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Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry

Publication details, including instructions for authors and subscription information: http://www.tandfonline.com/loi/lsrt19

Square-Planar Complexes of [p-[(p-Aminophenyl)thio] phenylpyrrole-2ylethylidene with Co(II), Ni(II), Cu(II) and Pd(II) Metalions

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To cite this article: Sanjay Vats & L. M. Sharma (1996) Square-Planar Complexes of [p-[(p-Aminophenyl)thio] phenylpyrrole-2-ylethylidene with Co(II), Ni(II), Cu(II) and Pd(II) Metalions, Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry, 26:6, 1087-1099, DOI: <u>10.1080/00945719608004353</u>

To link to this article: http://dx.doi.org/10.1080/00945719608004353

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SQUARE - PLANAR COMPLEXES OF [p-[(p-AMINOPHENYL)THIO] PHENYLPYRROLE-2-YL-ETHYLIDENE WITH Co(II), Ni(II), Cu(II) and Pd(II) METAL IONS

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ABSTRACT

A new bidentate ligand, [p-[(p-aminophenyl)thio] phenyl pyrrole-2yl-ethylidene [HL] (ATPE), was synthesised from bis-(p-aminophenyl)sulphide and 2-acetylpyrrole. Its metal complexes of the general formula ML₂, where M = Co(II), Ni(II), Cu(II) and Pd(II) have been prepared. On the basis of chemical analyses, magnetic moment measurements, electronic and IR spectra, conductance measurements and pH-metric studies, a square-planar geometry of the ligand around the bivalent metallic ions has been suggested. Some thermodynamic functions, such as changes in free energy (Δ F), entropy (Δ S) and enthalpy (Δ H) accompanying the complexation reactions, have been determined. The fungicidal activities of the ligand and its metal complexes have also been studied.

INTRODUCTION

From a survey of the literature it is evident that a number of coordination compounds with nitrogen, oxygen and sulphur as coordinating centres have been prepared under different conditions. Relatively less attention has been paid to the synthesis of transition metal complexes with a square-planar environment with substituted heterocyclic analogues of cyclopentadiene. In this communication, we report the synthesis of a keto-anil of pyrrole (ATPE), Fig. 1, its complexing behaviour towards bivalent Co(II), Ni(II), Cu(II) and Pd(II), the fungicidal activities and some thermodynamic parameters of these complexes.



Fig. 1. Structure of the ligand ATPE (HL)

EXPERIMENTAL

All reagents used were of A.R. grade. Elemental analyses were made by the microanalytical techniques. IR spectra were recorded on a Perkin Elmer-577 grating spectrophotometer using KBr pellets at room temperature. Electronic spectra were recorded on a Bausch and Lomb Spectronic-20 spectrophotometer and magnetic measurements were carried out at room temperature using the Guoy method. Conductometric titrations were carried out using a Phillips conductivity bridge, type LBR/B, pH-metric titrations were carried out with a Cambridge pH-meter in an inert atmosphere of nitrogen. The fungicidal activity of the ligand and its metal complexes was determined using the growth method¹⁶.

Preparation of the Ligand

Preparation of the ligand involves the following steps.

a. Preparation of p-Dinitrophenylsulphide¹. In a round bottom flask 20.0 g (0.12 mole) of p-nitrochlorobenzene were dissolved in 150 mL of alcohol on a water bath. A quantity of 5.0 g (0.06 mole) of sodium sulphide was dissolved in 15 mL of distilled water. The saturated solution of sodium sulphide was then added to the flask dropwise. The reaction mixture was refluxed for 5-6 hours. The color of the contents became orange. By keeping the reaction mixture at 20°C over night, orange colored crystals appeared. The orange mass was filtered, washed with alcohol and dried. The product was recrystallized from glacial acetic acid and orange plates were obtained. Yield 12.26 g (70%); m.p. 154°C. Calculated % for $C_{12}H_8N_2O_4S$: C 52.17; H 2.89; N 10.14; S 11.59. Found: C 52.76; H 3.01; N 10.64; S 11.19.

