

A Novel Route for the Preparation of Hydrotalcite and Synthesis of Intercalated Reversible Dioxygen-Carrying Cobalt(II) Complexes

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Reacting a solid $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ or $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 5\text{H}_2\text{O}$ (nesquehonite, hydromagnesite, dypingite) with an aqueous solution of sodium aluminate and sodium hydroxide is a novel procedure to synthesize solid solutions with desired stoichiometric Mg/Al ratios in the hydrotalcite series $[\text{Mg}_{3-x}\text{Al}(\text{OH})_{8-2x}]_2[(\text{CO}_3)(\text{H}_2\text{O})_{4-x}]$ ($0 \leq x \leq 1$).

By mixing of an intermediate solid solution of magnesium aluminium oxide obtained by thermal decomposition of hydrotalcite with an aqueous solution of mono- or α, ω -dicarboxylates which contain *N*-donor atom in the presence of ethylene glycol as a swelling agent pillared aminocarboxylate derivatives of hydrotalcite are produced. Nitrogen donor atoms of aminocarboxylate pillars may react with cobalt(II) complexes to form coordinatively unsaturated cobalt(II) chelates. The synthesized model Co(salen) and Co(salophen) complexes immobilized in the interlayer region of anionic clays reversibly bind dioxygen and enjoy high stability in the course of oxygenation-deoxygenation cycles.

A relatively scarce natural mineral of the chemical composition ranged from $[\text{Mg}_6\text{Al}_2(\text{OH})_{16}][(\text{CO}_3)(\text{H}_2\text{O})_4]$ to $[\text{Mg}_4\text{Al}_2(\text{OH})_{12}][(\text{CO}_3)(\text{H}_2\text{O})_3]$ occurs in two polytype modifications, CO_3 -hydrotalcite-3*R* (hydrotalcite) and CO_3 -hydrotalcite-2*H* (manasseite) [1, 2]. The typical chemical composition of hydrotalcites lies in the range $[\text{Mg}_{3-x}\text{Al}(\text{OH})_{8-2x}]_2[(\text{CO}_3)(\text{H}_2\text{O})_{4-x}]$ where ($0 \leq x \leq 1$) and $[\text{Mg}_{3-x}\text{Al}(\text{OH})_{8-2x}]$ is the formula unit of a layer having net charge $1+$. The structure of hydrotalcites and their structural analogues is derived from that of brucite, $\text{Mg}(\text{OH})_2$ [3–5]. When some of the Mg^{2+} in the brucite layer are isomorphously substituted with Al^{3+} , the mixed Mg^{2+} — Al^{3+} 2-*D* network bears one unit of positive charge per Al^{3+} , which is compensated by the incorporation of carbonate anions into the interlayers. In addition, some water molecules (about 20 mass %) are located in the interlayer region.

The interlayer region of hydrotalcite and its derivatives (anionic clays) behaves as a basic solid solvent and provides reactive medium not only for the counterions that ensure charge balance of the crystal structure, but also for a variety of intercalated polar or nonpolar molecules. Several attempts have been made recently for enlargement of the interlayer distance of hydrotalcite-like compounds by incorporation of large, preferably multiply charged anions into the interlayer space (pillared anionic clays) (Fig. 1).

The main goals in the development of new synthetic hydrotalcite-like compounds include: substitu-

tion of divalent cations (*e.g.* $\text{M}^{\text{II}} = \text{Mg}, \text{Zn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}$) and trivalent cations (*e.g.* $\text{M}^{\text{III}} = \text{Al}, \text{Fe}, \text{Co}, \text{Mn}, \text{Cr}, \text{V}$) into the brucite-like layers; replacing of anions (*e.g.* $\text{A}^{n-} = \text{CO}_3^{2-}, \text{ClO}_4^-, \text{HPO}_4^{2-}$, carboxylate and polyoxopolymetalate anions) and intercalated guest molecules (*e.g.* water, polyvalent alcohols, amines) by other species in the interlayer region. The general formula of these synthetic hydrotalcite derivatives may be written as $[\text{M}_{1-x}^{\text{II}} \text{M}_x^{\text{III}}(\text{OH})_2]^{x+}[\text{A}_{x/n}^{n-}]^{x-} \cdot y\text{L}$, with $0.25 \leq x \leq 0.33$. A diverse group of compounds containing various combinations of M^{II} , M^{III} , and A^{n-} ions, as well as molecules and complexes intercalated into hydrotalcite analogues can be synthesized [5–7].

Properties of hydrotalcite-like compounds depend on the chemical behaviour and distribution of cations incorporated in the brucite-like layers, as well as on the chemical composition, electronic structure, stereochemistry, and distribution of the interlayer anions and of the intercalated guest molecules. The preparation, structure, properties, and use of these materials for practical application have been reported in many research papers [6, 7]. In order to further exploit their potential, alternative processes, satisfactory from a technical and economical point of view, are desirable.

