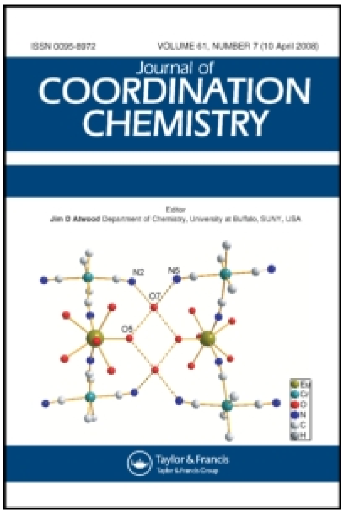

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DIAMINE COORDINATION TO NICKEL(II) IN AN AMORPHOUS ALUMINOSILICATE

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Treatment of an amorphous nickel(II)-substituted aluminosilicate (NiAS) with 1,2-diaminoethane (en), 1,2-diaminopropane (pnd), and 1,3-diaminopropane (tmd) gives materials (NiAS–en, NiAS–pnd and NiAS–tmd) that are characterized by a Ni/diamine ratio of 1:2, 1:1 and 1:1, respectively. The Ni^{2+} coordination environment is octahedral for NiAS–tmd (as it is for NiAS), tetragonally distorted octahedral for NiAS–en, and probably trigonal bypiramidal for NiAS–pnd. The tmd ligand in NiAS–tmd is coordinated as a monodentate.

Keywords: Aluminosilicates, nickel(II), diamines, adducts, properties

INTRODUCTION

In a previous paper[1] we studied the ligand exchange taking place when Ni(II)-substituted zeolite A is treated with some diamine ligands (1,2-diaminoethane, 1,2-diaminopropane and 1,3-diaminopropane). In another work[2] we have described the synthesis of an amorphous Ni(II)-substituted aluminosilicate that is in terms of its chemical composition related to the nickel(II)-substituted zeolite A.

The present work is aimed at obtaining products of the diamine ligand exchange at the amorphous nickel(II)-substituted aluminosilicate and at studying the Ni^{2+} coordination geometry in the materials. The purpose of the work is to gain an insight into the Ni(II) coordination chemistry inside an aluminosilicate environment since the latter may be expected to exert at least a two-fold influence. First, as we have shown earlier,[2] a Ni^{2+} ion can be coordinated by the O atoms of the aluminosilicate lattice so that the latter actually acts as a ligand. Secondly, the size of the aluminosilicate channels and cavities necessarily imposes significant steric requirements regarding possible coordination geometries around Ni^{2+}. As there are no data in the literature on the present system, the investigation will be of interest for any future study of catalytic properties of amorphous Ni^{2+}-aluminosilicates.

EXPERIMENTAL

Instrumentation

Infrared spectra were recorded on a Perkin-Elmer 457 spectrophotometer in the 4000–350 cm^{-1} range, with samples as KBr pellets. Diffuse reflectance spectra were obtained on a Beckman 5240 UV spectrophotometer in the 7500–29000 cm^{-1} region, with MgO as standard. X-ray powder diffraction analysis was conducted on a Siemens Kristalloflex 4 diffractometer using CuK$_\alpha$ radiation.

Electronic Spectra

Reflection data from the diffuse reflectance spectra were converted into $f(R_\infty)$ values using the Kubelka–Munk relationship.[3,4] Each resulting $f(R_\infty)$ curve was analyzed by a nonlinear least-squares technique[5,6] in order to be resolved into Gaussian-type components. The goodness-of-fit obtained was measured by the Hamilton R-factor,[7] values of $R < 2\%$ being accepted as satisfactory.[8]

Reagents

The starting material in the experiments described below was a nickel(II)-substituted aluminosilicate (NiAS), prepared by a previously published procedure.[2] It has the following characteristics. Oxide formula: $1.0NiO \cdot 0.1Na_2O \cdot 1.0Al_2O_3 \cdot 2.6SiO_2 \cdot 10.9H_2O$; IR spectrum ($cm^{-1}$): 3380(vs,b), 3180(sh), 2880(m), 2780(m), 2300(w), 1620(m,b), 1430(w,b), 1370(w), 1070(sh), 1000(vs,b), 850(s,b), 610(s,vb), 420(s,b) (vs = very strong; s = strong; m = medium; w = weak; vb = very broad; b = broad; sh = shoulder); colour light-green; diffuse reflectance spectrum (cm^{-1}): 26320, 15380, 14450, 8772. The curve resolution analysis of the corresponding $f(R_\infty)$ spectrum shows the presence of four Gaussian maxima (Table I). All other reagents were of "pro analysi" purity.

