Inorganica Chimica Acta, *158* (1989) 249–253

Electrical Studies and Characterisation of Complexes of Cobalt(II), Copper(II) and Zinc(II) with Diphenyl-2-pyridylmethane

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(Received March 31, 1988; revised September 21, 1988)

Abstract

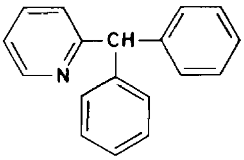
Complexes of the chlorides and bromides of cobalt(II), copper(II) and zinc(II) with diphenyl-2-pyridylmethane have been prepared. These complexes have stoichiometry ML_2X_2 where M is a metal ion, L is an organic ligand and X is a halide ion. Spectral and magnetic properties indicate that the likely environment of the metal ion is octahedral in the copper compounds and tetrahedral in the cobalt and zinc compounds.

Electrical measurements show that the room temperature conductivities range from 9.3×10^{-9} Ω^{-1} m^{-1} to 3.0×10^{-7} Ω^{-1} m^{-1}. The temperature dependencies of conductivity have been determined for the compounds and used to measure the activation energies for conduction. Some correlation between these activation energies and the coordination number of the metal atoms has been observed.

Introduction

Extensive structural studies involving spectral and magnetic measurements have been previously reported for the complexes formed by pyridine and the substituted pyridines with transition metal(II) halides. However, far fewer studies have been made on the electrical conductivity of such compounds.

The electrical properties of several different series of metallo-organic complexes have been investigated in these laboratories [1–6] and quinoxaline complexes have yielded the highest room temperature conductivities [3]. As the quinoxaline molecule contains a pyrazine ring attached to a benzene ring, it was anticipated that high conductivity may also be observed for diphenyl-2-pyridylmethane ($C_{18}H_{15}N$) complexes in which two benzene rings are attached via a carbon atom to a pyridine ring.



Diphenyl-2-pyridylmethane ($C_{18}H_{15}N$)

In this paper we describe and discuss the structural properties and some electrical conductivity measurements of diphenyl-2-pyridylmethane complexes with the first row transition metals cobalt, copper and zinc. The only coordination site for diphenyl-2-pyridylmethane is the ring nitrogen atom.

Experimental

The compounds were prepared as follows: 0.02 mol of diphenyl-2-pyridylmethane was dissolved in 50 cm^3 of warm ethanol; 0.02 mol of the metal halide was dissolved in 50 cm^3 of warm ethanol. The solutions were mixed and the volume reduced until the complexes precipitated. The compounds were filtered, washed with warm ethanol and dried in an oven at 40 °C.

The compounds prepared by this method are listed in Table 1. The analysis of the metal ion was determined by a Perkin-Elmer 373 atomic absorption spectrometer; the carbon, hydrogen and nitrogen analyses using a Carlo Erba elemental analyser. The magnetic moments given in the Table were measured by the Gouy method using $Hg[Co(SCN)_4]$ as calibrant. Each magnetic moment has been corrected for diamagnetism using Pascal's constants [7]. The per-

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0020-1693/89/$3.50

TABLE 1. Analyses and Magnetic Moments of Compounds

Compound	Colour	Theory (%)				Experimental (%)				μ (BM)
		M	C	N	H	M	C	N	H	
$Co(C_{18}H_{15}N)_2Cl_2$	blue	9.49	69.61	4.51	4.83	9.23	68.97	4.40	4.79	4.38
$Co(C_{18}H_{15}N)_2Br_2$	blue	8.30	60.88	3.94	4.22	8.07	60.13	3.79	4.08	4.59
$Cu(C_{18}H_{15}N)_2Cl_2$	brown	10.16	69.09	4.48	4.79	9.91	68.44	4.24	4.64	1.54
$Cu(C_{18}H_{15}N)_2Br_2$	green–brown	8.89	60.49	3.92	4.20	8.24	60.22	3.15	4.14	1.59
$Zn(C_{18}H_{15}N)_2Cl_2$	white	10.42	68.97	4.46	4.81	10.22	68.66	4.42	4.29	
$Zn(C_{18}H_{15}N)_2Br_2$	white	9.13	60.40	3.91	4.22	8.72	60.12	3.66	4.01	

$C_{18}H_{15}N$ = diphenyl-2-pyridylmethane.