Anionic clays have been prepared by coprecipitation procedures from mixtures of soluble magnesium and aluminium salts with different sodium hydroxide and sodium carbonate solutions [8–13], by simultaneous hydrolysis of magnesium and aluminium alkox-

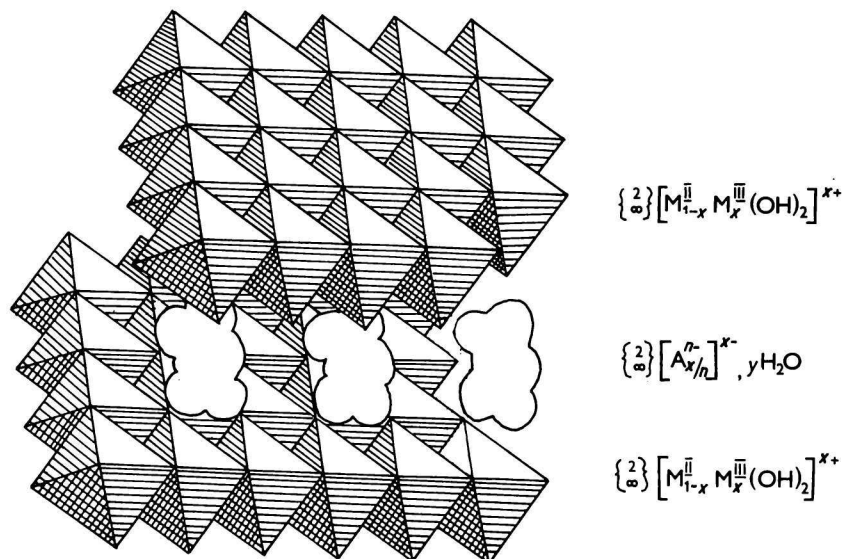


Fig. 1. Schematic representation of the layered structure of anion-intercalating hydrotalcite-like compounds. Water molecules situated in the interlayer are omitted for the sake of clarity.

ides [14], by reacting an aqueous solution of aluminium salt with magnesium oxide [15–17], by interaction of magnesium oxide and alumina gel [18–20], by heterocoagulation in mixed suspensions of magnesium hydroxide and aluminium hydroxycarbonate [21], and by reacting activated magnesium oxide with an aqueous sodium aluminate solution [22, 23]. Hydrotalcite can also be prepared (*Zikmund et al.* [24]) by simultaneous hydrolysis of aqueous solution of sodium aluminate [29, 30] and solid magnesium carbonate hydrates or magnesium carbonate hydroxide hydrates. Examples for nesquehonite, $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$, hydromagnesite, $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$, and dypingite, $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 5\text{H}_2\text{O}$ [25] are included [24].

This paper describes a method for synthesis of Mg—Al— CO_3 -hydrotalcites. The objectives are the synthesis and the study of the properties of pillared monocarboxylate derivatives attached to the internal surface of hydrotalcite, synthesis of cobalt(II) chelate complexes connected by donor-acceptor bonds to *N*-donor atom of aminocarboxylate pillars, and the study of the interaction of dioxygen with the coordinatively unsaturated cobalt(II) complexes immobilized in the interlayer region of hydrotalcite derivatives.

To make the interlayer region of hydrotalcite accessible to simple substrates, such as dioxygen or molecules of ligands, pillared aminocarboxylate derivatives were synthesized. Carboxylate and various other anionic derivatives of hydrotalcite were prepared by restructuring (reconstitution) reaction [26–28] of the mixed metal oxide solid solution formed by the thermal decomposition of CO_3 -hydrotalcite [5, 31–38]. In the present work, ethylene glycol was used instead of glycerol as swelling agent [39]. The interlayer arrangement of carboxylate anions has been studied

extensively [28, 40, 41]. The results obtained suggest that charge distribution (arrangement of Al^{3+}) within the electropositive hydrotalcite layers [42–44] will govern the placing and chain packing density of carboxylate anions (free distances between pillars) in the interlayer. The glycinate and isonicotinate monoanions are twice as numerous as glutamate dianions. The geometric orientation and accessibility of lone pair orbital which is capable of donating an electron pair from nitrogen atom to a vacant orbital on Co(II) are different. The σ -donor (aliphatic amines) and/or π -donor (aromatic amines) effects of the axial *N*-containing ligand influence changes in π bonding to an empty *p* orbital of superoxo anion radical coordinated to the cobalt atom.

Pillared derivatives of hydrotalcite containing tailored interlayer environment (structure, shape, packing, and orientation of the guests) have been used as interactive supports for various reagents. Reactions of nitrogen donor atoms from aminocarboxylate pillars with labile or coordinatively unsaturated cobalt(II) complexes may be utilized as an anchoring method for synthesis of neutral or charged cobalt(II) complexes (chelates) inside the interlayer [45, 46]. The exposure of attached cobalt(II) species to vapours of chelating ligands (*e.g.* ethylenediamine, salenH_2) affords a facile preparative procedure for synthesis of immobilized oxygen carriers. The attachment of planar cobalt(II) chelates containing a neutral didentate $(\text{NN}')_2$ or a dianionic tetradentate $(\text{N}_2\text{O}_2)^{2-}$ donor systems and a vacant coordination site (or, at most, a site that is only weakly coordinated to nitrogen atoms) in the structure of aminocarboxylate pillar eliminates the need for addition of a complementary axial ligand [47].

