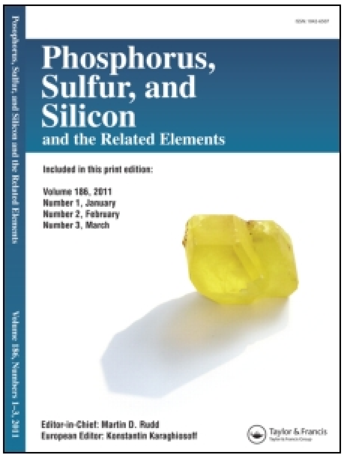

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INTERMEDIATES IN THE THERMAL DECOMPOSITION OF NORMAL COPPER(II), NICKEL(II) AND COBALT(II) SELENITE DIHYDRATES

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Thermal decomposition of normal transition metal selenite dihydrates, $MSeO_3 \cdot 2H_2O$; M = Cu(II), Ni(II), Co(II) was traced by TGA/DTA measurements from 50–700°C. The thermal products were obtained by heating the selenites in an air-oven to different temperatures, as determined from TGA/DTA curves, where different coloured products are obtained. The structures of the start selenites and the thermal intermediates were determined by chemical analyses and FT-IR spectral measurements. The start selenites proved to be equilibrium mixtures of the selenite, hydrogenselenite and/or pyroselenite anions. Gradual changes occurred in the FT-IR spectra of the nickel and cobalt selenites on thermal treatment till 225°C where, due to water loss, merely selenite anions are observed. In the case of the copper selenite, the selenito mixture persists till 250°C and the only change observed in the final product is the disappearance of one of the structurally non-equivalent water molecules present in the start selenite dihydrate.

Key words: Transition metal selenites, thermal analyses, IR of the metal selenites.

INTRODUCTION

The thermal behavior of some transition metal selenites have been previously reported.[1–4] However, the investigation of the solid state reactions have received very little attention.

Mel'nikova *et al.*[1–3] have studied the thermal analyses of $CoSeO_3 \cdot 2H_2O$, $NiSeO_3 \cdot 2H_2O$, $ZnSeO_3 \cdot 2H_2O$, $MnSeO_3 \cdot 2H_2O$ and $CuSeO_3 \cdot 2H_2O$. The inflection on the TGA curve of the former compound in vacuum, at 160°C corresponded to the formation of $CoSeO_3 \cdot \frac{1}{2}H_2O$.[1] However, they did not draw any definite conclusion about the formation of a similar intermediate hydrate in the dehydration of $NiSeO_3 \cdot 2H_2O$.[2] For both $ZnSeO_3 \cdot 2H_2O$ and $MnSeO_3 \cdot 2H_2O$, a monohydrate intermediate[3] was cited.

Khandelwal *et al.*[4] have studied the thermal decomposition of manganese(III) selenite hydrate, $Mn_2(SeO_3)_3 \cdot 4H_2O$, and obtained manganese(III) oxyselenite, $Mn_2O(SeO_3)_2$, at 430°C.

The present investigation studies the chemistry of the thermal dehydration products of copper(II), nickel(II) and cobalt(II) selenite dihydrates by means of thermal analyses (TGA and DTA), chemical analyses and FT-IR spectra.

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EXPERIMENTAL

Materials

Selenium dioxide (Merck) was used without any further purification. Copper(II), nickel(II) and cobalt(II) acetates and acetic acid were reagent grade chemicals.

Spectral Measurements

FT-IR spectra of the solids as KBr discs were recorded on an FT-IR Monson 4000 spectrometer at the Microanalytical Center, Faculty of Science, Ain-Shams University, Cairo, Egypt.

Elemental Analyses

Microanalyses of hydrogen was carried out at the Microanalytical Center, Cairo University, Giza, Egypt. Analyses of the metals followed dissolution of the solid in concentrated hydrochloric acid and then dilution with water. The selenite ion was reduced with sodium sulphite and the precipitated selenium was removed by filtration. Metal cations in the filtrate were titrated with EDTA. Selenium(IV) was estimated by reducing the selenite ion with potassium iodide and titrating the liberated iodine with standard thiosulphate solution. In the case of copper(II) selenite, selenium was estimated after the removal of the precipitated Cu_2I_2, as the copper(II) cations are also reduced by potassium iodide.

Thermal Analyses

TGA studies were carried out by blending the sample with 1% α-alumina. A TGA/DTA thermal analyzer manufactured by Theta Industries Inc., NY, USA was used provided with an electronic analytical balance model ER-180A manufactured by A&D Company Limited, Texas, USA. Specimen holder was alumina-silica of capacity 0.5 g. The data were collected by a microcomputer model TANDY 2500 via data acquisition system manufactured by Theta Industries Inc., NY, USA. TGA/DTA rate, from 25–150°C, was 10 degrees/min, and from 150–700°C, was 5 degrees/min.

Preparation of Cu(II), Ni(II) and Co(II) Selenite Dihydrates

Normal selenites of transition metal cations were previously prepared in our laboratory.[5] The following preparation exemplifies the method followed in their preparations: a solution of selenium dioxide 2.22 g (20 mmol) in 100 ml 50% acetic acid was added gradually to a hot solution of the metal acetate (10 mmol) in 100 ml glacial acetic acid, the latter solution was continuously stirred. The resulting normal selenite precipitate was filtered, washed with 50% acetic acid, methanol, ether then air dried.

Preparation of the Intermediate Thermal Products

The intermediate thermal products were obtained by heating the metal selenite dihydrates in an air-oven to the appropriate temperatures as determined from TGA/DTA curves, Figures 1–3.

