Structural and Spectroscopic Study
of the $(Mg, Ni)_2(OH)(AsO_4)$ Arsenates

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Compounds of general formula $(Mg_{2-x}Ni_x)(OH)(AsO_4)$ ($x = 0$ and 0.45) have been synthesized and characterized. The crystal structures of these compounds have been refined using X-ray powder diffraction data. The structure of the compounds contains two kinds of oxygen polyhedra coordinating to the metal atoms, an octahedron and a trigonal bipyramid. In the magnesium–nickel hydroxyarsenate the Ni(II) ions are preferentially placed in the hexacoordinated polyhedra. Diffuse reflectance study of the magnesium–nickel compound shows bands belonging to the two chromophores of the Ni(II) ions. The ESR spectrum of the $(Mg_{1.55}Ni_{0.45})(OH)(AsO_4)$ phase doped with 1% Co^{2+} exhibits signals of this cation in both octahedron and trigonal bipyramid coordination polyhedra. A comparative study with the homologous cobalt-hydroxyarsenate phases has also been carried out. © 1997 Academic Press

INTRODUCTION

Phosphate and arsenate minerals offer a considerable number of structures which can give rise to original physical properties. The complex structural chemistry of minerals of the formula $ABXO_4$ has been known for many years (1), and several structural types have been elucidated for this general formula. The adamite-type $M_2(O/OH)(XO_4)$ family includes different phases such as $Zn_2(OH)(AsO_4)$ (adamite) (2), $Mn_2(OH)(AsO_4)$ (eveite) (3), $Cu_2(OH)(PO_4)$ (libethenite) (4), $Cu_2(OH)(AsO_4)$ (olivenite) (5), and Al_2OSiO_4 (andalusite) (6). In addition, the $Co_2(OH)(AsO_4)$ phase has been found in solid solution with adamite (7). Synthetic $Co_2(OH)(PO_4)$ and $Zn_2(OH)(PO_4)$ compounds have recently been prepared in the laboratory (8). However, as far as we are aware, only a nickel hydroxyarsenate phase (nickelaustinite mineral) has been described (9).

The crystal structure of the adamite-type $M_2(O/OH)$ (XO_4) family contains a condensed three-dimensional network of vertex and edge-sharing MO_6, MO_5, and XO_4 subunits. In the structure the metal ions can be sited in two different topologies, such as the octahedral and trigonal bipyramidal. In this way, the presence of two different metal ions in these kinds of environments can give rise to interesting physical properties.

Most of the studies in these systems were carried out on mineral samples (10, 11). However, hydrothermal techniques could be used in the preparation of these kinds of compounds giving rise to new phases with interesting structural characteristics and physical properties.

In this work we report the structural characterization and spectroscopic properties of two new members of the adamite-type family, the $Mg_2(OH)(AsO_4)$ and $(Mg_{1.55}Ni_{0.45})$ $(OH)(AsO_4)$ compounds, which have been prepared under hydrothermal conditions. In the case of the magnesium–nickel compound, it is the first synthetic nickel hydroxyarsenate described.

EXPERIMENTAL

Preparation of the Compounds

The $(Mg_{2-x}Ni_x)(OH)(AsO_4)$ ($x = 0$, 0.45) compounds were prepared using hydrothermal conditions and starting from the $(Mg_{3-x}Ni_x)(AsO_4)_2 \cdot 8H_2O$ ($x = 0, 0.5$) precursors, which have recently been described (12). The $(Mg_{3-x}Ni_x)$ $(AsO_4)_2 \cdot 8H_2O$ compounds were heated for a week at approximately 180°C in a Teflon-lined steel autoclave 90% filled. Fine polycrystalline solids were separated by filtration, washed with water and acetone, and dried over P_2O_5 for 12 h. In the solution a slight amount of nickel(II) was detected probably due to the existence of another unknown phase. It has been verified that hydroxyarsenate compounds with a high nickel/magnesium ratio cannot be prepared as pure phases using the above experimental conditions. In this way, it was not possible to obtain the $Ni_2(OH)(AsO_4)$ phase which is not known as a mineral one. Preliminary results indicate that attempts performed at higher pressure and temperatures than the above described give rise to different structural phases.