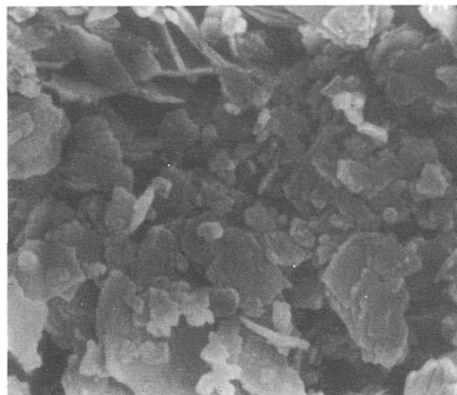


Fig. 2. Scanning electron micrograph of dypingite ($\times 20\ 000$).

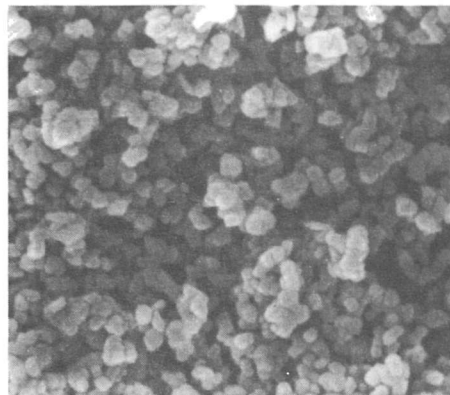


Fig. 3. Scanning electron micrograph of hydrotalcite ($\times 20\ 000$).

EXPERIMENTAL

Magnesium Carbonate Hydrates

Nesquehonite, $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$, was prepared by CO_2 -saturation of an aqueous suspension of magnesium hydroxide containing monoethanolamine, $\text{HO}(\text{CH}_2)_2\text{NH}_2$ (about 3 mass %) under continuous stirring [48, 49]. Transformation of nesquehonite into dypingite, $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 5\text{H}_2\text{O}$, was conducted by its controlled thermal decomposition using superheated water vapour (approx. 200°C , 1 h) [50]. The morphology of dypingite is shown in Fig. 2.

Hydrotalcites

CO_3 -hydrotalcite was prepared by reaction of a solid magnesium carbonate hydrate with aqueous solution of sodium aluminate. Desired Mg/Al ratios may be obtained by suitable choice of stoichiometric quantities of components. Depending on the reaction conditions, particularly on the chosen solution/solid, Al/NaOH and Mg/NaOH ratios, on the particle size of magnesium carbonate raw material (formation of pseudomorphs and agglomeration), as well as on the mixing conditions, the time and the temperature of crystallization, one can obtain hydrotalcite products of a high degree of crystallinity with required morphology and particle size and free of any other crystalline phases.

In a typical experiment, $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$ was obtained by adding, at room temperature, 2914 g (6 mol) of dypingite to a vigorously stirred aqueous solution ($15\ \text{dm}^3$) consisting of 1180 g (10 mol) of $\text{Na}[\text{Al}(\text{OH})_4]$ and 1200 g (30 mol) of NaOH. The resulting suspension was further stirred at ambient temperature for a period of about 4 h till homogeneity. The resulting slurry was charged to a stainless reaction vessel equipped with an anchor type agitator. Crystallization occurred, with constant stirring, at 95°C under autogenous pressure in 18 h. The cooled

mixture was then filtered, repeatedly washed with hot deionized water until the absence of sodium ions (Na^+ content $100\text{--}60\ \mu\text{g}$ of Na per 1 g of sample), and dried under reduced pressure at 100°C for 24 h. The yield was 3000 g (99.3 %).

The hydrophobing of hydrotalcite was achieved by surface reaction of sodium stearate or sodium palmitate in aqueous suspension. The wet, freshly prepared hydrotalcite (before filtration) was added to a dilute aqueous solution of sodium carboxylate and the reaction mixture was stirred at $50\text{--}90^\circ\text{C}$ for 3 h. The solid was then filtered, washed with deionized water (Na^+ content lower than $30\ \mu\text{g}$ of Na per 1 g of sample) and dried at 100°C .

