

## Synthesis and Characterization of some newly synthesized complexes of transition metal with ketoanil Schiff base

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### ABSTRACT

The present paper deals with the synthesis of some coordination compounds involving different d-orbital configurations in the environment of newly developed ligand systems of cubic symmetries and several structural features of new molecular models adopting spectral and magnetic moments. I.R. data of ligand have been compared with those of complexes in order to elaborate basic structural aspects including identification of various modes of vibrations and rotations and finally elucidation of structures of new species. E.S.R. spectra recorded at room and liquid nitrogen temperature reveals octahedral geometries of all the paramagnetics except compound of Cu (II), which is square planar.

**Key words:** Transition metals, PDTAG, ketoanil, Schiff base.

### INTRODUCTION

Thorough perusal of reports describing different studies on Schiff's bases including ketoanils and their complexes reveals that these compounds are of the highest choice among all other systems on account of their uses in diverse fields of development, viz., industries (as pigments and dyes<sup>1-8</sup> for synthetic fibres, plastics, cotton and wool; as high temperature stabilizers<sup>9</sup>, for lubricating oils; as sequestering agents<sup>10</sup>, to participate metal impurities of oils; as inhibitors<sup>11</sup> against acid corrosion of metals and alloys; as photographic developing agent<sup>12</sup> precursors etc.), medicinal sciences (as anticancerous<sup>13</sup>, inflammatory<sup>14,15</sup>, antituberculosis<sup>16</sup>, antibacterial<sup>17</sup>, fungicidal and as intermediates in synthetic organic chemistry<sup>18</sup>).

In many instances they form complexes of complicated structures, or equilibrium mixtures of two stereochemical or isomeric forms displaying abnormal physico-chemical behaviour. Dark colours of these complexes pointing towards high absorption in ultra-violet and visible regions may lead to very

specific solid state electronic phenomenon. Most peculiar structural features and high usefulness of ketoanils in general is the scarce knowledge in polydentate ligands particularly heterocyclic ketoanils. Keeping this view of its various applications and synthesizing various complexes of iron (III) of ketoanils<sup>19,20</sup>, the author now reports some studies on a few complexes of a typical ketoanil, para phenylenedianil of 2-thiophenrglyoxal (abbreviated as PDTAG).

### EXPERIMENTAL

Chemicals used in the syntheses were laboratory grade BDH or S.M. products. In electron spin resonance measurements finely pulverized complex samples were filled in the tube and the tube was placed in an absorption cell and the whole set up was placed in the magnetic field of known strength generated by a strong electromagnet. For each sample e.s.r. measurements were performed at room temperature (292 °K) and at liquid nitrogen temperature in Regional Sophisticated Instrumentation Centre Indian Institute of

Technology, Madras. Instrument used was E.P.R. E-4 spectrometer operating at 9.5 GHz-10.0 GHz, modulation and phase sensitive detections.

#### Calculation of Lande's splitting factor (g)

Different values of  $g$ ,  $g_{||}$  and  $g_{\perp}$  have been calculated at both the experimental temperatures from e.s.r. spectrum of each sample with the help of the following expression:

$$G = \nu h / \beta H$$

Where,

$h$  is the Planck's constant

$\nu$  is the frequency of X-band in  $\text{KHz}$

$\beta$  is the Bohr magneton value and

$H$  is the magnetic field in Gauss

#### Preparation of 2-Thiopheneglyoxal

It was prepared by the oxidation of 2-acetylthiophene with an equimolar amount of selenium dioxide in acetic acid-alcohol (3:2, v/v) by refluxing for 2 hours. Resultant solution was poured into hot water and the mixture solution was then boiled under reflux for 30 mins. On cooling dark brown viscous glyoxal settled in the bottom of the flask. It was then dissolved in alcohol and crystallized.

