

THERMAL, STRUCTURAL AND ELECTRICAL PROPERTIES

The chloro complex of nickel with 3-hydroxy-2-quinoxaline-carboxylic acid

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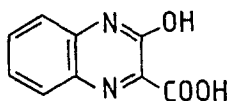
Abstract

The chloro compound of 3-hydroxy-2-quinoxalinecarboxylic acid with nickel(II) has been prepared in ethanolic solution from which a solid compound was isolated. Spectral and magnetic measurements show that the nickel ions are in an octahedral environment. Thermogravimetry, differential thermal analysis and electrical conductivity data are reported for 3-hydroxy-2-quinoxalinecarboxylic acid and its nickel complex. The conductivity measurements indicate that electron/hole traps are emptied during heating of the complex but repopulation occurs in about 24 h at room temperature.

Keywords: complexes, electrical properties, structural properties, thermal properties

Introduction

A number of papers have been published describing the preparation, thermal stability and electrical conductivity of transition metal complexes with various substituted pyrazines including quinoxaline [1], 2-methylquinoxaline [2, 3] and 6,7-dimethyl-2,3-di(2-pyridyl)quinoxaline [4]. Many of these complexes are polymeric in structure, containing both halogen and pyrazine bridges. Room temperature electrical conductivities greater than $1 \times 10^{-3} \Omega^{-1} \text{ m}^{-1}$ were reported for a bromoquinoxaline complex with manganese [1] and a chloroquinoxaline complex with cobalt [2]. However, much lower room temperature conductivities ($< 10^{-6} \Omega^{-1} \text{ m}^{-1}$) were also found [3, 4] for several complexes. For the upper end of the conductivity range there is a possibility of development of electronic devices and this, together with an interest in structures of metal complexes with other pyrazine derivatives, has led us to investigate the nickel-chloro complex with 3-hydroxy-2-quinoxalinecarboxylic acid.

3-hydroxy-2-quinoxalinecarboxylic acid ($C_9H_6N_2O_3$)

Experimental

Preparation of the metal complex

The nickel(II) chloride, $NiCl_2 \cdot 6H_2O$ (0.05 mol), was dissolved in a minimum of boiling ethanol. To the boiling solution, 0.10 mol of 3-hydroxy-2-quinoxalinecarboxylic acid in warm ethanol was added dropwise with stirring. The resulting solution was refluxed for 12 h and then cooled. The precipitated product was then isolated by filtration, washed with a minimum of warm ethanol and air dried.

Analytical, magnetic, spectral and thermal measurements

The concentration of nickel ion in the solid prepared as described above, was determined using a Perkin-Elmer 373 atomic absorption spectrophotometer; carbon, nitrogen and hydrogen concentrations were measured using a Carlo Erba elemental analyser.

Infrared spectra for both the 3-hydroxy-2-quinoxalinecarboxylic acid and its nickel complex were obtained using KBr discs (wavenumber range $4000-600\text{ cm}^{-1}$) and polyethylene discs ($600-200\text{ cm}^{-1}$ range) on a Perkin-Elmer spectrophotometer model 598. An electronic spectrum for the nickel complex was obtained on a Beckmann Acta MIV spectrophotometer as solid diffuse reflectance bands.

The magnetic moment per nickel ion present in the complex was measured by the Gouy method using $Hg[Co(SCN)_4]$ as calibrant.

Thermal analysis data, in the form of thermogravimetry (TG) and differential thermal analysis (DTA) traces, were obtained using a Stanton Redcroft STA thermobalance. Heating for these measurements was in static air at constant heating rate of 6°C min^{-1} and covering the temperature range $20-800^\circ\text{C}$.

Electrical measurements

Discs of diameter 13 mm and thickness in the range 0.26–0.49 mm were prepared by compressing powdered samples of the 3-hydroxy-2-quinoxalinecarboxylic acid ligand and its nickel complex. The compression was achieved using a hydraulic press set to apply a force of 100 kN. An electrode of diameter 5.91 mm was painted concentrically on the flat faces of each disc by application of a silver based conductive paint (Radiospares 555–156) through a mask.