Magnesium and nickel were determined by ICP-AES analysis. The results were consistent with the following

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stoichiometries: $Mg_2(OH)(AsO_4)$, found, Mg, 23.5; calculated, Mg, 23.8%; $(Mg_{1.55}Ni_{0.45})(OH)(AsO_4)$, found, Mg, 16.9, Ni, 11.7; calculated, Mg, 17.1, Ni, 12.0%). Thermogravimetric study was performed in a Perkin–Elmer TGS-1 thermobalance, in the range from 30 to 900°C. The decomposition curves of the compounds reveal weight losses of 0.5 and 4.5% at approximately 200 and 800°C, respectively. The initial weight loss is associated to surface effects and the second can be attributed to the loss of water obtained from the decomposition of two molecules of compound, as observed by Harrison *et al.* in other hydroxyphosphate compounds (8). The oxides and arsenates of nickel and magnesium were identified as final products.

X-ray Crystallography

X-ray powder diffraction patterns of $(Mg_{2-x}Ni_x)(OH)(AsO_4)$ ($x = 0$ and 0.45), used for the Rietveld analysis, were collected with a STOE diffractometer. Monochromated $CuK\alpha_1$ radiation was employed. The spectra were scanned in steps of 0.02°2θ for 12 s/step. Rietveld full-profile refinement was performed with the FULLPROF program (13), starting from the structural parameters of adamite compound (14). Details of the process are given in Table 1. The observed, calculated and difference X-ray powder diffraction patterns are shown in Fig. 1.

Physical Measurements

IR spectra (KBr pellets) were obtained with a Perkin–Elmer 1430 spectrophotometer. Diffuse reflectance spectra
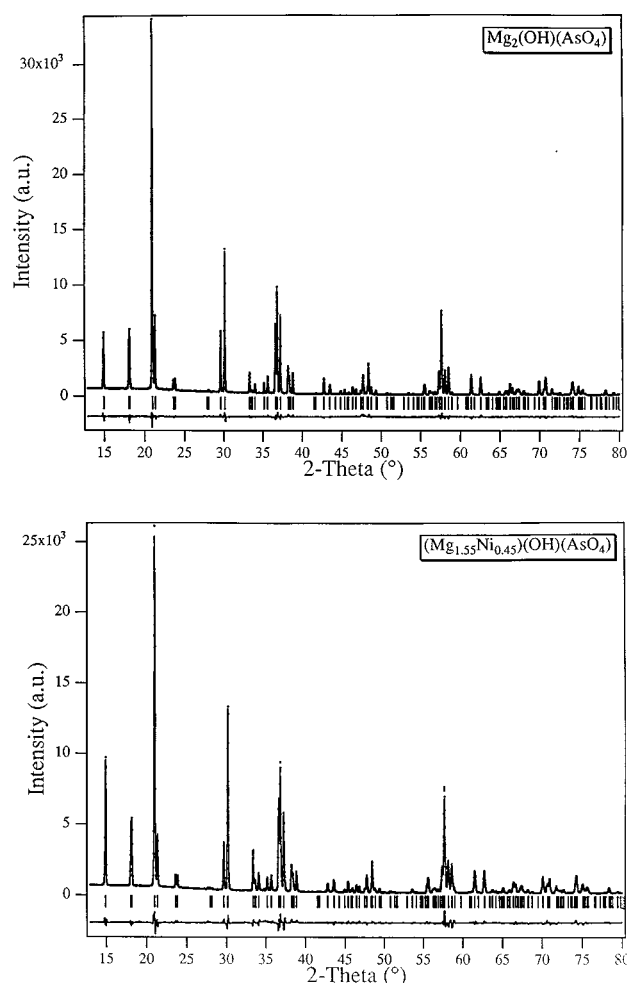

FIG. 1. Observed, calculated, and difference X-ray powder diffraction patterns of the $Mg_2(OH)(AsO_4)$ (I) and $(Mg_{1.55}Ni_{0.45})(OH)(AsO_4)$ (II) compounds, respectively. The observed data are shown by the dots; the calculated pattern is shown by the solid line.

were registered at room temperature on a CARY 2415 spectrometer in the range 5000–45,000 cm^{-1}. A Bruker ESP 300 spectrometer was used to record the ESR spectra at 4.2 K. The temperature was stabilized by an Oxford Instrument (ITC 4) regulator. The magnetic field was measured with a Bruker BNM 200 gaussmeter and the frequency inside the cavity was determined using a Hewlett–Packard 5352B microwave frequency counter.