The size of the particles ranged from $10\ \mu\text{m}$ to $50\ \mu\text{m}$. The N_2 BET surface areas for 80°C dried material were found to be in the range $15\text{--}30\ \text{m}^2\ \text{g}^{-1}$. The appearance of a product for application in polymer technology is shown in the SEM picture (Fig. 3). Fig. 4 shows the X-ray diffraction patterns obtained from the quasi-amorphous intermediate slurry before crystallization (a), from the solid phase (Fig. 3) after crystallization (b), and from the hydrotalcite prepared by regeneration reaction from the amorphous intermediate (a) heated at 500°C and then exposed to the aqueous solution of Na_2CO_3 for 1 h (c). The thermal behaviour of hydrophobized hydrotalcite is illustrated by the TG, DTG, and DTA curves (Fig. 5).

Aminocarboxylate Derivatives of Hydrotalcite

The synthesized $\text{Mg}_3\text{Al}\text{--CO}_3$ -hydrotalcite (alternatively its quasi-amorphous synthetic intermediate product formed before crystallization) was thermally decomposed in air at 500°C for 5 h. During this heat treatment a poorly crystalline mixed aluminium magnesium oxide solid solution was formed. Both hydrotalcite and its synthetic amorphous intermediate showed no significant differences in chemical properties of their decomposition products. The calcined

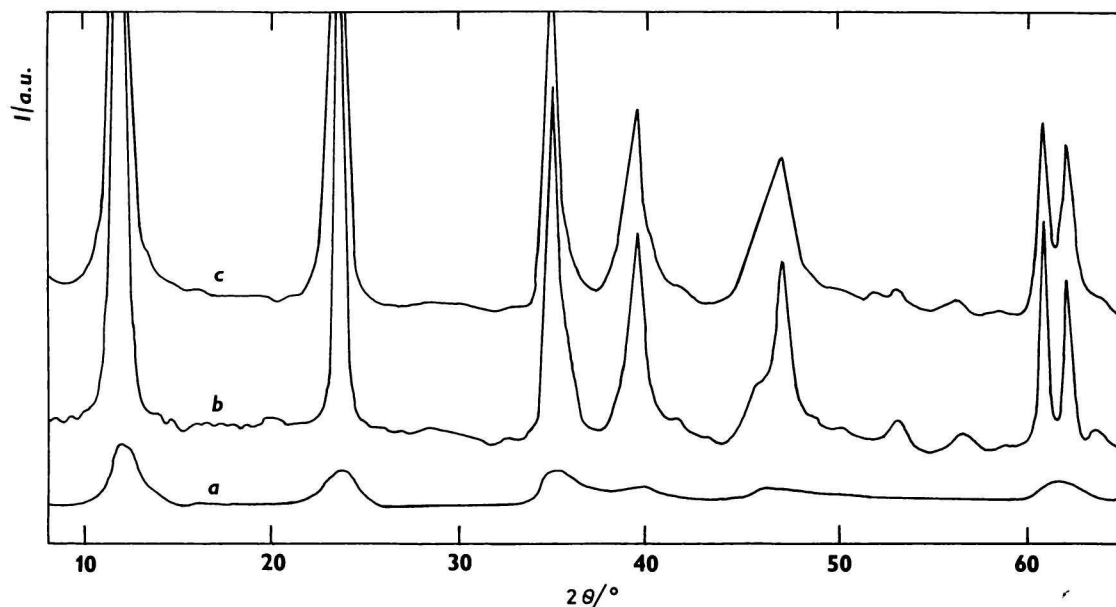


Fig. 4. X-Ray powder diffraction patterns corresponding to a) quasi-amorphous intermediate before crystallization, b) hydroxalcalcite after crystallization of quasi-amorphous intermediate, and c) hydroxalcalcite after regeneration from quasi-amorphous intermediate calcined at 500°C.

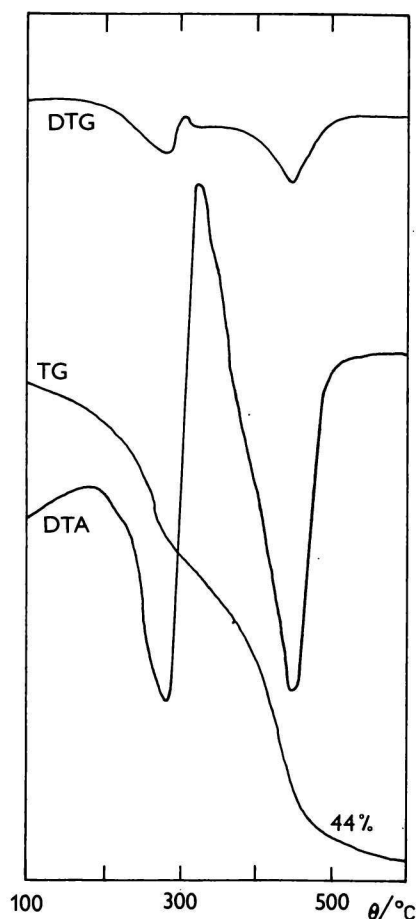


Fig. 5. TG, DTG, and DTA curves of hydrophobized hydroxalcalcite.

precursor was added into carbon dioxide-free distilled water and the resulting suspension was stirred for 24 h at room temperature under carbon dioxide-free conditions. After this treatment the formed OH-hydroxalcalcite (meixnerite), in the presence of stoichiometric amounts of ammonium aminocarboxylate dissolved in the ethylene glycol—water (2:1) mixture, was transformed into the aminocarboxylate derivatives of hydroxalcalcite. To achieve crystalline product, the reconstitution process of hydroxalcalcite-like structure was carried out at 95°C for 5 h. Once intercalated, the aminocarboxylate derivative of hydroxalcalcite in its dry state is stable.

