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THERMAL BEHAVIOUR OF COMPLEX CATION–COMPLEX ANION TYPE COORDINATION COMPOUNDS.
Part IV *

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ABSTRACT

This paper deals with the synthesis, thermal stability and non-isothermal decomposition kinetics of the coordination compound $[Ni(phen)_3][CuCl_4] \cdot 3.5H_2O$. The irreversible thermochromism of this compound, due to migration in the solid state of ligands between coordination spheres of the two metal ions, is reported. The migration of ligands is proved by means of thermogravimetric and EPR studies as well as by UV–visible and IR spectroscopic techniques.

INTRODUCTION

In previous papers [1–4] we reported the thermochromic behaviour of $[M(AA)_3][M'Cl_4]$-type coordination compounds, where AA = 2,2′-dipyridyl, 1,10-phenanthroline, M = Co, Ni, Cu, and M′ = Zn, Pd.

The irreversible thermochromism was assigned to the migration, in the solid state, of the ligands between the coordination spheres of two metal ions:

$$[M(AA)_3][M'Cl_4](s) \xrightarrow{T_t} [M(AA)_2Cl_2](s) + [M'(AA)Cl_2](s)$$

(T_t is thermochromic temperature **).

Following our research concerning chromotropic phenomena exhibited by complex cation–complex anion type coordination compounds, this paper deals with a new system, namely $[Ni(phen)_3][CuCl_4] \cdot 3.5H_2O$.

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* For Part III in this series, see ref. [4].

** The "T(°C)" values written above the arrow correspond to the maximum rates of the transformation (the values of the temperature depend on the heating rates [5]).

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EXPERIMENTAL

The compound $[Ni(phen)_3][CuCl_4] \cdot 3.5H_2O$ was synthesized by adding a stoichiometric amount of the ligand to a solution of $NiCl_2 \cdot 6H_2O$ in ethanol to give soluble $[Ni(phen)_3]Cl_2$. The target compound was precipitated by treating this solution with an ethanolic solution containing $CuCl_2$ and NH_4Cl (the ammonium chloride was added in order to achieve the formation of $[CuCl_4]^{2-}$ anion). The compound which precipitated from this solution as a yellow–orange microcrystalline powder was filtered off, washed with ethanol and dried in vacuum over P_4O_{10}. The results of elemental chemical analysis are in good agreement with the proposed formula. The synthesis of the related compound, $[Ni(dipy)_3][CuCl_4] \cdot nH_2O$ was unsuccessful: migration of ligands in solution leads to a mixture containing $[Ni(dipy)_2Cl_2]$ and $[Cu(dipy)Cl_2]$.

The thermogravimetric (TG), derivative thermogravimetric (DTG), differential thermal analysis (DTA) and temperature curves were recorded in a static air atmosphere in the range 20–700 °C, at various heating rates between 1.25 K min^{-1} and 20 K min^{-1}, using an MOM Budapest Q-1500D Paulike–Paulik–Erdey type derivatograph. The crystalline state of the powdered compound was determined using a Philips PW 1140 X-ray diffractometer with chromium $K\alpha$ radiation. The electronic spectra were recorded by a diffuse reflectance technique using MgO as the reference material. Infrared spectra were recorded in KBr pellets. The EPR spectra of the compounds were recorded on an ART-5 spectrograph in the X frequency band, with respect to Mn^{2+} as a standard.

RESULTS AND DISCUSSION

According to the derivatogram of the compound $[Ni(phen)_3][CuCl_4] \cdot 3.5H_2O$, after the loss of water molecules in the reaction:

$$[Ni(phen)_3][CuCl_4] \cdot 3.5H_2O(s) \xrightarrow{85\,°C} [Ni(phen)_3][CuCl_4](s) + 3.5H_2O(g) \tag{1}$$

the DTA curve exhibits an exothermic effect, without change of weight, corresponding to the migration of the ligands between the coordination spheres of two metal ions.