TABLE I
Parameters of the Gaussian maxima for the $f(R_x)$ curves of NiAS, NiAS-en, NiAS-pnd and NiAS-tmd.*

		I	II	III	IV	V	VI	R(%)
NiAS	ν	26250		15550	13660		8810	2.34
	δ	2282		1382	1228		1406	
	ε_0	1		0.569	0.297		0.693	
NiAS-en	ν	28170	18350	15670		10590	8757	1.23
	δ	4640	1570	1584		2113	954	
	ε_0	0.337	0.284	0.388		1	0.144	
NiAS-pnd	ν	27930		15770		10310	8606	1.36
	δ	5618		2228		1863	1329	
	ε_0	0.381		0.556		1	0.517	
NiAS-tmd	ν	26600		15870	14970		9066	1.35
	δ	2346		957	2111		1470	
	ε_0	0.396		0.167	0.391		1	

* $\nu(cm^{-1})$: position of the maximum; $\delta(cm^{-1})$: halfwidth of the maximum at half height; ε_0: relative intensity of the maximum; R(%): goodness-of-fit.

Treatment of NiAS with 1,2-diaminoethane (en)

4 g of finely ground NiAS ($7.8 \cdot 10^{-3}$ mol Ni) were suspended in 50 cm^3 of 1.67 mol dm^{-3} aqueous en (0.08 mol) and the suspension was kept in a closed flask for one day at room temperature with occasional stirring. The suspension was then

filtered, the solid washed with water and dried in air at room temperature to a constant mass. This yielded 3.38 g of a pale blue-violet product (NiAS–en). Elemental analysis (metals were determined by atomic absorption spectroscopy) gave the oxide formula $0.9NiO{\cdot}0.1Na_2O{\cdot}1.0Al_2O_3{\cdot}2.6SiO_2{\cdot}1.75en{\cdot}5.7H_2O$. IR spectrum ($cm^{-1}$): 3300(vs,b), 3290(w), 3240(w), 3120(sh), 2900(w), 2320(w), 2280(w), 1610(s,b), 1420(s), 1130(sh), 1000(vs,b), 850(s,b), 650(w,b), 550(w,b) 430(s,b). The curve resolution analysis of the $f(R_\infty)$ spectrum shows the presence of five Gaussian maxima (Table I).

Treatment of NiAS with 1,2-diaminopropane (pnd)

The procedure adopted was the same as in the en case above, except that 50 cm^3 of 1.35 mol dm^{-3} (0.0675 mol) of aqueous pnd was used. The work-up gave 3.43 g of a pale blue-green material (NiAS–pnd). Elemental analysis led to the oxide formula $0.85NiO{\cdot}0.1Na_2O{\cdot}1.0Al_2O_3{\cdot}2.6SiO_2{\cdot}1.0pnd{\cdot}7.1H_2O$. IR spectrum ($cm^{-1}$): 3360(vs,b), 3240(sh), 2900(w), 2320(w), 2280(w), 1610(w,b), 1430(w), 1130(sh), 1000(vs,b), 850(s,b), 650(s,b), 560(w,b), 430(s,b), 410(w). The curve resolution analysis of the $f(R_\infty)$ spectrum yielded four Gaussian maxima (Table I).

Treatment of NiAS with 1,3-diaminopropane (tmd)

The procedure was analogous to that used for the pnd reaction and resulted in 3.30 g of a blue-green product (NiAS–tmd). Elemental analysis gave the oxide formula $0.9NiO{\cdot}0.1Na_2O{\cdot}1.0Al_2O_3{\cdot}2.6SiO_2{\cdot}0.9tmd{\cdot}7.2H_2O$. IR spectrum ($cm^{-1}$): 3380(vs,b), 2900(w), 2300(w), 1610(w,b), 1520(w,b), 1000(vs,b), 840(w,b), 660(w,b), 580(w,b), 415(s,b). The curve resolution analysis of the $f(R_\infty)$ spectrum gave four Gaussian maxima (Table I).

X-ray Powder Diffraction

The analysis showed that NiAS-en, NiAS–pnd, and NiAS–tmd are all amorphous materials (as is the starting material, NiAS).

RESULTS AND DISCUSSION

A nickel(II)-substituted aluminosilicate has been treated with 1,2-diaminoethane, 1,2-diaminopropane and 1,3-diaminopropane, to yield solids NiAS–en, NiAS–pnd, and NiAS–tmd, respectively (see Experimental). The solids exhibit the following approximate Ni/diamine molar ratios: Ni/en 1:2, Ni/pnd 1:1, and Ni/tmd 1:1. Whereas the $Na_2O:Al_2O_3:SiO_2$ ratio in the products is the same as that in NiAS, the fraction of NiO is lower in the products than in NiAS by some 10% in NiAS–en and NiAS–tmd and by 15% in NiAS–pnd. This means that some Ni^{2+} is lost to solution when NiAS is treated with diamines. A likely explanation for this fact is that a corresponding fraction of the Ni^{2+} content in NiAS itself is present in the form of neutral $Ni(OH)_2$ subunits, whose Ni^{2+} centres attain coordinative saturation by also being bound to aluminosilicate O atoms and H_2O molecules. When NiAS is treated with an excess of diamine, the neutral species are converted into complex hydroxides, *e.g.*, $[Ni(diamine)_2(H_2O)_2](OH)_2$, that are water soluble[9] and therefore leave the aluminosilicate cavities.

