JOURNAL OF SOLID STATE CHEMISTRY 114, 550–555 (1995)

Organic Additive-Mediated Synthesis of Novel Cobalt(II) Hydroxides

J. Ismail, M. F. Ahmed, and P. Vishnu Kamath[1]

Department of Chemistry, Central College, Bangalore University, Bangalore 560 001, India

and

G. N. Subbanna,* S. Uma, and J. Gopalakrishnan[1]

**Materials Research Centre and Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560 012, India*

Received December 9, 1993; in revised form June 14, 1994; accepted June 16, 1994

Electrochemical precipitation of cobalt(II) hydroxide from nitrate solutions containing organic molecules, such as glucose, fructose, lactose, glycerol, and citric acid, yields a new modification of cobalt (II) hydroxide ($a = 3.09 \pm 0.03$ Å, $c = 23.34 \pm 0.36$ Å) that is isostructural with α-nickel hydroxide; precipitation in the absence of organic additives gives the stable, brucite-like, β-Co $(OH)_2$.

INTRODUCTION

The use of the inorganic/organic interface to achieve controlled synthesis of inorganic materials is an emerging soft chemical route to novel solids (1). Specific molecular interactions at the inorganic/organic interface seem to control nucleation and growth, often stabilizing new modifications (2). Calcium carbonate, for example, is stabilized in the vaterite modification in the presence of stearic acid (3). We have recently reported the synthesis of α-$Ni(OH)_2$ by a precipitation reaction in the presence of glucose or lactose (4).

We have for some time been interested in the hydroxides and oxide–hydroxides of cobalt, on account of their applications in alkaline secondary batteries (5–7). Cobalt(II) hydroxide, like its nickel counterpart, crystallizes in the hexagonal, brucite structure. Nickel(II) hydroxide is known to crystallize in two forms, a hydrated turbostratic structure with a large c parameter designated as α or α^* (8) and a compact form designated as β (see Fig. 1). In contrast to nickel(II) hydroxide, there is little reported work on cobalt(II) hydroxide. The Powder Diffraction File (PDF) has documented only two patterns ascribed to cobalt(II) hydroxide. Of them, one (30-443) corresponds to the β form; the pattern is similar to that of β-$Ni(OH)_2$. The other (2-925) is an impure phase of doubtful identity. A cobalt(II) hydroxide isostructural with α-$Ni(OH)_2$ has not been reported so far.

Synthesis of a stable hydrated form of cobalt(II) hydroxide with a large c parameter similar to α-$Ni(OH)_2$ holds exciting prospects, because such a phase would show superior electrochemical performance compared to the β form, reversibly incorporating water molecules, alkali metal ions, and mono- and divalent anions. We therefore investigated the synthesis of an α modification of cobalt(II) hydroxide in the presence of organic molecules as additives in the reaction medium. We tried 15 different additives of which glucose, fructose, lactose, glycerol, and citric acid yielded the α form, while maleic acid-mediated synthesis resulted in a new β-type phase with a doubling of the c parameter. We report the details of synthesis and characterization of these new forms of cobalt(II) hydroxide in this paper.

EXPERIMENTAL

Chemical synthesis of cobalt hydroxide in a simple precipitation reaction leads to autooxidation of cobalt(II) under high pH conditions. To circumvent this problem all cobalt hydroxide samples in the present study were electrochemically prepared (9) in a divided cell by cathodic reduction of a 0.1 mole dm^{-3} cobalt(II) nitrate solution containing 1 wt% of the additive. A Pt flag (1.5 cm^2 area) was used as the cathode. A 0.1 mole dm^{-3} potassium nitrate solution was used in the anodic chamber and a Pt wire was used as the anode. The electroreduction was done galvanostatically at a cathodic current density of 10 mA cm^{-2}. Cathodic reduction of nitrate ions yielded hydroxyl ions which precipitated Co^{2+} as a hydroxide. As the pH in the bulk of the solution did not increase

[1] To whom correspondence should be addressed.