RESULTS AND DISCUSSION

Structural Study

Atomic coordinates for the $Mg_2(OH)(AsO_4)$ and $(Mg_{1.55}Ni_{0.45})(OH)(AsO_4)$ compounds are given in Table 2. Interatomic distances and angles are presented in Tables 3 and 4.

TABLE 1
Details of Rietveld Full-Profile Refinement for the $Mg_2(OH)$ AsO_4) (I) and $(Mg_{1.55}Ni_{0.45})(OH)(AsO_4)$ (II) Compounds

Compound	(I)	(II)
Space group	*Pnnm*	*Pnnm*
a (Å)	8.3242(1)	8.297(1)
b (Å)	8.456(1)	8.442(1)
c (Å)	6.0349(1)	6.019(1)
V (Å³)	424.8(1)	421.7(1)
Radiation	$CuK\alpha_1$	$CuK\alpha_1$
Monochromator	Ge	Ge
Z	4	4
2θ range (°)	5–80	5–90
2θ Step-scan increment (°)	0.02	0.02
Time-step (s/step)	12	12
No. of reflections	148	196
No. of structural parameters	17	16
No. of profile parameters	11	12
$R_p = \sum|yi_{obs} - (1/c)yi_{calc}|/\sum yi_{obs}$	3.74	5.30
$R_{wp} = [\sum \omega i|yi_{obs} - (1/c)yi_{calc}|^2/\sum \omega i[yi_{obs}]^2]^{1/2}$	5.41	7.47
$R_B = \sum|I_{obs} - I_{calc}|/\sum I_{obs}$	3.85	4.30
GOF	1.90	3.77

TABLE 2
Fractional Atomic Coordinates, Occupancy Factors, and Temperature Factors for $Mg_2(OH)(AsO_4)$ and $(Mg_{1.55}Ni_{0.45})(OH)(AsO_4)$

Atom		P	K	x/a	y/b	z/c	B ($Å$)^2
				$Mg_2(OH)(AsO_4)$ compound			
Mg(1)		$4e$	1	0	0	0.2453(7)	1.06(5)
Mg(2)		$4g$	1	0.1354(4)	0.3667(4)	0	1.06(5)
As		$4g$	1	0.2541(1)	0.2457(1)	0.5	0.54(3)
O(1)		$4g$	1	0.0797(6)	0.1440(6)	0.5	0.20(5)
O(2)H		$4g$	1	0.1076(6)	0.1267(6)	0	0.20(5)
O(3)		$4g$	1	0.3965(5)	0.1052(6)	0.5	0.20(5)
O(4)		$8h$	1	0.2749(4)	0.3623(4)	0.2700(5)	0.20(5)
				$(Mg_{1.55}Ni_{0.45})(OH)(AsO_4)$ compound			
	Mg(1)		0.588(2)				
M(1)		$4e$		0	0	0.2456(7)	0.08(3)(−)
	Ni(1)		0.412(2)				
	Mg(2)		0.964(2)				
M(2)		$4g$		0.1380(5)	0.3647(5)	0	0.08(3)(−)
	Ni(2)		0.036(2)				
As		$4g$	1	0.2542(2)	0.2449(2)	0.5	0.08(3)(−)
O(1)		$4g$	1	0.0791(8)	0.1448(9)	0.5	0.08(3)(−)
O(2)H		$4g$	1	0.1082(8)	0.1253(9)	0	0.08(3)(−)
O(3)		$4g$	1	0.3971(8)	0.1053(9)	0.5	0.08(3)(−)
O(4)		$8h$	1	0.2755(5)	0.3628(6)	0.2715(7)	0.08(3)(−)

Both compounds are isostructural with the adamite mineral (14). The unit cell is illustrated in Fig. 2. Crystal structure of the adamite-type compounds contains two kinds of oxygen polyhedra coordinating to the metal atoms: an octahedron and a trigonal bipyramid. By edge-sharing, the octahedra give rise to linear chains propagated along the c-axis, whereas the trigonal bipyramids constitute dimeric entities. The chain of octahedra, the dimeric unit, and the arsenate anions share corners thereby forming a three-dimensional network.