b. Reduction of p-Dinitrophenylsulphide². A hot solution at 70°C of 72.5 g (0.29 mole) of SnCl₂.2H₂O in 80 mL of 12 N HCl was added during one minute to the hot solution at 70°C of 14.0 g (0.05 mole) of bis(p-nitrophenyl)sulphide in 150 mL of acetic acid. After 10 minutes the solution was evaporated to dryness under reduced pressure. The crystalline residue was dissolved in water and excess of 50% aqueous

KOH solution was added. The liberated base was filtered, washed with the KOH solution and again an excess of 50% KOH solution was added. The liberated base was again filtered, washed with KOH solution, then with water, dried and recrystallized from alcohol; yield 7.66 g (70%); m.p. 106°C. Calculated % for $C_{12}H_{12}N_2S$: C 66.66; H 5.55; N 12.96; S 14.81. Found: C 67.00; H 5.02; N 12.60; S 14.12.

2. Preparation of 2-Acetylpyrrole. Since the acetylation of pyrrole³ is typical, a unique method was employed. A mixture of phosphorusoxychloride (18 mL, 0.19 mole) and dimethylacetamide (10 mL, 0.103 mole) was kept for about 15-20 minutes at 10-20°C and then 25 mL (0.29 mole) of 1,2-dichloroethane was added to this mixture. The contents were cooled to 5°C in an ice-water bath and then were added slowly to 7.0 mL (0.08 mole) of pyrrole in 25 mL of 1,2-dichloroethane over a period of one hour. The reaction mixture was refluxed for about 20 minutes and then cooled to room temperature. To this liquid mass about 100 mL of a saturated solution of sodium carbonate was added and shaken vigorously. Two distinct layers form. The aqueous layer was extracted with 100 mL ether. The combined organic layers were washed with distilled water and dried when a crystalline mass was obtained. This was recrystallized from petroleum ether when to give white needles of 2-acetylpyrrole, m.p. 92°C; yield 5.92g (68%). Calculated % for C₆H₇NO: C 66.05; H 6.42; N 12.80. Found: C 66.40; H 6.60; N 12.60.

3. Preparation of [p-[(p-Aminophenyl)thio]phenylpyrrole-2-yl-ethylidene (ATPE). In a double necked round-bottomed flask fitted with a long (60-80 cm) reflux condenser, 5.0 g (0.045 mole) of 2- acetylpyrrole in 50 mL of absolute alcohol was mixed with 6.0 g (0.02 mole) of bis(p-aminophenyl)sulphide dissolved in 50 mL of acetic acid with constant stirring. The reaction mixture was refluxed for about 4-5 hours. The contents were then poured on ice. A dark brown colored crystalline mass was obtained. It was washed with hot water, dried and recrystallized from ethanol, m.p. 168°C; yield 6.62 g (60%). Calculated % for $C_{18}H_{17}N_2S$: C 73.72; H 5.80; N 9.55; S 10.92. Found: C 74.10; H 6.15; N 9.80; S 11.20.

Preparation of the Complexes

<u>Co(II) Complex.</u> A quantity of 2.37 g (0.01 mole) of cobalt chloride hexahydrate in 35 mL of ethanol was added dropwise to 5.86 g (0.02 mole) of the ligand in 50 mL of ethanol with constant stirring. The contents were digested on a water bath. The solution was cooled over ice when a dull red precipitate separated out. It was filtered, washed with acetone and dried in an oven at 80°C; yield 4.00 g (60%). <u>Ni(II) Complex.</u> A quantity of 5.86 g (0.02 mole) of the ligand in 50 mL ethanol was added slowly to a solution of nickel chloride hexahydrate (2.30 g (0.01 mol) in 30 mL of ethanol). The reaction mixture was boiled for 5 minutes. After cooling, a reddish brown precipitate was obtained. It was washed with water followed by alcohol and dried in an oven at 118°C; yield 4.40 g (68%).