RESULTS AND DISCUSSION

Transition metal selenites, $MSeO_3 \cdot 2H_2O$; M = Cu(II), Ni(II) or Co(II), are insoluble in all common solvents. These compounds exist as polymers due to strong hydrogen bonding between water molecules and the selenite ions.

Heating the selenites in an air-oven showed dramatic changes in their colours due to solid state chemical changes.

TGA/DTA studies of the selenites were carried out from 50 to 700°C. The thermograms (Figures 1–3) show complete decomposition at 680°C. TGA curves showed a series of weight loss stages. DTA curves showed that these stages are usually accompanied by endothermic peaks except that occurring at 446, 564 and 439°C in the case of copper(II), nickel(II) and cobalt(II) selenites, respectively. The results of the thermal analyses together with the interpretations of the weight loss due to the loss of water molecules and/or decomposition of the selenite anions, are based on

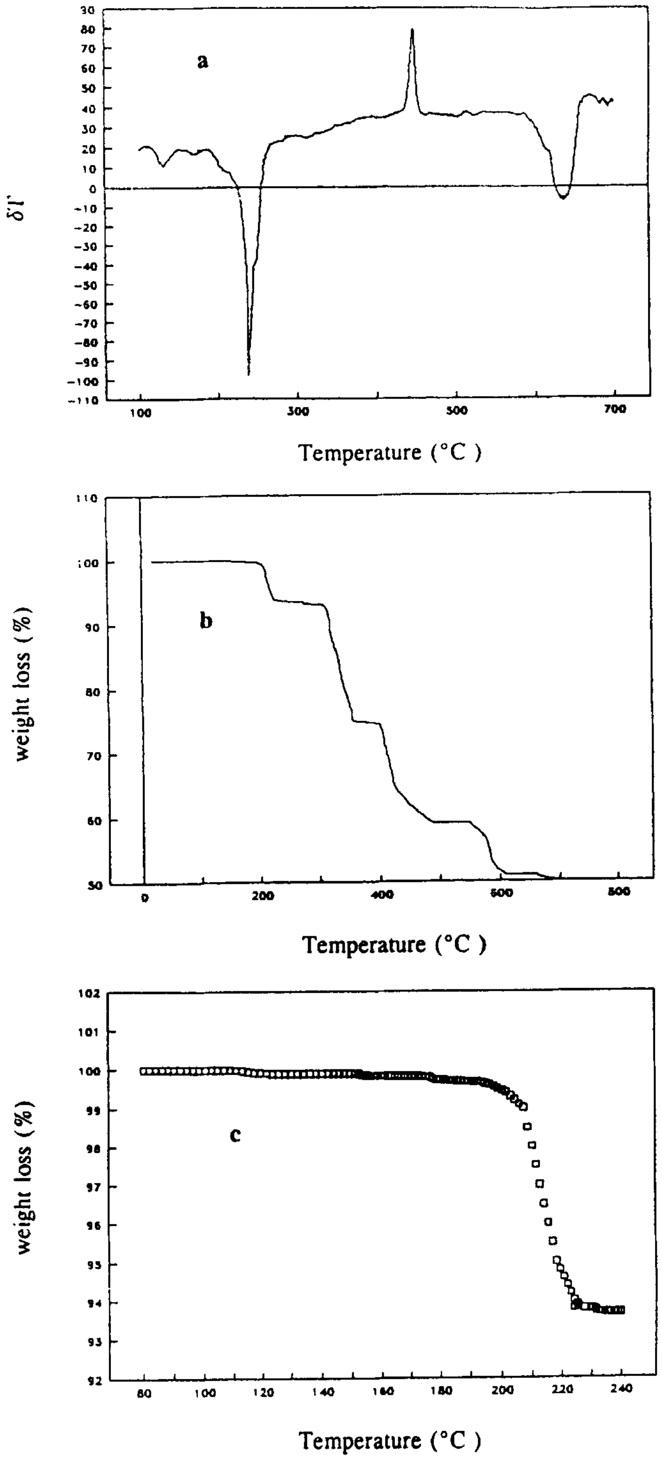

FIGURE 1 (a) DTA, (b) TGA curves of $CuSeO_3 \cdot 2H_2O$ at atmospheric pressure and (c) expansion of (b) in the region 80–240°C.