In the $Mg_2(OH)(AsO_4)$ compound, the Mg(1) atoms occur in elongated octahedra, with two long apical bond distances, Mg(1)–O(4)^i of 2.208(3) $Å$, and four shorter equatorial links, Mg(1)–O(1) of 2.070(4) $Å$ and Mg(1)–O(2)H of 2.035(5) $Å$. The Mg(2) atoms are fivefold coordinated by oxygen atoms in an approximately trigonal bipyramidal geometry. These atoms are placed at 0.082(4) $Å$ out of the equatorial plane formed by the O(3)^{ii} and two O(4) atoms. Another O(3)^{iii} atom and an O(2)H group are placed at slightly greater distances above and below this plane. The equatorial Mg(2)–O(3)^{ii} and Mg(2)–O(4) bond distances are 2.034(6) and 2.001(4) $Å$, respectively, whereas the apical Mg(2)–O(3)^{iii} and Mg(2)–O(2)H bond distances are 2.003(6) and 2.043(6) $Å$, respectively. The distortion of the coordination polyhedra of the metal ions, octahedron and trigonal bipyramid, has been calculated by quantification of the Muetterties and Guggenberger method (15–17). The values obtained for Mg(1)–O_6 octahedra and Mg(2)–O_5 trigonal bipyramid polyhedra are 5.5 and 15.3%, respectively, which

TABLE 3
Bond Distances ($Å$) and Angles ($°$) for the $Mg_2(OH)(AsO_4)$ Compound

Bond distances ($Å$)			
$Mg(1)O_4(OH)_2$ octahedron		$Mg(2)O_4(OH)$ trigonal bipyramid	
Mg(1)–O(1)	2.070(4) ×2	Mg(2)–O(2)H	2.043(6)
Mg(1)–O(2)H	2.035(5) ×2	Mg(2)–O(3)^{ii}	2.034(6)
Mg(1)–O(4)^i	2.208(3) ×2	Mg(2)–O(3)^{iii}	2.003(6)
		Mg(2)–O(4)	2.001(4) ×2

AsO_4 tetrahedron	
As–O(1)	1.687(5)
As–O(3)	1.678(5)
As–O(4)	1.711(3) ×2

Bond angles ($°$)			
$Mg(1)O_4(OH)_2$ octahedron		$Mg(2)O_4(OH)$ trigonal bipyramid	
O(1)–Mg(1)–O(1)^{iv}	84.1(2)	O(2)H–Mg(2)–O(3)^{iii}	90.3(2)
O(1)–Mg(1)–O(2)H	95.1(1) ×2	O(2)H–Mg(2)–O(4)	92.7(2) ×2
O(1)–Mg(1)–O(4)^v	89.6(2) ×2	O(3)^{ii}–Mg(2)–O(3)^{iii}	75.7(2)
O(1)–Mg(1)–O(4)^i	93.9(2) ×2	O(3)^{iii}–Mg(2)–O(4)	125.3(1) ×2
O(2)H–Mg(1)–O(2)H^{vi}	86.6(2)	O(3)^{ii}–Mg(2)–O(4)	95.4(2) ×2
O(2)H–Mg(1)–O(4)^i	82.7(2) ×2	O(4)–Mg(2)–O(4)^{vii}	109.0(2)
O(2)H–Mg(1)–O(4)^v	93.7(2) ×2	O(2)H–Mg(2)–O(3)^{ii}	166.0(3)
O(4)^i–Mg(1)–O(4)^v	175.2(2)		

AsO_4 tetrahedron	
O(1)–As–O(3)	104.3(2)
O(1)–As–O(4)	112.4(1) ×2
O(3)–As–O(4)	109.6(1) ×2
O(4)–As–O(4)^{viii}	108.4(2)

Symmetry code
$i = 1/2 − x, y − 1/2, 1/2 − z$ $ii = 1/2 − x, 1/2 + y, 1/2 − z$ $iii = x − 1/2, 1/2 − y, z − 1/2$
$iv = −x, −y, 1 − z$ $v = x − 1/2, 1/2 − y, 1/2 − z$ $vi = −x, −y, −z$
$vii = x, y, −z$ $viii = x, y, 1 − z$

is indicative of a larger distortion for the trigonal bipyramid environments. The balance of electrostratic charges has been calculated by the Brown (18) method. The results for Mg(1) and Mg(2) cations are 2.00 and 2.02 valence units (v.u.), respectively, being 4.79 v.u. for As(V) ions.

