

Studies on Oligomeric Polymers

Sachendra M Shah, F. B. Bux¹, Varsha Parmar² and Arun Singh^{*3}

¹Department of Chemistry, Govt. Geetanjali Girls College, Bhopal, M.P., India

²Department of Chemistry, Gargi Institute of Science and Technology, Bhopal, M.P., India

³Rajya Siksha Kendra, Pustak Bhawan Bhopal, M.P., India

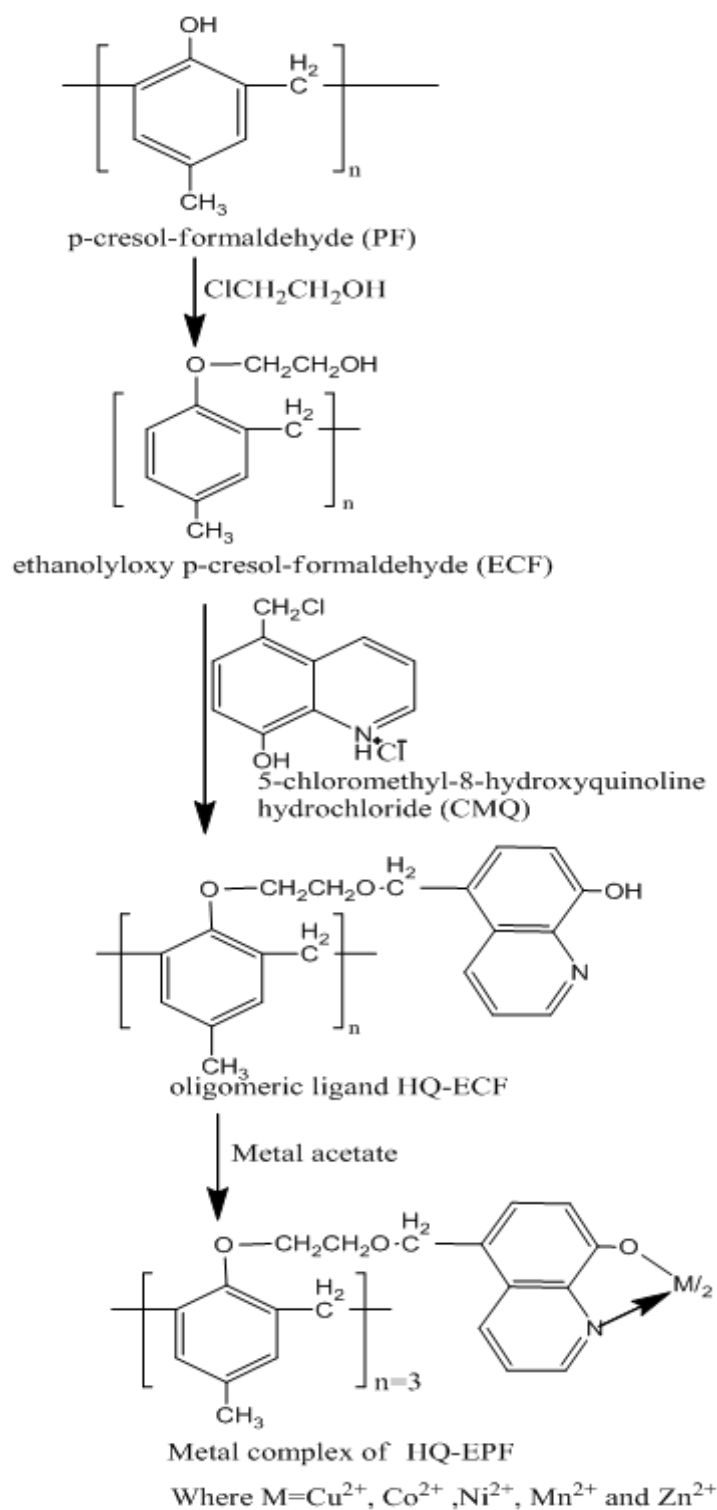
ABSTRACT

Acid catalyzed *p*-cresol-formaldehyde resin (CF) was prepared by well-known method. It was treated with 2-chloro ethanol. The resultant ethanolyloxy *p*-cresol-formaldehyde resin (ECF) was then treated with 5-chloromethyl-8-hydroxyquinoline hydrochloride (CMQ). The so called obtained oligomeric ligand HQ-ECF was characterized by elemental and spectral analysis. The oligomeric metal chlaties of HQ-ECF with Cu^{2+} , Co^{2+} , Ni^{2+} , Mn^{2+} and Zn^{2+} metal ions were prepared and studied for their metal:ligand (M/L), stoichiometry, magnetic moment, spectral features and by thermogravimetry.