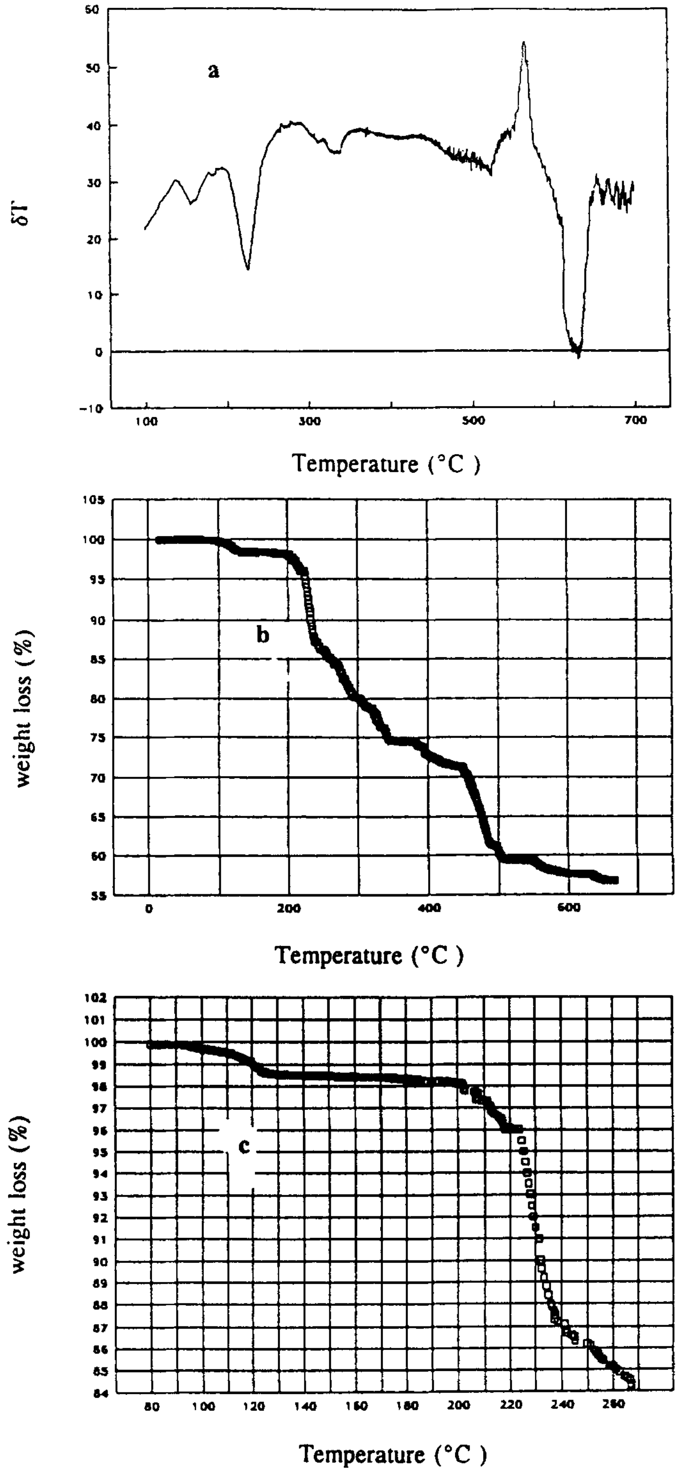

FIGURE 2 (a) DTA, (b) TGA curves of $NiSeO_3 \cdot 2H_2O$ at atmospheric pressure and (c) expansion of (b) in the region 80–260°C.

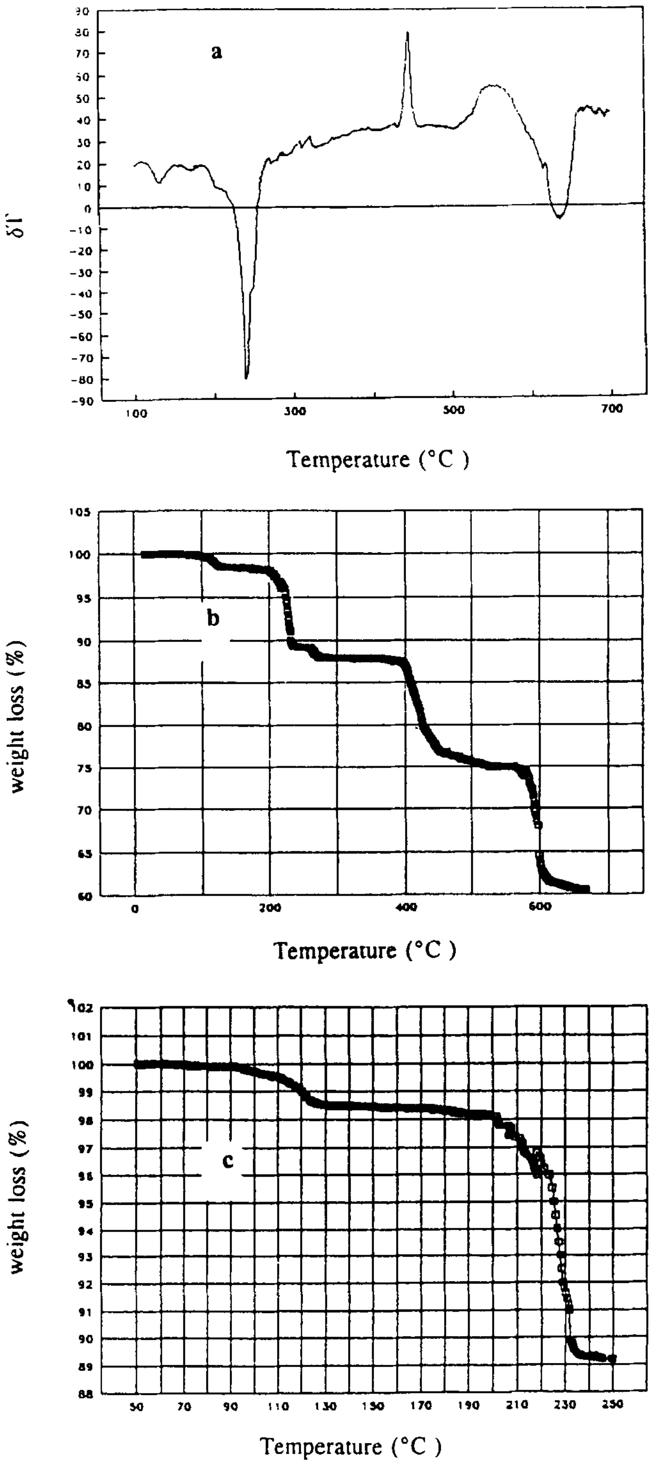

FIGURE 3 (a) DTA, (b) TGA curves of $CoSeO_3 \cdot 2H_2O$ at atmospheric pressure and (c) expansion of (b) in the region 50–250°C.

