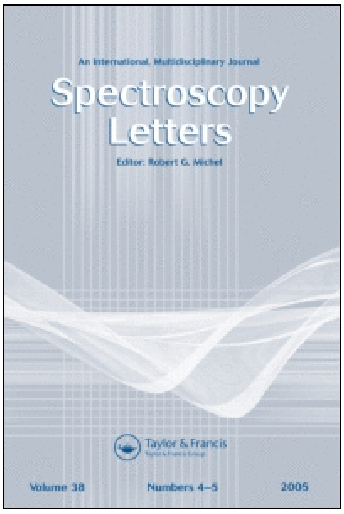

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Structural Chemistry of Some Imidazole Complexes

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Structural Chemistry of Some Imidazole Complexes

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Summary

Synthesis of benzimidazole and $\bar{4}$ (Imidazole 1-yl) acetophenone complexes derived from cobalt(II), nickel(II), copper(II), palladium(II) and platinum(IV) salts were carried out. The elemental analyses suggest the formation of 1:2 and 1:4 stoichiometries (M:L). Electronic spectra and magnetic susceptibility measurements are used

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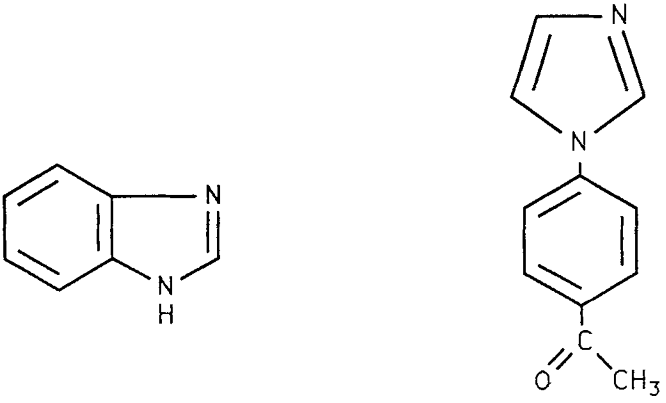
to infer the structures. The i.r. spectra of the ligands and their complexes are used to identify the type of bonding. Thermal analysis and electrical conductivity measurements were investigated in the temperature range 30-250°C. The results indicate slight semiconducting properties.

Introduction

Imidazole compounds are of potential biological importance from different scopes, for example, their antimicrobial and radio - therapeutic properties (1-6). The present work is undertaken to study the coordinating behaviour of some biologically active imidazole ligands (I) towards transition metal salts. This is achieved by determination of the geometry and the mode of bonding in the synthesized complexes using spectral and magnetic susceptibility methods of analysis. The data are correlated with electrical conductivity and thermal properties.



Benzimidazole 4- (Imidazole 1-yl) acetophenone

(I)

Results and discussion

The ^1H n.m.r. spectrum of benzimidazole in d_6-DMSO shows signals in the range 6.7-7.5 ppm which are equivalent to four protons of the benzene ring. The C_2 proton is absorbed at δ 8.1 ppm. The imino proton is not detected in the spectrum and shows no splitting of the C_2H peak to suggest that the NH proton is too labile to be detectable(7). However, the spectra of its Pd and Pt complexes show the down field shift by 0.15-0.4 ppm of the C_2 proton adjacent to the imino nitrogen atom to suggest M-N coordination(8). The ^1H n.m.r. spectrum of $\bar{4}$ (Imidazole 1-yl) acetophenone exhibits one sharp signal at δ 2.7 ppm assigned for the methyl group. The phenyl protons are expected at δ 7-7.3 ppm. Signals at δ 8.2, 7.9 and 7.6 ppm are due to C_2, C_5 and C_4 protons of the imidazole unit(9). Upon complexation with Pd and Pt ions, the signals due to C_2 and C_4 protons experience a clear down field shift by Cal.0.3-0.5 ppm suggesting that the N(3) atom of the imidazole unit is coordinated to the metal ions(10).