As we have previously shown,[2] the electronic spectrum of NiAS (Table I) is consistent with octahedrally coordinated Ni^{2+} ions in an O-donor ligand environment, the ligands being H_2O molecules and aluminosilicate oxygen atoms. Changes in the electronic spectrum occur following the partial replacement of O-donor ligands in NiAS by en, pnd or tmd. The smallest change is observed for the tmd adduct. The spectral pattern for NiAS–tmd (Table I) is essentially the same as that for NiAS, the only difference being that all four maxima in the former are somewhat shifted toward higher energies. This is to be expected since diamines exert a stronger ligand field than O-donor ligands.[10] It follows that an octahedral coordination environment at the Ni^{2+} site is maintained as NiAS is converted into NiAS–tmd. The IR spectrum of NiAS–tmd shows a weak band at 1520 cm^{-1} that is characteristic of the $-NH_3^+$ ion.[11] The ion is formed through an acid–base interaction of H_2O and tmd. Since the Ni/tmd ratio is 1:1 and the electronic spectrum shows the presence of only one kind of Ni^{2+} site,[1] the presence of the $-NH_3^+$ spectral feature necessarily suggests that tmd is coordinated to Ni^{2+} as a monodentate and not chelated as would normally be expected. This is in part probably a consequence of the greater length of the tmd molecule as compared to en and pnd. No $-NH_3^+$ bands are observed in the IR spectra of NiAS–en and NiAS–pnd.

The principal difference between the electronic spectra of NiAS and NiAS–en is the presence of five maxima for the latter. The spectral pattern observed for NiAS–en is frequently found for tetragonally distorted high-spin octahedral Ni^{2+} complexes.[12] For example, electronic spectra similar to that of NiAS–en have been reported for $[Ni(L)_4(H_2O)_2]^{2+}$, $[Ni(s\text{-}Et_2en)_2(H_2O)X]^+$ and $[Ni(s\text{-}Me_2en)_2(NO_3)_2]$ (L = pyridine or imidazole; X = Br or I; s-Et_2en = *sym-N,N'*-diethylethylenediamine; s-Me_2en = *sym-N,N'*-dimethylethylenediamine).[13,14] As the Ni/en ratio in NiAS–en is 1:2, the examples listed appear to be fairly suitable models for NiAS–en (which should accordingly contain $Ni(en)^{2+}$ subunits, the remaining two coordination positions around nickel being occupied by O-donor ligands). Therefore, on the basis of the electronic spectra, a tetragonally distorted octahedral geometry around Ni^{2+} can be proposed for NiAS–en.

Rather more puzzling is the electronic spectrum of NiAS–pnd (Table I). It features four absorption maxima and three of them lie approximately in the same spectral region as do the corresponding maxima for octahedral Ni^{2+} complexes. The fourth maximum (10310 cm^{-1}) is considerably shifted towards lower energy relative to the maximum for the octahedral case. Such a spectrum is quite uncommon for nickel(II) complexes. The only known Ni^{2+} systems exhibiting similar spectral patterns are some high-spin five coordinate complexes, *e.g.* $[Ni(trenMe]NO_3]NO_3$ (trenMe = tris(2-dimethylaminoethyl)amine) which has a trigonal bipyramidal (tbp) ligand environment[15] around Ni^{2+}. As tbp complexes are otherwise fairly numerous in nickel(II) chemistry, this geometry can therefore be tentatively suggested for NiAS-pnd.

A comparison should be made between Ni^{2+} ligand environments in the above three products and in the analogous products of diamine exchange in crystalline nickel(II) zeolite A.[1] The latter materials feature in most cases regular octahedral coordination geometry around Ni^{2+}, the only exception being a square planar site encountered in a tmd-exchanged Ni(II)–zeolite A. The greater variety of geometries found in the present work is probably due to a greater diversification in the size and shape of the aluminosilicate cavities and channels existing in amorphous NiAS as compared to Ni(II)–zeolite A. In the latter material there are some Ni^{2+} sites (those located in sodalite cavities) that do not exchange their O-donor ligands when treated with diamines,[1] since the sodalite cavities cannot accommodate complex species that are bulkier than aqua cations. In the diamine-exchanged NiAS compound no diamine-free Ni^{2+} sites have been found, indicating that Ni^{2+} ions in NiAS are more accessible to ligands entering the aluminosilicate network than are Ni^{2+} ions in Ni(II)-zeolite A.

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