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PREPARATION AND STUDY OF 1,8-OCTAMETHYLENEDIAMMONIUM CHLORONICKELATES

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ABSTRACT

The compound $(onH_2)[Ni_2Cl_6(H_2O)_4]$ (I), where on = 1,8-octamethylenediamine, is obtained as flat yellow crystals by reaction between nickel(II) chloride hexahydrate and the hydrochloride of the diamine. Dehydration of compound **I** leads to the reddish-yellow anhydrous compound $(onH_2)[NiCl_3]_2$ (II). Both compounds show diffuse reflectance spectra and magnetic moments typical of nickel(II) in an octahedral environment. The compounds were also studied by IR spectroscopy, differential thermal analysis and thermogravimetric analysis.

INTRODUCTION

Nickel(II) can adopt different geometries when forming coordination complexes with halide ions. Tetrahedral geometry is found in many compounds in which there are discrete intense blue $NiCl_4^{2-}$ anions [1]. In the compounds $(RNH_3)_2[NiCl_4]$, the nickel does not have a tetrahedral structure but is surrounded by six chloride ions in an octahedral environment [2,3].

Related to the tetrachloronickelates are the complex species $[NiCl_4(H_2O)_2]^{2-}$ and $[NiCl_4(ROH)_2]^{2-}$ which are octahedral and have a yellowish colour [3].

The compounds of formula $MNiX_3$ ($M = K^+$, Cs^+, $N(CH_3)_4^+$; $X = Cl^-$, Br^-) are generally reddish-yellow and the nickel achieves six coordination by the formation of $[NiX_3]_n^{n-}$ polymer chains in which octahedra share opposite faces [4,5].

The present work is the continuation of a series of experiments carried out in our laboratory aimed at preparing and characterising the chloronickelates of different diprotonated aliphatic diamines [6].

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EXPERIMENTAL

Instrumental techniques and reagents

The 1,8-octamethylenediamine and the nickel chloride hexahydrate were supplied by Aldrich. All chemicals were of analytical grade.

Fourier transform infrared (FTIR) spectra of the compounds were recorded using KBr pellets on a Perkin–Elmer M1700 apparatus equipped with a data station. The electronic spectra of the nickel compounds were recorded on a Varian–Techtron apparatus, Model 635, using the diffuse reflectance technique and barium sulphate as reference.

Thermogravimetric (TG) curves were obtained in flowing air and argon (45 cm^3 min^{-1}) using a Perkin–Elmer Model 3600 instrument coupled to a data station; the heating rate was 5 °C min^{-1}. Differential thermal analysis (DTA) was performed using a Perkin–Elmer 3600 instrument with the same conditions as for the TG curves and using alumina as the reference. The sample weights employed for thermal analysis were 7–12 mg.

Magnetic susceptibilities were determined at room temperature using a Stanton MC-5 Gouy-type balance. The diamagnetic corrections for the ligands were performed using Pascal's constants.

The powder diffractograms were recorded on a Siemens X-ray diffractometer Model D500, using Ni-filtered copper $K\alpha$ radiation.

Preparation of the compounds

The preparation procedure is similar to that previously described by us [6]. A solution of nickel chloride hexahydrate (0.10 mol and 20 cm^3 of HCl) was added to a solution of the diamine hydrochloride (0.05 mol and 10 cm^3 of water), onH_2Cl_2. The resulting solution was concentrated at 50 °C until the volume was reduced to 10 cm^3, and placed in a desiccator with calcium chloride. After standing for several days, flat yellow crystals of hydrated compound **I** were obtained. By heating at 120 °C in an oven, the compound **I** loses water molecules and the reddish-yellow anhydrous compound **II** is obtained. On standing compound **II** in a moist air atmosphere, it returns to the initial yellow compound **I** which shows the typical IR spectrum of the hydrated nickel compound.

The powder diffractogram of compound **II** no longer shows the characteristic lines of the $NiCl_2$ or on H_2Cl_2 spectrum and, therefore, the dehydration is as follows

$$(onH_2)[Ni_2Cl_6(H_2O)_4] \rightleftharpoons (onH_2)[NiCl_3]_2 + 4H_2O \qquad (1)$$

The metal content of compound **I** was determined complexometrically with EDTA using murexide as the indicator. The analysis of C, N, H and Cl were determined at the Institute of Bio-organic Chemistry of the CSIC

(Barcelona, Spain). Analytical results were: Ni, 21.5%; N, 5.8%; C, 18.0%; H, 5.6%; and Cl, 38.0%. $(C_8H_{22}N_2)[Ni_2Cl_6(H_2O)_4]$ calculated is: Ni, 21.42%; N, 5.11%; C, 17.51%; H, 5.47%; and Cl, 38.80%.