The migration of ligands which occurs according to the equation:

$$\underset{\text{yellow–orange}}{[Ni(phen)_3][CuCl_4](s)} \xrightarrow{\sim 250\,°C} \underbrace{[Ni(phen)_2Cl_2](s) + [Cu(phen)Cl_2](s)}_{\text{green}} \tag{2}$$

is accompanied by a change in colour from yellow–orange to green. The electronic spectra of the green mixture $[Ni(phen)_2Cl_2] + [Cu(phen)Cl_2]$,

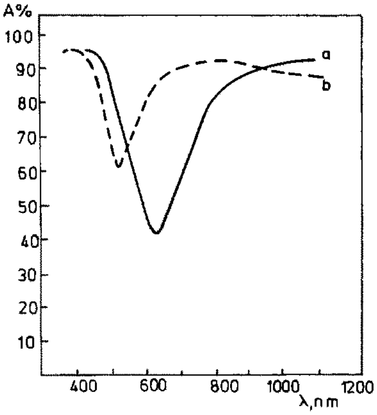

Fig. 1. Diffuse reflectance spectra of (a) $[Ni(phen)_3][CuCl_4]\cdot3.5H_2O$ and (b) $[Ni(phen)_2Cl_2]$ + $[Cu(phen)Cl_2]$.

together with the spectrum of the parent complex $[Ni(phen)_3][CuCl_4]\cdot 3.5H_2O$, are represented in Fig. 1. By treating the green mixture $[Ni(phen)_2Cl_2]$ + $[Cu(phen)Cl_2]$ with ethanol, we separated the two complexes: $[Ni(phen)_2Cl_2]$ which is soluble in ethanol and $[Cu(phen)Cl_2]$ which is sparingly soluble. $[Ni(phen)_2Cl_2]$ complex was crystallized by removing the ethanol. The electronic spectra of these two complexes are given in Fig. 2. It is interesting to note that the yellow–orange colour of the initial complex $[Ni(phen)_3][CuCl_4]\cdot 3.5H_2O$ suggests a pseudotetrahedral configuration of the $[CuCl_4]^{2-}$ anion (the square planar $[CuCl_4]^{2-}$ anion is green). Indeed, Bloomquist et al. [6] proved that such a configuration for $[CuCl_4]^{2-}$ anion, the so-called "hot" form, is obtained by a first order phase

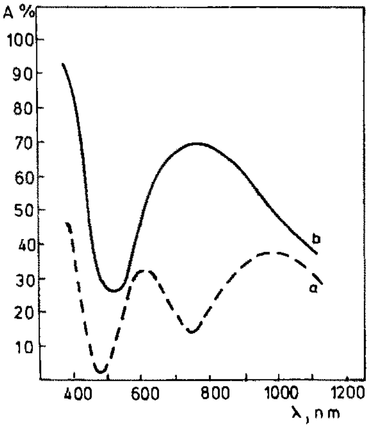

Fig. 2. Diffuse reflectance spectra of (a) $[Ni(phen)_2Cl_2]$ and (b) $[Cu(phen)Cl_2]$. Both complexes were separated from the green mixture which resulted from the migration of ligands.

