

Dielectric Properties of Pt(NO₂acac)₂ and Their Molecular Complexes with Heterocyclic N-Bases

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The dipole moments of Pt(NO₂-acac)₂ and its molecular complexes formation with heterocyclic N-bases have been studied by refractive index, Guggenheim and dielectric plot methods. The formation of charge transfer complexes Pt(NO₂-acac)₂ with heterocyclic N-bases is further supported by dipole moment studies. It is found that acetylacetonone has larger dipole moment than its metal chelates, which may be interpreted due to its non-planar structure. The symmetry of Pt(acac)₂ is disturbed when γ -H of this chelate is replaced by the nitro group. An increase in the dipole-moment was observed in these systems after complexation. The maximum dipole moment of Pt(NO₂-acac)₂ pyridine complex was observed which indicates stronger interaction with pyridine in comparison to other donors. The dipole moment of these complexes has been found in consistent with those of K₁ values obtained from conductometric methods. It is also observed that the value of dipole moment increases with increase in the temperature for Pt(NO₂-acac)₂-pyridine or quinoline complex. The values are greater for pyridine system at different temperatures. The dielectric titration technique has indicated 1:1 stoichiometry of these charge-transfer complexes. From this study it has been observed that more polar is the solute the larger is the expected increase in its dipole moment values. It is suggested that the interaction of Pt(NO₂-acac)₂ with N-bases is governed by dipole electrostatic attraction.

Key Words: Dipole moment, Molecular complex, Pyridine, Quinoline, Conductometric method, Heterocyclic-N-bases.

INTRODUCTION

It has been observed that the measurements of equilibrium and rate constants of Pt(NO₂-acac)₂-pyridine molecular complexes provide about the stability of these complexes. The studies of dielectric constants of substances have given as useful information for the elucidation of the structure of molecular complexes. Dielectric properties of the metallic complexes have been used to provide information about the life-time of these complexes¹ and charge redistribution² on them. Dipole moment has been found to be directly related to the dative contribution to the ground state of the charge-transfer complexes. Thus, it provides good deal of information about the polarity, structure and stability of these molecular complexes. A comparison of dipole moment of the component molecules may provide valuable

information on charge redistribution on the complex formation and a measure of the strength of the interaction between donor and acceptor molecules^{1,2}.

A survey of the chemical literature³⁻⁷ reveals that the dielectric studies on $M(\text{NO}_2\text{-acac})_n$ and its molecular complexes with heterocyclic bases are scanty. Although spectrophotometric^{2,8-12} and NMR¹³ studies have been used extensively to study the molecular interactions, but spectrophotometric technique is not feasible when there is only slight perturbation of either donor or acceptor absorption band due to weak interactions or there is overlapping of charge-transfer band with those of either donor or acceptor absorption band.

The purpose of the present study is to investigate the dielectric properties of $M(\text{NO}_2\text{-acac})_n$ and their molecular complexes with heterocyclic bases, such as, pyridine, quinoline, 2-methyl pyridine, 3-methyl pyridine, 4-methyl pyridine in non-polar solvents. They have zero dipole moment. This study may provide substantial information on the geometry of such molecular complexes as well as the role of π - and n -electrons in metal acetylacetonate chelate rings.

EXPERIMENTAL

$M(\text{NO}_2\text{-acac})_n$ were prepared as reported in the literature¹⁴.

(A) The procedure for the nitration of $M(\text{NO}_2\text{-acac})_n$ with copper nitrate or concentrated nitric acid as nitrating agent was essentially the same as reported in the literature¹⁴. In place of copper nitrate, nitrates of Ni(II), Co(II), Al(II) and Fe(II) were also used as nitrating agent in acetic anhydride medium under similar reaction conditions.

(B) Acetylacetone (0.02-0.23 mol) or 1,3-diphenyl propane-1,3-dione (0.03 mol) and acetic anhydride (10-20 mL) were placed in a 250 mL Erlenmeyer flask fitted with a calcium chloride drying tube and stirred magnetically for 15 min at 0 °C. Crystals of the metal nitrate (0.01 mol) were pulverized and added in portions to the stirred solution during 0.5 h. After 1-2 h the ice bath was removed and stirring was continued. The contents of the flask slowly dissolved though an exothermic reaction.

Pressures which develop inside the flask were released by occasional lifting of the stopper and undue rise in temperature was checked by dipping the flask in ice-cold water. A coloured deposit of nitro derivative was stirred 2-3 h more at room temperature and then poured *ca.* 200 mL of ice-cold water containing sodium acetate and stirred for a further 1 h. The precipitated nitro derivative was filtered under suction and washed with water and then with ethanol. After air drying recrystallization from a suitable solvent gave the pure product.

