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A Study of Bis(iminodiacetate)nickelates

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Introduction

Nickel(II) iminodiacetate, Niida$\cdot$2H_2O, and sodium bis(iminodiacetate)nickelate, $Na_2[Ni(ida)_2]\cdot 7H_2O$, were prepared by Laitinen [1]: their electronic and infrared spectra, magnetic properties and thermal stability have been studied. The structures of the cesium and lithium salts of bis(iminodiacetate) nickelic acid, $Cs_2[Ni(ida)_2]\cdot 4H_2O$ and $Li_2[Ni(ida)_2]\cdot 4H_2O$, were determined [2]. The coordination polyhedron has the shape of an irregular octahedron. Both the nitrogen atoms are coordinated in the *trans* position and the substances are not isostructural. The present paper is aimed at the preparation and study of bis(iminodiacetate)-nickelic acid, not yet described in the solid state, and of its potassiim and barium salts, together with the earlier described lithium and sodium salts. The paper is a part of the study of complexes of iminodiacetic acid with the metals from the first row of the transition elements [3,4].

Experimental

Niida$\cdot$2H_2O, $Li_2[Ni(ida)_2]\cdot 4H_2O$ and $Na_2[Ni(ida)_2]\cdot 7H_2O$ were prepared according to Mammano [2] and Laitinen [1] from iminodiacetic acid, nickel(II) carbonate and the appropriate hydroxide. This method has also been applied for the preparation of $K_2[Ni(ida)_2]\cdot 2H_2O$ and $Ba[Ni(ida)_2]\cdot 6H_2O$. $H_2[Ni(ida)_2]\cdot 4H_2O$ was prepared by the conversion of the barium salt with 0.1 *N* H_2SO_4. After filtering off $BaSO_4$ and partial evaporation, the product was precipitated with ethanol.

Nickel was determined complexometrically in the substances prepared after combustion of samples and their dissolution in HCl, nitrogen was determined by distillation as NH_3 after the sample mineralization, alkali metals were determined by atomic absorption and barium as $BaSO_4$. The water content was determined by thermal decomposition, with a temperature

TABLE I. Analytical and Physical Data.[a]

Substance	Results of Analyses				Dehydration		No. of H_2O molecules	IR (cm^{-1})		
	%Ni found (calc.)	%N found (calc.)	%M found (calc.)	%H_2O found (calc.)	beginning °C	end °C		NH	COO^- antis.	COO^- sym.
Niida$\cdot$2H_2O	26.05	6.28	–	16.5	100	250	–2	3285	1570	1410
	(26.00)	(6.20)	–	(16.0)					1600sh	
$Li_2[Ni(ida)_2]\cdot 4H_2O$	14.52	7.04	3.45	17.8	70	130	–4	3235–3280	1625	1415
	(14.43)	(6.88)	(3.41)	(17.7)						
$Na_2[Ni(ida)_2]\cdot 7H_2O$	12.02	6.80	9.35	25.6	30	140	–7	3230	1635	1405
	(11.91)	(5.68)	(9.33)	(25.6)				3300		
$K_2[Ni(ida)_2]\cdot 2H_2O$	13.60	6.45	17.93	8.7	50	85	–1	3240–3260	1625	1405
	(13.49)	(6.43)	(17.97)	(8.3)	100	150	–1			
$Ba[Ni(ida)_2]\cdot 6H_2O$	10.43	5.00	23.9	19.1	30	50	–3	3275–3300	1610	1405
	(10.37)	(4.94)	(24.2)	(19.1)	80	100	–2			
					100		–1			
$Ba[Ni(ida)_2]$	–	–	–	–	–	–		3280	1585	1410
$H_2[Ni(ida)_2]\cdot 4H_2O$	14.76	6.85	–	18.1	50	120	–1	3280	1585	1405
	(14.87)	(7.09)	–	(18.2)	170	210	–3		1710	

[a] ida = $NH(CH_2COO^-)_2$.

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TABLE II. The Diffuse Reflectance Spectra.

Band	ν_3 [nm]		ν_2 [nm]			ν' [nm]		ν_1 [nm]
Assignment	$^3A_{2g} \to {}^3T_{1g}(P)$		$^3A_{2g} \to {}^3T_{1g}(F)$			$^3A_{2g} \to {}^1E_g(D)$		$^3A_{2g} \to {}^3T_{2g}$
$Li_2[Ni(ida)_2]\cdot 4H_2O$	350 sh	370	570	600	640 sh	760 sh		910
$Na_2[Ni(ida)_2]\cdot 7H_2O$	350 sh	370	590		670 sh	760 sh		910
$K_2[Ni(ida)_2]\cdot 2H_2O$		380	585		650 sh	700 sh	760 sh	980
$Ba[Ni(ida)_2]\cdot 6H_2O$	355	380	580		650 sh	780		1015
$Niida\cdot 2H_2O$		380		630		740 sh		1050
$H_2[Ni(ida)_2]\cdot 4H_2O$		390		600sh	640	740 sh		1050
$Ba[Ni(ida)_2]$		390		630		780		1050

increase of 10 °C in 8 hours. The results of analyses and the dehydration temperatures are given in Table I.