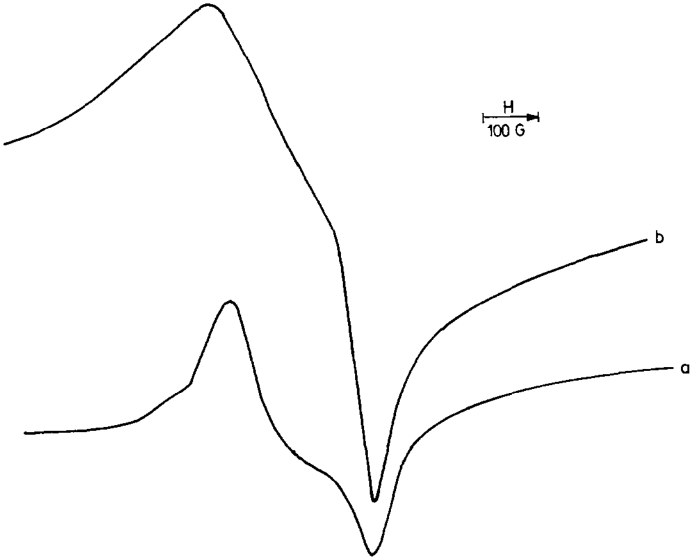

Fig. 3. The EPR spectra of (a) powdered $[Ni(phen)_3][CuCl_4]\cdot 3.5H_2O$; (b) $[Ni(phen)_2Cl_2]+[Cu(phen)Cl_2]$.

transition at 50 °C, exhibited by the green complex compound $(IPA)_2[CuCl_4]$ (IPA = isopropylammonium):

$$\underset{\text{green}}{\underset{D_{4h}}{(IPA)_2[CuCl_4]}} \xrightarrow{50\,^\circ C} \underset{\text{yellow}}{\underset{D_{2d}}{(IPA)_2[CuCl_4]}}$$

Figure 3a represents the EPR spectrum of the complex $[Ni(phen)_3][CuCl_4]\cdot 3.5H_2O$, whose shape is identical to that reported by Bloomquist et al. [7] for $(IPA)_2[CuCl_4]$ (hot form). Consequently, we conclude that in our complex the $[Ni(phen)_3]^{2+}$ cation stabilizes the hot form of $[CuCl_4]^{2-}$ anion at room temperature, with a flattened tetrahedral (D_{2d}) symmetry. The EPR spectrum of the green mixture obtained after migration is shown in Fig. 3b.

Supplementary information regarding the migration of the organic ligand may be obtained from the infrared spectra. The IR spectra recorded within the range 400–4000 cm^{-1} for $[Ni(phen)_3][CuCl_4]\cdot 3.5H_2O$ and $[Ni(phen)_2Cl_2]+[Cu(phen)Cl_2]$ samples exhibit some differences: the triplet centered around 1580 cm^{-1} is slightly modified, going from 1570, 1590 and 1610 cm^{-1} for $[Ni(phen)_3][CuCl_4]\cdot 3.5H_2O$ to 1560, 1595, 1605 cm^{-1} in the spectrum of $[Ni(phen)_2Cl_2]+[Cu(phen)Cl_2]$. At the same time, the relative intensities of these bands are also modified: the most intense peak in the spectrum of the unheated sample is located at 1610 cm^{-1}, whereas in the spectrum of the green sample the most intense peak is located at 1560 cm^{-1}. This triplet near 1590 cm^{-1} is assigned to C–C and C–N stretching vibrations on the heterocyclic ring system [8]. These differences between the

TABLE 1

Interplanar distances, relative intensities and mean crystallite size for $[Ni(phen)_3][CuCl_4]\cdot 3.5H_2O$

d (Å)	10.69	8.83	8.23	6.43	5.31	4.87	4.78	4.24	3.89	3.86	3.71	3.69	3.52	3.42	3.21	2.70	2.63	2.56
Relative intensities	90	4	16	23	100	3	4	3	3	4	7	14	11	4	5	3	11	2
l (Å)					205													

TABLE 2

Interplanar distances, relative intensities and mean crystallite size for the mixture of $[Ni(phen)_2Cl_2]$ and $[Cu(phen)Cl_2]$

d (Å)	8.77	8.25	7.95	7.35	6.66	6.31	5.67	5.46	4.92	4.42	4.03	3.71	3.65	3.25
Relative intensities	38	68	40	15	64	34	16	21	12	21	47	23	27	100
l (Å)														152

IR spectra may be accounted for by the inequivalence of the coordinated phenanthroline molecules in the green mixture. Indeed, as a consequence of different degrees of interaction in phenanthroline–nickel(II) and phenanthroline–copper(II), the C–N stretchings become inequivalent.