RESULTS AND DISCUSSIONS

Infrared spectra

The important IR bands of the nickel complexes and the hydrochloride of the diamine, and their assignments, are collected in Table 1. The IR spectrum of compound **I** shows an intense broad band in the 3500–3200 cm^{-1} zone which contains the OH and NH stretching modes of water molecules and alkyldiammonium cations. The intense band at 1624 cm^{-1} present in compound **I** (absent in compound **II**) is assigned to the OH deformation vibration mode. The NH deformation mode appears in both nickel compounds at 1602 cm^{-1}. The broad central band at 2030–2060 cm^{-1} present in the nickel compounds and onH_2Cl_2, is assigned to the $-NH_3^+$ vibration group [7]. The NH stretching bands of onH_2Cl_2 are shifted towards longer wavenumbers in the nickel compounds as a consequence of hydrogen bond formation (NH ··· O or NH ··· Cl), between the chlorocomplex anions and the diammonium cations [7,8].

Visible diffuse reflectance spectra

The diffuse reflectance spectra of the nickel complexes appear in Fig. 1 and are consistent with an octahedral environment for Ni(II) [9]. The shoulder located at 13400 cm^{-1} in the reflectance spectrum of compound **I** is associated with the transition to the ^1E_g state. Table 2 contains the

TABLE 1

Important IR bands (cm^{-1}) [a]

Compound	ν(OH) ν(NH)	δ(NH)	Other
$(onH_2)[Ni_2Cl_6(H_2O)_4]$	(3500–3200s, b)	1602s	2032m, b 1624s 1467m 600m
$(onH_2)[NiCl_3]_2$	(3436–3200s, b)	1602s	2038m, b 1467m 633w
onH_2Cl_2	– 2978s, b 3196sh	1603s	2062w, b 1516s 1467s

[a] onH_2^{2+} = 1,8-octamethylenediammonium; s = strong, m = medium, w = weak, b = broad.

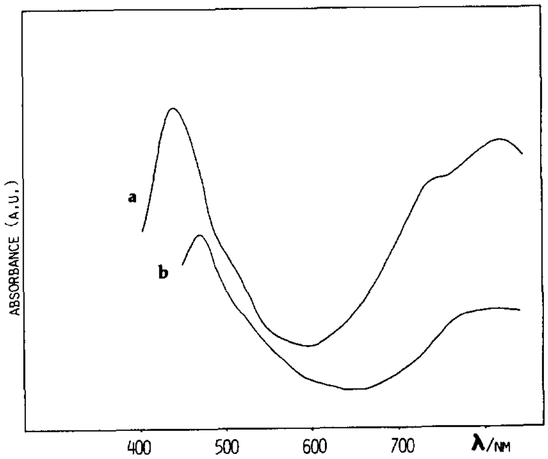

Fig. 1. Diffuse reflectance spectra of the nickel compounds: a, $(onH_2)[Ni_2Cl_6(H_2O)_4]$; b, $(onH_2)[NiCl_3]_2$.

observed ν_2 and ν_3 transitions and the lowest energy transition, ν_1, which was calculated from ν_2 and ν_3 using Lever's method [10]. The same method was also used for the calculation of the inter-electronic repulsion parameter, B. The transition ν_1 coincides with the crystal field energy 10 Dq, and their values are consistent with an octahedral environment for $NiCl_4(H_2O)_2$ and $NiCl_6$ in compounds **I** and **II**, respectively. The theoretical values of 10 Dq may be determined from f and g, Jørgensen's parameters [11], and they show good agreement with the Lever's method values

$$10\ Dq[NiCl_6] = fg = 0.78 \times 8.7 = 6.78\ kK \tag{2}$$

$$\begin{aligned}10\ Dq[NiCl_4(H_2O)_2] &= 2/6 \times 10\ Dq[Ni(H_2O)_6] + 4/6 \times 10\ Dq[NiCl_6] \\ &= 7.42\ kK\end{aligned} \tag{3}$$

For the hydrated compound, **I**, the Ni/Cl ratio and their stoichiometry do not permit the formation of discrete octahedral anions $[NiCl_4(H_2O)_2]^{2-}$ so

TABLE 2

Crystal field and magnetic data

Compound	$\nu_1[^3A_{2g} \rightarrow {}^3T_{2g}]$	$\nu_2[^3A_{2g} \rightarrow {}^3T_g(F)]$	$\nu_3(^3A_{2g} \rightarrow {}^3T_g(P)]$	B	μ(BM)
$(onH_2)[Ni_2Cl_6(H_2O)_4]$	7360 [a] 7400 [b]	12300	22900	860 [a]	2.9
$(onH_2)[NiCl_3]_2$	6800 [a] 6780 [b]	12150	21400	850 [a]	2.8

[a] Calculated from Lever's method.