When nitrates of metal (0.015-0.025 mol) which form more stable chelates were used for the nitration of less stable metal chelates (0.015 mol) in acetic anhydride medium (10-15 mL), the metal atom of the nitrate replaced the ring metal atom of labile chelate during the nitration process. The nitro derivatives of new chelates were obtained as a result of such metal replacement reactions.

Acetylacetone (AR grade) was used after distillation. All the solvents and donors used were AR grade (BDH) and were purified as reported in the literature¹⁴.

Preparation of the solutions: Stock solution of Pt(NO₂-acac)₂ was prepared in different solvents by weighing on an analytical balance and subsequent dilution of the required volume in volumetric flasks in appropriate solvents. The solution employed for the measurement of dipole moment was prepared from the stock solutions by pipetting the calculated volume in 10 mL volumetric flasks. All the stock solution was made on the day of study for dipole moment.

Determination of refractive index: The refractive index (n) of all the solutions of Pt(NO₂-acac)₂ and their complexes with different donor and in different solvents was measured with the help of Abbe's refractometer with an accuracy of ± 0.0002 at 30 °C.

Measurement of density: The density of the solute in different solvents and complexes were measured by usual relative density bottle (5 mL) method.

Determination of dielectric constant: The RCL bridge has been used to measure the capacitance of the solutions. For this purpose, we have made small capacitors of two brass plates having the same thickness as well as the same area of cross section and are joined in such a way that they are separated by a non-conducting material with a fixed distance. Now these plates (capacitors) are connected by 2 leads to the RCL bridge. The capacitance of this capacitor in vacuum is directly measured by the bridge. Then this capacitor is dipped in the mixture of Pt(NO₂-acac)₂ and heterocyclic bases in different solvent at different temperatures, whose density and refractive index have already been measured to obtain the capacity of the mixture. These measurement have been made after 20 h on mixing acceptor Pt(NO₂-acac)₂ and donors (pyridine, 2-methyl pyridine, 3-methyl pyridine, 4-methyl pyridine and quinoline) in different solvents CCl₄, C₅H₅N and tetrahydrofuran at different temperature (30, 35, 40 and 45 °C). The ratio of the capacitance in solution to the capacitance in vacuum will measure the dielectric constant of the solution. These measurements were carried out at 20 °C. At a radio frequency of 1 MHz. RCL bridge works on a well-known principle of heterodyne beat method. The resulting beat frequency is projected on the screen of a cathode ray tube (CRT) with a 50 cycle/second. A Lissajous figure is obtained on the screen. The readings were recorded at the resonance point indicated on the cathode ray tube screen. When dielectric constant, refractive index and density have been obtained, the dipole moment (μ), was calculated from eqns. (1, 5 and 11) in each case.

When dielectric constant and refractive index have been obtained, the dipole moment (μ) was calculated from eqn. (1).

In the present study, the dipole moment of the polar solutes and charge transfer complexes have been determined by using the following methods:

Refractive index method: In this method eqn. 1 has been used to calculate the dipole moment (μ) of the solutes and complexes¹⁵,

$$\mu = 0.0127 \times 10^{-18} \sqrt{(P - P_D)T} \quad (1)$$

where P is the total polarization and PD (PE + PA) is the distortion polarization. P and PD were calculated using eqns. 2 and 3;

$$P = \frac{(\epsilon - 1) M}{(\epsilon - 2) d} \quad (2)$$

$$P_D = \frac{(n^2 - 1) M}{(n^2 + 2) d} \quad (3)$$

where ϵ is the dielectric constant, M is molecular weight, d is the density and n is the refractive index of the solution.

Guggenheim method: The dipole moment of polar solutes has been calculated using this method by plotting¹, Δ against the concentration C in moles of polar solutes (Figs. 1-4) given by the relation¹⁶,

$$\Delta = (\epsilon_{12} - n_{12}^2) (\epsilon_1 - n_1) \quad (4)$$

where ϵ_1 , n_1 and ϵ_{12} , n_{12} represent the dielectric constant and refractive index of pure solvent and solution, respectively. The slope $(\Delta/C)_0$ of a curve at C=0 is then used to evaluate the dipole moment of the solutes by eqn. 5¹⁷,

$$\mu^2 = \frac{9kT}{4N} \cdot \frac{3}{(\epsilon_1 + 2)(n_1^2 + 2)} (\Delta/C)_0 \quad (5)$$

where k is the Boltzmann's constant, N, Avogadro's number, ϵ_1 and n_1 are the dielectric constant and refractive index of the solvent at temperature T, respectively.