TABLE I

Thermoanalytical results of the metal selenite dihydrates

Dehydration/decomposition transition	Temp. (°C)		Wt. loss (%)	
	TGA	DTA	Calc.	Found
$\{[(CuSeO_3)_2(OH_2)_4] \rightleftharpoons [CuO.Cu(HSeO_3)_2(OH_2)_3] \rightleftharpoons [CuO.CuSe_2O_5(OH_2)_4]\}$ (I)				
(I) $\rightleftharpoons$ (II)*		132 (endo)	0.0	0.0
(II) $\xrightarrow{-1\frac{1}{2}H_2O}$ $\{[(CuSeO_3)_2(OH_2)_{2\frac{1}{2}}] \rightleftharpoons [CuO.Cu(HSeO_3)_2(OH_2)_{1\frac{1}{2}}] \rightleftharpoons [CuO.CuSe_2O_5(OH_2)_{2\frac{1}{2}}]\}$ (III)	150-221	173 (endo)	6.0	6.2
(III) $\xrightarrow{-1\frac{1}{2}H_2O}$ $\{[(CuSeO_3)_2(OH_2)] \rightleftharpoons [CuO.Cu(HSeO_3)_2] \rightleftharpoons [CuO.CuSe_2O_5(OH_2)]\}$ (IV)	221-319	238 (endo)	11.9	11.8
(IV) $\xrightarrow[-\frac{1}{2}SeO_2]{-1\frac{1}{2}H_2O}$ $[\frac{1}{2}CuO.1\frac{1}{2}CuSeO_3]$ (V)	319-400			25.8
	400-407		28.2	28.9
	407-421			34.8
(V) $\xrightarrow{-\frac{1}{2}SeO_2}$ $[CuO.CuSeO_3]$ (VI)	421-481	446 (exo)	40.4	41.3
	550-583			45.3
	583-607			49.1
	657-681	623 (endo)		50.0

$\{[(NiSeO_3)_2(OH_2)_4] \rightleftharpoons [NiO.Ni(HSeO_3)_2(OH_2)_3] \rightleftharpoons [NiO.NiSe_2O_5(OH_2)_4]\}$ (I)				
(I) $\xrightarrow{-\frac{1}{3}H_2O}$ $\{[(NiSeO_3)_2(OH_2)_{3\frac{2}{3}}] \rightleftharpoons [NiO.Ni(HSeO_3)_2(OH_2)_{2\frac{2}{3}}] \rightleftharpoons [NiO.NiSe_2O_5(OH_2)_{3\frac{2}{3}}]\}$ (II)	86-125		1.4	1.3
(II) $\xrightarrow{-\frac{2}{3}H_2O}$ $\{[(NiSeO_3)_2(OH_2)_3] \rightleftharpoons [NiO.Ni(HSeO_3)_2(OH_2)_2]\}$ (III)	182-221	182 (endo)	4.1	4.0
(III) $\xrightarrow{-2H_2O}$ $[(NiSeO_3)_2(OH_2)]$ (IV)	221-237	229 (endo)	12.2	12.9
	237-337	307, 336 (endo)		25.2
(IV) $\xrightarrow[-\frac{1}{2}SeO_2]{-H_2O}$ $[\frac{1}{2}NiO.1\frac{1}{2}NiSeO_3]$ (V)	337-445		28.7	28.6
	445-484			38.6
	484-504		41.2	41.6
		525 (endo)		
	545-590	564 (exo)		42.7
	629-645	630 (exo)		43.4

TABLE I (*Continued*)

Dehydration/decomposition transition	Temp. (°C)		Wt. loss (%)	
	TGA	DTA	Calc.	Found
$\{[(CoSeO_3)_2(OH_2)_4] \rightleftharpoons [CoO.CoSe_2O_5(OH_2)_4]\}$ (I)				
(I) $\xrightarrow{-\frac{1}{2}H_2O} \{[(CoSeO_3)_2(OH_2)_{3\frac{1}{2}}] \rightleftharpoons [CoOCoSe_2O_5(OH_2)_{3\frac{1}{2}}]\}$ (II)	71-192	131 (endo)	2.0	1.9
(II) $\xrightarrow{-\frac{1}{2}H_2O} \{[CoSeO_3)_2(OH_2)_3] \rightleftharpoons [CoOCoSe_2O_5(OH_2)_3]\}$ (III)	192-218	218 (endo)	4.1	3.8
(III) $\xrightarrow{-1\frac{3}{4}H_2O} [CoSeO_3)_2(OH_2)_{1\frac{1}{4}}]$ (IV)	218-237	237 (endo)	11.1	10.8
(IV) $\xrightarrow{-\frac{1}{4}H_2O} [CoSeO_3)_2(OH_2)]$ (V)	237-265 385-452	247 (endo) 439 (exo)	12.2	11.9 23.0
(V) $\xrightarrow[-\frac{1}{3}SeO_2]{-H_2O} [\frac{1}{3}CoO.1\frac{2}{3}CoSeO_3]$ (VI)	452-517		24.5	25.0
(VI) $\xrightarrow{-\frac{2}{3}SeO_2} [CoO.CoSeO_3]$ (VII)	571-608 608-671	632 (endo)	41.2	39.5

* Phase transition without weight loss.