[b] Calculated from Jørgensen's parameters.

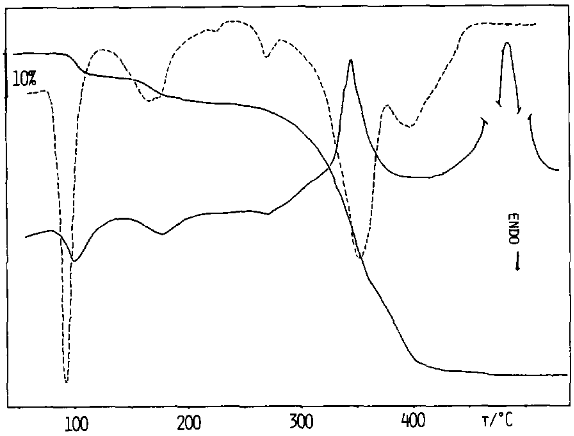

Fig. 2. Thermal analysis of $(onH_2)[Ni_2Cl_6(H_2O)_4]$. The TG weight losses in air are represented by a solid line (———), the DTA curve in air by a solid line and the DTA curve in argon by a dashed line (— — —).

that it may be present as a dimer or polymer. It is possible to propose a dimer structure for the anion complex of compound **I**, i.e. $[Ni_2Cl_6(H_2O)_4]^{4-}$. This anion consists of two octahedra joined at an edge by two chlorine bridges whose axial positions are occupied by water molecules; this has been described for the analogous chlorometallates [12,13].

The reflectance spectrum of compound **II** is analogous to other trichloronickelate spectra previously described [4,5] that contain the polymeric anion $[NiCl_3]_n^{n-}$ in which $NiCl_6$ octahedra share opposite faces.

Thermal analysis

Figure 2 shows the TG and DTA curves of compound **I** and Table 3 contains its thermal data. The TG curve of compound **I** recorded in air

TABLE 3

Thermal analysis of $(onH_2)[Ni_2Cl_6(H_2O)_4]$

DTA (air)	DTA (Ar)	Observations and TG weight loss (% calc./obs.)	E_a (kJ mol^{-1})
93.3 (end)	85.5 (end)	Loss of $2H_2O$ (6.5/6)	257
176 (end)	165.5 (end)	Loss of $2H_2O$ (13.1/12)	127
–	175 (end)		
–	225 (end)		
274 (end)	271 (end)		
241 (exo)	252 (end)	NH_4Cl (sublimation)	
469 (exo)	–	C + NiO (72.8/72)	
–	401 (end)	C + Ni(78.6/74)	

atmosphere shows water loss in two steps. The activation energy, E_a, of the dehydration steps has been calculated for a first-order kinetic process [14]. The final residue of TG in air atmosphere ($\approx 500\,^\circ$C) was identified as NiO. In argon, the residue obtained at $\approx 500\,^\circ$C consists of carbon and metallic nickel. Both final residues were identified by X-ray diffractograms.

In the DTA curves (air and argon), the dehydration process appears as an endothermic effect. The peak at 340–350 °C (air and argon) is produced by the sublimation of NH_4Cl, identified by IR spectroscopy. The DTA curve of onH_2Cl_2 recorded in air shows an exothermic peak at 381°C for the loss of NH_4Cl.

Additional peaks in the DTA curve of onH_2Cl_2 recorded in air appear at 185, 284 and 296 °C, with no weight loss. These peaks show solid state phase transitions in the chain conformation of the diammonium cation, forming a *cis* conformation from the all *trans* C–C hydrocarbon chain. Similar endothermic changes have been observed in other alkanediammonium compounds [15–17]. In our compound **I**, the peaks which appear at 275 °C (air), 255 °C (argon) and 271°C (argon) can be also assigned to the same alkanediammonium conformational changes.

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