Electronic spectra and magnetic properties

All the synthesized complexes are coloured. They are generally insoluble in the common organic solvents except that the palladium(11) and platinum(IV) complexes are soluble in $CHCl_3$ and DMSO. The insolubility may be taken as favouring a polymeric structure. Co^{II} and Ni^{II} complexes of benzimidazole show identical spectra having only one band in the visible region with λ_{max} at 580 and 520 nm assignable to $^4A_2(F)\rightarrow{}^4T_1(P)$ and $^3T_1(F)\rightarrow{}^3T_1(P)$ transitions, respectively. The μeff value of the cobalt(II) complex (4.2 B.M.) suggests tetrahedral geometry around cobalt(II) ion. However, the room temperature magnetic moment of Ni^{II} complex is 2.6 B.M. which is below the spin only value for two unpaired electrons to suggest the existence of some quenching property possibly by Ni-Ni interaction. However, we are in favour to suggest an equilibrium between high spin (S=1) and low spin (S=0) configurations(11). The red copper(II)- benzimidazole complex with μeff=0.88 B.M. is consistent with strong antiferromagnetic spin-spin interaction through molecular association(12). This is in concordance with tetragonal distorted O_h geometry about Cu^{II} of approximate D_{4h} symmetry. However, the pale blue copper(II) $\bar{4}$.(Imidazole 1-yl)-acetophenone complex has μeff 2.03 B.M. to be of pseudotetrahedral(12). The Pd^{II} and Pt^{IV} complexes are diamagnetic and show a strong band at 370-400 nm and a weak one at 640-670nm which are usually observed for square planar configuration(13).

Infrared spectra and mode of bonding

The i.r. spectrum of benzimidazole ligand shows weak bands above 3200 cm^{-1} which are apparently due to the imidazole CH vibrations. Those at 2900 and 3080 cm^{-1} are assigned to the CH vibrations of the benzene ring(14). The strong band appearing at 3130 cm^{-1} may be due to the ν NH of the ligand. Several ring stretching bands are expected in the region 1600-1200 cm^{-1}. Sharp bands at 1360-1340 cm^{-1} may be due to the NH bending vibration. The i.r.

spectrum of the free ligand shows dramatic changes on complexation, the ν NH and δ NH bands were completely absent in the spectra of Pd^{II}, Pt^{IV} and Cu^{II} complexes i.e., the NH group is participated in bond formation with the metal ion through deprotonation. However, formation of Co^{II} and Ni^{II} complexes does not affect the ν CH and ν NH ligand bands since both complexes contain neutral and monodeprotonated anion of benzimidazole. The characteristic M-N frequencies are situated at 520-535 cm^{-1} and 460 cm^{-1}. However, the ν NH absorption occuring at 3130 cm^{-1} in benzimidazole is absent in $\bar{4}$ (Imidazole 1-yl) acetophenone indicating the absence of the NH group in the latter. The sharp bands at 1670, 1420 and 1310 cm^{-1} are attributed to the ν C=O and asymmetric and symmetric deformation vibrations of the methyl group , respectively. The ligand has ν C=N at 1580-1550 cm^{-1} which is shifted to 1520-1510 cm^{-1} in the complexes. Burger et al(15) reported, on the basis of ν C=N frequency shifts that the lower the νC=N value, the stronger the metal--- N=C doner π bond. The very weak band appearing at 900 cm^{-1} in all the complexes may be attributed to the ring mode of coordinated imidazole which appears at 930 cm^{-1} in the free ligand. The bands at 340 and 360 cm^{-1} are due to stretching vibrations of Pd-Cl and Pt-Cl bonds which suggest that the chlorine atoms are at the trans position(16).

Thermal an electrical conductivity date :

The TGA curves of the complexs show a very minute loss in weight in the range 25-250°C. This weight loss may be due to the evaporation of the adsorbed water. Again the above complexes were subjected to differential thermal analysis (DTA).The measurements were performed from 25°C up to 250°C. No change is detected in the behaviour of these samples, indicating that they do not suffer any phase transformation in the above temperature range.