Keywords: *p*-cresol-formaldehyde (PF), 5-chloromethyl-8-hydroxyquinoline hydrochloride (CMQ), Spectral studies, Thermogravimetric analysis (TGA), Magnetic moment, Antibacterial and Antifungal activities.

INTRODUCTION

Polymeric ligands derived from 8-hydroxylquinoline are reported in literature and its derivatives are good metal precipitant and ion-exchangers [1-10]. The *p*-cresol-formaldehyde resins are important material in industries [11-12], but its clubbing with 8-hydroxylquinoline(HQ) has not been developed so far. This may afford good ion-exchanger material. Though the 8-hydroxylquinoline (HQ) derivative say 5-chloromethyl-8-hydroxy quinolinol(CMQ) precursor for the synthesis of many coordination polymers, biological active compounds as well as ion-exchanger[12-17].Thus the present article expresses the synthesis and characterization of a novel oligomeric ligand having *p*-cresolic-8-hydroxylquinoline clubbed system and its metal chelates Cu^{2+} , Co^{2+} , Ni^{2+} , Mn^{2+} and Zn^{2+} metal ions. The synthetic route is shown in scheme 1.



Scheme-1

MATERIALS AND METHODS

All the chemicals used were of AR grade and were obtained from local dealer.

Synthesis of Oligomeric Ligand HQ-ECF

The 5-chloromethyl-8-hydroxyquinoline hydrochloride (m.p. 280°C) was prepared by method reported in literature[18]. The ethanolyloxy p-cresol-formaldehyde resin (ECF) prepared by simple reaction of sodium salt of p-cresol-formaldehyde resin (CF) resin with 2-chloroethanol [19].

HQ-ECF was prepared by following a method reported for 5-alkoxymethyl-8-quinoline¹⁶. According to this method, Sodium Bicarbonate (0.1mole) was added to a suspension of 5-chloromethyl-8-hydroxyquinoline hydrochloride (0.1 mole) and ethyloxy p-cresol-formaldehyde resin (ECF)(0.1mole) in THF. The reaction mixture was refluxed for 2.5hrs with frequently stirring. The resulting solution was then made alkaline with dilute ammonia to precipitate out HQ-ECF ligand, which was then filtered and air dried. The yield of was 76% and its melting point was 214-216°C (uncorrected). The predicted structure and formation of polymeric ligand is shown in Scheme-1.

Preparation of Polymeric Chelates

All Polymeric Chelates were synthesized by using metal acetates in a general method described as follows:

A warm clear solution of HQ-ECF in 20% aq.formic acid (200ml) was added to a solution of copper acetate (0.01mole) in 50% aq.formic acid (50ml) with constant stirring. After complete addition of metal salt solution, the pH of reaction mixture was adjusted to about 5 with dilute ammonia solution. The polymer chelate is separated out in the form of suspension was digested on a water bath for one hour and eventually filtered, washed with hot water followed by acetone and dimethyl formamide (DMF) and then dried in air at room temp. The yields of all co-ordination polymers were almost quantitative.

TABLE 1 ANALYTICAL AND SPECTRAL DATA OF THE CO-ORDINATION POLYMERS OF HQ-ECF (H₂L)