The X-ray diffractograms have been recorded for the compound $[Ni(phen)_3][CuCl_4] \cdot 3.5H_2O$, as well as for the mixture $[Ni(phen)_2Cl_2] + [Cu(phen)Cl_2]$. The values of interplanar relative intensities and mean crystallite size obtained by using Scherrer's formula for the most intense line are given in Tables 1 and 2.

As far as the residual product of decomposition is concerned, the X-ray diffractogram showed the presence of CuO and NiO [9]. In order to evaluate the non-isothermal kinetic parameters the Coats–Redfern method [10], Flynn–Wall method for constant heating rate [11], modified Coats–Redfern method [12], and Doyle–Gorbachev method [13,14] have been used. As for the migration of the ligand described by eqn. 2, we tried to determine the activation energy from the shift of the corresponding DTA peak with heating rate using Reich's method [15]. The experimental data have been computed using a program written in BASIC [16]. The same program allowed us to regenerate the TG curves in coordinates α, $T\,°C$ using the experimental values of the kinetic parameters, and to superpose the experimental values of α. The values of the non-isothermal kinetic parameters are given in Table 3.

There is quite good agreement between the values obtained using the different methods described. Taking into account the value of the pre-exponential factor, which differs from that predicted by transition state theory [17], we conclude that the value of the reaction order, close to unity, is only an apparent one. The value $n \approx 1$ shows merely that the reaction 1 is described by the JMAYK equation [18–22] for instantaneous nucleation and uni-dimensional growth of the nuclei [23].

The TG curve regenerated using the Coats–Redfern values for the non-isothermal kinetic parameters (in α, $T\,°C$ coordinates) for $\beta = 3.6$ K min^{-1}, as well as the experimental points in the same coordinates, are given in Fig. 4. The experimental points practically lie on the curve, thus proving the

TABLE 3

Values of the non isothermal kinetic parameters for reaction 1 at $\beta = 3.6$ k.min^{-1} (temperature corresponding to maximum rate = 78 ° C)

Method	n	A (s^{-1})	E (kcal mol^{-1})	r [a]
Coats–Redfern	1.1	2.57×10^3	10.26	−0.99975
Flynn–Wall	1.1	1.72×10^4	11.10	−0.99980
M. Coats–Redfern	1	3.00×10^3	10.30	−0.99973
Doyle–Gorbachev		2.67×10^3		

r [a] = correlation coefficient of the corresponding linear regression.

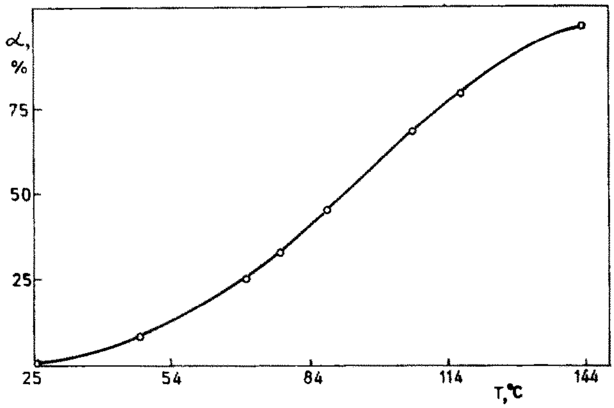

Fig. 4. The regenerated α, T curve for reaction 1 at $\beta = 3.6$ K min^{-1}, using the value of the non-isothermal kinetic parameters obtained by application of the Coats–Redfern method.

correctness of the kinetic description of the experimental data provided by the method applied.

As far as the activation energy for the migration (eqn. 2) is concerned, we obtained the value $E_m = 23.7$ kcal mol^{-1}.

CONCLUSIONS

A novel migration of ligands between two coordination spheres, described by eqn. (2), was demonstrated. The kinetic parameters for the dehydration of the compound $[Ni(phen)_3][CuCl_4] \cdot 3.5H_2O$ were determined. A rough estimate of the activation energy for migration, E_m, was obtained.

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