In order to avoid experimental error arising from the uncertainty in the extrapolation of the curve between solute polarization (P_2) and its mole fraction (X_2) and in measurement of solution densities, the dipole moment of the complex was calculated by the Guggenheim¹⁶ procedure. The procedure is based upon the Debye equation¹⁵ and employs the relation:

$$P_0 = \frac{4}{9} \frac{\mu^2}{KT} = \frac{3M_2}{\rho_1(\epsilon_1 + 2)^2} \lim_{W_2 \rightarrow 0} W_2 - 0 \frac{\delta\epsilon_{12}}{W_2} - \frac{\delta\epsilon_{12}n_{12}^2}{W} \quad (6)$$

where P_0 , μ , M_2 and W_2 are the orientation, polarization, dipole moment, molecular weight and weight fraction of the solute, ρ_1 and ϵ_1 are the density and dielectric constant of the pure solvent and ϵ_{12} and n_{12} are the dielectric constant and refractive index of the solution, respectively.

Now from a plot of ϵ_{12} versus W_2 , one can obtain a curve which fits the expression.

$$\epsilon_{12} = \epsilon_1 + a W_2 + a W_2^2 \quad (7)$$

with a limiting slope of the curve at $W_2 = 0$ given by eqn. 8;

$$\frac{\delta\epsilon_{12}}{W_2} = a \quad (8)$$

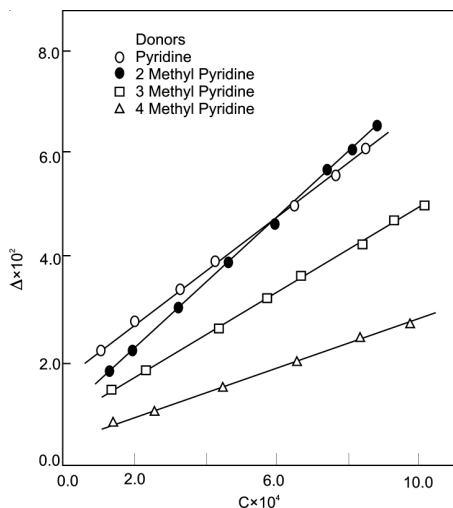


Fig. 1. Plot of Δ vs. C for Pt(NO₂-acac)₂ complex with pyridine donor in carbon tetrachloride at 20 °C

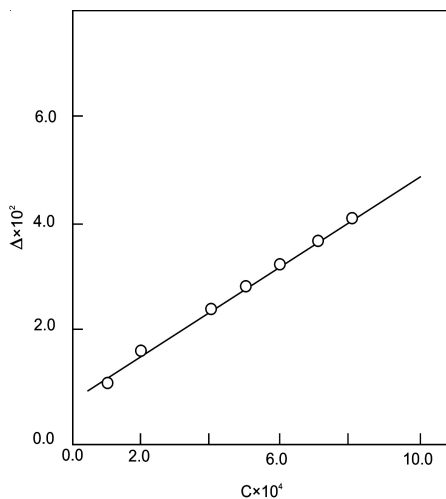


Fig. 2. Plot of Δ vs. C for Pt(NO₂-acac)₂-Py complex in pyridine at 20 °C

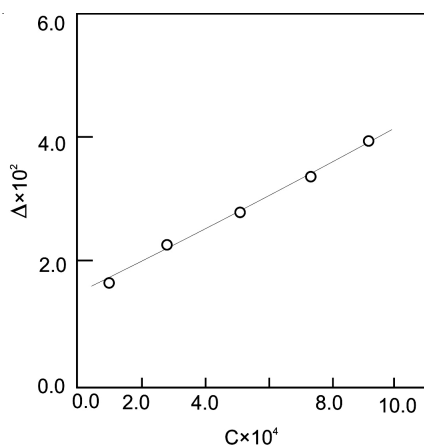


Fig. 3. Plot of Δ vs. C for Pt(NO₂-acac)₂-quinoline complex in carbon tetrachloride at 20 °C

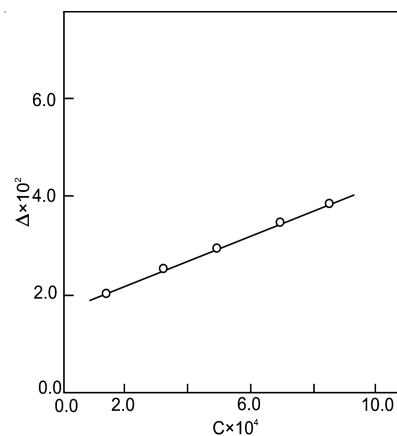


Fig. 4. Plot of Δ vs. C for Pt(NO₂-acac)₂-Py complex in tetrahydrofuran at 20 °C

Similarly, a plot of n_{12}^2 versus W_2 gives a curve which fits the expression,

$$n_{12}^2 = n_1^2 + a_n W_2 + a_n W_2^2 \tag{9}$$

With the limiting slope of the curve at $W_2=0$ given by eqn. (10);

$$\frac{\delta n_{12}^2}{\delta w_2} = a_n \tag{10}$$

Now, substituting the eqn. (8 and 10) into eqn. (6), we get,

$$\mu^2 = \frac{27kT}{N} \cdot \frac{M_2}{4\pi\rho_1(\epsilon_1 + 2)^2} (a_\epsilon - a_n) \quad (11)$$