<u>Cu(II)</u> Complex. A solution of 1.70 g (0.01 mole) of copper chloride dihydrate in 25 mL of distilled water was added dropwise to a solution of 5.86 g (0.02 mole) of the ligand in 50 mL of ethanol. The mixture was refluxed for 10 minutes. A dark purple solid mass was obtained. It was filtered and washed with water and alcohol. The crystals were dried in an oven at 90°C; yield 4.37 g (65%).

<u>Pd(II) Complex.</u> A quantity of 1.77 g (0.01. mole) of palladium chloride in 20 mL of distilled water was added to 30 mL of an alcoholic solution containing 5.86 g (0.02 mole) of the ligand. The mixture was warmed on a water bath for 10 minutes and then poured into a beaker containing ice-cold water. A brown precipitate was obtained. It was washed with water followed by alcohol and dried in an oven at 110°C; yield 4.34 g (60%).

RESULTS AND DISCUSSION

The analytical data of the complexes and pH-metric studies suggest that the complexation reactions take place according to the following stoichiometric equation

$$2HL + M^{++} = ML_2 + 2H^{+}$$

The analytical results of the isolated solid complexes, their colors and melting points are compiled in Table I. A general formula ML_2 has been found for all metal compounds which are stable up to 300°C. The results of electronic spectra, magnetic moments and molar conductance measurements are given in Tables II and III, respectively.

IR Spectra

The IR spectrum of the ligand (ATPE) in KBr shows sharp bands at 3420 cm⁻¹ and 1470 cm⁻¹ which are assignable to v(N–H) and v(C=N) vibrational modes, respectively. Some other bands of varying intensities have also appeared in the regions 1350-1650 cm⁻¹ and 700-875 cm⁻¹ which are assignable to characteristic skeletal and δ (C–H) or β -ring vibrational modes, respectively. The v(C=N) vibrational frequency has been observed as shifted to lower energy invariably in all the complexes by 40-50 cm⁻¹. This shift suggests the participation of the azomethine nitrogen in the coordination of the ligand with the metal ions. Simultaneously, the disappearance of the band at 3420

pnenyipyrro	ne-2-yi-eu	iyndene	Complex	kes with	CO(II), N	1(11), Cu	(11) and \mathbf{F}	<u>a(n)</u>
Complex	Color	M.P. °C	% Yield	% M calcd (obsd)	% C calcd (obsd)	% H calcd (obsd)	% N calcd (obsd)	% S calcd (obsd)
CoL ₂ C ₃₆ H ₃₂ N ₆ CoS ₂	Dull red	320	60	8.78 (9.10)	64.38 (63.98)	4.76 (4.74)	12.51 (12.57)	9.53 (9.00)
$\begin{array}{c} \text{NiL}_2\\ \text{C}_{36}\text{H}_{32}\text{N}_6\text{NiS}_2 \end{array}$	Reddish Brown	310	68	8.75 (9.02)	64.40 (64.70)	4.77 (5.21)	12.52 (12.60)	9.52 (9.12)
CuL ₂ C ₃₆ H ₃₂ N ₆ CuS ₂	Dark Purple	315	65	9.40 (9.52)	63.94 (64.26)	4.73 (4.70)	12.43 (12.50)	9.47 (9.52)
$\begin{array}{c} \operatorname{PdL}_2\\ \operatorname{C}_{36}\operatorname{H}_{32}\operatorname{N}_6\operatorname{PdS}_2\end{array}$	Brown	305	60	14.81 (15.30)	60.13 (59.88)	4.45 (4.50)	11.69 (12.20)	8.90 (8.87)

 Table I

 Analytical Data, Color and Melting Points of Bis[p-[(p-Aminophenyl)thio]thenylpyrrole-2-yl-ethylidene Complexes with Co(II), Ni(II), Cu(II) and Pd(I

 cm^{-1} on coordination, indicates the deprotonation and the involvement of the pyrrole nitrogen in the complexation. Participation of the pyrrole nitrogen in the complexation has already been suggested by other authors earlier⁴.

