Inorganica Chimica Acta, *134* (1987) 259–264

Spectral, Magnetic and Electrical Studies on Complexes of Cobalt(II), Nickel(II) and Copper(II) with Aminopyrazine

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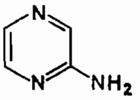
(Received March 16, 1987)

Abstract

The preparation and some properties of complexes of aminopyrazine with the thiocyanates and chlorides of cobalt(II), nickel(II) and copper(II) are described. Magnetic moments, electronic, infrared and Raman spectra indicate that coordination takes place through the ring nitrogen atoms. Electrical conductivity measurements made at room temperature and as a function of temperature over the range 300 to 383 K are reported. The conduction is ohmic and the temperature dependence of the conductivity is interpreted in terms of the ionization of impurities. The compounds are all novel with the exception of dichlorobis(aminopyrazine) cobalt(II) for which no electrical measurements have previously been reported.

Introduction

This work is an extension of previously reported studies on pyrazines and transition metal elements [1, 2]. The present work reports the structural properties and the electrical measurements for complexes of aminopyrazine with the thiocyanates and chlorides of cobalt(II), nickel(II) and copper(II). The pyrazines are predominantly bidentate ligands and complexes formed between pyrazine and transition metal ions are known [3–6]. However, little is known about the complexes of α-aminopyrazine.



2-aminopyrazine (Apz)

Information about the stereochemistry of such complexes has been obtained by studying their magnetic moments and their electronic, infrared and Raman spectra.

Experimental

Three methods of preparation were used:

(a) 5 g of the metal salt dissolved in 50 ml of warm ethanol was added to 4 g of aminopyrazine in 50 ml of warm ethanol. The solution was boiled and stirred until the complex precipitated. The precipitated complexes were washed with warm ethanol and dried over calcium chloride.

(b) 1.8 g of nickel(II) nitrate dissolved in 60 ml of warm ethanol was added to 1.9 g of potassium thiocyanate in 60 ml of warm ethanol. The resulting precipitate was filtered off and 2 g of aminopyrazine was added to the filtrate. The precipitated complex was filtered, washed with warm ethanol and dried over calcium chloride.

(c) The copper(II) thiocyanate complex was prepared by dissolving 1.6 g of copper(II) nitrate and 2 g of aminopyrazine in 120 ml of de-ionized water. 2 g of potassium thiocyanate were added to the solution and the thiocyanate complex was formed by displacement of the nitrate ion. The complex was filtered, washed with warm water and dried over calcium chloride.

The complexes prepared by these methods are listed in Table I and are considered to be novel except where reference is given to a previous preparation. The magnetic moments (given in Table I) were obtained by the Gouy method using $Hg[Co(SCN)_4]$ as calibrant. Each magnetic moment has been corrected for diamagnetism using Pascal's constants [5]. The electronic spectra were obtained using a Beckman ACTA MIV spectrophotometer. The infrared

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0020-1693/87/$3.50

TABLE I. Analyses and Magnetic Moments

Compound	Colour	Method of preparation	% Cation		% Anion		μ (BM)
			Theory	Expt.	Theory	Expt.	
$Co(Apz)_2(CNS)_2$	brown	a	16.30	16.06	31.79	31.65	5.24
$Co(Apz)_2Cl_2$ [a]	grey	a	17.38	16.92	21.48	21.08	5.26
$Ni(Apz)_2(CNS)_2$	green	b	16.08	16.02	31.81	31.68	3.02
$Ni(Apz)_2Cl_2$	green	a	18.36	18.24	22.17	22.09	3.14
$Cu(Apz)_2(CNS)_2$	brown	c	17.18	17.10	31.40	31.22	1.75
$Cu(Apz)Cl_2$	green	a	27.68	27.48	30.84	30.68	1.69

[a] Ref. 8.