TABLE 2. Yield and Melting Points of the Compounds

Compound	Yield (%)	Melting point (K)
$Co(C_{18}H_{15}N)_2Cl_2$	77	463–473[a]
$Co(C_{18}H_{15}N)_2Br_2$	34	473–483
$Cu(C_{18}H_{15}N)_2Cl_2$	47	453[b]
$Cu(C_{18}H_{15}N)_2Br_2$	14	443–448
$Zn(C_{18}H_{15}N)_2Cl_2$	15	463
$Zn(C_{18}H_{15}N)_2Br_2$	9	473

$C_{18}H_{15}N$ = diphenyl-2-pyridylmethane. [a]Compound discolours at 453 K and subsequently melts at 463–473 K. [b]The quoted temperature (453 K) is a decomposition temperature.

TABLE 3. Infrared Spectra of Compounds (4000–200 cm^{-1})

Compound	Ring vibrations		ν (M–N)	ν (M–X)	
$(C_{18}H_{15}N)$	1590	1433			
$Co(C_{18}H_{15}N)_2Cl_2$	1603	1434	430	336	305
$Co(C_{18}H_{15}N)_2Br_2$	1605	1434	428	260	
$Cu(C_{18}H_{15}N)_2Cl_2$	1600	1434	435	308	
$Cu(C_{18}H_{15}N)_2Br_2$	1610	1435	438	226	
$Zn(C_{18}H_{15}N)_2Cl_2$	1611	1438	426	290	329
$Zn(C_{18}H_{15}N)_2Br_2$	1609	1439	425	240	

$C_{18}H_{15}N$ = diphenyl-2-pyridylmethane. All listed wavenumbers correspond to strong vibrations.

TABLE 4. Electronic Spectra of Compounds

Compound	Peak position[a] (cm^{-1})	Dq[b] (cm^{-1})	B[c]	β[d]
$Co(C_{18}H_{15}N)_2Cl_2$	6944 14749 (ϵ = 29.3)	376	694	0.72
$Co(C_{18}H_{15}N)_2Br_2$	6757 14970 (ϵ = 51.6)	366	716	0.74
$Cu(C_{18}H_{15}N)_2Cl_2$	12833 (ϵ = 19.8)			
$Cu(C_{18}H_{15}N)_2Br_2$	12559 (ϵ = 24.6)			

$C_{18}H_{15}N$ = diphenyl-2-pyridylmethane. [a]ϵ is the molar extinction coefficient, $m^2\ mol^{-1}$. [b]Dq is the ligand field strength expressed in terms of wavenumber. [c]B is the Racah parameter. [d]$\beta = B/B_0$ is the nephelauxetic ratio (B_0 in free ion; B in complex).

centage yields and melting points are listed in Table 2. These melting points were obtained using a Griffin and George melting point apparatus. The infrared spectra, Table 3, using KBr discs, 4000–600 cm^{-1} and polyethylene discs, 600–200 cm^{-1} were obtained with a Perkin-Elmer infrared spectrophotometer model 598. The electronic spectra, Table 4, were obtained on a Beckman Acta MIV spectrometer as solution spectra using chloroform as the solvent.

For electrical measurements the compounds were formed into discs of diameter 13 mm and thicknesses in the range 0.54 to 1.00 mm. The discs were prepared by compressing the powder material in a hydraulic press set to apply a force of 100 kN. Concentrically, on the flat faces of each disc, electrodes of 4.9 mm diameter were provided by applying a silver-based conductive paint through masks. After the paint had dried one electrode was placed on a copper heat sink and contact was made to the other electrode by a spring-loaded pad. Current (I) *versus* voltage (V) d.c. characteristics at room temperature were obtained as point by point measurements with current measured by a Keithley 610C electrometer. This instrument was placed in the circuit so that it registered only the current drawn by the disc. To test that the contacts were ohmic, the voltage was increased in stages from zero to 30 V, then reduced in stages back to zero and this was next repeated with reversed polarity. Agreement between the four readings of current so obtained for any given applied voltage to a disc was within 5%. The disc thickness, which is needed for the conductivity determination, was measured using a micrometer.

The temperature dependence of electrical conductivity for each compound was obtained by placing the disc of the compound, still in its mount, in an electrically heated oven and monitoring the current during heating for a fixed applied voltage of 10 V.