A sharp band characteristic of the v(M-N) frequency has also appeared in the region 500-550 cm⁻¹ which corresponds to the coordination of the metal with the nitrogen⁵. From the above assignment of the bands it is concluded that the ligand is coordinated with the metal in a bidentate manner.

Electronic Spectra

<u>Co(II) complex.</u> Co(II) is a d⁷ system. It can form either spin-free or spin-paired complexes. The environment of the ligand around the Co(II) ion may be square-planar or tetrahedral and may be distinguished from both magnetically and spectroscopically⁶. The spin-paired complexes of Co(II) may have square-planar geometry with magnetic moments between 2.1 and 2.8 B.M. In the present study the observed magnetic moment of 1.84 B.M. for CoL₂ is higher than 1.76 B.M., the spin only value corresponding to a square-planar environment of the ligand around the Co(II) ion. This abnormal value of magnetic moment for the present complex may be attributed to Jahn-Teller distortions and some unquenched orbital momentum of the excited state causing the lowering of the octahedral symmetry. The magnetic moment⁴ of 1.80 B.M. has been reported for a square-planar complex of Co(II) with [[1-(1H-pyrrole-2-yl)ethylidene]amino]benzene. The reason for the higher value of μ_{eff} for square-planar Co(II) complexes is not

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Electronic Spectra and Magnetic Moment Data of Bis[p-[(p-Aminophenyl)thio]-phenylpyrrole-2-yl-ethylidene Complexes with Co(II), Ni(II), Cu(II) and Pd(II)

H	² osition of the bands cm ⁻¹ 16875 18280 20570 27880	Assignments $d_{xy} \rightarrow d_{x^2} - y^2$ $d_{z^2} \rightarrow d_{x^2} - y^2$ Charge transfer Intra ligand	Δ ₁ cm ⁻¹	$\Delta 2 \text{cm}^{-1}$	∆3cm ^{−1}	μ _{eff} B.M. 1.84	Suggested Geometries sp ^a	Remarks
	21010 30675 33590 35500	${}^{1}A_{1g} \rightarrow {}^{1}A_{2g}$ ${}^{1}A_{1g} \rightarrow {}^{1}B_{1g}$ Charge transfer	25870	13985		1.8	sp	Using B=1080 cm ⁻¹ C=4860 cm ⁻¹
	16550 19995 22685	${}^{2}B_{1g} \rightarrow {}^{2}A_{1g}$ ${}^{2}B_{1g} \rightarrow {}^{2}E_{g}$ Charge transfer				1.82	sp	
	18235 20008 29995	$\begin{tabular}{ll} \begin{tabular}{ll} A_{1g} & \rightarrow {}^{1}A_{2g} \\ \end{tabular} \end$	20891	5093	9157	0.54	sp	Using B=830 cm ⁻¹ C=2656 cm ⁻¹
sq.	iare planar							

Complex	Molar conductance, (0.001 M) Solution				
	Nitrobenzene	Dimethylsulphoxide			
CoL ₂	5.64				
NiL ₂	4.84	11.02			
CuL ₂	_	9.86			
PdL2	8.78	10.20			

Table III

satisfactorily resolved. This square-planar environment of the ligand around the Co(II) ion is further supported by the ligand field reflectance spectrum. Some intense absorption bands at 16875 cm⁻¹ corresponding to $d_{xy} \rightarrow d_{x^2-y^2}$, at 18280 cm⁻¹ attributed to $d_{z^2} \rightarrow$ $d_{x^2-y^2}$ and two additional bands of varying intensities at 20570 cm⁻¹ and 27880 cm⁻¹ which may be due to charge transfer and intraligand transitions, respectively, make their appearance in the spectrum. However, in other square-planar complexes of Co(II) a sharp band near 20,000 cm⁻¹ is also seen.