absorption spectra were obtained from KBr discs in the region 4000–650 cm^{-1} using a Perkin-Elmer 598 spectrometer. The Raman spectra were obtained on an Anaspec 33 spectrometer using the 647.1 nm line of a krypton ion laser. The analysis of the metal ion was determined using a Perkin-Elmer 373 atomic absorption spectrophotometer and the carbon, hydrogen and nitrogen analyses were performed on a Carlo Erba Elemental Analyser. Electrical measurements were made on disc-shaped samples of the compounds. These discs of diameter 13 mm and approximately 1 mm thickness were prepared by compressing sample powder in a hydraulic press set to apply a force of 100 kN. Circular electrodes of diameter 5.9 mm were applied concentrically on the flat faces of the discs using a silver-based conducting paint. The current passed by each disc was measured as a function of applied voltage at room temperature in a d.c. circuit. A Keithley 610C electrometer was used to register the current. With reversal of polarity of any given applied voltage the magnitude of the current was always constant within ±10% indicating that the painted electrodes are non-blocking. For all discs the current (I)–voltage (V) characteristics were approximately linear over the investigated range (0–120 volt) and conductivities were calculated from the gradient of these characteristics assuming that the field lines are perpendicular to the electrodes. The disc thicknesses needed in these calculations were measured with a micrometer. The same technique for electrical conductivity measurement has recently been described [1, 2].

The temperature dependence of conductivity for each disc was obtained by measuring the current passing between the electrodes under a fixed applied voltage in the range 30–50 volt whilst the disc was in an electrically-heated oven. For temperature measurement a calibrated copper–constantan thermocouple made from 44 S.W.G. wires was mounted on the disc. The temperature range investigated was from room temperature up to a maximum of 110 °C. To avoid problems of pick-up into the high impedance disc circuit from the a.c. heater circuit of the oven, the oven current was temporarily switched off each time the disc current was measured.

Results and Discussion

Analytical Results

The analytical results for the complexes are given in Table I. These are in agreement with the given formulae and show that the maximum number of aminopyrazine molecules present in any complex is either one or two. The aminopyrazine is therefore acting as a monodentate or bidentate ligand in these complexes.

Magnetic Moments

The magnetic moments for the cobalt complexes (Table I) are in the range 4.8–5.3 BM suggesting that an octohedral arrangement of ligands about the cobalt atom is likely [7]. The magnetic moments for the nickel complexes are in the range 2.8–3.4 BM suggesting that the nickel is in an octahedral environment [7] (Table I) and those for the copper complexes are similar to the spin only value of 1.73 BM.

Electronic Spectra

The d–d bands from the electronic spectra of the complexes are given in Table II. The electronic spectra of the cobalt compounds show absorption bands in the regions 8810–9900 and 19 400–20 900 cm^{-1} which are assigned to the $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ (ν_1) and $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ (ν_3) transitions. The values of ν_1 and ν_3 have previously been used to calculate spectral parameters $10Dq$, B and β [8]. The spectra are characteristic of cobalt(II) in an octahedral environment as these complexes have values of $Dq > 440$ cm^{-1} [7, 9].

The electronic spectra of the nickel compounds show absorption bands in the regions 25 900–27 000, 15 700–16 100 and 9500–10 020 cm^{-1} which are assigned to the $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)(\nu_3)$,

TABLE II. Electronic Spectra (cm^{-1})

Compound	Peak position (cm^{-1})	*Dq*	*B*	*β*
$Co(Apz)_2(CNS)_2$	$\nu_1 = 6756$ $\nu_3 = 19802$	781	940	0.98
$Co(Apz)_2Cl_2$	$\nu_1 = 6494$ $\nu_3 = 19008$	750	901	0.93
$Ni(Apz)_2(CNS)_2$	$\nu_1 = 8640$ $\nu_2 = 17094$ $\nu_3 = 23256$	864	962	0.92
$Ni(Apz)_2Cl_2$	$\nu_1 = 8335$ $\nu_2 = 15036$ $\nu_3 = 24005$	833	936	0.90
$Cu(Apz)_2(CNS)_2$	$\nu_1 = 13222$			
$Cu(Apz)Cl_2$	$\nu_1 = 13899$			

$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ (ν_2) and $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ (ν_1) transitions respectively. The values ν_1, ν_2 and ν_3 have been used to calculate spectral parameters $10Dq$, B and β [8]. The spectra are characteristic of the nickel(II) ion in an octahedral environment, shown by the values for Dq [7, 9].

The copper complexes have a single band between 13 200–14 100 cm^{-1} which is assigned to the $^2Eg(D) \rightarrow {}^2T_{2g}(D)$ (ν_1) transition. This would suggest an octahedral environment for the copper atom [7].