The prepared discs were then kept in a desiccator for a week to ensure that no trace of water could be present, and then d.c. measurements were obtained of: (i) the current (I) as a function of applied voltage (V) for increasing and decreasing magnitude of V in both polarities for room temperature and (ii) the current passing as a function of temperature, over the range 22–70°C, under application of a constant potential difference (200 V for the ligand and 40 V for the complex). For all these electrical measurements the disc was mounted on a holder so that its lower electrode made contact to a brass block and connection to the upper electrode was by a spring-loaded aluminium pad. A hole drilled into the brass block of the holder accommodated a mercury-in-glass thermometer and, during the measurements, the holder was placed inside an oven. Measurements of current were by a Philip Harris analogue pico-ammeter and voltage by a digital meter.

The thickness of each disc, which is required for inferring the conductivity of the disc material from the above measurements, was obtained as the mean of many determinations using a micrometer.

Results and discussion

Analytical

From the experimentally determined analyses for nickel ion, carbon, nitrogen and hydrogen in the yellow metal complex the formula $\text{Ni}(\text{C}_9\text{H}_6\text{N}_2\text{O}_3)\text{Cl}_2$ was inferred for the compound. On the basis of this formula, the theoretical analysis was calculated and compared with the original experimental data giving the following results:

| | Metal | Carbon | Nitrogen | Hydrogen |
|------------|-------|--------|----------|----------|
| Found/wt% | 18.14 | 33.54 | 8.66 | 1.86 |
| Theory/wt% | 18.35 | 33.79 | 8.75 | 1.89 |

The good agreement between the observed and theoretical analyses indicates a high degree of purity of the complex.

Electronic spectrum, infrared spectra and magnetic moment

Bands observed at the wavenumbers 8621, 15152 and 18692 cm^{-1} in the electronic spectrum of the metal complex correspond to the $d-d$ transitions from ${}^3A_{2g}(\text{F})$ to the respective terminal states ${}^3T_{2g}(\text{F})$, ${}^3T_{1g}(\text{F})$ and ${}^3T_{1g}(\text{P})$. By analogy with assignments made for similar nickel complexes, the electronic spectrum indicates that the nickel ion is in an octahedral environment [5]. The observed magnetic moment of 3.12 BM per nickel ion provides supporting evidence for the suggested structure because it lies within the range 2.8–3.2 BM

known to be appropriate for a nickel ion in an octahedral environment [5]. Further evidence for the proposed environment of nickel ions is obtained from the infrared spectrum which exhibits an absorption band at 256 cm^{-1} and this wavenumber is consistent with assigning it to a Ni-Cl vibration for octahedrally-surrounded nickel ions [6].

The IR spectra of the 3-hydroxy-2-quinoxalinecarboxylic acid and its nickel complex both show a strong absorption band at 3318 cm^{-1} and this is considered to be due to a hydrogen-bonded OH group since a non-hydrogen-bonded OH group would give absorption at about 3600 cm^{-1} . A broad absorption band at $3000\text{--}2500\text{ cm}^{-1}$, assigned to a hydrogen-bonded COOH group, was also observed in the IR spectrum for each compound.

In the wavenumber range $2500\text{--}600\text{ cm}^{-1}$ there is similarity between the IR absorption spectra for 3-hydroxy-2-quinoxalinecarboxylic acid and its nickel complex except that in the latter the formation of the complex has shifted the aromatic ring vibrations to higher frequencies. This shift suggests that the nitrogen atoms of the aromatic ring are co-ordinated to a nickel atom [1-4].

In the wavenumber range below 300 cm^{-1} in the IR spectrum for the nickel complex, a band is observed at 298 cm^{-1} which is identified as due to a Ni-N vibration [7] and, as previously mentioned when discussing the evidence for the octahedral environment of nickel ions, there is a band at 256 cm^{-1} assigned to a Ni-Cl vibration.