0022-4596/95 $6.00

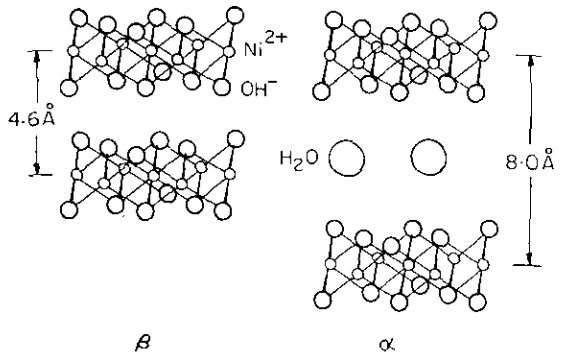

FIG. 1. Schematic view of the stacking of nickel hydroxide layers in the α and β polymorphic forms.

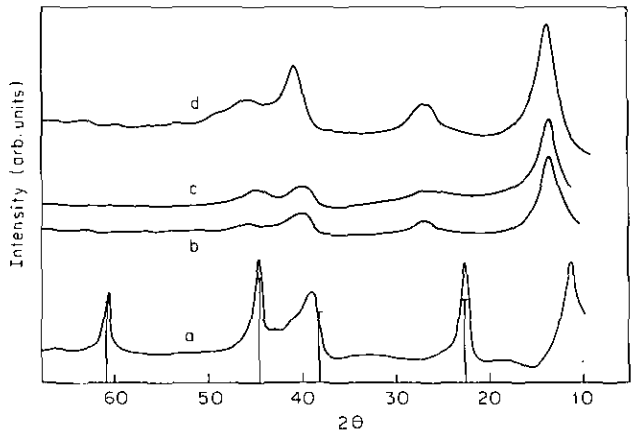

FIG. 2. Powder X-ray diffraction patterns of cobalt(II) hydroxide samples obtained in the presence of maleic acid (a), glucose (b), glycerol (c), and fructose (d) as additives. Vertical bars represent the peak positions and intensities due to β-$Co(OH)_2$ obtained in the absence of any additives.

beyond 7 in the course of the reaction, oxidation of Co^{2+} was completely suppressed and a rose-red sample of β-$Co(OH)_2$ was obtained with a negligible Co^{3+} content (10). The reaction was carried out for 2 to 4 hr until sufficient material was electroprecipitated in the cathodic chamber.

Fifteen organic additives were used, one by one, in the synthesis of cobalt hydroxide. These are listed in Table 1. The hydroxide precipitates obtained in the presence of additives were filtered out, washed in water, and dried to constant weight at 55°C. Each sample was characterized in detail and compared with the control sample of cobalt(II) hydroxide obtained in the absence of any additive.

All X-ray diffraction (XRD) patterns were recorded with a Philips X-ray diffractometer using Co$K\alpha$ (λ = 1.7902 Å) radiation as the source. Infrared spectra were recorded using a Perkin–Elmer 580 IR spectrometer in thin KBr pellets at a resolution of 3 cm^{-1}. Thermogravimetric (TG) analysis was carried out using a Cahn TG-131 thermobalance at a heating rate of 5°C min^{-1}. Transmission electron microscopy was carried out on a Jeol JEM 200 CX microscope operated at 200 kV. The powdered samples were dispersed on holey carbon grids of 200 mesh size.