From eqn. 11, the dipole moment of the complex has been evaluated. In eqn. (11), M_2 is the molecular weight of the complex and ρ_1 and ϵ_1 are the density and dielectric constant of the solution, respectively. The a_ϵ and a_n represent the slopes of a plot of dielectric constant and square of the refractive index, against the weight fraction of the complex in solution. Dielectric constant (permittivity) determinations are adequately described in the literature^{1,17-23}.

RESULTS AND DISCUSSION

The dipole moment of Hacac and $\text{Pt}(\text{NO}_2\text{-acac})_2$ in carbon tetrachloride are reported in Tables 1 and 2, respectively. The large value of dipole moment of acetylacetone can be attributed due to the non-polar (asymmetric) structure. The decrease in the dipole moment after chelation with platinum may be explained due to enhanced symmetrical structure of the chelate. Thus, it can be assumed that $\text{Pt}(\text{NO}_2\text{-acac})_2$ is more symmetrical as compared to acetylacetone. The $\text{Pt}(\text{NO}_2\text{-acac})_2$ has an octahedral structure.

TABLE-1
DIPOLE MOMENT DATA OF Hacac AT DIFFERENT
CONCENTRATION IN CCl_4 AT 30 °C

Hacac $\times 10^4$ (M)	n	ϵ	$\mu \times 10^{18}$ (e.s.u.)
1.0	1.447	16.90	2.11
2.0	1.451	17.40	2.13
3.0	1.458	17.80	2.18
4.0	1.465	18.10	2.20
5.0	1.469	18.25	2.24
6.0	1.490	18.60	2.28

TABLE-2
DIPOLE MOMENT DATA OF $\text{Pt}(\text{NO}_2\text{-acac})_2$ AT DIFFERENT
CONCENTRATION IN CCl_4 AT 30 °C

$\text{Pt}(\text{NO}_2\text{-acac})_2 \times 10^4$ (M)	n	ϵ	$\mu \times 10^{18}$ (e.s.u.)
1.0	1.448	5.09	2.08
2.0	1.453	5.12	2.10
3.0	1.465	5.33	2.16
4.0	1.471	5.45	2.18
5.0	1.476	5.87	2.20
6.0	1.479	6.00	2.22

Molecular complexes of $\text{Pt}(\text{NO}_2\text{-acac})_2$ with heterocyclic bases: In the molecular complexation of $\text{Pt}(\text{NO}_2\text{-acac})_2$ with heterocyclic bases, two types of experimental procedure were adopted: (a) By keeping the concentration of the

acceptor Pt(NO₂-acac)₂ solution constant and varying the concentration of the donor solutions in different solvents. (b) By keeping the concentration of the acceptor and donor solutions constant in different solvents.

Molecular complexes by keeping the concentration of the acceptor constant and varying the concentration of the donors in different solvents: The dipole moment data have been measured for the charge-transfer complexes of Pt(NO₂-acac)₂ with heterocyclic bases in different solvents (carbon tetrachloride, pyridine and THF). The concentration of the acceptor was kept constant (0.05 M) throughout the experiment and the concentration of the donors (pyridine, 2-methyl pyridine, 3-methyl pyridine, 4-methyl pyridine and quinoline) was varied in different solvents. The value of n_{12}^2 , ϵ_{12} and $\mu \times 10^2$ for these charge-transfer complexes are listed in Tables 3-9 at 20 °C. The dipole moments (μ) have been calculated for these molecular complexes from eqns. 1 and 11 are given in Table-14. It is observed that the addition of a small amount of donor solution generates an equal amount of the molecular complex. The permittivity of the system also increases on addition of the donor solution. The permittivity of the system continues to increase until the equivalent quantities of the donor and acceptor as present. This situation is schematically shown in Figs. 5-8, which indicates 1:1 stoichiometry of these complexes. Similar results have also been observed by electrical conductance studies for these charge-transfer complexes, which further supports 1:1 stoichiometry.