The diffuse reflectance spectra of the solid substances were measured on a VSU-2 instrument from Zeiss, Jena, GDR. Magnesium oxide was used as the reference material. The IR spectra were measured on a UR 20 instrument from Zeiss, Jena, GDR, in KBr pellets, nujol and tripene.

Results and Discussion

The prepared salts of bis(iminodiacetate)nickelic acid readily crystallize from aqueous solutions as hydrates and the anhydrous substances can be prepared by dehydrating them. Dehydration of $Ba[Ni(ida)_2]\cdot 6H_2O$ is accompanied by the change in colour from blue to green. $H_2[Ni(ida)_2]\cdot 4H_2O$ had to be precipitated by ethanol: its dehydration is completed only at a temperature of about 200 °C, with ligand decomposition following immediately.

In the study of the IR spectra, our attention was centred on the valence vibrations of the carboxyl group and of N–H, from the point of view of the coordination of the two groups to the central atom (Table I). The absorption band of the antisymmetrical valence vibration of the carboxyl group in the salts of bis(iminodiacetate)nickelic acid is shifted (except for that of $Ba[Ni(ida)_2]$) to a value of 1620–1635 cm^{-1}. These shifts, together with the values of the differences in the wavenumbers of symmetrical and antisymmetrical vibration bands, indicate monodentate coordination of the carboxyl group, in agreement with the determined structure of $Li_2[Ni(ida)_2]\cdot 4H_2O$. The shift of the absorption band of antisymmetrical valence vibration of the carboxyl group to 1570–1585 cm^{-1} in nickel(II) iminodiacetate, bis(iminodiacetate)nickelic acid and its dehydrated barium salt $Ba[Ni(ida)_2]$ suggest possible bidentate coordination of the carboxyl, similar to $Cuida\cdot 2H_2O$ [1, 5, 6]. The absorption band at 1710 cm^{-1} in the spectrum of $H_2[Ni(ida)_2]\cdot 4H_2O$ indicates the presence of an uncoordinated carboxyl group.

The absorption bands of the N–H group valence vibration were always shifted to lower values (on average by 30 cm^{-1}) compared with the wavenumber in the spectrum of K_2ida. This shift corresponds to those in the spectra of the complexes of iminodiacetic acid with manganese and iron [3] and cobalt [4]. In the electronic reflectance spectra, absorption bands were found that correspond to nickel(II) compounds with octahedral surroundings (Table II). The bands for ν_2 and ν_3 transitions were split for the hydrates of lithium, sodium, potassium and barium bis(iminodiacetate)nickelate. A decrease in the symmetry of the coordination surroundings cannot be deduced from this splitting, especially as the bands of the ν_1 transition were not split [6]. The bands of the ν_2 and ν_3 transitions were not split in the spectrum of nickel(II) iminodiacetate. The band of the ν_2 transition was shifted from 540–590 nm in the spectrum of the alkali bis(iminodiacetate)nickelate to 630 nm. This shift is apparently caused by a change in the coordination surroundings of nickel(II) cation from (2N; 4O) to (N; 5O), in agreement with the above mentioned similarity between the structures of $Niida\cdot 2H_2O$ and $Cuida\cdot 2H_2O$ and the results obtained from the IR spectra. The closest coordination surrounding of nickel in $Niida\cdot 2H_2O$ then consists of two water molecules, one nitrogen atom, two oxygen atoms from the two carboxyl groups and one oxygen atom from a carboxyl group of the neighbouring ligand. The electronic spectra of $H_2[Ni(ida)_2]\cdot 4H_2O$ and $Ba[Ni(ida)_2]$ are both virtually identical with that of $Niida\cdot 2H_2O$.

This fact, together with the assumed bidentate coordination of the carboxyl group and release of three molecules of water at a temperature as high as 200 °C, indicate that the structural motif of $H_2[Ni(ida)_2]\cdot 4H_2O$ is similar to that of complexes with the metal-to-ida ratio of 1:1. This similarity between acids and 1:1 complexes was also observed with $H_2[Mn(ida)_2]$ [3] and $H_2[Co(ida)_2]\cdot6H_2O$ [4]. In the dehydration of $Ba[Ni(ida)_2]\cdot6H_2O$, the coordination surrounding of nickel probably also changes into N; 5O) and a polymeric structure is formed through bridge carboxyl.

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