The variation of the electrical conductivity of the complexes with temperature in the range from 30-250°C are represented in Fig (1). All the complexes under investigation exhibit similar behaviour where two lines intersect each other. The temperature of intersection for the systems lies in the range 72-160°C. The conductivity data vary exponentially with the absolute temperature according to the Arrhenius relation $\sigma=\sigma o\ e^{-\Delta E/2kT}$ where σ is the electrical conductivity, σo is the pre-exponential term, and ΔE, K and T have their usual meanings. The values of ΔE obtained are tabulated in table (2). The fact that both ΔE_1 and ΔE_2 values depend on the type of the compound examined is taken to indicate extrinsic conductance. The disparity in the ΔE values may be ascribed either to possible movement of impurities in disorder regions of grain boundaries, existence of phase transformations or the varying lattice imperfections. Grain boundary effects seem to be negligible since all samples were pressed under the same high pressure. From DTA measurements on the same samples, no phase transformation within the temperature range was recorded. The Cu^{II} benzimidazole complex possesses low electrical conductivity.So, such complex exists in molecular association achieved through a direct copper - copper

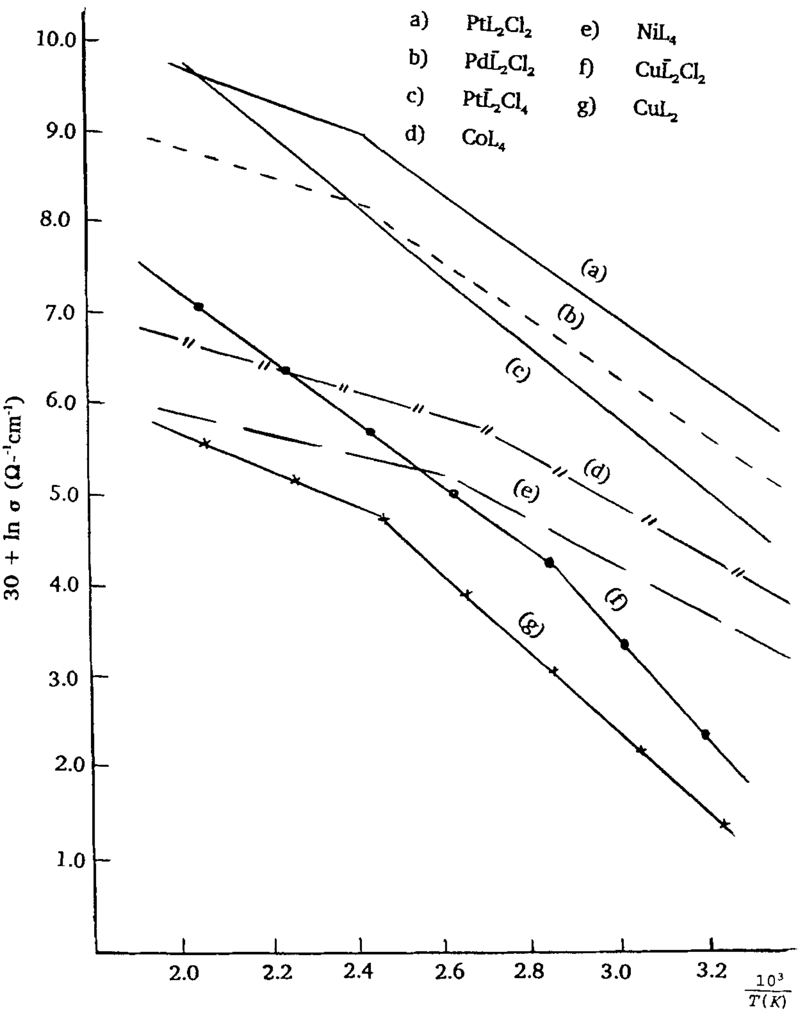


Fig. 1. ln σ versus 1/T of some Imidazole complexes.

interaction and/or a bridged ligand system. This is in harmony with the measured low magnetic moment value of 0.88 B.M. However, Co^{II} and Ni^{II} complexes of benzimidazole ligand have ΔE values nearly the same, i.e., that both the concentrations of the charge carriers as well as the current transfer mechanism are the same for these complexes. The palladium and platinum complexes have higher electrical conductivities compared to those of other complexes as a result of forming strong coordinate bonds between Pd^{II} and Pt^{IV} ions and the ligand molecules.