TABLE-3
DIPOLE MOMENT DATA FOR Pt(NO₂-acac)₂ PYRIDINE COMPLEX IN CCl₄ AT 20 °C

$C \times 10^4$ (M)	n_{12}	ϵ_{12}	$\mu \times 10^2$
1.0	2.17	2.21	0.60
2.0	2.19	2.24	1.20
3.1	2.25	2.28	1.80
4.0	2.26	2.29	2.39
5.2	2.28	2.31	3.00
6.0	2.29	2.34	3.59
7.5	2.32	2.39	4.30

TABLE-4
DIPOLE MOMENT DATA FOR Pt(NO₂-acac)₂ -
2 METHYL-PYRIDINE COMPLEX IN CCl₄ AT 20 °C

$C \times 10^4$ (M)	n_{12}^2	ϵ_{12}	$\mu \times 10^2$
1.0	2.10	2.12	1.25
2.0	2.14	2.16	1.80
3.1	2.16	2.19	2.55
4.0	2.17	2.22	3.05
5.0	2.20	2.24	3.96
6.0	2.22	2.26	4.42

TABLE-5
 DIPOLE MOMENT DATA FOR Pt(NO₂-acac)₂-3 METHYL-
 PYRIDINE COMPLEX IN CCl₄ AT 20 °C

C × 10 ⁴ (M)	n ₁₂ ²	ε ₁₂	μ × 10 ²
1.0	2.10	2.12	2.00
2.0	2.12	2.15	2.40
3.0	2.14	2.17	3.00
4.0	2.15	2.19	3.25
5.0	2.18	2.22	3.70
6.0	2.20	2.25	4.50
7.0	2.23	2.28	4.52

TABLE-6
 DIPOLE MOMENT DATA FOR Pt(NO₂-acac)₂-4 METHYL-
 PYRIDINE COMPLEX IN CCl₄ AT 20 °C

C × 10 ⁴ (M)	n ₁₂ ²	ε ₁₂	μ × 10 ²
3.0	2.10	2.10	0.21
4.0	2.11	2.11	1.61
5.0	2.13	2.18	3.24
6.1	2.15	2.19	4.26
6.5	2.20	2.25	5.10

TABLE-7
 DIPOLE MOMENT DATA FOR Pt(NO₂-acac)₂-PYRIDINE
 COMPLEX IN C₅H₅N AT 20 °C

C × 10 ⁴ (M)	n ₁₂ ²	ε ₁₂	μ × 10 ²
1.0	2.26	2.28	1.02
2.0	2.26	2.29	1.75
3.0	2.27	2.30	2.13
4.0	2.28	2.31	2.75
5.0	2.29	2.32	3.38
6.0	2.30	2.34	3.75
7.0	2.32	2.37	4.46

TABLE-8
 DIPOLE MOMENT DATA FOR Pt(NO₂-acac)₂-QUINOLINE
 COMPLEX IN CCl₄ AT 20 °C

C × 10 ⁴ (M)	n ₁₂ ²	ε ₁₂	μ × 10 ²
3.0	2.16	2.18	2.51
4.0	2.19	2.19	2.56
5.0	2.21	2.92	2.90
6.0	2.25	3.01	3.01
7.0	2.27	3.26	3.26
8.0	2.29	3.42	3.41
9.0	2.31	3.78	3.74

TABLE-9
 DIPOLE MOMENT DATA FOR $\text{Pt}(\text{NO}_2\text{-acac})_2$ -PYRIDINE COMPLEX IN THF AT 20 °C

$C \times 10^4$ (M)	n_{12}^2	ϵ_{12}	$\mu \times 10^2$
2.0	2.10	2.10	1.60
3.0	2.10	2.12	1.89
4.0	2.14	2.16	2.21
5.0	1.16	2.20	2.70
6.0	2.20	2.23	3.01
7.0	2.22	2.56	3.36
8.0	2.24	2.69	3.52

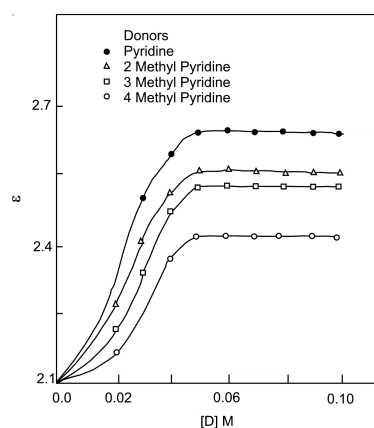


Fig. 5. Plot of molecular concentration of donor vs. dielectric constant of the molecular complex in CCl_4 at 20 °C keeping acceptor concentration constant (0.05 M)

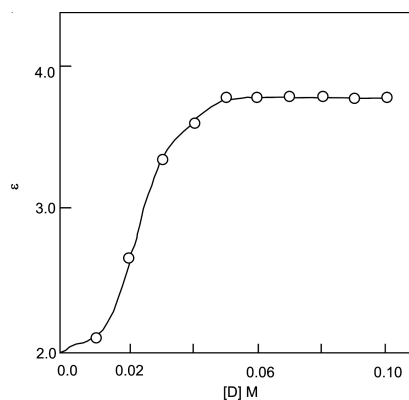


Fig. 6. Plot of molecular concentration of quinoline vs. dielectric constant of the molecular complex in CCl_4 at 20 °C keeping acceptor concentration constant (0.05 M)