#### Synthesis of p-phenyldianil of 2-thiopheneglyoxal (PDATG)

Solutions of p-phenylenediamine and 2-thiopheneglyoxal containing equimolecular quantities (glyoxal in slight excess) in chloroform, when mixed together showed a sharp and deep colour change from light orange to dark brown indicating the formation of a new compound in the mixture solution. The reaction mixture was concentrated on a water bath and dried in air at 45 °C. The solid thus obtained was repeatedly washed with ether to remove unreacted glyoxal, if any. The product was purified by recrystallization from acetone. Analytical data (Carbon (%): Calcd. 61.36, found 61.01; Hydrogen (%): Calcd. 7.96, found 8.12) showed the high purity of the new product.

#### Isolation of Complexes

PDATG was dissolved in acetone whereas metal salt solutions were prepared in acetone or in its mixture with alcohol or water. On mixing the

reacting solution in appropriate proportions (PDATG in excess), complexes of Ti (III), Cr (III), Co (III), Ni (II) and Hg (II) chlorides. The precipitates were purified by reprecipitation from their solution in acetone. Final products were dried in hot air oven at ~ 50 °C and collected in air tight tubes.

## RESULTS AND DISCUSSION

Structure of PDATG shows the presence double of each, carbonyl, azomethine and thienyl groups in the ligand indicating its six coordination abilities. Perusal of orbital descriptions of these coordinating groups reveals that sulphur of thienyl group which has been attached with adjacent carbon atoms through  $\sigma$  and  $\pi$  bonds can spare its 3s  $\sigma$ -bonding and 3p<sub>x</sub>  $\sigma$ -bonding orbitals for coordination whereas carbonyl oxygen (in quinonoid structure) can offer 2s  $\sigma$ -bonding and 2p<sub>x</sub> and 2p<sub>y</sub>  $\pi$ -bonding orbitals for coordination and azomethine nitrogen, however, could make available its only 2s  $\sigma$ -bonding orbital for complexation.

In order to investigate the stoichiometries and structures of ligand and complexes, isolated solids were analyzed for their various important component elements and infrared spectra were recorded to mark the different characteristic groups and bonds in them. Molecular formulae deduced from analytical data are recorded in table-1.

With the knowledge of characteristic absorption of different atoms, groups and bonds, bands in the spectra of PDATG and its complexes were identified. Comparison of infrared data of ligand with those of complexes was done in order to investigate the structural change in ligand, if any, during the complexation with metal ions and to identify coordination seats.

Although all infrared frequencies of PDATG are the subject of disturbance, those corresponding to carbonyl and azomethine groups of ligand are subjected to highest perturbation on complexation; medium intensity doublet band corresponding to 1:4 disubstitution observed at 830  $\text{cm}^{-1}$  in ligand, is little disturbed in its frequency value but peak structure is changed from doublet to singlet invariably in all the complexes. Lowering in the carbonyl and azomethine group frequencies may be accounted

for considering their participation in complexation. However, disturbance in frequency corresponding to 1:4 disubstitution could be attributed to some structural change in ligand during complexation possibly benzenoid to quinonoid and this may be

substantiated by change in frequency of benzene ring breathing. Participation of carbonyl and azomethine groups in coordination is confirmed by the new bands appeared in the region  $600\text{ cm}^{-1}$ - $400\text{ cm}^{-1}$  and  $430\text{ cm}^{-1}$  –  $310\text{ cm}^{-1}$  corresponding to

**Table 1: Analytical results of complexes**

Complex	Molecular weight	Elemental analysis					
		Carbon (%)		Hydrogen (%)		Nitrogen (%)	
		Calcd.	Found	Calcd.	Found	Calcd.	Found
Ti(PDATG)Cl <sub>2</sub> .7H <sub>2</sub> O	561.5	38.47	38.45	4.63	4.45	4.99	5.10
Cr(PDATG)Cl <sub>2</sub> .9H <sub>2</sub> O	601.5	35.91	35.70	4.99	5.24	4.65	4.72
Co <sub>2</sub> (PDATG)Cl <sub>2</sub> .5H <sub>2</sub> O	631.0	34.23	34.30	3.49	3.38	4.44	4.33
Ni <sub>2</sub> (PDATG)Cl <sub>2</sub> .7H <sub>2</sub> O	667.0	32.38	32.55	3.90	4.01	4.20	4.08
Cu(PDATG).4H <sub>2</sub> O	487.5	44.31	44.23	4.10	4.15	5.74	6.00
Zn(PDATG).6H <sub>2</sub> O	525.3	41.12	41.23	4.57	4.68	5.33	5.48
Hg(PDATG).6H <sub>2</sub> O	660.0	32.73	32.95	3.64	3.72	4.24	4.33