In the $(Mg_{1.55}Ni_{0.45})(OH)(AsO_4)$ compound, the results of the structural refinement show a strong preference of the Ni(II) ions for the hexacoordinated position. The Ni(II) cation occupies approximately 41% of the $M(1)$–O_6 sites, whereas only 4% of the $M(2)$–O_5 polyhedra are occupied by this cation; see Table 2. For this compound, a free refinement of the thermal factor converged to −0.08(3), an unrealistic negative value, although quite close to zero. The bond distances in the $(Mg_{1.55}Ni_{0.45})(OH)(AsO_4)$ compound are similar to those described above for $Mg_2(OH)(AsO_4)$. In the $M(1)$–O_6 octahedron, the long apical distances are $M(1)$–O(4)^i 2.196(5) $Å$, whereas the equatorial distances are $M(1)$–O(1) 2.067(6) and $M(1)$–O(2)H 2.027(6) $Å$. In the $M(2)$–O_5 trigonal bipyramid the equatorial distances are $M(2)$–O(3)^{ii} 2.052(9) and $M(2)$–O(4) 1.993(5) $Å$, the

TABLE 4
Bond Distances (Å) and Angles (°) for the $(Mg_{1.55}Ni_{0.45})(OH)$ (AsO_4) Compound

		Bond distances (Å)		
$M(1)O_4(OH)_2$ octahedron			$M(2)O_4(OH)$ trigonal bipyramid	
$M(1)$–O(1)	2.067(6) $\times 2$		$M(2)$–O(2)H	2.037(9)
$M(1)$–O(2)H	2.027(6) $\times 2$		$M(2)$–O(3)[ii]	2.052(9)
$M(1)$–O(4)[i]	2.196(5) $\times 2$		$M(2)$–O(3)[iii]	2.015(8)
			$M(2)$–O(4)	1.993(5) $\times 2$

AsO_4 tetrahedron	
As–O(1)	1.681(7)
As–O(3)	1.672(7)
As–O(4)	1.707(5) $\times 2$

		Bond angles (°)		
$M(1)O_4(OH)_2$ octahedron			$M(2)O_4(OH)$ trigonal bipyramid	
O(1)–$M(1)$–O(1)[iv]	84.3(2)		O(2)H–$M(2)$–O(3)[iii]	90.2(3)
O(1)–$M(1)$–O(2)H	95.2(2) $\times 2$		O(2)H–$M(2)$–O(4)	93.5(2) $\times 2$
O(1)–$M(1)$–O(4)[v]	89.6(2) $\times 2$		O(3)[ii]–$M(2)$–O(3)[iii]	74.6(3)
O(1)–$M(1)$–O(4)[i]	94.4(2) $\times 2$		O(3)[iii]–$M(2)$–O(4)	124.7(2) $\times 2$
O(2)H–$M(1)$–O(2)H[vi]	86.4(3)		O(3)[ii]–$M(2)$–O(4)	95.1(2) $\times 2$
O(2)H–$M(1)$–O(4)[i]	82.3(3) $\times 2$		O(4)–$M(2)$–O(4)[vii]	110.2(3)
O(2)H–$M(1)$–O(4)[v]	93.8(3) $\times 2$		O(2)H–$M(2)$–O(3)[ii]	164.9(4)
O(4)[i]–$M(1)$–O(4)[v]	174.6(3)			

AsO_4 tetrahedron	
O(1)–As–O(3)	105.0(4)
O(1)–As–O(4)	112.5(2) $\times 2$
O(3)–As–O(4)	109.7(2) $\times 2$
O(4)–As–O(4)[viii]	107.4(2)

Symmetry code

i $= 1/2 - x, y - 1/2, 1/2 - z$ ii $= 1/2 - x, 1/2 + y, 1/2 - z$ iii $= x - 1/2, 1/2 - y, z - 1/2$
iv $= -x, -y, 1 - z$ v $= x - 1/2, 1/2 - y, 1/2 - z$ vi $= -x, -y, -z$
vii $= x, y, -z$ viii $= x, y, 1 - z$

FIG. 2. Crystal structure of the $(Mg, Ni)_2(OH)(AsO_4)$ compounds.

$M(2)$–O(3)[iii] and $M(2)$–O(2)H apical distances being 2.015(8) and 2.037(9) Å, respectively. In this compound, the $M(2)$ cations are placed at 0.064(3) Å out of the equatorial plane. The distortion of the coordination polyhedra for $M(1)$–O_6 octahedron and $M(2)$–O_5 trigonal bipyramid are 5.2 and 15.5%, respectively. These values are similar to those obtained for the magnesium hydroxyarsenate. The balance of electrostatic charges gives the values 1.96 and 1.87 v.u. for $M(1)$ and $M(2)$ cations, respectively, and 4.84 v.u. for As(V) ions.