Specific anions used for intercalation in this study include ammonium salts of (i) *L*-glutamic acid ((*S*)-(+)-glutamic acid), $\text{HO}_2\text{C}(\text{CH}_2)_2\text{CH}(\text{NH}_2)\text{CO}_2\text{H}$, and (ii) 4-pyridinecarboxylic acid (isonicotinic acid), $\text{N}(\text{CH}_2)_4\text{CCO}_2\text{H}$. They will be abbreviated to glu (i) and ina (ii) in the following text. The hydroxalcalcite-like materials containing glutamate and isonicotinate ions can be denoted simply as glu-HT and ina-HT, respectively.

Anchored Cobalt(II) Complexes

For further investigation two starting hydroxalcalcite derivatives (*A*, *B*) containing cobalt(II) chloro complexes were synthesized. The Co complexes were introduced in the form of ethylene glycol solution of 1,3-diammoniumpropane tetrachlorocobaltate(2-), $[\text{H}_3\text{N}(\text{CH}_2)_3\text{NH}_3][\text{CoCl}_4] \cdot 3\text{H}_2\text{O}$, into interlayer of hydroxalcalcite derivative and attached (probably in the form of ion pair species) to donor nitrogen atom of

glutamate (*A*, 0.15 mmol g⁻¹ Co) and isonicotinate (*B*, 0.17 mmol g⁻¹ Co). These compounds were chosen to be precursors for synthesis of coordinatively unsaturated square planar cobalt(II) chelates inside the hydrotalcite interlayer region. The central Co(II) atom in these chelate complexes was connected with nitrogen donor atom of aminocarboxylate pillar as axial ligand. The chelating ligands used were Schiff bases *N,N'*-ethylenebis(salicylideneiminato)(2-) (salen), C₁₆H₁₄N₂O₂²⁻, m.p. = 126 °C (*A*, *B*) and *N,N'*-1,2-phenylenebis(salicylideneiminato)(2-) (salophen), C₂₀H₁₄N₂O₂²⁻, m.p. = 166 °C (*B*). (Kinetic diameter of salenH₂ is about 0.65 nm, maximum diameter of Co(salen) is about 1.2 nm.)

Typically, cobalt(II)-containing hydrotalcite (*A*, *B*) was dried in air at 160 °C and mixed with an excess of salenH₂ (alternatively with salophenH₂). The reaction vessel was kept under argon atmosphere and heated under reduced pressure (< 10 Pa) to 120 °C (alternatively to 160 °C) for 48 h. After cooling, the sample was extracted in an inert atmosphere with dichloromethane to remove surface species and free base ligand. The solid product was dried at 80 °C *in vacuo* overnight and stored in sealed ampoules under an argon atmosphere.

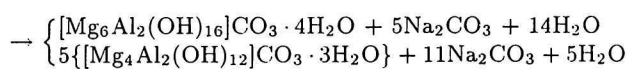
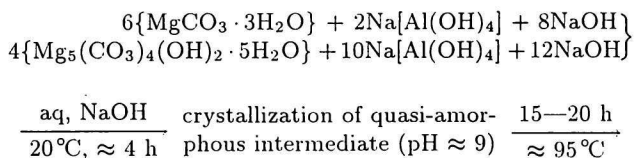
Methods of Characterization

The starting materials and reaction products were analyzed by standard chemical methods. Mg, Al, Na, Co were determined *via* atomic absorption spectroscopy (Instrumentation Laboratory Model AAS/AES Video 12) after dissolution of the solids in 0.1 M hydrochloric acid. In selected samples, Co was determined both by chemical analysis and AAS, the two methods giving similar results. All reagents were from commercial sources. Solvents were purified by standard procedures before using. Thermal analysis (TG/DTA) was performed with a MOM Derivatograph (Budapest). A heating rate of 10 K min⁻¹ and an air flow rate of 10 cm³ min⁻¹ were used. X-Ray powder diffraction patterns were recorded on a Philips diffractometer using CuK α and CoK α radiation. Phase purity of selected synthesized starting materials and products was confirmed using data reported in the literature (Powder Diffraction File. Inorganic Phases. 1989. Nesquehonite, File 20-669; Dypingite, File 23-1218; Hydrotalcite, File 14-191). UV VIS spectra were obtained on a Specord M-40 spectrometer (Zeiss, Jena). Diffuse reflectance spectra in the $\bar{\nu}$ region of 30 000–11 000 cm⁻¹ were recorded on a type I reflectance attachment using MgO as a reference. The spectra were processed by computer obtaining *Kubelka/Munk* function $F(R_\infty)$ as a function of wavenumber. The electronic diffuse reflectance spectra [51], infrared spectra [52], and X-ray powder diffraction patterns [53] of selected air- and moisture-sensitive substances were taken by using procedures

for preparation in a controlled atmosphere without dry box. Electron spin resonance (ESR) spectra were recorded in X-band with a modulation frequency of 100 kHz in the range of 100–300 K. The apparatus was Bruker SRC-200 D. The morphology of selected specimens was observed by scanning electron microscopy (Cambridge Stereoscan 2A).