Infrared Spectra

The infrared data obtained are detailed in Table III. The spectrum of aminopyrazine is almost identical to those of the complexes in the region 2000–625 cm^{-1}, excepting the bands due to ring vibrations which move to higher wavenumbers on complex formation. This suggests that coordination takes place through the ring nitrogen atom to the transition metal [10]. In the region 3100–3600 cm^{-1} a difference is observed in the ν(N–H) bands of the spectrum. In the spectrum of a dilute solution of aminopyrazine in tetrachloromethane bands are observed between 3500 and 3400 cm^{-1}, which are assigned to free NH_2 ν(N–H). Comparison of the spectra of aminopyrazine and its complexes shows that the frequencies of these bands are lowered to 3320 and 3170 cm^{-1}. It is suggested that this is due to the transition from the monomeric to the dimeric form of the molecule by intermolecular dimerization.

Raman Spectra

The bands which are absent in the Raman spectrum of aminopyrazine but present in the spectra of the complexes have been assigned as metal–halogen and metal–nitrogen vibrations and are given in Table IV.

Solubility

The poor solubility of the compounds in both polar and non-polar solvents indicates that the compounds have polymeric structures [7].

Without X-ray diffraction data no definite structures can be described for the complexes. Attempts to grow single crystals of these complexes to enable such analyses to be carried out were unsuccessful. However, the spectroscopic and magnetic data enable predictions to be made of the possible structures. The $M(Apz)_2X_2$ complexes have octahedral structures and the bands in the Raman spectra corresponding to ν(M–Cl) and ν(M–Br) are consistent with similar modes in halogen-bridged polymeric structures. The presence of a band around 2150 cm^{-1} in the infrared spectra of the thiocyanate complexes would indicate the presence of bridging thiocyanate groups in these complexes [11]. It is therefore suggested that the structure of these complexes is made up of a plane of metal atoms with bridging halogen or thiocyanate groups with the aminopyrazine bonded above and below the plane of the chain to each metal atom through a lone pair of electrons or one of the ring nitrogen atoms. It is further postulated, by comparison of the N–H vibrations in the infrared spectra of the complexes to those observed for aminopyrazine (using KBr disc and tetrachloromethane solution), that the aminopyrazine molecules are con-

TABLE III. Infrared Spectra (4000–600 cm^{-1})

Compound	$\nu_a(NH_2)$	$\nu_s(NH_2)$	$S(NH_2)$	Ring vibrations	
Apz	3325(s)	3150(s)	1650(m)	1530(m)	1425(m)
$Co(Apz)_2(CNS)_2$	3420(s)	3195(s)	1620(m)	1535(m)	1435(m)
$Co(Apz)_2Cl_2$	3410(s)	3200(s)	1635(m)	1530(m)	1440(m)
$Ni(Apz)_2(CNS)_2$	3415(s)	3296(s)	1620(m)	1530(m)	1435(m)
$Ni(Apz)_2Cl_2$	3420(s)	3180(s)	1635(m)	1535(m)	1445(m)
$Cu(Apz)_2(CNS)_2$	3340(s)	3180(s)	1620(m)	1530(m)	1440(m)
$Cu(Apz)Cl_2$	3375(s)	3105(s)	1640(m)	1540(m)	1470(m)

s = strong, m = medium.

TABLE IV. Raman Spectra (100–650 cm^{-1})

Compound	ν(M–X)	ν(M–N)
$Co(Apz)_2(CNS)_2$		367, 607
$Co(Apz)_2Cl_2$	239	366, 607
$Ni(Apz)_2(CNS)_2$		604
$Ni(Apz)_2Cl_2$	209	372, 607
$Cu(Apz)_2(CNS)_2$		365, 607
$Cu(Apz)Cl_2$	250	366, 605

nected to each other by hydrogen bonding between the amine groups.

The compound $Cu(Apz)Cl_2$ also has an octahedral structure. The assignment of the Cu–Cl bond in the Raman spectrum of this compound would suggest the presence of bridging chlorine atoms [12]. Hence it is postulated that the structure of this complex consists of a chain of copper atoms bonded to chlorine atoms in which the copper atoms in adjacent chains are linked by aminopyrazine molecules. Each copper atom has a coordination number of 6, being surrounded by four planar chloride ions with a ring nitrogen atom from the aminopyrazine above and below the Cl–Cu–Cl plane [13]. The N–H vibrations in the infrared spectrum of this complex would seem to suggest that the aminopyrazine molecules are linked by hydrogen bonding involving the amine groups.