Summary of suggested structure of the nickel complex

To obtain definite information on the structure of the complex one needs to grow large crystals suitable for single crystal X-ray diffractometry but the preparation procedure used by us yielded the complex in the form of a powder. However, from the spectroscopic and magnetic data, a possible structure can be suggested.

In the suggested structure there are parallel chains of nickel atoms bonded to chlorine atoms with molecules of 3-hydroxy-2-quinoxalinecarboxylic acid acting as bridging agents between adjacent chains to form a sheet structure. Hydrogen bonding exists between the OH and COOH groups within each 3-hydroxy-2-quinoxalinecarboxylic acid molecule. The nickel ions are in an octahedral environment being surrounded by four planar chloride ions with a ring nitrogen atom from the 3-hydroxy-2-quinoxalinecarboxylic acid on each side of the Cl-Ni-Cl plane.

Thermal decomposition

The thermogravimetric (TG) and differential thermal analysis (DTA) traces obtained for the 3-hydroxy-2-quinoxalinecarboxylic acid are shown in Fig. 1. The TG trace shows that no chemical change occurs until the temperature reaches 190°C and this change, which is a pyrolytic decomposition is rapid near

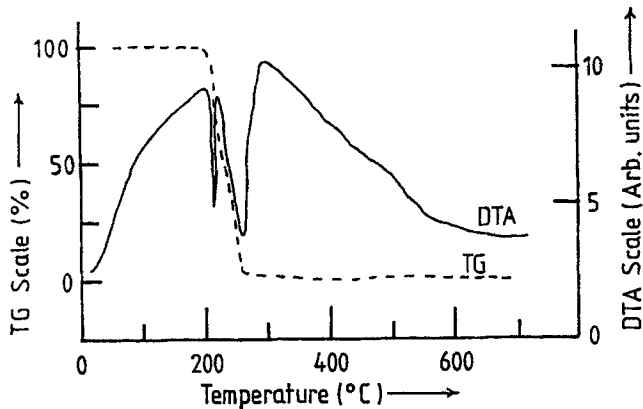


Fig. 1 Thermogravimetric (TG, - - -) and differential thermal analysis (DTA, —) traces for 3-hydroxy-2-quinoxalinecarboxylic acid. Sample weight = 1.42 mg

270°C. Thereafter, up to 402°C, a much slower change occurs which we suggest is due to decomposition of a tar.

The DTA trace shown in Fig. 1 exhibits an endothermic peak at 206°C corresponding to fusion. The liquefied compound immediately decomposes and this is manifested as another endothermic peak at 262°C in the DTA trace.

Figure 2 shows TG and DTA traces for the nickel complex, $\text{Ni}(\text{C}_9\text{H}_6\text{N}_2\text{O}_3)\text{Cl}_2$. It is observed from the TG trace that the decomposition begins at 70°C and thereafter there is progressive weight loss which becomes rapid a few degrees below the temperature of 460°C after which there is no further loss. The weight of the residue, which is 24.8% of the original sample weight, is in good agreement with that (25.0%) predicted from theory for NiO

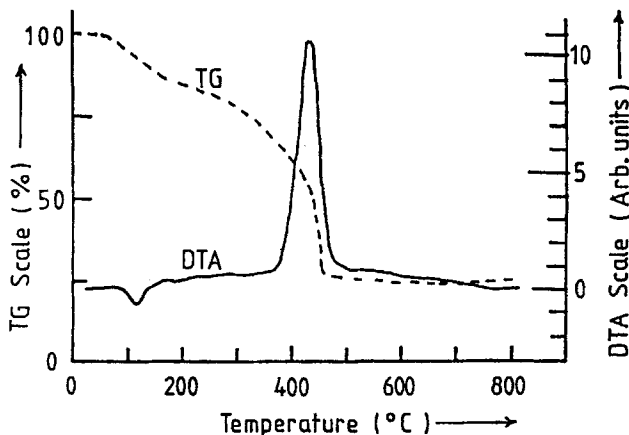


Fig. 2 Thermogravimetric (TG, - - -) and differential thermal analysis (DTA, —) traces for $\text{Ni}(\text{C}_9\text{H}_6\text{N}_2\text{O}_3)\text{Cl}_2$. Sample weight = 8.52 mg