Ligand/ Co-ordination polymers	Empirical Formula	Formula Weight	Analyses				$\mu_{\text{eff.}}$ (B.M.)	\overline{M}_n (± 60)	\overline{D}_p
			%Found(Calculated)						
			%M	%C	%H	%N			
HQ-ECF	(C ₂₀ H ₁₉ NO ₃) _n	321	-	67.2 (67.22)	5.3 (5.32)	3.9 (3.92)	-	-	-
[Cu(HQ-ECF)(H ₂ O) ₂] _n	(Cu.C ₂₀ H ₁₈ NO ₃ .2H ₂ O) _n	419.54	15.1 (15.14)	57.1 (57.20)	5.2 (5.24)	3.3 (3.33)	2.03	2584	6
[Co(HQ-ECF)(H ₂ O) ₂] _n	(Co.C ₂₀ H ₁₈ NO ₃ .2H ₂ O) _n	414.94	14.1 (14.20)	57.8 (57.83)	5.2 (5.30)	3.3 (3.37)	2.92	2140	5
[Ni(HQ-ECF)(H ₂ O) ₂] _n	(Ni.C ₂₀ H ₁₈ NO ₃ .2H ₂ O) _n	414.71	14.1 (14.15)	57.8 (57.87)	5.2 (5.30)	3.3 (3.37)	4.01	2146	5
[Mn(HQ-ECF)(H ₂ O) ₂] _n	(Mn.C ₂₀ H ₁₈ NO ₃ .2H ₂ O) _n	410.94	13.3 (13.36)	58.3 (58.40)	5.3 (5.35)	3.3 (3.40)	4.85	2535	6
[Zn(HQ-ECF)(H ₂ O) ₂] _n	(Zn.C ₂₀ H ₁₈ NO ₃ .2H ₂ O) _n	421.38	15.5 (15.51)	56.9 (56.95)	5.2 (5.22)	3.3 (3.32)	Diamagnetic	2177	5

Measurements

Elemental analysis of HQ-ECF and its polymeric chelates were carried out on a C,H,N elemental analyzer (Italy). IR spectra of H₂L and the polymeric chelates were scanned on a Nicolet-760D FTIR spectrophotometer in KBr. The metal content analyses of the polymeric chelates were performed by decomposing a weighed amount of each polymeric chelates followed by EDTA (disodium ethylene diamine tetra acetate) titration as reported in the literature[20]. Magnetic susceptibility measurements of all the polymeric chelates were carried out at room temperature by the Gouy method. Mercury tetrathiocyanatocobaltate (II), Hg[Co(NCS)], was used as a calibrant. Molar Susceptibilities were corrected for diamagnetism of component atoms using Pascal's constant. The diffuse reflectance spectra of the solid polymeric chelates were recorded

on a Beckman DK-2A spectrophotometer with a solid reflectance attachment. MgO was employed as the reference compound.

Thermogravimetric analysis of co-ordination polymers were carried on DuPont 950 TGA analyzer in air at a heating rate of 20C/min.

TABLE 2 THERMO GRAVIMETRIC ANALYSIS OF HQ-ECF

Ligand/ Co-ordination polymers	% weight loss at temperature T(°C)					
	100	200	400	500	600	700
H ₂ L	-	5.8	10.6	40.7	45.8	48.7
[CuL(H ₂ O) ₂] _n	2.8	5.5	13.5	42.9	48.3	53.9
[CoL(H ₂ O) ₂] _n	4.9	9.0	16.9	22.6	43.8	59.7
[NiL(H ₂ O) ₂] _n	5.2	8.8	15.3	26.9	45.6	59.9
[MnL(H ₂ O) ₂] _n	5.3	7.2	9.9	15.7	25.5	36.6
[ZnL(H ₂ O) ₂] _n	2.6	3.8	5.4	15.6	23.9	35.9

Antibacterial activities

Antibacterial activity of HQ-ECF ligand and its co-ordination polymers were studied against gram-positive bacteria (*Bacillus subtilis* and *staphylococcus aureus*) and gram-negative bacteria (*E.coli* and *salmonella typhi*) at a concentration of 50µg/ml by agar cup plate method. Methanol system was used as control in this method. The area of inhibition of zone measured in mm.

TABLE 3 ANTIBACTERIAL ACTIVITIES OF HQ-ECF

Compounds	Zone of Inhibition(mm)			
	Gram +Ve		Gram -Ve	
	<i>Bacillus subtilis</i>	<i>Staphylococcus aureus</i>	<i>Salmonella typhi</i>	<i>E.coli</i>
[CuL(H ₂ O) ₂] _n	60	68	65	67
[CoL(H ₂ O) ₂] _n	66	69	60	65
[NiL(H ₂ O) ₂] _n	67	67	64	62
[MnL(H ₂ O) ₂] _n	64	64	63	67
[ZnL(H ₂ O) ₂] _n	66	63	67	65

Antifungal activities

The fungicidal activity of all the compounds was studied at 1000 ppm concentration in vitro. Plant pathogenic organisms used were *penicillium expansum*, *Nigrospora Sp.*, *Trichothesium Sp.*, and *Rhizopus nigricum*. The antifungal activity of ligand and its co-ordination polymers was measured on each of these plant pathogenic strains on a potato dextrose agar (PDA) medium. Such a PDA medium contained potato 200gm, dextrose 20gm, agar 20gm and water one liter. Five days old cultures were employed. The compounds to be tested were suspended (1000ppm) in a PDA medium and autoclaved at 120° C for 15 min. at 15atm. pressure. These medium were poured into sterile Petri plates and the organisms were inoculated after cooling the petri plates.