TABLE 1
Additives Used in the Synthesis of Cobalt(II) Hydroxide

Additive	Concentration (wt%)	Major phase obtained
Glucose	1	α
Fructose	0.1	α
Lactose	0.5	α
Sucrose	1	β
Starch	1	β
Ethanol	1	β
Glycol	1	β
Glycerol	1	α
Polyethylene glycol	1	β
Malonic acid	1	β
Maleic acid	1	β*
Citric acid	0.5	α
Urea	1	β
Glycine	1	β
Lysozyme	1	β

RESULTS

Electroreduction of cobalt(II) nitrate readily yields cobalt(II) hydroxide. We show in Fig. 2 the XRD patterns of cobalt(II) hydroxides electrosynthesized in the absence and presence of different additives. In the absence of additives, a well-crystallized sample of brucite-like β-$Co(OH)_2$ is obtained which shows major reflections at 4.65, 2.75, and 2.36 Å. This pattern matches with the PDF pattern 30-443 which has been assigned to β-$Co(OH)_2$ with a = 3.181 Å and c = 4.653 Å. The cobalt(II) hydroxides obtained in the presence of glucose, fructose, lactose, glycerol, and citric acid as additives, on the other hand, exhibit a completely different pattern. Table 2 lists the observed d values. These patterns are all alike and match with that reported in the literature for α-$Ni(OH)_2$ (8). The patterns could be indexed on a hexagonal cell of parameters a = 3.1 Å and c = 23.3 Å. We call this phase α-$Co(OH)_2$ in keeping with the nomenclature used for the hydroxides of Ni(II).

In Fig. 2 we also show the XRD pattern of cobalt(II) hydroxide synthesized in the presence of maleic acid (1 wt% concentration). While all the reflections in this sample match with those of the control sample (β-$Co(OH)_2$), there is an additional reflection at 9.3 Å which suggests a

TABLE 2

Powder X-Ray Diffraction Patterns of Cobalt(II) Hydroxide Synthesized in the Presence of Different Additives Compared with Those of α-Nickel Hydroxide

hkl[a]	α-Ni(OH)$_2$[b] *d* (Å)	*d* (Å) for α-Co(OH)$_2$			
		Glucose	Fructose	Glycerol	Citric acid
003	7.79	7.73	7.73	7.67	7.76
006	3.908	3.86	3.95	3.83	3.83
101	2.676	2.60(b)	2.61(b)	2.64	2.62(b)
012	2.604			2.60	
015	2.321	2.291	2.319	2.329	2.359
018	1.972	1.907			

Note. (b), broad.

[a] The patterns could be indexed using these (*hkl*) values on a hexagonal cell, and the lattice parameters of the cobalt(II) hydroxide samples obtained in the presence of different additives are in the range $a = 3.09 \pm 0.03$ Å and $c = 23.3 \pm 0.36$ Å.

[b] The *d* values of α-nickel hydroxide are taken from Ref. (8).

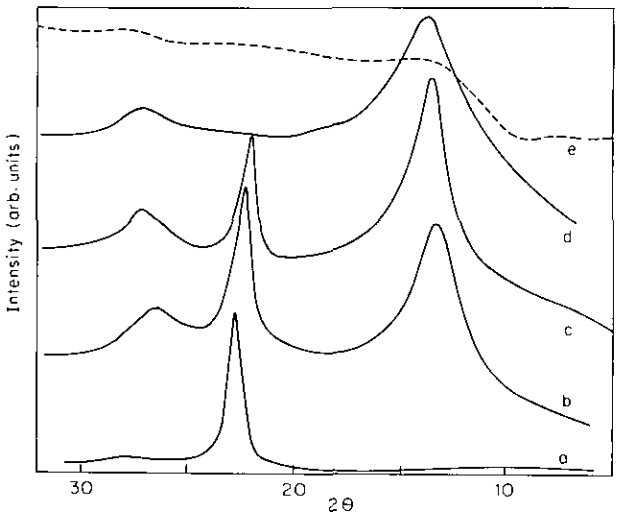

FIG. 3. Powder X-ray diffractograms of cobalt(II) hydroxide samples obtained in the presence of lactose as additive. Curves a–e are for 0, 0.1, 0.2, 0.5, and 1 wt% lactose concentrations, respectively.

possible doubling of the *c* parameter, since this *d* value is approximately twice the *d* value of the (001) reflection of β-Co(OH)$_2$ (Table 3). Accordingly we have indexed this pattern on a hexagonal cell of parameters $a = 3.17$ Å and $c = 9.26$ Å. We designate this new form of cobalt(II) hydroxide as β*-Co(OH)$_2$.