**Table 2: Analytical and spectral data**

Compound	Characteristic I.R. Frequencies (cm <sup>-1</sup> )			1:4 di-substitution	M-O	M-N
	Carbonyl group	Azomethine group	Thienyl group			
PDATG	1720	1645	660,520	830m, d	-	-
Ti(PDATG)Cl <sub>2</sub> .7H <sub>2</sub> O	1625	1590	-	825	490	400
Cr(PDATG)Cl <sub>2</sub> .9H <sub>2</sub> O	1645	1580	665	830	490	430
Co <sub>2</sub> (PDATG)Cl <sub>2</sub> .5H <sub>2</sub> O	1695	1620	655,630	825	400	400
Ni <sub>2</sub> (PDATG) <sub>2</sub> .7H <sub>2</sub> O	1630	1630	660,525	830	430	400
Cu(PDATG).4H <sub>2</sub> O	1625	1625	520	830	445	-
Zn(PDATG).6H <sub>2</sub> O	1670	1630	665	840	405	405
Hg(PDATG).6H <sub>2</sub> O	1670	1620	520	825d	410	380

**Table 3: Values of g, g<sub>||</sub> and g<sub>⊥</sub> from E.S.R. spectra at RT and LNT**

Complex	g		g <sub>  </sub>		g <sub>⊥</sub>	
	RT	LNT	RT	LNT	RT	LNT
Ti(III)-Cl-PDATG	2.023	2.017	1.924	1.987	1.974	1.999
Cr(III)-Cl-PDATG	2.027	1.993	1.745	1.838	2.142	2.096
Co(II)-Cl-PDATG	2.084	-	1.946	-	1.975	-
Ni(II)-Cl-PDATG	2.023	-	1.877	-	2.091	-
Cu(II)-Cl-PDATG	2.122	2.009	2.064	2.101	2.198	2.018

RT = Room Temp., LNT = Liquid Nitrogen Temp.

metal-oxygen and metal-nitrogen bonds respectively. Prevention of sulphur atom from coordination may be attributed to its lower electron donating ability than carbonyl oxygen and azomethine nitrogen atoms and its greater distance from carbonyl oxygen than that between oxygen and nitrogen which, most probably, owes to the free rotation of thiophene ring attached with chain carbon through a single bond.

Higher frequencies of metal-oxygen bond than metal-nitrogen bond of ligand in complexes very well confirm the quinonoid form of ligand in complexes. On this basis of infrared spectral studies, the mechanism of complex formation may be shown as under.