Ni(II) Complex. Square-planar complexes of the d⁸ configuration are of the spin-paired type. They show much charge transfer and ligand field bands which have not been established with certainty in their spectra. Square-planar complexes of Ni(II) can be distinguished from octahedral or tetrahedral structures in that no electronic transitions occur below 10,000 cm⁻¹. This is due to the large crystal field splitting in a square complex. The energy separation between the $d_{x^2-y^2}$ orbital and the next lowest orbital is invariably greater than 10,000 cm⁻¹. In the present case the observed transitions, have been assigned based on the assignments of other workers⁸.

The first major band near 21,010 cm⁻¹ has been assigned to the ${}^{1}A_{1g} \rightarrow {}^{1}A_{2g}$ transition $(b_{2g} \rightarrow b_{1g})$ and the second major band observed at 30,675 cm⁻¹ to the ${}^{1}A_{1g} \rightarrow {}^{1}B_{1g}$ transition $(a_{1g} \rightarrow b_{1g})$, respectively. In addition to these bands two other strong bands also appear at 33,590 cm⁻¹ and 35,500 cm⁻¹ and are probably charge transfer bands. These bands of comparatively high intensities may be due to π -bonding interactions. The transition energies may be determined by using the following equations⁹.

$$\begin{aligned} d_{xy} (b_{2g}) &\to d_{x^2 - y^2} (b_{1g}) E [{}^{1}A_{1g} \to {}^{1}A_{2g}] = \Delta_{1-C} \\ d_{z^2} (a_{1g}) &\to d_{x^2 - y^2} (b_{1g}) E [{}^{1}A_{1g} \to {}^{1}B_{1g}] = \Delta_1 + \Delta_{2-4B-C} \\ d_{xz}, d_{yz} (e_g) \to d_{x^2 - y^2} (b_{1g}) E [{}^{1}A_{1g} \to {}^{1}E_g] = \Delta_1 + \Delta_{2-3B-C} + \Delta_3 \end{aligned}$$

These equations have been solved by inserting the assumed values of B (1080 cm⁻¹) and C (4860 cm⁻¹). The values of Δ_1 , Δ_2 and Δ_3 of the respective metal compounds are given in Table II. It is argued that in the absence of π -bonding it is likely that the three non-bonding levels $e_g (d_{xz}, d_{yz})$, $b_{2g}(d_{xy})$ and $a_{1g}(d_{z}^*)$ lie fairly close together. In the present investigation, because of the negligible contribution of the bonding, the transitions are about at the same energy levels which is the requirement for square-planar complexes of amines. On the spin-paired assumption the d⁸ configuration leads to the configuration b_{2g}^2 . e_g^4 . a_{1g}^2 (S = 0). In keeping with this observation it is found that many square-planar complexes of bivalent nickel are diamagnetic and exhibit magnetic moments between zero and the value normal for octahedral complexes (3.2 B.M.) when dissolved in coordinating solvents. The magnetic moment for the present divalent nickel complex NiL₂ is found to be 1.8 B.M. which supports its square-planar geometry. This observation is in conformity with other square-planar complexes of Ni(II), viz. μ_{eff} for Ni(N-methyl-salicylaldoxime)₂ lies between zero and 2.8 B.M. and that of Ni-(2,3-butylenediamine)₂-Cl₂, μ_{eff} 1.7 B.M.

<u>Cu(II)</u> Complexes. The Cu(II) ion with d⁹ electronic configuration possesses an unpaired electron in the b_{1g} orbital. It is, therefore, apparent that its magnetic moment value should be 1.73 B.M. The present complex CuL₂ has a magnetic moment value 1.82 B.M. indicating that the orbital contribution is almost quenched by the crystal field. In addition, the value visualises two other possibilities viz; the complex could be distorted octahedral in geometry¹⁰⁻¹² or the Cu(II) is substituted into a tetrahedral lattice site leading to a molecule of D₂d symmetry. If it is, the Jahn-Teller effect has to work against the forces maintaining the lattice and hence distortion is expected to be minimised. Thus, it is predicted that both bands will move to higher energy levels supporting the square-planar environment of the ligand around the metal ion. In the present case two bands were noticed at 16550 cm⁻¹ and 19,995 cm⁻¹ and one strong band at 22685 cm⁻¹. The first two bands have been assigned as the transitions ${}^{2}B_{1g} \rightarrow {}^{2}A_{1g}$ and ${}^{2}B_{1g} \rightarrow {}^{2}E_{g}$, respectively, and the third band at the higher energy level may be a charge transfer band¹³.