To further investigate the effect of additives, syntheses were carried out at different additive concentrations. At low additive concentrations, for example, at 0.1 and 0.2 wt% of lactose, a mixture of α and β phases was obtained. At 0.5 wt% of lactose, a pure α phase was observed, and at higher (>1 wt%) concentrations, a completely disordered sample was obtained (Fig. 3). The critical concentration of the additive required to synthesize a pure α phase varied from case to case (see Table 1).

In Fig. 4 we give thermogravimetric data for β-Co(OH)$_2$ along with that of cobalt(II) hydroxide synthesized in the presence of glucose. β-Co(OH)$_2$ shows a single loss starting at 100°C up to 250°C, giving a total weight loss of 13.7%. The product of decomposition was found to be Co_3O_4 ($a = 8.08$ Å). This weight loss matches exactly with the formula Co(OH)$_2$ (calculated weight loss 13.6%, observed weight loss 13.7%), indicating that there is no water of hydration in the control sample. The α-cobalt hydroxide obtained from a glucose-mediated synthesis, on the other hand, shows two loss peaks starting at 100 and 170°C, respectively, and a total weight loss of 30%.

TABLE 3

Powder X-Ray Diffraction Pattern of Cobalt(II) Hydroxide Prepared in the Presence of Maleic Acid (β* Modification) Compared with That of β-Cobalt Hydroxide

β-Co(OH)$_2$				β*-Co(OH)$_2$			
hkl	d_{obs}	d_{calc}	I_{obs}	*hkl*	d_{obs}	d_{calc}	I_{obs}
				001	9.3	9.256	80
001	4.653	4.640	100	002	4.628	4.628	95
100	2.749	2.745	32	100	2.682	2.748	59
101, 002	2.364	2.362	73	102	2.364	2.363	100
102	1.772	1.772	43	104	1.769	1.770	56
110	1.586	1.585	27	110	1.584	1.587	51
$a = 3.17$ Å, $c = 4.64$ Å				$a = 3.17$ Å, $c = 9.26$ Å			

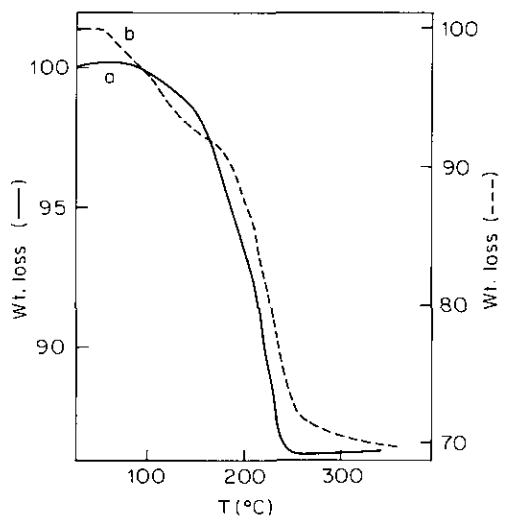

FIG. 4. Thermogravimetric analysis of β-Co(OH)$_2$ (full line) (a) compared with that of cobalt(II) hydroxide obtained in the presence of glucose as additive (broken line) (b).