RESULTS AND DISCUSSION

Reactions for transforming magnesium carbonate hydrates and sodium aluminate aqueous solution into hydrotalcite can be represented by the following scheme



The proposed method enables hundreds of grams of pure material to be produced. The whole process is technologically simple; it requires only a few common processing steps; energy demands are modest. The technological procedure is a closed cycle in which waste waters contaminated by anions, such as Cl⁻ or NO₃⁻, arise. The raw materials are widely available and rather inexpensive.

To improve the dispersive properties in nonpolar liquid suspensions and in organic polymers (*e.g.* poly(vinyl chloride), polypropylene), amphiphilic organic long-chain anions, such as stearate or palmitate sodium salts, may be used as surface-modifiers of hydrotalcite powders. After the chemical reaction between the carboxylate anions and >AlOH or >MgOH groups present on the outer surface of hydrotalcite, the powder is coated with a monomolecular layer of >AlOOR and/or >MgOOR chain which provides a convenient protection of dry hydrotalcite against direct contact with water.

Pillared hydrotalcite derivatives have been generally prepared by anion exchange, by reconstitution reactions, as well as *via* direct synthesis in the presence of pillaring anion with and without use of preswelling agents [8, 27, 28, 39–41, 54–61]. Since CO₃-hydrotalcite has a relatively high layer charge density, it is hard to swell and difficult to exchange interlayer counterions when compared to OH-hydrotalcite or to cationic smectite clay minerals. The interlayer separation of hydrotalcite diminishes with the increase in Al³⁺ due to the increase in an electrostatic attraction between positive layers and negative interlayer species. The interlayer spacing varies with number and design (charge, length, size, shape, orientation) of the interlayer aminocarboxylate anions and

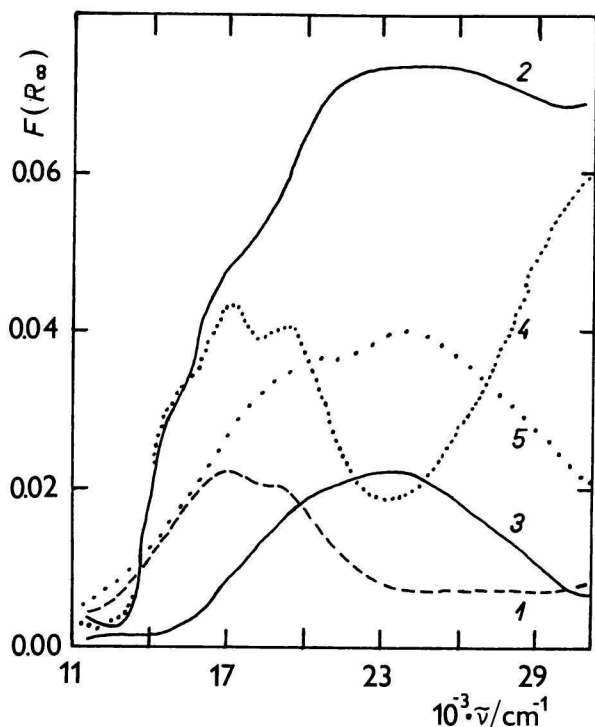


Fig. 6. Diffuse reflectance spectra of the cobalt complexes attached to aminocarboxylate pillared hydrotalcite: 1. model complex $\text{Co}(\text{salen})$ (recorded under an air atmosphere); 2. $\text{CoCl}_3\text{-glu-HT}$ (dehydrated at 160°C); 3. O_2 adduct of $\text{Co}(\text{salen})\text{-glu-HT}$; 4. $\text{CoCl}_3\text{-ina-HT}$ (dehydrated at 160°C); 5. O_2 adduct of $\text{Co}(\text{salen})\text{-ina-HT}$.

anchored cobalt(II) complexes.

In a prototype pure crystalline $\text{Co}(\text{salen})$ complex, the catalytic reaction must necessarily take place in the solid surface so that only coordinatively unsaturated $\text{Co}(\text{II})$ atoms at surface sites (without axially coordinated amine ligands) may be accessible and effective in heterogeneous catalysis. All complexes situated in the bulk of crystal structure (not present at the surface) remain unexploited. By contrast, the individual complexes anchored and regularly arranged in the pillared interlayer have not only definite stoichiometry and uniform active structure, but all are theoretically available for reactants as catalytically active species. This heterogenized system can have the reactivity different from its crystalline analogue and is potentially more efficient in terms of portion of catalyst needed to catalyze a given amount of reactants.