residue. The DTA trace shows a small endothermic peak at 110°C and a much larger exothermic peak at 410°C as consequences of two distinct processes in the overall change from the starting material to the nickel oxide.

As previously stated, decomposition of 3-hydroxy-2-quinoxalinecarboxylic acid molecules, as determined from the TG traces, begins at 190°C for the free ligand and at 70°C when incorporated into the nickel complex. It is suggested that the lower decomposition temperature in the latter case is a consequence of the irregular packing of the ligand molecules between the nickel chloride chain.

Electrical

The disc of 3-hydroxy-2-quinoxalinecarboxylic acid used for the electrical measurements was of thickness 0.49 mm and in tests at room temperature the applied voltage ranged from zero to 415 V, corresponding, therefore, to a maximum applied field of 0.85 MV m⁻¹. Ohmic behaviour was observed over the full range of these measurements and the value deduced for the room temperature (24°C) conductivity, assuming the conduction pathway to be through the bulk material (as opposed to surface leakage), is 5.3 × 10⁻¹² Ω⁻¹ m⁻¹. A plot of the conductivity (using a logarithmic scale) against reciprocal absolute temperature for the 3-hydroxy-2-quinoxalinecarboxylic acid is shown in Fig. 3. Over the temperature range for heating from 317 K to the maximum temperature reached (353 K) the plot is linear and the value of ΔE in the equation $\sigma = \sigma_0 \exp(-\Delta E/2kT)$ corresponding to this linear section is 2.15 eV. During cooling back to room temperature, the conductivity, as can be seen from the fig-

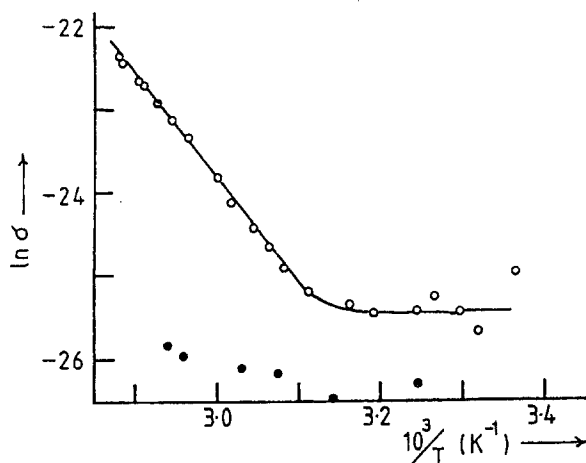


Fig. 3 Plot of $\ln(\sigma)$ against $10^3/T$ for 3-hydroxy-2-quinoxalinecarboxylic acid where $\sigma = \text{conductivity}/\Omega^{-1} \text{ m}^{-1}$ at absolute temperature T . The activation energy ΔE in the equation $\sigma = \sigma_0 \exp(-\Delta E/2kT)$, as obtained from the linear section during heating, is 2.12 eV. Heating (○); cooling (●)

ure, was much lower than for heating even though the highest temperature reached (353 K) was far below the TG result of 463 K for the onset of thermal decomposition. After the disc had cooled to room temperature the conductivity was approximately one third of its preheating value for this temperature. These results indicate that during the heating, part of the current was thermally-stimulated due to carrier traps emptying without replenishment.