Electrical Properties

The measured electrical properties are summarized in Table V. For each compound the room temperature conductivity and the temperature dependence of conductivity refer to the same disc. In view of the observed ohmic behaviour of the discs it follows that the conductivities are independent of voltage. The range of observed room temperature conductivities is from 3.2×10^{-9} Ω^{-1} m^{-1} for $Co(Apz)_2(CNS)_2$ to 2.2×10^{-5} Ω^{-1} m^{-1} for $Co(Apz)_2Cl_2$.

Figures 1 and 2 show plots of ln σ *versus* $1/T$, (σ = conductivity, T = absolute temperature). From the gradients of the linear sections of these plots the energies ΔE in the equation $\sigma = \sigma_0 \exp -\Delta E/2kT$ were determined and are listed in Table V. For intrinsic semiconductors in which the temperature dependence of the carrier mobilities is weak compared to that of the free carrier concentrations, ΔE corresponds to the energy gap between valence and conduction bands [14]. If ionization of a donor or acceptor impurity level without significant compensation is the dominant process for free carrier generation, again with a negligible temperature dependence of mobility, then ΔE corresponds to the ionization energy of the impurity [14, 15]. If the mobility is controlled by an activation energy as has been suggested for phthalocyanine [16], then the interpretation of ΔE is more complicated since both mobility and carrier concentration are strongly dependent on temperature. The hopping mechanism is a case in which the mobility is an exponential function of T^{-1} [17].

For $Co(Apz)_2(CNS)_2$ and $Cu(Apz)_2Cl_2$ the ln σ *versus* $1/T$ plots, Fig. 1, each show a well defined linear region followed at higher temperature by independence of σ on T. The gradients of the linear regions lead to values of 0.94 and 0.92 eV respectively for ΔE. The simplest interpretation for the shapes of the ln σ *versus* $1/T$ plots is that a single impurity level is ionized in each compound and at the higher temperatures these impurity levels are completely ionized. According to this view the values determined for ΔE correspond to donor or acceptor ionization energies.

The ln σ *versus* $1/T$ graph for $Cu(Apz)_2(CNS)_2$, Fig. 2, exhibits two linear regions KL and MN with a short range of near temperature independence bridging these regions. The values determined for ΔE from

TABLE V. Summary of Electrical Properties

Compound	Room temperature conductivity (Ω^{-1} m^{-1})	Graph of ln σ *vs.* $1/T$	Values of ΔE in the equation $\sigma = \sigma_0 \exp\left(\frac{-\Delta E}{2kT}\right)$ (eV)	Range of ln σ *vs.* $1/T$ graph used to determine ΔE
$Co(Apz)_2(CNS)_2$	3.2×10^{-9}	Fig. 1	0.94	AB
$Co(Apz)_2Cl_2$	2.2×10^{-5}	Fig. 2	0.35	EF
$Ni(Apz)_2(CNS)_2$	6.4×10^{-7}	Fig. 2		
$Ni(Apz)_2Cl_2$	8.7×10^{-6}	Fig. 2	0.39 and	GH
			0.31	IJ
$Cu(Apz)_2(CNS)_2$	5.6×10^{-7}	Fig. 2	0.88 and	KL
			0.36	MN
$Cu(Apz)Cl_2$	4.5×10^{-8}	Fig. 1	0.92	CD

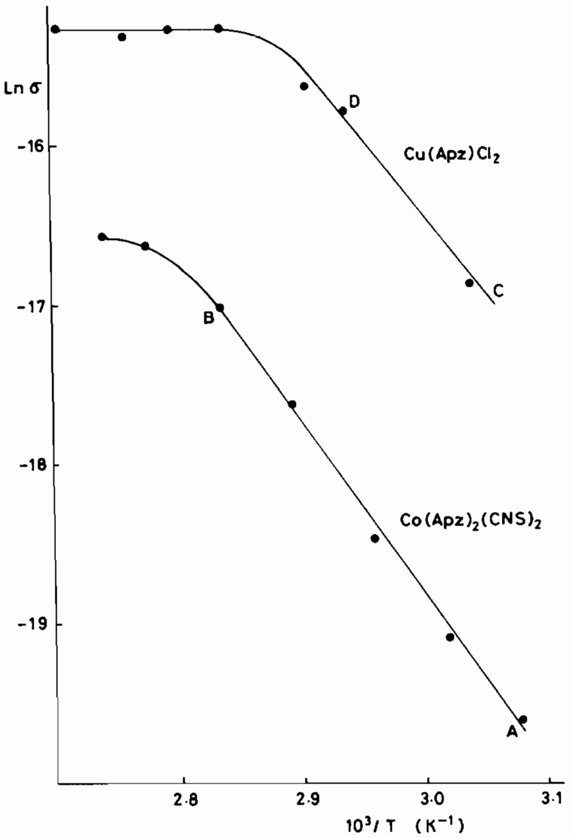

Fig. 1. Plots of ln σ *vs.* $1/T$ for $Co(Apz)_2(CNS)_2$ and $Cu(Apz)Cl_2$. σ is in units of Ω^{-1} m^{-1}. AB and CD are linear regions referred to in the text.