The percentage inhibition for fungi was calculated after five days using the formula given below:

$$\text{Percentage of inhibition} = 100(X-Y) / X$$

Where, X = Area of colony in control plate

Y = Area of colony in test plate

TABLE 4 ANTIFUNGAL ACTIVITIES OF HQ-ECF

Compounds	Zone of Inhibition at 1000 ppm (%)			
	<i>Penicillium Expansum</i>	<i>Nigrospora Sp.</i>	<i>Trichothesium Sp.</i>	<i>Rhizopus Nigricum</i>
[CuL(H ₂ O) ₂] _n	65	66	64	62
[CoL(H ₂ O) ₂] _n	63	68	65	66
[NiL(H ₂ O) ₂] _n	67	69	69	62
[MnL(H ₂ O) ₂] _n	66	65	66	68
[ZnL(H ₂ O) ₂] _n	63	63	67	65

RESULTS AND DISCUSSION

The synthesis of the oligomeric ligand HQ-ECF has not been reported in the literature. The ligand HQ-ECF was isolated in the form of a reddish brown powder. It was soluble organic solvents such as in DMSO (dimethyl sulfoxide), DMF. The results of elemental analyses of the HQ-ECF ligand (Table-1) are agreed with those predicted on the basis of formula.

The IR spectrum of HQ-ECF features are a broad band extending from 3450-3160 cm⁻¹ with maximum at 3320 cm⁻¹, attributed to the OH group. The weak bands around 2893 and 2950 cm⁻¹ may be due to asymmetric and symmetric stretching vibrations of methylene groups(-CH₂-). The bands around 1634, 1575, 1500 and 1440 cm⁻¹ are attributed to the 8-hydroxyquinoline nucleus [21]. The others bands are at their respective positions.

The ¹H NMR(δ ppm) spectrum of HQ-ECF also show the signals 2.78(2H,s,CH₂); 3.84-4.45 (4H,t,CH₂) ; 5.04 (2H,s, CH₂) ; 4.22 (1H,s,OH) ; 7.30-6.76(2H,m,Ar-H,); 6.54-8.11 (5H,m,Quinoline). These features confirm the proposed structure of ligand HQ-ECF. The NMR Data of HQ-ECF shown in experimental part are also confirming the structure of HQ-ECF.

The polymeric chelates derived from HQ-ECF are insoluble in common organic solvents like acetone, methanol, ethanol etc. Hence it is not possible to characterized the co-ordination polymers by molecular mass using conventional methods like osmometry, viscometry etc. These co-ordination polymers do not melt up to 360°C.

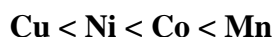
On the basis of the proposed structure shown in Scheme-1, the molecular formula of the HQ-ECF ligand is C₂₀H₁₉NO₃, which, upon chelation coordinates with two central metal atom at four co-ordination sites and two water molecules. Therefore, the general molecular formula of the resulting co-ordination polymer is given by [M (HQ-ECF)₂.2H₂O] as shown in scheme-1. This has been confirmed by the results of elemental analyses of all of the five co-ordination polymers and their parent ligand. The data of elemental analyses reported in Table I are in agreement with the calculated values of C,H and N based on the above-mentioned molecular formula of the parent ligand as well as co-ordination polymers. Examination of data of the metal content in each polymer (Table-1) revealed a 1:1 metal: ligand (M/L) stoichiometry in all of the co-ordination polymers. Comparison of the IR spectrum of the ligand HQ-ECF and those of the co-ordination polymers reveals certain characteristic differences. The broad band at 3400-3100 cm⁻¹ for HQ-ECF has almost disappeared for the spectra of polymers. However, the weak bands around 3200 cm⁻¹ in the spectra of HQ-ECF -Co²⁺, HQ-ECF -Ni²⁺, HQ-ECF -Mn²⁺ indicate the presence of water molecules which may have been strongly absorbed by the polymer sample. The weak band around 1115cm⁻¹ is attributed to the C-O-M stretching frequency [21]. The band at 1435 cm⁻¹ in the IR spectrum of HQ-ECF is attributed to the in-plane OH deformation [21]. The band is shifted towards higher frequency in the spectra of the polymers indicating formation of metal-oxygen bond. These feature suggest that the structure of the co-ordination polymer.