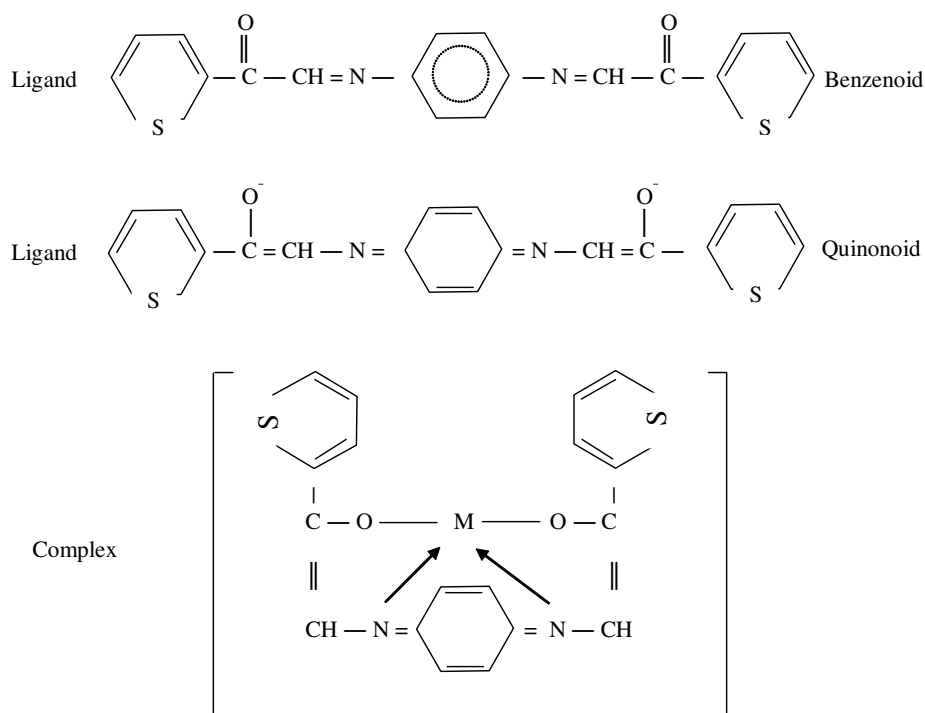
### Electron Spin Resonance Studies

Perusal of literature on e.s.r. studies of transition metal complexes reveals that complexes of Schiff's bases have been studied in the highest number to complexes of any other class of organic ligands in the past few decades whereas studies on ketoanil Schiff's base complexes<sup>22</sup> could not be conducted recently, and no reference is yet available

on polydentate ketoanil complexes. Values of  $g$ ,  $g_{||}$  and  $g_{\perp}$  of the synthesized compounds are reported in Table 3.

Perusal of  $g$ ,  $g_{||}$  and  $g_{\perp}$  values calculated at different temperatures from e.s.r. spectra of Ti (III) complex reveals that change in temperature is insignificant to bring any considerable effect in the splitting of  $M_J$  levels. High values of  $g_{||}$  and  $g_{\perp}$  in the present case indicate that ligand field component of magnitude compared to  $\lambda$  be present. This follows because the near isotropy of  $g$  and its proximity to the spin value, 2.00, corresponds to almost complete quenching of orbital angular momentum. The large component is not unexpected in view of the inequivalence of the ligand groups. Thus experimental values evidently show the presence of octahedral cubic ligand field around the metal ion in the complex.

E.S.R spectra of Cr (III) complex are typical of the compounds involving  $d^3$  configuration and  ${}^4A_{2g}$  ground term. Experimental values at both the temperatures are nearly isotropic and are consistent with cubic symmetry of the complex.



(Where M is bivalent metal having 4 coordination number)

However, little deviation in observed values from spin only value is indicative of very small departure from the proposed cubic symmetry. Temperature does not seem to affect the octahedral symmetry of the complex considerably. The contribution of spin orbit coupling effect also seems to be very small.

For high spin Co (II) complex involving  ${}^4T_{1g}$  ground state, if ligand field component is large compared to  $\lambda$ , the observed  $g$  value would be isotropic and near to 2.00. In the present complex  $g_{||}$  and  $g_{\perp}$  obtained from room temperature e.s.r. spectrum are almost the same and  $g$  is nearing spin only value. These results clearly indicate octahedral geometry of the complex.

In Ni (II)-PDATG complex  $g$  at room temperature (2.023) is very nearly isotropic. Values of  $g_{||}$  and  $g_{\perp}$  having insignificant difference indicate resonance possibility at room temperatures or at relatively lower temperatures and octahedral cubic symmetry of ligand field component. However, even very small difference of  $g$  from spin only value leads to small distortions in the proposed octahedral

geometry of the complex. Spin orbit coupling effect does not seem to play any effective role in the present complex.