TABLE II

Analytical data of the products obtained on heating metal selenite dihydrates to specified temperatures

Compd.	Temp. (°C)	Colour	Chemical analyses of the products (Found/(Calcd.))		
			%M	%Se	%H
			$CuSeO_3.2H_2O$		
Start (I)		Light blue	27.8 (28.1)	35.5 (34.9)	2.7 (1.8)
(II)*	132	Blue	28.4 (28.1)	34.8 (34.9)	----
(III)	218	Greenish blue	29.9 (29.8)	36.9 (37.1)	----
(IV)	250	Green	32.2 (31.8)	40.1 (39.6)	0.8 (0.5)
			$NiSeO_3.2H_2O$		
Start (I)		Light green	26.4 (26.5)	34.7 (35.6)	2.9 (1.8)
(II)	131	Green	26.4 (26.9)	36.8 (36.1)	----
(III)	218	Cumin	27.2 (27.2)	37.1 (37.1)	----
(IV)	225	Brown	30.8 (30.3)	41.1 (40.5)	1.0 (0.5)
			$CoSeO_3.2H_2O$		
Start (I)		Rose	26.5 (26.6)	36.1 (35.6)	2.5 (1.8)
(II)	131	Pink	27.7 (27.1)	35.7 (36.3)	----
(III)	218	Magenta	28.3 (27.7)	36.5 (37.1)	----
(IV)	225	Violet	30.2 (29.9)	41.0 (40.1)	1.1 (0.6)

* Compound (II) retained the same structure as start compound (I) at this temperature.

the chemical analyses and FT-IR data of the start selenites and their thermal products. These results are listed in Table I.

The thermal intermediates were obtained by heating the start selenites to the appropriate temperatures as determined from the TGA/DTA curves. These temperatures together with the chemical analyses of the start selenites and their thermal products are listed in Table II. Table III lists their characteristic IR frequencies.

The IR spectra of the start selenite dihydrates, Table III, Figures 4(I)–6(I), show many absorption bands for both the stretching and bending vibrations of the O—H and Se—O bonds. The broad bands at 2911–3505 and 1449–1667 cm^{-1} are attributed to the stretching and bending vibrations of the coordinated water molecules.

TABLE III

FT-IR frequencies of the metal selenite dihydrates and their thermal intermediates (cm^{-1})[a]

Compd.[b]	νO-H (H_2O)	νOH ($HSeO_3$)	δO-H (H_2O)	δO-H ($HSeO_3$)	νSe-O-Se (Se_2O_5)	νSe-O (SeO_3 + $HSeO_3$ + Se_2O_5)[c]	νSe-OH ($HSeO_3$)	δSe-O-Se (Se_2O_5)	δSe-O (SeO_3 + $HSeO_3$ + Se_2O_5)[c]
(I) Cu	3505 vs, 3375 s, b, 3189 s, b, 2915 vs, b	2402 m	1652 m, 1607 m, 1559 m, 1449 m, b	1218 w	940 m, 911 m, sh	839 m, sh, 812 s, sh, 778 vs, b, 716vs, b	643 s	570 s	536 s, sh, 462 m
(IV) Cu	3505 vs, 3189 s, b, 2911 s, b	2402 m	1667 m, b, 1561 m, b	1218 w	940 m	842 s, sh, 774 vs, b 716 vs, b	643 s	569 s	539 s, 458 m
(I) Ni	3420 vs, 3330 s, b, 3180 s, b, 3110 s, b, 3010 s, b, 2940 s, b	2430 s, b	1654 m, b, 1546 m, b	1256 w, 1137 w-m		850 s, sh, 820 s, 808 vs, 723 vs, 711 s, sh	635 s	565 s	504 s, 465 m
(III) Ni	3455 s, 3397 s, b, 3216 s, b, 2930 s, b		1638 w, b, 1526 w, b	1241 vw		857 s, sh, 839 s, sh, 709 vs, b, 670 vs, b	643 vs, sh		508 s, b, 473 s, sh
(IV) Ni	3397 m, b, 3312 m, b 2980 m, b		1654 m, b, 1561 m, b			848 m, sh, 714 vs, sh, 670 vs, b			520 m, b, 489 m, b
(I) Co	3439 s, b, 3223 s, b, 2961 s, b		1623 m, b, 1522 m, b		911 m, sh	824 s, 800 s, 708 vs		585 m	496 s
(IV) Co	3439 m, b, 3235 m, 3135 m, b, 2969 m, b		1626 w, b, 1522 w, b			804 s, b, 720 vs, b			504 s, 472 m, sh 444 m

(a) s = strong, m = medium, w = weak, v = very, sh = shoulder.

(b) See Tables (1) & (2) for characterization of the compounds.

(c) The stretching and bending vibrations are those of the terminal SeO_2 groups of the $Se_2O_5^{2-}$.