Experimental

The ligands were obtained as reagent grade materials and were used without further purification.

The solid complexes were prepared by mixing the required weights of the metal salt solutions (Co, Ni, Cu, Pd and Pt) with the ligand dissolved in H_2O or EtOH. The compounds formed were revised by filtration and dried in vacuo over P_4O_{10}. Attempts to prepare Co^{II} and Ni^{II} complexes derived from $\bar{4}$ (Imidazole 1-yl) acetophenone were not successful. The analytical data of the complexes are collected in table (1). The i.r. spectra were recorded on a perkin Elemer 1430 recording infrared spectrophotometer. ^1H n.m.r. spectra were obtained in d_6 DMSO using a EM-390 90 MHZ NMR spectrometer. The room temperature Faraday measurements on powdered complexes were used for obtaining the magnetic moments.

Table 1. Physical properties of benzimidazole and $\bar{4}$-(Imidazole1-yl) acetophenone complexes

Complex	Colour	Found (Calcd.) %			
		C	H	M	Cl
CoL_4	purple	63.1	4.0	11.0	-
		(63.3)	(4.2)	(11.4)	-
NiL_4	violet	63.1	4.2	10.7	-
		(63.6)	(4.2)	(11.1)	-
$Cu L_2$	brick red	56.0	3.8	21.0	
		(56.0)	(3.4)	(21.3)	
PdL_2	pale yellow	49.3	2.9	30.8	-
		(49.1)	(2.9)	(31.0)	-
$Pt L_2Cl_2$	yellow	33.5	2.3	-	14.1
		(33.8)	(2.0)	-	(14.1)
$Cu \bar{L}_2 Cl_2$	blue	51.8	4.0	12.3	13.6
		(52.1)	(4.0)	(12.6)	(13.8)
$Pd\bar{L}_2 CL_2$	pale yellow	48.5	3.9	19.0	12.6
		(48.2)	(3.6)	(19.3)	(12.8)
$Pt \bar{L}_2Cl_4$	yellow	37.0	3.0	-	20.0
		(37.3)	(2.8)	-	(20.1)

L and $\bar{L}$ are abbreviated for benzimidazole and $\bar{4}$ (Imidazole 1-yl) acetophenone respectively.

Table 2. Values of the activation energies of the benzimidazole and 4(Imidazole l-yl) acetophenone complexes

Complex	Activation energy (ev)	Temperature range (°C)
CoL_4	0.81	40-97
	0.70	111-203
NiL_4	0.83	40-97
	0.70	112-250
CuL_2	1.20	30-112
	0.48	144-240
$PtL_2\,Cl_2$.	0.09	30-127
	0.20	160-250
$Cu\bar{L}_2\,Cl_2$	0.52	30-72
	0.02	84-250
$Pd\bar{L}_2\,Cl_2$	0.88	30-127
	0.39	152-250
$Pt\bar{L}_2\,Cl_4$	1.04	30-250

$Hg[Co(SCN)_4]$ were used for calibration and diamagnetic corrections were made using Pascal's constants.

The differential thermal analysis (DTA) and thermogravimetric analysis (TGA) measurements were made with general V22 A Dupont 9900 analyser. The heating rate used was 10 deg. min^{-1}, with a 60 mg sample in a cylindrical heat resistant ceramic crucible. For electrical conductivity measurements, samples were prepared in the form of tablets of 0.1-0.2 cm thickness at a pressure of 5 $tons/cm^2$ and held between two copper electrodes with a silver paste, then inserted with the holder vertically into a cylindrical electrical furnace. The potential across the heater was varied gradually through a variac transformer to produce a slow rate of temperature. The electrical conductivity measuring circuit consisted of Healthkit d.c. regulated power supply (0-400 V) and electrometer (Keithley 610) for measuring current. The temperature was measured within ±0.1°K using a digital thermometer (Keithley 871 Type KTC Nicr-NiAL) The conductivity was obtained using the general equation $\sigma = I/V_c . d/a$

where I is the current in ampere and V_c is the potential drop across the sample of cross -sectional area "a" in cm^2 and thickness "d" in cm.

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