the regions KL and MN are 0.88 and 0.36 eV respectively. These energies possibly correspond to ionization energies of two sets of impurities although, contrary to observation, one would have expected the impurities of lower ionization energy to be preferentially ionized first as the temperature is increased.

The conductivities for $Co(Apz)_2Cl_2$ and $Ni(Apz)_2Cl_2$ which are also displayed in Fig. 2, each pass through a maximum as the temperature is increased. After heating through the maximum conductivity further conductivity measurements were taken as cooling back to room temperature occurred. As can be seen from the Figure, σ is constant during this cooling phase. When the discs were again heated the conductivity remained at its room temperature value. Evidently heating has produced an irreversible chemical range. With freshly prepared discs the conductivity maxima were again observed. Approximate values for ΔE obtained from the ln σ *versus* $1/T$ plots in the range between room temperature and the conductivity maxima are listed in Table V. For $Ni(Apz)_2Cl_2$ there is weak evidence for the existence of two linear regions, marked as GH and IJ in Fig. 2, before the temperature corresponding to maximum conductivity is reached.

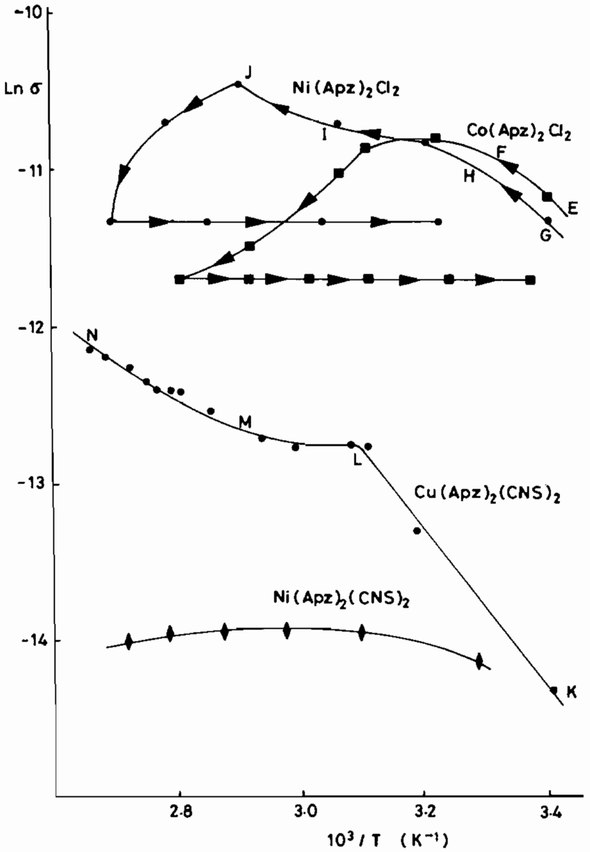

Fig. 2. Plots of ln σ *vs.* $1/T$ for $Ni(Apz)_2(CNS)_2$, $Cu(Apz)_2(CNS)_2$, $Co(Apz)_2Cl_2$ and $Ni(Apz)_2Cl_2$. σ is in units of Ω^{-1} m^{-1}. Lettering is to identify regions of the curves which are discussed in the text.

The compound $Ni(Apz)_2(CNS)_2$ exhibits little change in conductivity with temperature as may be seen by reference to Fig. 2. A possible explanation is that the species of impurity resulting in the room temperature conductivity is essentially fully ionized at 300 K and the intrinsic mechanism is not significantly activated until temperatures higher than those investigated are reached.

The temperature dependencies of electrical conductivity observed have been tentatively explained in terms of impurity ionizations. There is some evidence that impurities play a major role in governing the temperature dependence of conductivity since neither the room temperature conductivities or the activation energies ΔE show any obvious trend with the composition.

Acknowledgement

Permission to publish this paper has been given by the British Petroleum Company p.l.c.

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