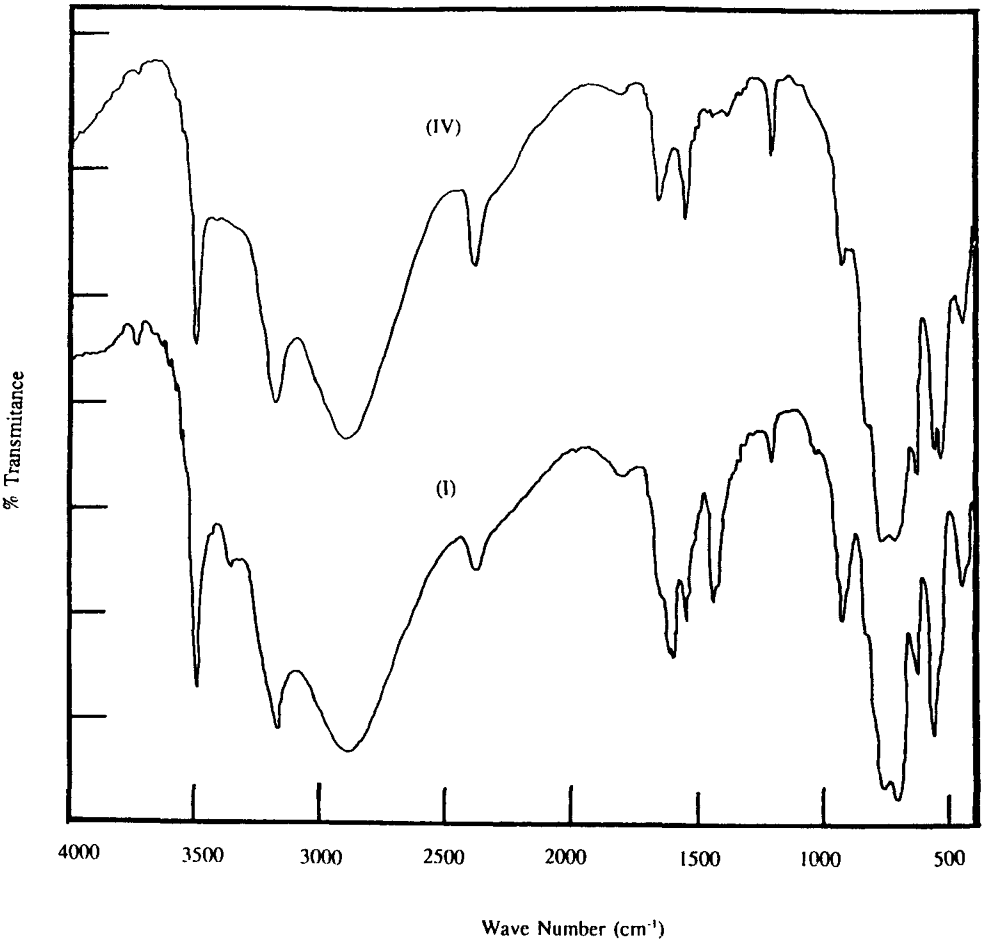

FIGURE 4 Infrared spectra of the start $CuSeO_3 \cdot 2H_2O$ (I) and its thermal product heated at 250°C (IV).

Splitting of the stretching absorption bands to three or more and the bending bands to either two or four are observed. The presence of the lower stretching and bending bands indicate H-bonding between water molecules and the oxygen atoms of the selenite anions. In the case of copper(II) selenite dihydrate, four bending vibrations of the water molecules are observed at 1652, 1607, 1559, and 1449 cm^{-1}. The first two bands indicate the presence of two structurally non-equivalent types of water molecules and the latter (c.f. Figure 4(I)) two bands are due to their H-bonded counterparts. This observation was previously cited for $ZnSeO_3 \cdot 2H_2O$ and $CoSeO_3 \cdot 2H_2O$ where the splitting of the stretching bands of water molecules was interpreted as due to the presence of two structurally different water molecules in the lattice.[1]

The splitting of the Se—O bands was previously interpreted as due to the lowering of the symmetry of the SeO_3^{2-} anions from C_{3v} in its ionic form to C_S when coordinated to transition metal cations.[5] FT-IR spectra of the selenites, in this work, produced better splitting of the bands. Thus, besides the aforementioned splitting of the selenite anion bands due to lowering of the anion symmetry, it was observed that the start selenites show new bands which indicate that the start selenites are in

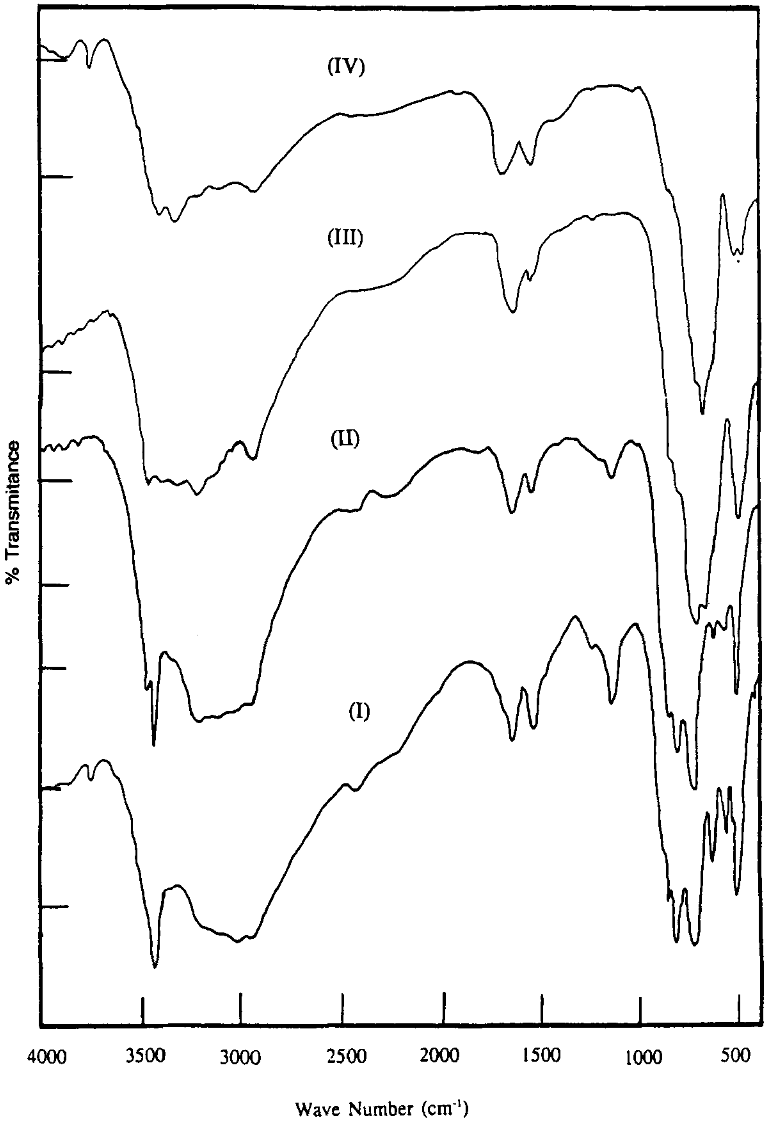

FIGURE 5 Infrared spectra of the start $NiSeO_3 \cdot 2H_2O$ (I) and its thermal products: (II), (III), (IV) heated at 131, 218, 225°C, respectively.