To our knowledge, the reversible formation of cobalt(II)—dioxygen complexes attached within the interlayer region of derivatized hydrotalcite as a potential route for an efficient method for chemical separation of dioxygen from air and other gaseous mixtures and for catalytic oxygenations and oxidations has not been investigated. However, many low-spin mono- and dicobalt complexes of various amine and Schiff base ligands in solution [e.g. 62] were reported to bind

dioxygen reversibly. Several cationic [63–66], neutral [67], and anionic [68] cobalt(II) complexes, encapsulated inside negatively charged supercages of zeolite Y and attached to the surface of cationic clay (hectorite) [69], represent further examples of reversible oxygen carriers [66]. These inclusion and attached compounds show promise of combining the advantages and eliminating the disadvantages of homogeneous and heterogeneous catalytic systems. In addition, the stability of the catalyst can be influenced by its immobilization, since degradation pathways involving reactions such as the formation of peroxo-bridged dimers of the catalytically active complex can be avoided.

The reaction between cobalt(II)-containing hydrotalcite and salenH_2 leads undoubtedly to the formation of hydrotalcite supported complex $\equiv\text{N}-\text{Co}(\text{salen})$, which cannot be extracted with dichloromethane. The result is demonstrated by the characteristic bands in the visible region of the electronic spectra, obtained by the reflectance technique for the extracted products, as well as in the extraction residue previously dissolved in hydrochloric acid and extracted with dichloromethane. The $d-d$ diffuse reflectance spectra of the attached complexes (Fig. 6) are similar to those of analogous complexes formed in solution and inside the zeolite Y. X-Ray powder diffractograms of hydrotalcite derivatives under investigation show retention of the hydrotalcite-type structure. The X-ray diffraction patterns show increased $d(003)$ spacings, and hence increased interlayer distances, which is consistent with the expectation of the replacement of a small anion (e.g. carbonate) by a bulkier one (aminocarboxylate). We have found $d(003) = 1.31$ nm for glycine pillared hydrotalcite containing $\text{Co}(\text{salen})$, $\text{Co}(\text{salen})\text{-gly-HT}$, and $d(003) = 1.16$ nm for analogous hydrotalcite derivative containing $\text{Co}(\text{salophen})$, $\text{Co}(\text{salophen})\text{-gly-HT}$. The observed (001) reflections indicate that the stacking is not fully rhombohedrally ordered.

From the thermal decomposition data we can conclude that the aminocarboxylate derivatives of hydrotalcite are stable up to about 240°C . The two samples under investigation (A, B) behaved similarly during the thermal study. The TG and DTA curves for $\text{CoCl}_3\text{-glu-HT}$ (A) and $\text{CoCl}_3\text{-ina-HT}$ (B) are shown in Fig. 7. Thermogravimetric (TG) analysis has shown that the mass loss begins at ambient temperature and continues progressively up to ca. 350°C . Physically adsorbed and interlayer water is removed between room temperature and about 200°C . The differential thermal analysis (DTA) indicated that the thermal decomposition of aminocarboxylate pillars is a two-stage process. The exothermic effect in the temperature range between 250°C and 400°C can be ascribed to the thermal destruction of the aminocarboxylate anions. The second complex exothermic effect above this temperature, corresponding to the further mass loss due to coupled release of water and carbon diox-

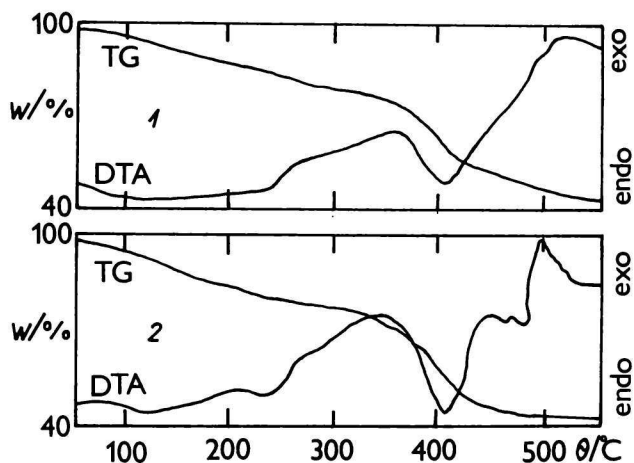


Fig. 7. TG and DTA diagrams of the cobalt(II) complexes attached to aminocarboxylate pillared hydrotalcite: 1. $\text{CoCl}_3 \cdot \text{ina-HT}$; 2. $\text{CoCl}_3 \cdot \text{glu-HT}$.