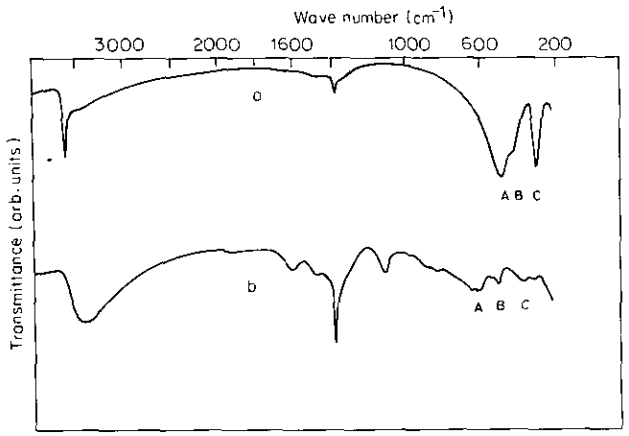

FIG. 5. Infrared spectra of β-$Co(OH)_2$ (curve a) compared with that of cobalt(II) hydroxide obtained in the presence of glucose as additive (curve b).

The low-temperature weight loss corresponds to 0.5 mole of adsorbed water, while the high-temperature loss corresponds to loss of structural water and decomposition taking place simultaneously. The weight loss is consistent with the formula $[Co(OH)_2 \cdot 0.66H_2O]\ 0.5H_2O$ [calculated weight loss 7.9%, 21.6%, observed weight loss 8.2%, 21.8%]. This formula agrees with the observation of 0.66 mole of structural water reported for α-$Ni(OH)_2$ (PDF No. 22-444) (11).

In Fig. 5 we show the infrared spectra of β-$Co(OH)_2$ and those of the samples obtained from additive-mediated synthesis. The spectrum of β-$Co(OH)_2$ is typical of the brucite lattice, showing a sharp non-hydrogen bonded OH stretch at 3620 cm^{-1} followed by three bands at 485 (A), 410 (B), and 310 (C) cm^{-1} which can be assigned to the in-plane OH bending, Co–O stretching, and out-of-plane OH bending, respectively (12). In the α-$Co(OH)_2$ obtained from glucose-mediated synthesis, the hydroxyl groups are extensively hydrogen bonded as seen from the broad band at 3440 cm^{-1}. The A, B, and C bands are blue shifted to 650, 560, and 385 cm^{-1}, respectively, and are split into two each. The blue shift of the bending modes is a natural consequence of hydrogen bonding (13).

The striking feature of the IR spectrum of α-$Co(OH)_2$ is the strong absorption seen in the 2000–1000 cm^{-1} region. The peaks at 1480, 1375, 1330, and 1030 cm^{-1} and the weak doublet at 980 and 835 cm^{-1} are all characteristic of nitrate ions intercalated in the C_{2v} symmetry (14). These features which are also seen in the IR spectra of α-$Ni(OH)_2$ (14) are considered diagnostic of the α modification. The nitrate content in the α modifications is however low (14), and accordingly the loss of nitrate is not resolved in the TG data (15).

In Fig. 6, we show the results of electron microscopic investigations of cobalt(II) hydroxide samples obtained in the absence and presence of additives. β-$Co(OH)_2$ consists of well-defined crystalline platelets. A bright field image of one such platelet and the corresponding electron diffraction pattern are shown in Figs. 6a and 6b, respectively. The α-$Co(OH)_2$ obtained from a glucose-mediated synthesis consists of scaly particles (Fig. 6c). A high resolution electron micrograph of one of the particles viewed edge on reveals a layer spacing of about 7.8 Å (Fig. 6d), corresponding to the c parameter of α-$Co(OH)_2$. Samples obtained from additive-mediated synthesis are generally found to be electron beam sensitive as prolonged exposure leads to loss of crystallinity.

DISCUSSION

Despite the similarity in the structure and chemistry of the hydroxides and oxide–hydroxides of nickel and cobalt, a stable well-characterized, α modification of cobalt(II) hydroxide has not been reported to date, while its nickel counterpart is well known (8, 13–15). Cobalt(II) hydroxide is known to exist in blue and pink forms, but the former rapidly ages to the latter and only the pink β phase has been unambiguously characterized and reported in the literature. Additive-mediated synthesis appears to fill this lacuna, as the cobalt(II) hydroxide samples synthesized in the presence of glucose, fructose, lactose, glycerol, and citric acid exhibit XRD patterns identical to those reported for α-$Ni(OH)_2$. Besides, the α-$Co(OH)_2$ so obtained was stable against aging (in mother liquor), washing, and drying at 55°C.