In both phases the arsenate groups exhibit three different bond lengths and four different bond angles, although they are very similar in both $Mg_2(OH)(AsO_4)$ and $(Mg_{1.55}Ni_{0.45})$ $(OH)(AsO_4)$ compounds. The mean values are 1.69(2) Å and 108(3)°.

Spectroscopic Study

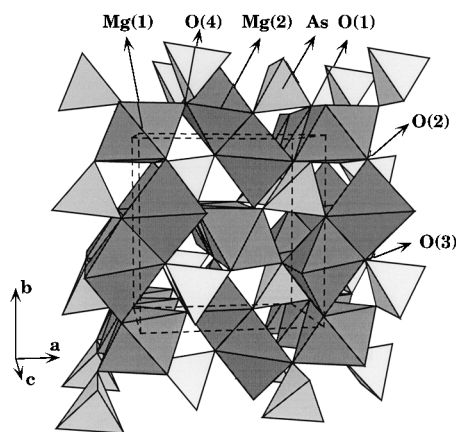IR spectroscopy is a useful technique for the identification of different types of phosphates and arsenates. Good correlations between the essential vibrational features and the structural data can be obtained (19,20). An infrared spectroscopic study of the olivenite, $Cu_2(OH)(AsO_4)$, and adamite, $Zn_2(OH)(AsO_4)$, compounds has been already carried out by Braithwaite (21). The IR spectra of the title compounds show practically the same features. In both compounds there is a band at approximately 3560 cm^{-1} belonging to the stretching mode of the O–H bond. This band appears at a frequency similar to those observed for the adamite (14) and olivenite (21) compounds, 3520 and 3500 cm^{-1}, respectively. The spectra do not show any absorption band near 1620 cm^{-1}, which is indicative of the absence of crystal-hydrate water (21) in good agreement with the structural results. The bands observed in the 900–700 cm^{-1} region for the title compounds are attributed to the stretching vibration modes of the $(AsO_4)^{3-}$ groups. The v_3 asymmetrical stretching mode $[v_{as}(As–O)]$ appears at frequencies 865, 845, and 815 cm^{-1} for $Mg_2(OH)(AsO_4)$ and at 865, 825, and 795 cm^{-1} for $(Mg_{1.55}Ni_{0.45})(OH)(AsO_4)$. The v_1 symmetrical stretch $[v_s(As–O)]$ is detected at frequencies 710 and 720 cm^{-1} for the magnesium and magnesium–nickel phases, respectively. The asymmetrical deformation vibrations $[\delta_{as}(O–As–O)]$ can be observed at 545, 495, and 425 cm^{-1} for the magnesium hydroxyarsenate and at 545, 495, and 415 cm^{-1} for the magnesium–nickel phase. These bands appear at frequencies similar to those observed for the adamite and olivenite phases (14, 21), but at frequencies lower than those observed for the homologous hydroxyphosphates, as corresponds to shorter P–O bond distances in the latter compounds (8, 21, 22). The bands corresponding to the O–H deformation modes, which appear in this region, could be obscured by the vibrations of the $(AsO_4)^{3-}$ groups (21). The absence of bands in the 1300 and 2700 cm^{-1} regions confirms that no acidic As–OH groups are present in the structure (23). Finally, the bands in the lower-frequency region of the spectra, which appear at 375 and

305 cm^{-1} for Mg$_2$(OH)(AsO$_4$) and at 370 and 295 cm^{-1} for (Mg$_{1.55}$Ni$_{0.45}$)(OH)(AsO$_4$), can be attributed to the stretching vibrations of the metal–oxygen bonds, according to observations by Hill (14) in the adamite phase (380 and 320 cm^{-1}).