<u>Pd(II) Complex.</u> Pd(II) is a d^8 system. The d^8 ion complexes are generally fourcoordinate and square-planar¹⁴ involving dsp^2 hybridization of the metal ion and are diamagnetic in nature. Vats *et al.*⁴ have studied the complexing behavior of substituted pyrroles and amines with Pd(II) and found the complexes to be square-planar and diamagnetic. These observations are in agreement with the Pd(II) complex of Nethoxycarbonylpyrrole-2-thiocarboxamide. The authors, on carefully resolving the spectra, came to the conclusion that three spin allowed transitions are anticipated corresponding to transitions from the three lower lying d levels to the empty $d_{x^2-y^2}$ orbital; two electronic transitions are very weak and are ignored. The ground state is ${}^{1}A_{1g}$ and the excited states corresponding to these transitions are ${}^{1}A_{2g}$, ${}^{1}B_{1g}$, ${}^{1}E_{g}$ in order of increasing energy. The spectra of the present complex consist of three bands of varying intensities, the first band at 18235 cm⁻¹ is assigned to ${}^{1}A_{1g} \rightarrow {}^{1}A_{2g}$, the second at 20,008 cm⁻¹ assigned to ${}^{1}A_{1g} \rightarrow {}^{1}B_{1g}$. With the help of these transitions the ligand field parameters are calculated and listed in Table II.

From the pattern of the transitions visible in the electronic spectra and the magnetic behaviour of the present complex, $\mu_{eff} = 0.54$ B.M., we suggest a square-planar environment of the ligand around Pd(II) metal ion which is diamagnetic.

pH-Measurements

The stoichiometric composition and stability of the metal-ligand complexes were determined by the pH-metric method. The pH-metric titration of the ligand alone and in the presence of metal ions reveals that the average number of ligand molecules attached per metal ion increases gradually with increase of the pH value. The formation of the chelate between metal ion and the ligand may be assumed to take place in successive steps. The observations are in good agreement with the ligand acting in the deprotonated ionic form and forming the bis-complex with different metal ions.

The values of stability constants determined for the systems would not be the real values but would be the apparent ones. The values of the apparent stability constants suggest the stoichiometry of the ligand and the metal ion to be 2:1 as shown in Fig.2.

Conductance Measurements

The non-ionic nature of the present complexes was established by measuring their conductivities. The conductivities of the individual complex have been measured in the specific solvents in which they are soluble. Conductance data confirm the non-ionic behaviour of the complexes. Although the Ni(II), Pd (II) and Cu(II) complexes in DMSO exhibit somewhat higher conductance values than in nitrobenzene, these conductance values do not support a 1 : 1 electrolyte (Table III).

Thermodynamic Functions

A state of chemical equilibrium is established during complexation reactions. Hence, utilizing the values of the apparent stability constants, the values of overall changes in the free energy (ΔF), enthalpy (ΔH) and entropy (ΔS) accompanying complexation reactions have been determined at 25°C by using standard equations¹⁵ (Table IV).



Fig. 2. Structure of the complex, $M(ATPE)_2$, where M = Co(II), Ni(II), Cu(II) and Pd(II)

The value of the free energy change (ΔF) is determined from the expression

$$\Delta F = -RT \ln \beta_2$$

where $\beta_2 = K_1K_2$, the overall apparent stability constants for Co(II), Ni(II), Cu(II) and Pd(II) metal ions. The values of other thermodynamic parameters, ΔH and ΔS , were determined by making use of Vant Hoff's isochore and the third law of thermodynamics, e.g.

$$\frac{d (\ln \beta_2)}{dT} = \frac{\Delta H}{RT^2}$$
 and $\Delta S = \frac{\Delta H - \Delta F}{T}$

The observed values of enthalpy (ΔH) show that all the complexation reactions are exothermic.