The α modifications are characterized by a low-angle reflection at 7.5 to 7.8 Å due to the (003) plane, followed by a reflection at 3.7 to 3.9 Å due to the (006) plane. The β form, on the other hand, has a more compact cell, and its first reflection appears at 4.6 Å due to the (001) plane.

The large c parameter of α-$Co(OH)_2$ is due to the presence of interlamellar water which is bound to the hydroxyl groups by hydrogen bonds. Apparently considerable disorder exists in the layers of water molecules as indicated by the broad peaks in the XRD patterns. Indeed the exact synthetic conditions employed and the thermal history of the sample affect the c parameter of α-cobalt hydroxide. Similar observations have been made for α-$Ni(OH)_2$ as well (15). β-$Co(OH)_2$, on the other hand, has no water of hydration and its XRD pattern is sharper, indicative of a higher degree of crystallinity.

From TG data, the interlamellar water can be estimated and α-cobalt(II) hydroxide can be formulated as $Co(OH)_2 \cdot 0.66H_2O$, a composition consistent with that of α-$Ni(OH)_2$ (11). This structural water is lost in a single step along with the cobalt(II) hydroxide decomposition reaction. In contrast, α-$Ni(OH)_2$ shows multiple steps in its TG data (15). Understandably the compact packing of

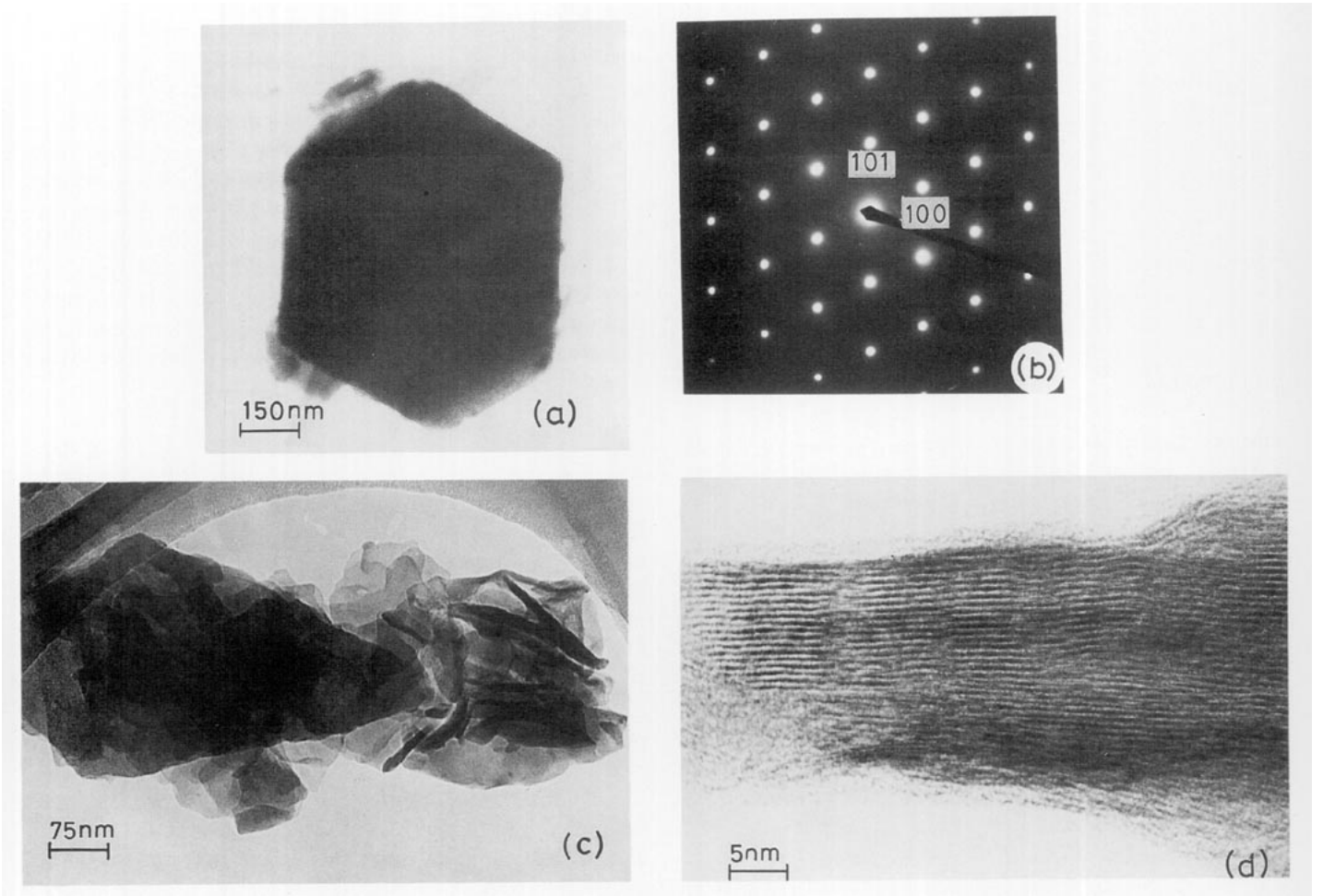

FIG. 6. (a) Transmission electron micrograph of β-$Co(OH)_2$. (b) Electron diffraction pattern of platelet seen in (a). (c) Transmission electron micrograph of cobalt(II) hydroxide obtained in the presence of glucose as additive. (d) HREM of one of the scales seen in (c).

layers in β-$Co(OH)_2$ does not permit the existence of any intercalated species.