The value of the degree of polymerization of all the co-ordination polymers listed in Table-1 suggest that the average Dp for all the polymers in a range of 5 to 6. Magnetic moments (μ_{eff}) of polymeric chelate are given in Table-1.

The diffusion electronic spectrum of HQ-ECF -Cu²⁺ co-ordination polymers shows two broad bands around 15,392 cm⁻¹ and 22,738 cm⁻¹. The first bands may be due to ${}^2T_{2g} \rightarrow {}^2E_g$ transition. While the second may be due to charge transfer. The first band shows structure suggestion a distorted octahedral structure for the HQ-ECF -Co²⁺ polymers. The higher value of μ_{eff} of the HQ-ECF -Cu²⁺ polymer support this view [22,23]. The HQ-ECF -Ni²⁺ and HQ-ECF -Co²⁺ polymers give two absorption bands respectively at 17,263 and 24,021 cm⁻¹ and at 17,256 and 23742 cm⁻¹ which can be assigned respectively to ${}^4T_{1g} \rightarrow {}^2T_{2g}$, ${}^4T_{1g} \rightarrow {}^4T_{1g(P)}$ transitions. These absorption bands and the values of μ_{eff} indicate an octahedral configuration for the HQ-ECF -Ni²⁺ and HQ-ECF -Co²⁺ polymers [24,25]. The spectrum of [Mn(HQ-ECF)₂(H₂O)₂] show weak bands at 16,475, 17,694 and 23,171 cm⁻¹ assigned to the transitions ${}^6A_{1g} \rightarrow {}^4T_{1g}(4G)$, ${}^6A_{1g} \rightarrow {}^4T_{2g}(4G)$ and ${}^6A_{1g} \rightarrow {}^4A_{1g}, {}^4E_g$ respectively, suggesting an octahedral structure for the [Mn(HQ-ECF)₂(H₂O)₂] polymer²³. As the spectrum of the [Zn (HQ-ECF)₂(H₂O)₂] polymer is not well resolved, it is not interpreted, but its μ_{eff} value shows that it is diamagnetic as expected.

The TGA data for the polymers are presented in Table-2. The weight loss of the polymer samples at different temperatures indicates that the degradation of the polymers is noticeable beyond 300°C. The rate of degradation becomes a maximum at a temperature lying between 400 °C and 500 °C depending upon the nature of the polymers. Each polymer lost about 56% of its weight when heated up to 700 °C. Inspection of the thermograms of HQ-ECF -Co²⁺, HQ-ECF -Mn²⁺ and HQ-ECF -Ni²⁺ samples revealed that these samples suffered appreciable weight loss in the range 150 to 280°C. This may due to the presence of water strongly absorbed by the polymers. It has also been indicated earlier that the IR spectra of these three polymer samples have OH bands at around 3200 cm⁻¹ due to associated water.

On the basis of the relative decomposition (% wt. loss) and the nature of thermograms, the co-ordination polymers may be arranged in order in increasing stability as:



This trend also coincides with the stability order already reported for the metal oxinates¹⁹ and for co-ordination polymers of HQ-ECF[3].

The antimicrobial activity of HQ-ECF and its co-ordination polymers are presented in Table-3 and 4. The data suggest that all the samples are toxic to bacteria or fungus. The data also suggest that the % age of bacteria or fungus is inhibited in the range of 58 to 80% depending upon the biospecies and co-ordination polymers.

CONCLUSION

Polycondensation of 5-chloromethyl-8-hydroxyquinoline hydrochloride and ethyloxy p-cresol-formaldehyde resin (ECF) yielded a novel oligomeric ligand HQ-ECF. The applicability of the polymeric ligand was explored by preparing polymeric chelates using different divalent metal ion indicating that the HQ-ECF polymeric ligand has good chelating property and high thermal stability.