equilibrium with the hydrogenselenites and/or pyroselenites. The following equations illustrate the different equilibria present in the case of both copper(II) and nickel(II) selenite dihydrates.

$$\begin{array}{lcc} 2MSeO_3 \cdot 2H_2O \rightleftharpoons & M(HSeO_3)_2 \cdot 2H_2O & + \; M(OH)_2 \\ (M = Cu(II) \text{ or } Ni(II)) & \Updownarrow & \Updownarrow \\ & MSe_2O_5 \cdot 3H_2O & MO + H_2O \end{array}$$

The stretching vibration of the Se—OH bond of the hydrogenselenite anions appears at ~640 cm^{-1}, reported values are 608 cm^{-1} for $NaHSeO_3$[6]; 624 cm^{-1} for

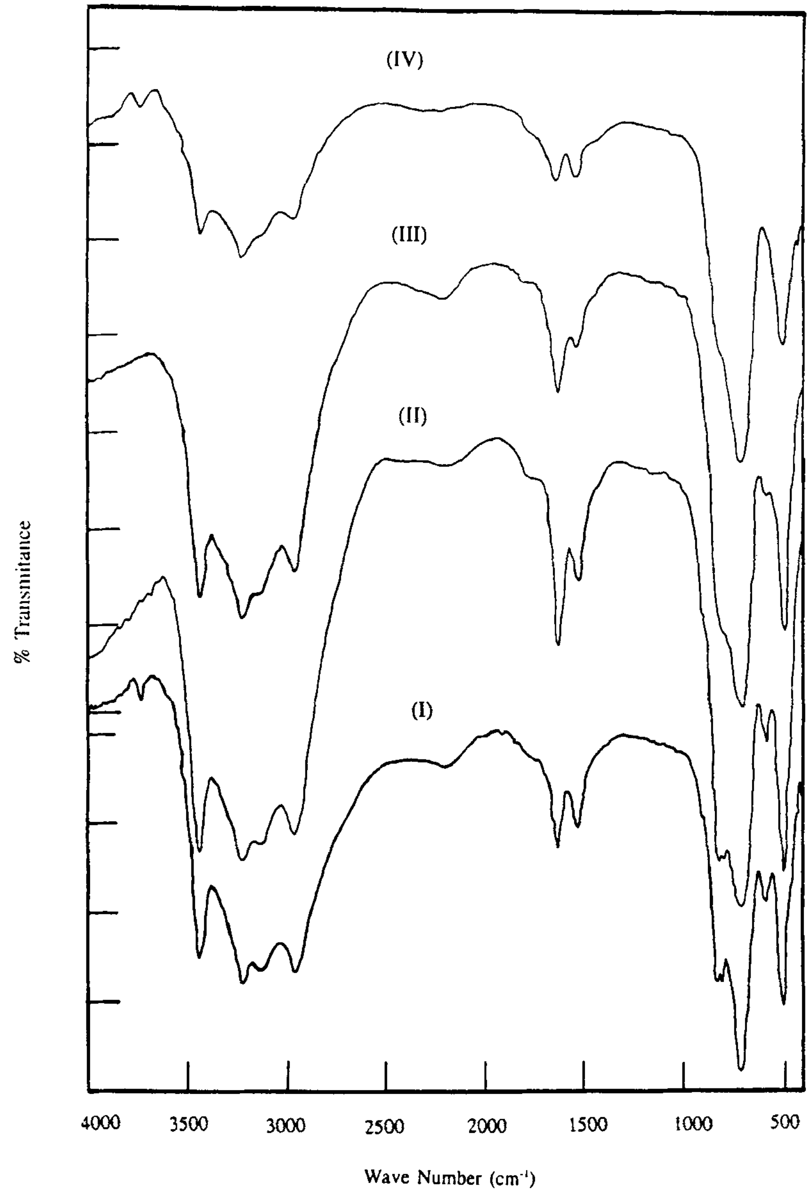

FIGURE 6 Infrared spectra of the start $CoSeO_3 \cdot 2H_2O$ (I) and its thermal products: (II), (III), (IV) heated at 131, 218, 225°C, respectively.