These compositional features of α and β-$Co(OH)_2$ are also reflected in the infrared spectra. Infrared spectroscopy is a useful tool for revealing aspects of short-range structure, especially in poorly ordered materials. α-$Co(OH)_2$ is characterized by the presence of hydrogen bonded hydroxyl groups and intercalated nitrate ions. Many conflicting hypotheses have been proposed to explain the presence of nitrate ions in α-$Ni(OH)_2$, such as (i) hydroxide vacancies that accommodate nitrate ions in the brucite structure, (ii) simultaneous inclusion of protons together with nitrate ions, and (iii) partial oxidation of nickel(II) to nickel(III) to compensate for the excess negative charge arising from the inclusion of nitrate ions (10, 16). However, none of these hypotheses have been incontrovertibly accepted.

β-$Co(OH)_2$, like its nickel counterpart, is crystalline and exhibits a hexagonal platelet morphology. α-$Co(OH)_2$ exhibits scaly particles which under high resolution reveal a lattice spacing of 7.8 Å, similar to α-$Ni(OH)_2$.

Maleic acid-mediated synthesis yielded a novel β-like phase (which we designate as β^*) with a doubling of the c parameter. Similar observation has been made with Li_xCoO_2 (17). Such a modification arises due to the gliding of alternate layers without the breaking of any Co–O bonds. No other additive was able to stabilize this modification.

Too small or too large organic molecules were found to be quite ineffective at bringing about a change in the structure and morphology of cobalt hydroxide. Thus the addition of methanol, ethanol, urea, and glycine, as well as large polymeric molecules such as polyethylene glycol, starch, and lysozyme, yielded β-$Co(OH)_2$, as in the control reaction carried out without the presence of additives. Medium-sized molecules such as glucose, fructose, lactose, glycerol, and citric acid stablized the α modification. Mann *et al.* have made a similar correlation between the

size of the organic additive and the nature of the inorganic phase stabilized (18).