Major distortion to Cu (II)-PDATG complex in an approximately octahedral environment causes  $g_{||}$  and  $g_{\perp}$  values to approach  $\sim 2.00$ . In a square planar molecule, a special octahedral case, due to considerable increase in  $\Delta E(d_{x^2-y^2} - d_{xy})$  and  $\Delta E(d_{x^2-y^2} - d_{xz}, d_{yz})$   $g$  values come out to be  $\sim 2.00$ . In the present case a single very broad isotropic derivative centred at  $g = 2.1220$  is although consistent with square planar geometry, possibility of very weak axial interactions in the solid, however, cannot be ruled out. Moreover, small difference in  $g_{||}$  and  $g_{\perp}$  values at room temperature which is further reduced at liquid nitrogen temperature evidently shows that this complex is not perfectly square planar.

The results of e.s.r. study, in general, reveal octahedral geometry for all paramagnetic complexes except that of Cu (II) in their solid state. It is interesting to note that octahedral cubic symmetry is stable in both, solid and solution, states.

## REFERENCES

- Baumann, H., U.S. (Cl, 260-145A C09 B45/02), 04 Oct. (1977).
- Baumann, H. and Grychtol, K., Ger. Offen. **2**, 614, 201 (Cl. C09 B55/48) 20 Oct. (1977).
- Baumann, H. and Grychtol, K., Ger. Offen. **2**, 617, 748 (Cl. C09 B55/00) 03 Nov. (1977).
- Hunger, K., Ger. Offen. **2**, 653, 481 (Cl. C09 B55/00) 01 June (1978).
- Hunger, K., Ger. Offen. **2**, 653, 482 (Cl. C09 B55/00) 01 June (1978).
- Hunger, K., Ger. Offen. **2**, 653, 483 (Cl. C09 B55/100) 01 June (1978).
- Chamberlain, T. R., Campbell and McCrae, J. M., Ger. Offen. **2**, 728, 863 05 Jan. (1978).
- Pakhomova, L. F., Babel, V. G., Bebikh, G. F. and Proskuryakov, V.A., Zh. Prikl Khim (Leningard), **48**(8): 1841 (1976).
- Pakhomova, L. F., Babel, V. G., Bebikh, G. F. Proskuryakov, V.A. and Antropyanskaya, E. A., Otkrytie Izolbret. Prom. Obratzsy Tovarnya, Znaki, **55**(B): 78 (1978).
- Chenieek, T. A., U. S. **2**: 249, 602 (1941).
- Costain, W. and Terry, B. W. H., Brit., **1**, 434, 354 (Cl. C23F11/00), 5<sup>th</sup> May (1976).
- Pupo, D. A., Haist, G. M. and Klijanowicz, E., *Res. Diesel*, **151**: 63 (1976).
- Popp, F. D. and Kirsch, W., *J. Org. Chem.*, **26**: 3858 (1961).
- Kher, N. J., Subnis, S.S. and Bhide, M. B., *Bull. Haffkine Inst.*, **5**(1): 60 (1977).
- Kher, N. J., Subnis, S.S. and Bhide, M. B., *Bull. Haffkine Inst.*, **5**(2): 69 (1977).
- Cohen, V. I., Rist, N. and Duponchel, C., *J. Pharma Sci.*, **66**(9): 1322 (1977).
- Bekstch, Z., Kowlik, R. and Zwier, W., *Dissertation Pharm.*, **15**(5): 369 (1964).

18. Snyder, J. P., Heyman, M. and Gundestrup, M., *J. Org. Chem.*, **43**(11): 2224 (1978).
19. Km. Saxena, Hemlata, Prabhakar, Prem and Pathak Vishal., *J. Chemtracks*, **11**(1): 333 (2009).
20. Pathak, Prince, Singh, Monal and Pathak, Vishal, *Asian J. Chem.*, **22**(3): 1773 (2010).
21. Upadhyay, R. K., *Chromatographics*, **11**, 197 (1978).
22. Gupta, H. C., Ph. D. Thesis, Agra Univ., Agra (1981).