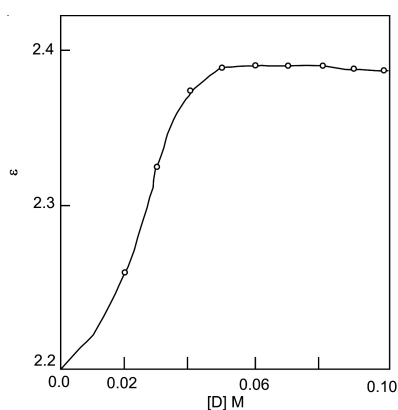


Fig. 7. Plot of molecular concentration of pyridine vs. dielectric constant of the molecular complex in pyridine at 20 °C keeping acceptor concentration constant (0.05 M)

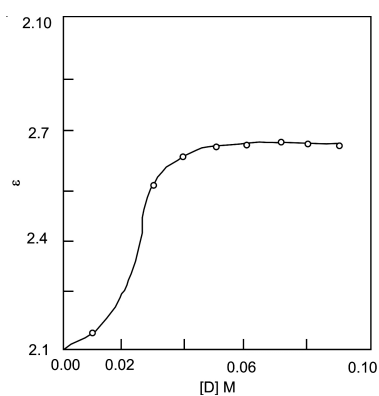
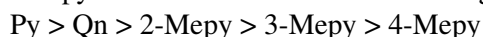


Fig. 8. Plot of molecular concentration of pyridine vs. dielectric constant of the molecular complex in THF at 20 °C keeping acceptor concentration constant (0.05 M)

Molecular complexes in Pt(NO₂-acac)₂ heterocyclic bases in carbon tetrachloride: The dipole moment for the charge-transfer complexes of Pt(NO₂-acac)₂ heterocyclic bases (Py, Qn, 2-Mepy, 3-Mepy and 4-Mepy) in carbon tetrachloride were calculated from eqns. 1 and 11. The dipole moment data of these complexes were measured by mixing 5 mL solution of Pt(NO₂-acac)₂ (0.05) M in carbon tetrachloride and 5 mL base at 30 °C. The dipole moment of these molecular complexes calculated by refractive index method is recorded in Table-10. The dipole moment data for charge-transfer complex of Pt(NO₂-acac)₂ with pyridine or quinoline in carbon tetrachloride at different temperatures (30, 35, 40 and 45 °C) are also calculated from eqn. 1. These data are given in Tables 11 and 12. From Table-10, it is evident that an appreciable increase in dipole moment may be interpreted due to the charge-transfer complexation at infinite time. This appreciable increase in dipole moment may be interpreted due to the charge-transfer complexation of Pt(NO₂-acac)₂ with heterocyclic bases. Further, the maximum increase in the dipole moment of the complex is observed in the case of Pt(NO₂-acac)₂-pyridine system. This indicates stronger interaction with pyridine and it follows the following trend:



A comparison of dipole moment values calculated by refractive index and Guggenheim methods is shown in Table-14. It was observed that the values of dipole moments calculated by the both methods agree well within the limit of experimental error.

TABLE-10
DIPOLE MOMENT DATA OF Pt(NO₂-acac)₂ WITH HETEROCYCLIC
BASE COMPLEX IN CCl₄ AT 30 °C

Donor	Donor*	n	A		B	
			ε	μ × 10 ¹⁸ (esu)	ε	μ × 10 ¹⁸ (esu)
Py	6.219	1.453	23.05	2.87	23.10	2.92
Qn	3.186	1.396	18.34	2.86	19.50	2.87
2-Mepy	5.377	1.357	17.25	2.85	17.53	2.86
3-Mepy	5.377	1.357	17.20	2.83	17.27	2.85
4-Mepy	5.377	1.357	17.15	2.81	17.12	2.83

*The concentration of the acceptor [Pt(NO₂-acac)₂] was 0.05M in each case.
A. At initial time (Zero); B. At final time (infinite)

TABLE-11
DIPOLE MOMENT DATA OF Pt(NO₂-acac)₂-Py COMPLEX IN
CCl₄ AT DIFFERENT TEMPERATURES*

Temperature (°C)	n	A		B	
		ε	μ × 10 ¹⁸ (esu)	ε	μ × 10 ¹⁸ (esu)
30	1.453	23.01	2.87	23.10	2.92
35	1.453	23.15	2.94	23.20	2.98
40	1.453	23.25	3.02	23.31	3.05
45	1.453	23.65	3.07	23.72	3.11

*The concentration of Pt(NO₂-acac)₂ and pyridine was 0.05 M and 6.33 M respectively in each case; A. At initial time (zero); B. At final time (infinite).