Room temperature measurements of current against voltage, shown in Fig. 4, for the disc of the nickel complex verify that it, like the 3-hydroxy-2-quinoxalinecarboxylic acid, is ohmic and without electrical hysteresis. The conductivity obtained from these measurements is $3.8 \times 10^{-10} \Omega^{-1} \text{ m}^{-1}$ which, although very low, is a factor of 72 greater than that of the 3-hydroxy-2-quinoxalinecarboxylic acid.

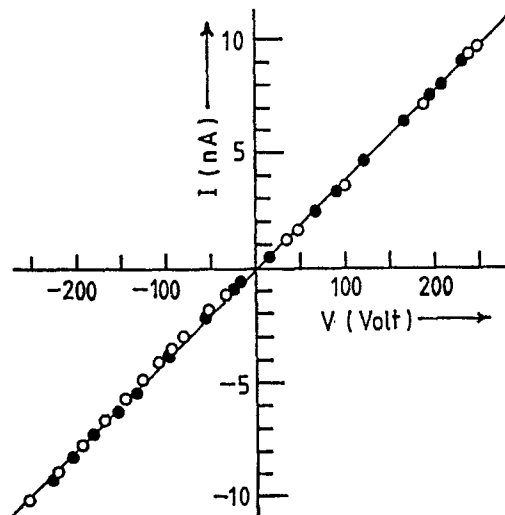


Fig. 4 Room temperature dependence of current (I) on applied potential (V) for a disc of $\text{Ni}(\text{C}_9\text{H}_6\text{N}_2\text{O}_3)\text{Cl}_2$ of thickness 0.26 mm. Increasing V (o); decreasing V (•)

An Arrhenius plot for the electrical behaviour of the nickel complex is shown in Fig. 5. From the gradient of the broken straight lines drawn in the figure, the values of ΔE in the equation $\sigma = \sigma_0 \exp(-\Delta E/2kT)$ for heating and cooling are, respectively, 1.99 eV and 1.62 eV. The highest temperature attained during the heating and cooling cycles was 339 K which is just below the temperature of 343 K determined from the TG trace for onset of decomposition. Again, like the 3-hydroxy-2-quinoxalinecarboxylic acid, conductivities for cooling were less than for the same temperature during heating but with less average fractional difference. The points marked A and B in Fig. 5 were obtained, in that order, 24 h after the thermal cycle and with the disc unmoved from its holder. The proximity of points A and B to the curve for the heating phase of

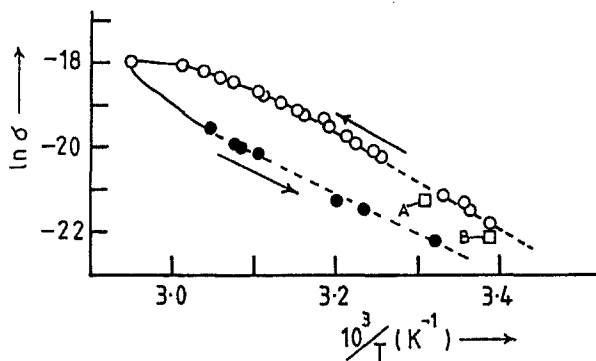


Fig. 5 Plot of $\ln(\sigma)$ against $10^3/T$ for $\text{Ni}(\text{C}_9\text{H}_6\text{N}_2\text{O}_3)\text{Cl}_2$ where $\sigma = \text{conductivity}/\Omega^{-1} \text{ m}^{-1}$ and $T = \text{absolute temperature}$. Heating (o); cooling (\bullet). The points labelled A and B were obtained 24 h after the cooling cycle

the thermal cycle shows that, electrically, the complex nearly recovers during 24 h at room temperature to its pre-heating condition. A test showed that the new relation between current and voltage at room temperature was still ohmic and non-hysteretic. These results indicate that during heating, the conductivity was enhanced due to carrier release from traps which did not have time to replenish but, during 24 h subsequent delay at room temperature, the carrier population in the traps nearly recovered to the pre-heating value.

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