$LiHSeO_3$[7]; 625 cm^{-1} for $[Ni(HSeO_3)(SeO_3)_{1/2}(OH_2)_{3/2}]$[8]; and 640 cm^{-1} for $[Cu(HSeO_3)(Se_2O_5)(OH_2)_{1/2}]$.[8] The stretching vibrations of the coordinated SeO_2 group of the $HSeO_3^-$ anion together with those due to SeO_3^{2-} and $Se_2O_5^{2-}$- anions (the $Se_2O_5^{2-}$ anions consist of two terminal SeO_2 groups and a bridging SeOSe group) appear in the range 670–850 cm^{-1}, reported values are 825–835 cm^{-1} for $NaHSeO_3$[6]; 837, 805 and 670 cm^{-1} for $LiHSeO_3$[7]; 770–880 cm^{-1} for $[Cu(HSeO_3)(Se_2O_5)_{1/2}(OH_2)_{1/2}]$[8];

and 735–870 cm^{-1} for [Ni($HSeO_3$)(SeO_3)$_{1/2}$(OH_2)$_{3/2}$].[8] Characteristic stretching and bending bands of the OH group of the $HSeO_3^-$ anion appear at 2400–2430 and 1137–1256 cm^{-1}, respectively. These bands appear at quite low frequencies due to strong hydrogen bonding between the $HSeO_3^-$ anions and the water molecules. Similar bands were cited for copper(II) complexes containing $HSeO_3^-$ anions.[8] The bending vibrations of the Se—O bonds in the $HSeO_3^-$ anions together with those of the SeO_3^{2-} and $Se_2O_5^{2-}$ anions occur at 444–489 and 496–539 cm^{-1}, reported values are 450–495 cm^{-1}.[8] The stretching and bending vibrations of the bridging SeOSe group of the $Se_2O_5^{2-}$ anion occur at 911–940 and 565–585 cm^{-1}, respectively. Reported values are 760–870[8] and 930 cm^{-1}[19] for the stretching vibrations, also 510–595[8] and 535 cm^{-1}[19] for the bending vibrations.

The IR spectrum of the start cobalt(II) selenite dihydrate did not show the band characteristic of the $HSeO_3^-$ anions, but showed bands which indicate that it is an equilibrium mixture of the selenite and pyroselenite anions

$$2CoSeO_3 \cdot 2H_2O \rightleftharpoons [CoOCoSe_2O_5(OH_2)_4]$$

The IR spectra of the start complexes, however, did not show the band characteristic of the bending vibration of the O—H bond in the metal hydroxides which would be produced by the dissociation of water to hydrogen ions, which transfer to the selenite ions producing the $HSeO_3^-$ ions and consequently the $Se_2O_5^{2-}$ ions, and the hydroxide ions forming the metal hydroxides and consequently the metal oxides. This band due to the metal hydroxides is expected to occur at ~1389 cm^{-1} as previously reported in the case of basic selenites of transition metals.[10] Thus, the metal hydroxides are expected to transfer instantly to the metal oxides. The start selenites thus seems to have a complex structure of their oxides together with the selenite, hydrogenselenite and/or pyroselenite ions.

The behaviour of transition metal selenites, studied in this work differs on thermal treatment. The IR spectra of the thermal products obtained on heating the copper(II) selenite dihydrate did not change till 250°C and showed the presence of bending vibrations of only one type of water molecules compared to the start compound which showed two different types of coordinated water molecules. Thus, the equilibria between different types of the selenito species still persist in the thermal products of $CuSeO_3 \cdot 2H_2O$, Figure 4 and Table III.

On the other hand, the IR spectra of the thermal products of both $NiSeO_3 \cdot 2H_2O$ and $CoSeO_3 \cdot 2H_2O$ showed gradual changes, Figures 5, 6 and Table III, which indicate the disappearance of both the $HSeO_3^-$ and $Se_2O_5^{2-}$ anions in the case of the nickel salt and the latter anions in the case of the cobalt salt. The products obtained at 225°C for both salts show simple IR pattern of the Se—O bonds characteristic of the SeO_3^{2-} anions which would be present in an ionic form. Three stretching bands appear for the final thermal product of the nickel salt at 848, 714 and 670 cm^{-1}, the former two bands appear as shoulders for the latter one. Two stretching bands appear for the final thermal product of the cobalt salt at 804 and 720 cm^{-1}. Two bending bands appear at 520, 489 and at 504, 444 cm^{-1} for both products, respectively. These vibrations are similar to the vibrations cited for ionic Na_2SeO_3 salt, where the stretching vibrations occur at 790 and 742 cm^{-1} and the bending vibrations at 460 and 400 cm^{-1}.[10]

The thermal analyses indicate that there are equilibria between the metal selenites, hydrogenselenites and/or pyroselenites. In the case of $CuSeO_3 \cdot 2H_2O$, these equilibria remained till 238°C. However, in the case of $NiSeO_3 \cdot 2H_2O$, these equilibria persist till 125°C, afterwards, the IR data indicated the disappearance of the pyroselenite anions and only an equilibrium between the selenite and hydrogenselenite anions persist till 182°C. On the other hand, $CoSeO_3 \cdot 2H_2O$ showed an equilibrium between the selenite and pyroselenite anions which persist till 218°C. Also, it was observed in the case of $CuSeO_3 \cdot 2H_2O$ that the start compound (I) undergoes a phase transition at 132°C without any change in its constituents as indicated from its chemical analysis and IR spectrum.

It could be concluded that the structures of the start selenite salts are in equilibrium with the selenite, the hydrogenselenite and/or the pyroselenite anions together with the metal oxide. The coordinated water molecules are highly hydrogen bonded to the selenite anions. Transfer of the water protons to the selenite anions do occur producing other selenito species.

A recent study on the electric conductance of solid transition metal selenites has shown that they have high conductance which decrease with increasing the temperature over the range 28–60°C. This was attributed to the threshold of the transfer of the protons of water molecules to the selenite anions along the line of the hydrogen-bond.[11] However, on increasing the temperature over the range 60–130°C the selenites behave as semiconductors. The increase of temperature may lead to the breakdown of the mother-crystal where it splits into microblocks, separated by cracks or localized zones. The movement of the protons, in the latter case, may be due to the localized or jump mechanism.

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