TABLE-12
 DIPOLE MOMENT DATA OF Pt(NO₂-acac)₂-Qn COMPLEX IN
 CCl₄ AT DIFFERENT TEMPERATURES*

Temperature (°C)	n	A		B	
		ε	μ × 10 ¹⁸ (esu)	ε	μ × 10 ¹⁸ (esu)
30	1.65	15.21	2.84	15.27	2.88
35	1.65	15.28	2.91	15.29	2.95
40	1.65	15.32	2.97	15.81	3.02
45	1.65	15.89	3.04	16.35	3.09

*The concentration of Pt(NO₂-acac)₂ and quinolene was 0.05 and 3.816M, respectively in each case; A. At initial time (Zero); B. At final time (infinite).

It is observed from Tables 11 and 12 that dipole moment of Pt(NO₂-acac)₂-pyridine complex is higher than Pt(NO₂-acac)₂-quinoline complex at various temperatures in carbon tetrachloride. This clearly indicates that Pt(NO₂-acac)₂ forms stronger complex at different temperature with pyridine than that of quinoline. The dipole moment of these complexes also increases with temperature in both systems. The higher is the temperature, stronger is the interaction with heterocyclic bases. In both the systems, the dipole moment follows the same order with temperature and there is linear relationship (Figs. 9 and 10) of the dipole moment with temperature above 35 °C. Similar results have also been observed by conductometric method.

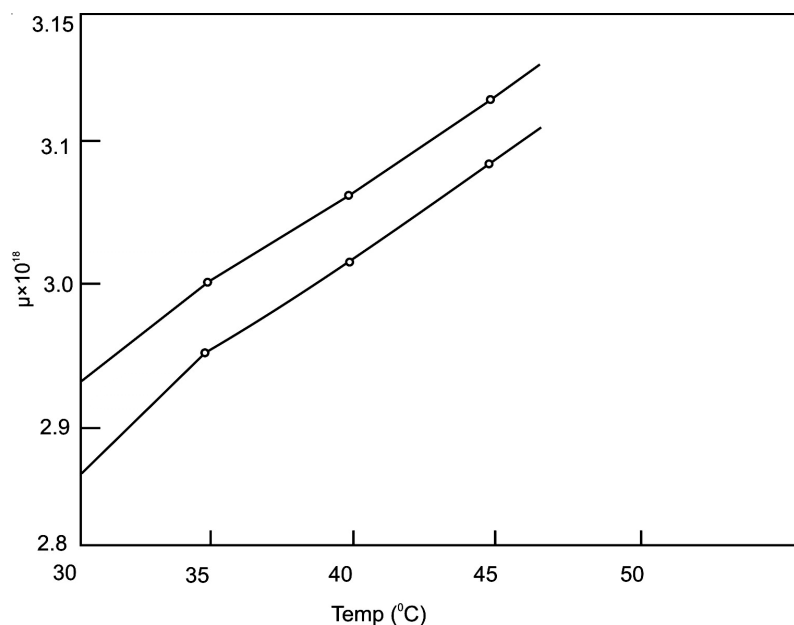


Fig. 9. Plot of temperature vs. dipole moment for the molecular complex of Pt(NO₂-acac)₂ with pyridine in CCl₄

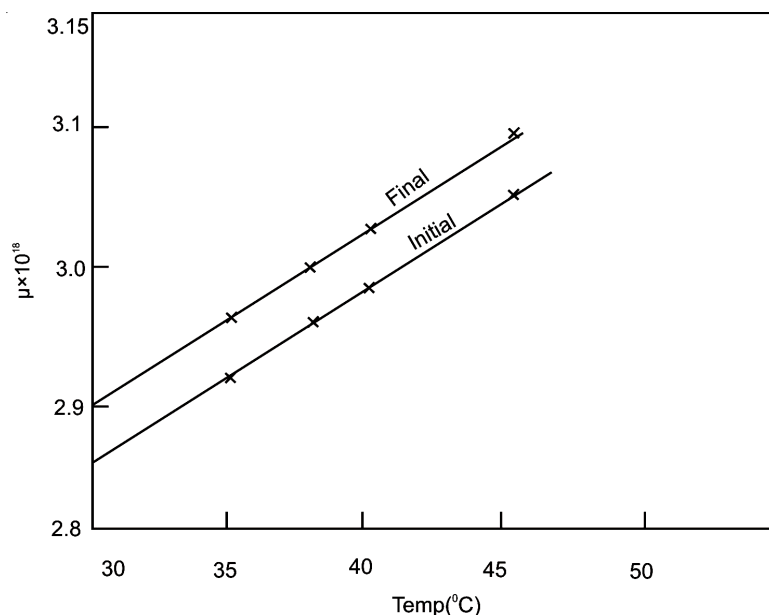


Fig. 10. Plot of temperature vs. dipole moment for the molecular complex of $\text{Pt}(\text{NO}_2\text{-acac})_2$ with quinoline in CCl_4