Further, the polymeric ligand is thermally more stable than its polymeric chelates. Among the five polymeric chelates, M-HQ-ECF chelate is least stable, whereas M-HQ-ECF polymeric chelates is the most stable having a thermal stability comparable to that of chelates may be used as heat resistant material up to 350°C. The polymeric ligand follows a two steps thermal degradation whereas polymeric chelates follow a single step thermal degradation.

A evaluation of the thermal stability of the present polymeric chelates with those of 5-chloromethyl-8-hydroxyquinoline hydrochloride and ethyloxy p-cresol-formaldehyde (ECF) as a parent groups of polymeric chelates reveals that the HQ-ECF polymeric chelates are thermally more stable. Finally, the magnetic susceptibility results indicate that polymeric chelates of Cu^{+2} , Ni^{+2} and Co^{+2} are paramagnetic, whereas that of Zn^{+2} is diamagnetic in nature.

All the polymers have good microbicidal activity.

REFERENCES

- [1] H.S. Patel, D.J.Pate, *International Journal of Polymeric Materials*, **2010**,59,307.
- [2] C. U. Pittman, K. S. Ramachandran Jr and K.R. Lowyer, *J. Coat. Technol.*,**1982**,54,27.
- [3] R.Purohit and S.Devi, *Analyst*. **1991**,16,825.
- [4] M.Bankova, N Manolova and I.Rashkov, *Eur. Polym. J.*,**1994**,30(10),1179.
- [5] N.Angelova, N. Manolova, and I.Rashkov, *Eur. Polym. J.* **1995**,31(8), 741.
- [6] M.Bankova, T. Petrova, N.Manolova and I.Rashkov, *Eur. Polym. J.* **1996**,32(3), 325.
- [7] M.Bankova, T.Petrova, N.Manolova and I.Rashkov, *Eur. Polym. J.* **1996**,32(5), 569.
- [8]N. Manolova, M. Ignatova and I. Rashkov, *Eur. Polym. J.*,**1998**, 34(8),1133.
- [9] M. Bankova, N. Manolova, N.Markova, T.Radoucheva, K.Dilova and I.Rashkov, *Eur. Polym. J.* **1999**,34(2), 247.
- [10] H.K. Sharma, N.I. Verma and J. K.Kapoor, *Advances in Applied Science Research*, **2011**,2(5),522-537 .
- [11] Alexandratos, S.D., *Ind. Eng. Chem. Res.*, **2009**,48,388.
- [12] M.I.Kuo, D. Adams, D. Myers, D. Curry, H. Heemstra, J.L. Smith, and Y. Bian., *Forest Products Journal*,**1998**,48(2),71.
- [13] R. D. Patel, S. R. Patel and H. S. Patel, *Eur. Polym. J.* **1987**,23(3), 229.
- [14] T. B. Shah, H. S. Patel, R. B. Dixit and B. C.Dixit, *Int. J. of Polym. Anal. and Charact.* **2003**,8,369.
- [15] D.K.Patel and Arun Singh, *E-Journal of Chemistry*, **2009**,6(4),1017.
- [16] W.Abraham, D.Abraham, R.Guy and P.Abraham, , *Reactive polymers, ion Exchangers, Sorbents.*,**1984**,2(4),301.
- [17] A.D.Patel, N.K.Prajapati, S.P.Patel and G.R.Patel,*Der Chemica Sinica*,**2011**,2(2):130.
- [18] J. H. Burckhalter and R. I. Leib, *J. Org. Chem.*,**1961**,26,4078.
- [19] A. I.Vogel,*A Text book of Quantitative Inorganic Analysis*, 5th ed., (Longman, London), **1989**,584.
- [20] H.S. Patel, R.B. Dixit, and T.B.Shah, *Int. J. Polym. Material.*, **2001**,49,27.
- [21] R.G. Charles, H.Freiser, R.Priedel, L.E. Hilliand and R.D.Johnston,*Spectrochim Acta*,**1958**,8,1.
- [22] D. C. Patel and P. K. Bhattacharya, *J. Indian Chem. Soc.* **1972**,49, 1041.
- [23] D. Oza, K. N. Kaul and R. K. Mehta, *Indian J. Chem.* **1996**,7, 927.
- [24] J. Lewis and R.S. Wilkins, *Modern Co-ordination Chemistry*,*Intersci.*,NY,**1960**,290.
- [25] R.Papplardo, *J. Chem. Phys.* **1960**, 33, 613.