ligand through azomethine nitrogen is well established in Pt(IV) complex.

On the basis of the above results octahedral structures have been proposed for the Pt(IV), Co(II) and Ni(II) complexes, square-planar for the Pd(II) complex, tetrahedral for the Zn(II), Cd(II) and Hg(II) complexes and linear polymeric structures for the Ag(I) complexes. The ligand molecules coordinate to the metal ions through thio sulfur after deprotonation and with azomethine nitrogen.

REFERENCES

1. R. Belcher, M. Pravica, W.I. Stephen and P.C. Vden, *Chem. Commun.*, 42 (1971); S. Dill and E. Patasalides, *J. Chromatogr.*, **270**, 354 (1983).
2. B.Ramchandra and B Narayana, *J. Indian Chem. Soc.*, **76**, 239 (1999).
3. N.G Bhat and B. Narayana, *Synth. React. Inorg. Met.-Org. Nano Met. Chem.*, **260**, 35 (2005).
4. B. Sridhar, K. Ravikumar, H.S. Yathirajan, H.G. Anilkumar and B. Narayana, *Acta Cryst.*, **26**, 382 (2006).
5. F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, Interscience, New York, edn. 3 (1972).
6. A.B.P. Lever, *Inorg. Chem.*, **4**, 763 (1965).
7. B.N. Figgs and J. Lewis, *Prog. Inorg. Chem.*, **6**, 37 (1964).
8. A.B.P. Lever, Inorganic Electronic Spectroscopy, Elsevier, New York (1968).
9. R.H. Holm and F.A. Cotton, *J. Chem. Phys.*, **31**, 788 (1959).
10. S.K. Sengupta, S.K. Sahni and R.N. Kapoor, *Synth. React. Inorg. Metal-Org. Chem.*, **10**, 269 (1980); S.N. Dubey and B. Kaushik, *Indian J. Chem.*, **24A**, 950 (1965).
11. L. Sacconi, *Transition Met. Chem.*, **4**, 199 (1968).
12. A.B.P. Lever, *J. Chem. Educ.*, **45**, 711 (1968).

(*Received*: 16 February 2007; *Accepted*: 2 November 2007) AJC-6053