Molecular complexes of $\text{Pt}(\text{NO}_2\text{-acac})_2$ with heterocyclic bases in different solvents: The dipole moment for the charge-transfer complex of $\text{Pt}(\text{NO}_2\text{-acac})_2$ with pyridine in different solvents ($\text{C}_5\text{H}_5\text{N}$, CCl_4 and tetrahydrofuran) are calculated from eqn. 11. The dipole moment data for these systems are measured by mixing 5 mL solution of $\text{Pt}(\text{NO}_2\text{-acac})_2$ (0.05 M) in different solvents and 5 mL of pyridine at 30 °C. The dipole moment for this molecular complex in various solvents are recorded in Table-13. It was observed that the dipole moment for $\text{Pt}(\text{NO}_2\text{-acac})_2$ -pyridine complex has different values in different solvents. The dipole moment is highest in the pyridine solvent for the above system. The dipole moment values calculated by refractive index and Guggenheim methods are given in Table-14. It is evident from this Table that the values of dipole moment calculated by the both methods agree well within the limit of experimental error.

The dipole moment gives a measure of the strength of the interaction between the acceptor and donor molecules. The fact that $\text{Pt}(\text{NO}_2\text{-acac})_2$ -pyridine complex is relatively stable as indicated from high value of its dipole moment in non-polar solvent is due to the rearrangement of electronic charge between donor and acceptor molecules. The above discussed results are further evidence on the complexation of $\text{Pt}(\text{NO}_2\text{-acac})_2$ with heterocyclic bases. Although spectroscopic, conductometric, treatment of hard soft acid and base studies, towards solving the problems of aromaticity in metal acetylacetonates and nature of bonding in molecular complexes of $\text{M}(\text{NO}_2\text{-acac})_n$ and with heterocyclic N-bases reported in recent years²⁴⁻³⁵.

TABLE-13
DIPOLE MOMENT DATA OF Pt(NO₂-acac)₂-Py COMPLEX AT 30 °C

Solvent	Pyridine* (M)	n	A		B	
			ε	μ × 10 ¹⁸ (esu)	ε	μ × 10 ¹⁸ (esu)
Py	12.658	1.540	25.90	4.02	27.02	4.29
CCl ₄	6.392	1.453	22.01	2.87	23.10	2.92
THF	6.392	1.390	12.30	2.00	12.50	2.09

*The concentration of the acceptor [Pt(NO₂-acac)₂] was 0.05 M in each case.
A. At initial time (zero); B. At final time (infinite).

TABLE-14
DIPOLE MOMENT (μ) OF SOME Pt(NO₂-acac)₂-
HETEROCYCLIC BASE COMPLEX AT 20 °C

Complex	Solvent	μ × 10 ¹⁸ (e.s.u.)*	
		Guggenheim method	Refractive index method
H(acac)	CCl ₄	2.95	2.91
Pt(NO ₂ -acac) ₂	CCl ₄	2.01	1.89
Pt(NO ₂ -acac) ₂ -Py	CCl ₄	2.90	2.62
Pt(NO ₂ -acac) ₂ -2-Mepy	CCl ₄	2.16	2.00
Pt(NO ₂ -acac) ₂ -3-Mepy	CCl ₄	2.14	1.99
Pt(NO ₂ -acac) ₂ -4-Mepy	CCl ₄	2.11	2.96
Pt(NO ₂ -acac) ₂ -Qn	CCl ₄	2.85	2.61
Pt(NO ₂ -acac) ₂ -Py	Py	4.28	4.02
Pt(NO ₂ -acac) ₂ -Py	THF	1.83	1.79

*A standard deviation of 0.03-0.80 % has been estimated in the values of dipole moment.

Abbreviations:

ε	:	Dielectric constant
ε ₁	:	Dielectric constant of the solvent
ε ₁₂	:	Dielectric constant of solution
P	:	Total polarization
P _D	:	Distorted polarization
K	:	Boltzman's constant
N	:	Avagadro's number
M	:	Molecular weight of the complex
n ₁	:	Refractive index of solvent
n ₁₂	:	Refractive index of the solution
ρ	:	Solute polarization
W ₂	:	Weight fraction of solute
μ _{inert}	:	Dipole moment of solute in the non-interacting solvent
μ _{sol}	:	Dipole moment of solute in interacting solvent
μ _{ind}	:	Induced dipole moment
CRT	:	Cathode ray tube

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