The disc temperature was obtained from the e.m.f. of a previously calibrated copper–constantan junction (formed from S.W.G. 44 wires) with the hot junction on the disc surface. The discs were raised to a maximum temperature of 371 K and during each measurement of disc current the oven heater current was temporarily switched off so as to avoid any problem of electrical pick-up from the heater circuit into the disc circuit. Further measurements of the disc current were obtained during cooling back to room temperature and these reproduced the results obtained during heating to within a few percent, showing that thermal degradation had not occurred.

Results and Discussion

Analytical

In Table 1 the analytical results for the complexes are shown. These results agree with the given formulae which show that in each complex the number of diphenyl-2-pyridylmethane molecules present is two. All of the compounds are anhydrous.

Infrared Spectra

The wavenumbers of the infrared absorption bands as well as their descriptions and assignments are given in Table 3. The infrared spectra, throughout the range 4000–600 cm^{-1}, are almost the same for diphenyl-2-pyridylmethane and its complexes, except that the frequencies of the aromatic ring vibrations are slightly shifted to higher values in the complexes. This implies that the nitrogen atom in the aromatic ring is coordinated to a metal atom [8]. Metal–halogen and metal–nitrogen bands are observed for the complexes and are reported in Table 3. The assignments of the frequencies of the metal–halogen vibrations show that the metal ion is in an octahedral environment in the copper complexes [9] and in a tetrahedral environment in the cobalt and zinc complexes [9, 10].

Electronic Spectra

Table 4 gives the parameters relating to the d–d bands in the electronic spectra of the cobalt and copper complexes in chloroform solution. No visible change was observed in the colour of the complexes when they were dissolved in the chloroform and hence it is assumed that compounds have the same stereochemistry in the solid state as in the solution. The positions of these d–d bands in the cobalt complexes indicate that the cobalt ion is in a tetrahedral environment [11]. The values of the ligand field strength Dq and the molar extinction coefficient ϵ for these complexes are also consistent with this stereochemistry [12]. The copper compounds have a single broad absorption band between 10000–15000 cm^{-1}. Since a square planar copper(II) compound would show a set of bands of near equal intensity at about 15000–18000 cm^{-1} [13–15] and regular and pseudo tetrahedral compounds both exhibit bands below 10000 cm^{-1} [16, 17], none of which were observed, an octahedral environment for the copper atom is suggested. The ϵ values are also consistent with the copper ion being in an octahedral environment [18].

Proposed Stereochemistry

Attempts to grow single crystals from various solvents for X-ray structure analysis were unsuccessful hence, as only powders were isolated, no complete structure determination was made. However, the magnetic and spectroscopic data listed in Tables 1 and 4 enable us to infer that the metal environment in the cobalt and zinc compounds is tetrahedral whilst in the copper complexes the metal environment is octahedral. The six-coordinate environment for the copper ions is obtained by considering the complexes to have a planar arrangement of ligands with the apical positions being free so that the metal can coordinate to halogens of further $Cu(C_{18}H_{15}N)_2Cl_2$ groups [9]. The resulting values of the ligand field strength, Dq, the Racah parameter, B, and the nephelauxetic ratio, β, are reported in Table 4. The value for Dq indicates that diphenyl-2-pyridylmethane is a weak ligand and would occur below pyridine in the spectrochemical series. The values for B and β suggest some electron delocalisation between the metal and the ligands.

Electrical Measurements

The room temperature current (I) *versus* voltage (V) graphs are all linear and the examples of $Zn(C_{18}H_{15}N)_2Br_2$, $Co(C_{18}H_{15}N)_2Cl_2$ and $Cu(C_{18}H_{15}N)_2Br_2$ are shown in Fig. 1. Electrical conductivities, as calculated from the gradients of the I *versus* V plots and with the assumption that current is perpendicular in direction to the electrodes, are given in Table 5. These conductivities are too low for most device applications but it is anticipated that they may be raised by many orders of magnitude by appropriate doping.

The highest room temperature conductivity found for any of the complexes is $3.0 \times 10^{-7}\ \Omega^{-1}\ m^{-1}$, which is lower by a factor of 7.7×10^3 than the highest value found amongst quinoxaline complexes previously reported by us [3]. Possibly, the relatively low conductivity of the $M(C_{18}H_{15}N)_2X_2$ complexes is due to the benzene rings being linked to the pyridine ring within each molecule only via an intermediate carbon atom. In contrast, for quinoxaline the pyrazine ring and benzene ring are directly attached which enhances electron transport across the molecule.