The exact mechanism of additive-mediated stabilization of the α form is not clear to us. Mann *et al.* have invoked a template effect where an ordered monolayer of organic additive molecules nucleates a novel inorganic phase (3). In the present instance, the additive molecules are completely dissolved in the reaction medium and are presumably randomly oriented, ruling out a template effect. The $\alpha \rightarrow \beta$ transformation of these layered hydroxides is known to take place through a dissolution–nucleation mechanism. It is possible that the additive molecules present in the reaction medium prevent the nucleation of the β phase and thereby stabilize the α phase. There is no incorporation of the additive molecule in the inorganic phase as evidenced by infrared spectroscopy. But the possibility of additive adsorption onto the particles of the α phase exists, which may prevent the nucleation of the β phase. However, we do not have a definitive evidence in support of this mechanism.

SUMMARY

In conclusion, we have, for the first time, synthesized an α modification of cobalt(II) hydroxide by electrochemical precipitation from nitrate solution in the presence of organic additives. Like α-$Ni(OH)_2$, α-$Co(OH)_2$ is poorly crystalline and exhibits an increased interlayer spacing. Maleic acid-mediated synthesis leads to the stabilization of a new β-like phase with a doubling of the c parameter.

REFERENCES

1. S. Mann, D. D. Archibald, J. M. Didymus, B. R. Heywood, F. C. Meldrum, and V. J. Wade, *MRS Bull.*, October, 32 (1992), and references therein.
2. S. Mann, D. D. Archibald, J. M. Didymus, T. Douglas, B. R. Heywood, F. C. Meldrum, and N. J. Reeves, *Science* **261,** 1286 (1993).
3. S. Mann, B. R. Heywood, S. Rajam, and J. D. Birchall, *Nature* **334,** 692 (1988).
4. P. V. Kamath, J. Ismail, M. F. Ahmed, G. N. Subbanna, and J. Gopalakrishnan, *J. Mater. Chem.* **3,** 1285 (1993).
5. P. V. Kamath and S. Ganguly, *Mater. Lett.* **10,** 537 (1991).
6. J. Ismail, M. F. Ahmed, and P. V. Kamath, *J. Power Sources* **36,** 507 (1991); **41,** 223 (1993).
7. P. V. Kamath and M. F. Ahmed, *J. Appl. Electrochem.* **23,** 225 (1993).
8. J. J. Braconnier, C. Delmas, C. Fouassier, M. Figlarz, B. Beaudouin, and P. Hagenmuller, *Rev. Chim. Miner.* **21,** 496 (1984).
9. J. A. Switzer, *Am. Ceram. Soc. Bull.* **66,** 1521 (1987).
10. P. V. Kamath and N. Y. Vasanthacharya, *J. Appl. Electrochem.* **22,** 483 (1992).
11. H. Bode, K. Dehemelt, and J. Witte, *Z. Anorg. Allg. Chem.* **366,** 1 (1969).
12. S. S. Mitra, *Solid State Phys.* **13,** 1 (1962).
13. P. Oliva, J. Leonardi, J. F. Laurent, C. Delmas, J. J. Braconnier, M. Figlarz, and F. Fievet, *J. Power Sources* **8,** 229 (1982).
14. F. Portemer, A. Delahaye-Vidal, and M. Figlarz, *J. Electrochem. Soc.* **139,** 671 (1992).
15. B. Mani and J. P. de Neufville, *J. Electrochem. Soc.* **135,** 800 (1988).
16. C. Faure, C. Delmas, and M. Fouassier, *J. Power Sources* **35,** 279 (1991).
17. C. Delmas, J. J. Braconnier, and P. Hagenmuller, *Mater. Res. Bull.* **17,** 117 (1982).
18. S. Mann, J. M. Didymus, N. P. Sanderson, B. R. Heywood, and E. J. AsoSamper, *J. Chem Soc. Faraday Trans.* **86,** 1873 (1990).