The absorption bands observed in the diffuse reflectance spectrum of (Mg$_{1.55}$Ni$_{0.45}$)(OH)(AsO$_4$) are shown in Table 5. These bands correspond to the two different chromophores of the Ni(II) ions, with octahedral and trigonal bipyramidal symmetries. For the NiO$_6$ chromophore the three spin allowed transitions $^3A_{2g} \rightarrow {}^3T_{2g}$, $^3T_{1g}(F)$, and $^3T_{1g}(P)$ appear at the following frequencies: $\nu_1 = 8890$, $\nu_2 = 11,560$, and $\nu_3 = 24,690$ cm^{-1}. The spin forbidden transitions $^3A_{2g} \rightarrow {}^1E_g$ and $^1T_{2g}$ were also observed at $\nu_4 = 14,490$ and $\nu_5 = 22,725$ cm^{-1}, respectively. The Dq and Racah parameters, calculated by fitting the experimental frequencies to an energy level diagram for octahedral d^8 systems (24), are: $Dq = 890$, $B = 990$, and $C = 3615$ cm^{-1}. These values are in the range usually found for octahedrally coordinated Ni(II) compounds (24). The trigonal bipyramidal chromophores exhibit bands at frequencies 7405, 10,870, 17,700, 19,045, and 20,830 cm^{-1}. These bands are assigned to the five spin allowed transitions $^3E' \rightarrow {}^3E''$, $^3A_1''$, $^3A_2''$; $^3A_2'$, $^3E''(P)$, and $^3A_2'(P)$ of the Ni(II) ions in a trigonal bipyramidal environment, in good agreement with other related Ni(II) compounds (24).

At this point we consider interesting to introduce a comparative study with the homologous (Mg,Co)$_2$(OH)(AsO$_4$) phases the magnetic behavior of which was presented in a previous article (25). The ESR spectrum of Mg$_2$(OH)(AsO$_4$) doped with 1% Co^{2+} at 4.2 K showed only one signal with the g values characteristic of an octahedral environment (25). To corroborate the optical results discussed before, we have performed the reflectance spectrum of the (Mg$_{1.5}$Co$_{0.5}$)(OH)(AsO$_4$) phase. The bands observed and their assignments are shown in Table 5 with those corresponding to the Co$_2$(OH)(AsO$_4$) phase for comparison. The positions of the bands are in the range usually found for the Co(II) compounds in octahedral and trigonal bipyramidal geometries (24). In the case of the octahedral environments the values of the Dq and Racah parameters are also characteristic of Co(II) ions. It can be seen that similar spectra are observed for both compounds which is indicative of the presence of two chromophores for the cobalt(II) ions. These results are similar to those observed for the (Mg$_{1.55}$Ni$_{0.45}$)(OH)(AsO$_4$) phase in which the two crystallographic sites are occupied for the Ni(II) ions in good agreement with the structural results.

The ESR spectrum of (Mg$_{1.55}$Ni$_{0.45}$)(OH)(AsO$_4$) doped with 1% Co^{2+} at 4.2 K is shown in Fig. 3. The spectrum can be described in terms of a spin doublet $S = 1/2$ interacting with a single ^{59}Co nucleus ($I = 7/2$). This effective spin doublet arises from the splitting of the $^4T_1$ term through spin–orbit coupling and local distortion of the octahedral sites (26). It shows the strong anisotropy of the g factor and hyperfine coupling constant characteristic of Co^{2+} ions in distorted octahedral environments. The observed g values are $g_1 = 6.25$, $g_2 = 3.01$, and $g_3 = 2.03$. The deviation

TABLE 5
Diffuse Reflectance Data for the (Mg$_{1.55}$Ni$_{0.45}$)(OH)(AsO$_4$) and (Mg$_{2-x}$Co$_x$)(OH)(AsO$_4$) ($x = 0.5$, 2) Compounds (Energy Values Are Given in cm^{-1})