Plots of $\ln \sigma$ *versus* $1/T$ (σ = conductivity, T = absolute temperature) have been obtained for each compound and, with the exception of $Co(C_{18}H_{15}N)_2$-

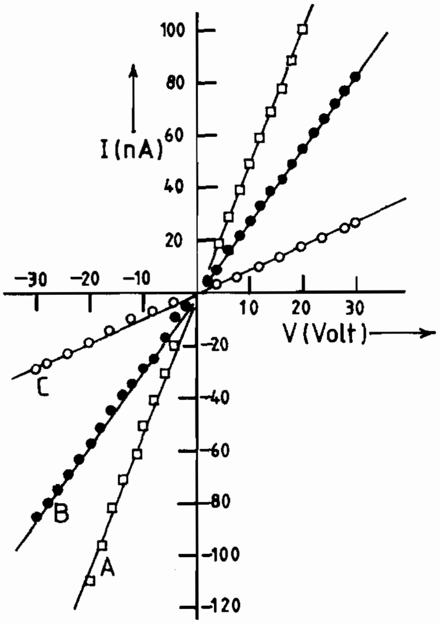

Fig. 1. Current (*I*)–voltage (*V*) characteristics for discs of the compounds at room temperature (290 K). A: $Zn(C_{18}H_{15})_2Br_2$ of thickness 1.00 mm. B: $Co(C_{18}H_{15}N)_2Cl_2$ of thickness 0.56 mm. C: $Cu(C_{18}H_{15}N)_2Br_2$ of thickness 0.84 mm.

TABLE 5. Electrical Properties of the Compounds

Compound	Electrical conductivity at 290 K ($\Omega^{-1}\,m^{-1}$)	ΔE [a] (eV)
$Co(C_{18}H_{15}N)_2Cl_2$	8.4×10^{-8}	0.69
$Co(C_{18}H_{15}N)_2Br_2$	3.0×10^{-7}	0.50
$Cu(C_{18}H_{15}N)_2Cl_2$	2.3×10^{-8}	1.41
$Cu(C_{18}H_{15}N)_2Br_2$	4.1×10^{-8}	1.41
$Zn(C_{18}H_{15}N)_2Cl_2$	9.3×10^{-9}	1.12
$Zn(C_{18}H_{15}N)_2Br_2$	2.9×10^{-7}	0.56

$C_{18}H_{15}N$ = diphenyl-2-pyridylmethane. [a] ΔE is the activation energy appearing in the equation $\sigma = \sigma_0 \exp(-\Delta E/2kT)$ and is determined from the gradient of the high temperature linear region of the ln σ *vs.* $10^3/T$ plot.

Cl_2 which has been omitted to avoid crowding of the graphs, are shown in Figs. 2 and 3. The activation energy ΔE which appears in the equation $\sigma = \sigma_0 \exp(-\Delta E/2kT)$ has been determined for each complex from the gradient of the high temperature linear region of the corresponding ln σ *versus* $1/T$ plot and is listed in Table 5. Possible interpretations for ΔE if the band model is assumed are that it represents the energy barrier for electron release from the valence to the conduction bands [19] or the ionisation energy for donor or acceptor centres [19]. Hopping conduction also exhibits a wide temperature range in which ln σ varies linearly with $1/T$ [20]. For $Cu(C_{18}H_{15}N)_2Br_2$ and $Co(C_{18}H_{15}N)_2Br_2$, Fig. 2, and $Cu(C_{18}H_{15}N)_2Cl_2$, Fig. 3, it can be seen that at the lower end of the temperature range investigated (*i.e.* near room temperature) there is clear evidence of a tendency towards saturation of the conductivity. This is consistent with regarding the determined ΔE values for these compounds as being the energy gap between valence and conduction bands and the room temperature conductivity would then be considered as controlled by exhaustion of donor or acceptor impurities. For both of the zinc compounds, the linearity of the ln σ *versus* $1/T$ plots, Figs. 2 and 3, is maintained down to room temperature which suggests that the conductivity at this temperature is the intrinsic value. For $Co(C_{18}H_{15}N)_2Cl_2$ there is only a very slight tendency for the ln σ *versus* $1/T$ plot to deviate from linearity towards saturation as the temperature approaches room temperature from above.