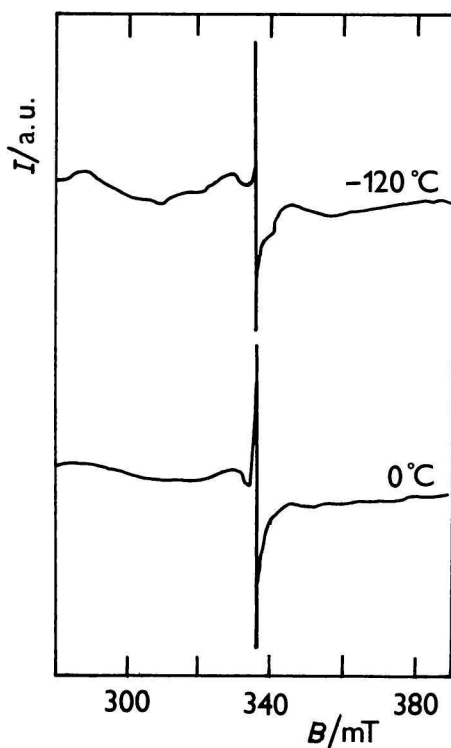


Fig. 8. ESR spectra of O_2 adduct of $\text{Co}(\text{salophen})\text{-ina-HT}$ in air (10^5 Pa).

ide, can be attributed to the degradation and/or combustion of the rest of the aminocarboxylate pillars and to the simultaneous partial crystallization of intermediate mixed aluminium magnesium solid solution.

Two paramagnetic species were detected when air was contacted with hydrotalcite derivatives containing $\text{Co}(\text{salen})$ or $\text{Co}(\text{salophen})$ attached to isonicotinate pillar (Fig. 8). The ESR spectrum consists of two overlapping signals: the narrow ($\delta H = 120$ mT) sym-

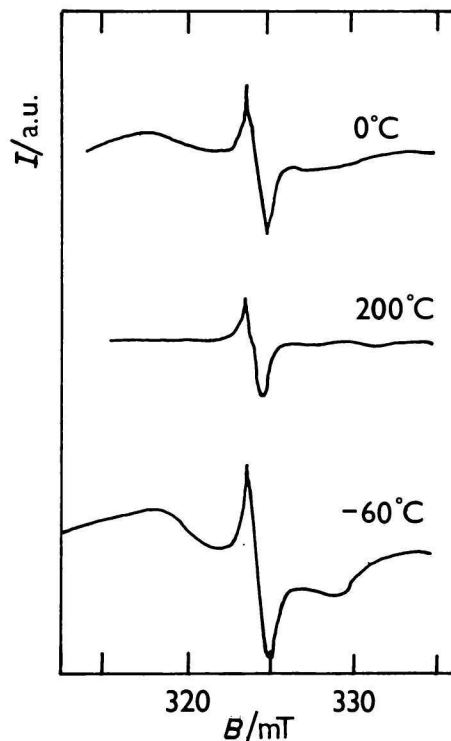


Fig. 9. ESR spectra of O_2 adduct of $\text{Co}(\text{salen})\text{-ina-HT}$ after exposure to air (0°C , 10^5 Pa); after heating at 200°C (recorded under argon atmosphere); further oxygen added (-60°C , 10^5 Pa).

metric signal (*I*) showing hyperfine structure and a second signal (*II*) with $g = 2.02$ and $\delta H = 950$ mT. The two signals could be separated by heating the sample to 300°C , which removes signal *II* while signal *I* reduces in intensity. After a decrease in temperature both signals were restored. Both signals were stable in the presence of air at 25°C and unchanged at -60°C , but their intensity was reduced slowly on heating above that temperature (Fig. 9). The oxygenation—deoxygenation—re-oxygenation process during cycling the temperature changes was repeated several times with no measurable loss in the low-temperature absorption ability. No ^{59}Co hyperfine splitting is observed in signal *I*, and g is close to g_e , which indicates that O_2^- is not bonded to the cobalt atom. Therefore we tentatively assign signal *I* to O_2^- in interaction with Al^{3+} centre on internal surface of derivatized hydrotalcite. The ESR signal *II* closely resembles the signal observed previously from other immobilized $\text{Co}(\text{salen})$ —dioxygen complexes, *i.e.* the oxygen complex should be formulated as $\text{Co}^{\text{II}}\text{-O}_2^{\cdot-}$. Cobalt(II) chelate complexes attached to derivatized hydrotalcite offer several advantages over analogous species formed in solution. These are as follows: *a*) The number, basicity, and arrangement of axially coordinated *N*-donor atoms in the structure of aliphatic and/or aromatic amines can be successively altered; *b*) the active complexes in intracrystalline environment

are immobilized; *c*) the large separation between the pairs of Co(II) atoms eliminates the possibility that the two adjacent cobalt species might simultaneously bind the same oxygen molecule, *i.e.* the dimerization (irreversible autoxidation, inactivation) process may be retarded; *d*) the synthesized intercalated cobalt(II) complexes exhibit reversible binding of dioxygen also in the presence of water vapour.

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