Compound	Cromophore	Assignment					Dq	B	C
(Mg$_{1.55}$Ni$_{0.45}$)(OH)(AsO$_4$)	NiO$_6$	$^3A_{2g} \rightarrow$ $^3T_{2g}$ 8890	$^3A_{2g} \rightarrow$ $^3T_{1g}(F)$ 11,560	$^3A_{2g} \rightarrow$ $^3T_{1g}(P)$ 24,690	$^3A_{2g} \rightarrow$ ^1E_g 14,490	$^3A_{2g} \rightarrow$ $^1T_{2g}$ 22,725	890	990	3615
	NiO$_5$	$^3E' \rightarrow$ $^3E''$ 7405	$^3E' \rightarrow$ $^3A_1''$ 10,870	$^3E' \rightarrow$ $^3A_2''$ 17,700	$^3E' \rightarrow$ $^3A_2'$ 19,045	$^3E' \rightarrow$ $^3E''(P)$ 20,830			
(Mg$_{1.5}$Co$_{0.5}$)(OH)(AsO$_4$)	CoO$_6$	$^4T_{1g} \rightarrow$ $^4T_{2g}$ 7900	$^4T_{1g} \rightarrow$ $^4A_{2g}$ 15,500	$^4T_{1g} \rightarrow$ $^4T_{1g}(P)$ 18,350			760	850	
	CoO$_5$	$^4A_2' \rightarrow$ $^4A_1'', ^4A_2''$ 5000	$^4A_2' \rightarrow$ $^4E''$ 6450	$^4A_2' \rightarrow$ $^4E'$ 10,870	$^4A_2' \rightarrow$ $^4A_2'(P)$ 16,130	$^4A_2' \rightarrow$ $^4E''(P)$ 20,000			
Co$_2$(OH)(AsO$_4$)	CoO$_6$	$^4T_{1g} \rightarrow$ $^4T_{2g}$ 7700	$^4T_{1g} \rightarrow$ $^4A_{2g}$ 15,500	$^4T_{1g} \rightarrow$ $^4T_{1g}(P)$ 18,020			780	815	
	CoO$_5$	$^4A_2' \rightarrow$ $^4A_1'', ^4A_2''$ 5000	$^4A_2' \rightarrow$ $^4E''$ 6250	$^4A_2' \rightarrow$ $^4E'$ 10,870	$^4A_2' \rightarrow$ $^4A_2'(P)$ 16,000	$^4A_2' \rightarrow$ $^4E''(P)$ 19,800			

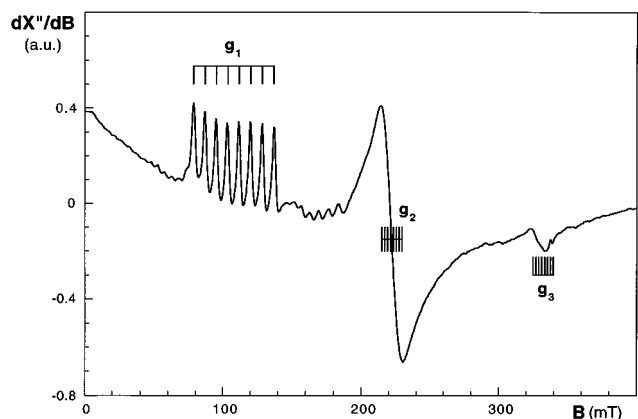**FIG. 3.** ESR spectrum of $(Mg_{1.55}Ni_{0.45})(OH)(AsO_4)$ doped with 1% Co^{2+}, at 4.2 K.

observed for the sum of the three orthogonal g-values from the theoretical value near 13 proposed by Abragam and Pryce (27) could be attributed to the simultaneous presence of the magnetic Ni(II) cations in the structure of this compound. The hyperfine splitting parameters, $A_1 = 240 \times 10^{-4}$ cm^{-1}, $A_2 < 20 \times 10^{-4}$ cm^{-1}, and $A_3 < 20 \times 10^{-4}$ cm^{-1}, are similar in magnitude to those observed in $Mg_2(OH)$ (AsO_4) doped with 1% Co^{2+} and other related cobalt(II) compounds (25, 28, 29) with six O^{2-} ions as the nearest neighbors of Co^{2+}. Likewise, in the ESR spectrum of the title compound other weak signals, which could be attributed to a small portion of Co(II) ions placed in the trigonal bipyramidal positions of the crystal structure, can also be observed. The g values of these positions cannot be calculated due to the overlapping of the signals with those corresponding to the octahedral sites.

CONCLUDING REMARKS

Two new compounds with adamite-type structure have been synthesized and characterized. The results obtained from the crystallograhic study of $(Mg_{1.55}Ni_{0.45})(OH)$ (AsO_4) show a preferential localization of the Ni^{2+} ions in the octahedral sites of the crystal structure. Spectroscopic studies by diffuse reflectance in the nickel and cobalt hydroxyarsenates reveal bands which can be adscribed to the two coordination polyhedra, octahedral and trigonal bipyramidal. The ESR measurements of $(Mg_{1.55}Ni_{0.45})(OH)$ (AsO_4) doped with 1% Co(II) at 4.2 K show the strong anisotropy of the g factor and the hyperfine structure of Co(II) ions. So, we can conclude that in the $(Mg,M)_2(OH)$ (AsO_4) (M = Ni and Co) hydroxyarsenate phases the two

crystallographic sites are occupied by the magnetic cations, showing the preference of these ions for the octahedral positions.

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