Fungicidal Activity

The fungicidal activity has been evaluated against pathogenic fungi, viz. Pestalotia sp. and Alternaria sp. The fungicidal activities of the ligand and its metal complexes were evaluated in Czapek-Dox medium. Czapek-Dox medium contains sucrose (30.0 g), NaNO₃ (2 g), KH₂PO₄ (1 g), MgSO₄.7H₂O (0.5 g), KCl (0.5 g), FeSO₄ (0.01 g), Agar-agar (30.0 g) and distilled water to make 1 litre. DMSO was used as a solvent for the preparation of different concentrations (0.01% and 0.1%) of the ligand and its metal complexes. The growth inhibition percent was calculated on the basis of the average diameter of the fungal colony¹⁶. The percentage inhibition of various compounds are recorded in the Table V.

Percentage Inhibition =
$$\frac{(C - T) \times 100}{C}$$

Complex		$Log K_2$	3.928	1.70 Kcal/Mole	0.26 Kcal/Mole	<pre>9 cal/deg/Mole</pre>
	Pd(II)	Log K ₁	4.998	$\Delta F = -11$	$\Delta H = -10$	$\Delta S = 4.6$
5°C	Complex	Log K ₂	3.867	47 Kcal/Mole	.02 Kcal/Mole	cal/deg/Mole
Functions at 2.	Cu(II)	Log K ₁	5.846	ΔF = - 13.	$\Delta H = -12$	ΔS = 4.69
Thermodynamic	Complex	Log K ₂	3.468	34 Kcal/Mole	29 Kcal/Mole	cal/deġ/Mole
Г	Ni(II)	Log K ₁	5.246	$\Delta F = -10.3$	ΔH = – 9.2	$\Delta S = 5.03$
Co(II) Complex	Complex	$Log K_2$	4.023	73 Kcal/Mole	23 Kcal/Mole	cal/deg/Mole
	Log K ₁	6.146	$\Delta F = -14.$	$\Delta H = -10.$	$\Delta S = 15.10$	

Table IV

		Table V			
Complex	<u>A</u>	verage Percent In	hibition after 8 da	ys	
		Orga	nism		
	Pestalotia sp. Concentration used		Altern Concentr	aria sp. ation used	
	0.1%	0.01%	0.1%	0.01%	
CoL ₂	-	-	-	-	
NiL ₂	81.9	93.4	83.1	91.0	
CuL ₂	79.6	92.8	54.0	69.3	
PdL ₂	78.1	89.8	21.0	53.5	
Ligand (APTE)	82.7	94.4	32.7	57.9	

(-) Insoluble in DMSO.

Where C = diameter of the fungus colony in the control plate after 8 days; T = diameter in mm of the fungus colony in the treated plates after 8 days.

It is found that on applying the pestalotia sp. the complexes are less toxic than the ligand. But the toxicity of the complexes decreases with increase in the order of atomic numbers, covalent radii, ionization potentials and electronegativities (with the exception of Pd) of the metals. In case of Alternaria sp. the Ni(II) and Cu(II) complexes are more toxic than the ligand while the Pd(II) complex is found to be less toxic than the ligand. The metallic character decreases with decreasing toxicity of the metals.

The fineness of the particles of the fungicides and the solubility of the compounds which affect the adhesiveness and toxicity are important factors for their biological activity¹⁶. Because of the solubility factor, the toxicity differs between ligand and complexes.

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Received: 31 January 1995 Accepted: 22 March 1996 Referee I: G. A. Pearse, Jr. Referee II: K. Moedritzer Downloaded by [University of Cambridge] at 10:48 31 December 2014