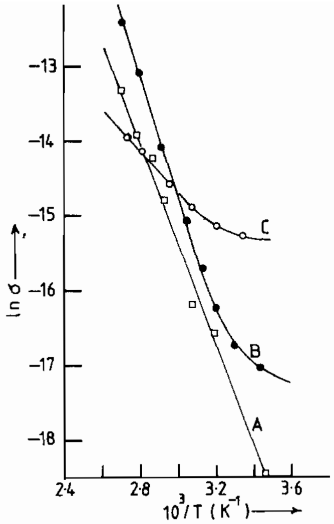

Fig. 2. Plots of ln σ *vs.* $10^3/T$ for discs of the compounds as measured with $V = 10$ V (σ = conductivity in units of $\Omega^{-1}\,m^{-1}$, T = absolute temperature in units of K). A (□): $Zn(C_{18}H_{15}N)_2Cl_2$. B (●): $Cu(C_{18}H_{15}N)_2Br_2$. C (○): $Co(C_{18}H_{15}N)_2Br_2$.

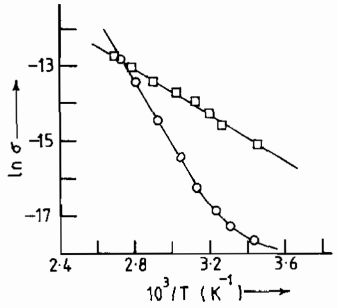

Fig. 3. Plots of ln σ *vs.* $10^3/T$ for discs of the compounds as measured with $V = 10$ V (σ = conductivity in units of $\Omega^{-1}\,m^{-1}$, T = absolute temperature in units of K). ○, $Cu(C_{18}H_{15}N)_2Cl_2$; □, $Zn(C_{18}H_{15}N)_2Br_2$.

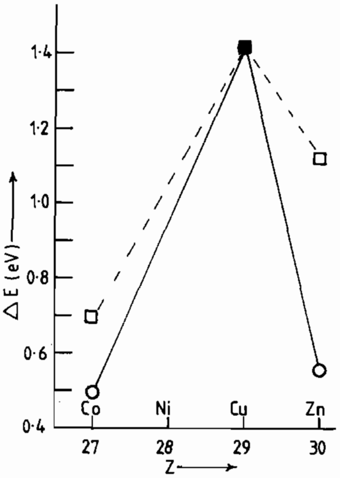

Fig. 4. Plot of the activation energy ΔE [defined by the equation $\sigma = \sigma \exp(-\Delta E/2kT)$] *versus* atomic number Z of the metal atom. – –□– –, $M(C_{18}H_{15}N)_2Cl_2$ complexes; –○–, $M(C_{18}H_{15}N)_2Br_2$ complexes; ■, coincident point for both the chloride and bromide series. No points plotted for $Z = 28$ because the nickel complexes were not prepared.

The activation energies (ΔE) obtained as described above are plotted, Fig. 4, as a function of the atomic number (Z) of the metal atom for both the bromide and chloride series. No points appear for the nickel complexes as these were not prepared. The plots for the two series are qualitatively similar, both exhibiting a peak corresponding to the copper complex. With some caution on account of the lack of data for the nickel complexes, we suggest that it is significant that ΔE peaks for the copper complexes since, as previously noted, copper is in an octahedral environment in contrast to cobalt and zinc which are in tetrahedral environments. Within the experimental uncertainty the value of ΔE for both of the copper complexes is the same. This leads us to the tentative suggestion that for the $M(C_{18}H_{15}N)_2X_2$ complexes the energy gap between valence and conduction bands is nearly independent of which halogen is represented by X if M is in an octahedral environment but not if M is in a tetrahedral environment.

Electrical conductivity measurements can form a basis of a test for thermal stability and, using this technique, we have previously reported [2, 3, 6] the occurrence of thermal degradation below 353 K in other coordination compounds. The compounds described in the present paper exhibited reproducible electrical properties after heating to 370 K, showing that their decomposition temperatures had not been reached. Further work is in progress in our laboratories on the relative conductivities of directly and indirectly linked ring systems as exemplified by quinoxaline and diphenyl-2-pyridylmethane respectively.

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