ELECTRONIC STATE OF IRON COMPLEXES IN THE INTERLAYER OF HYDROTALCITE-LIKE MATERIALS

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Abstract—Infrared and Mössbauer spectroscopic studies were made on hydrotalcite-like materials, $Mg_6Al_2(OH)_{16}(NO_3)_2\cdot4H_2O$, anion exchanged in aqueous solution of $K_3Fe(CN)_6$, $K_4Fe(CN)_6\cdot3H_2O$, or $Na_2Fe(CN)_5NO\cdot2H_2O$. The material anion-exchanged in aqueous solution of $K_3Fe(CN)_6$ gave infrared (IR) absorption bands at 2120 and 2040 cm^{-1} in the $C\equiv N$ stretching region, suggesting that part of the ferrate(III) complex was reduced to ferrate(II) complex on the intercalation chiefly because pure $K_3Fe(III)(CN)_6$ and $K_4Fe(II)(CN)_6\cdot3H_2O$ gives bands at 2120 and 2040 cm^{-1}, respectively. On the intercalation of $Fe(CN)_6^{4-}$, no change in the oxidation state of iron was observed. These features were confirmed by Mössbauer spectroscopy. In the IR spectra of material anion-exchanged in aqueous solution of $Na_2Fe(CN)_5NO\cdot2H_2O$, the intensity of bands due to $N\equiv O$ (1940 cm^{-1}) and $C\equiv N$ stretching was much less than that observed for $Na_2Fe(CN)_5NO\cdot2H_2O$, indicating that most of $N\equiv O$ ligand was eliminated during the intercalation. Four bands were observed in the $C\equiv N$ stretching region: a band at 2143 cm^{-1} was assigned to $C\equiv N$ groups in $Fe(CN)_5NO^{2-}$; a band at 2120 cm^{-1} was tentatively assigned to $Fe(CN)_5H_2O^{2-}$; bands at 2040–2050 cm^{-1} were assigned to $Fe(CN)_5H_2O^{3-}$.

Key Words—Anion exchange, Infrared spectroscopy, Hexacyanoferrate, Hydrotalcite, Intercalation, Iron oxidation.

INTRODUCTION

Hydrotalcite, $Mg_6Al_2(OH)_{16}CO_3\cdot4H_2O$, is one of the naturally occurring anionic clay minerals (Frondel, 1941; Allmann, 1970). Hydrotalcite-like materials can be synthesized in which other cations and anions proxy for the Mg, Al, and CO_3 ions and which can be expressed by a general formula (Miyata, 1975, 1980; Miyata and Okada, 1977).

$$[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}[A^{n-}_{x/n}\cdot mH_2O]^{x-},$$
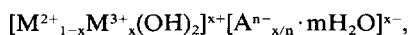
where M^{2+} and M^{3+} are metal cations, A^{n-} is an anion (such as NO_3^-, Cl^-, CO_3^{2-}, SO_4^{2-}, or CrO_4^{2-}), and $x = 0.2$–0.33. The divalent (M^{2+}) and trivalent (M^{3+}) cations are distributed among the octahedral layers to form positively charged sheets. Negatively charged interlayers between the sheets contain interlayer anions, A^{n-}, and water molecules.

Anions can be intercalated into the interlayer sites of these materials by an anion-exchange method (Miyata, 1983). Inasmuch as the interlayer spacing can be changed depending on the size of the intercalated anions, the surface area (Cavalcanti *et al.*, 1987) or the adsorption capacity for hydrocarbons (Cavalcanti *et al.*, 1987; Suzuki *et al.*, 1989) or for carbon dioxide (Miyata and Kumura, 1973; Miyata and Hirose, 1978) of the materials can be greatly modified by the intercalation of large anions, such as $Fe(CN)_6^{3-}$ or $Fe(CN)_6^{4-}$. Although the phenomenon of the intercalation for hydrotalcite-like materials has been well established, the state of the intercalated anions or the processes involved in the anion exchange have not yet been studied in detail.

In this work, the chemical states of $Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$, and $Fe(CN)_5NO^{2-}$ in a hydrotalcite-like material containing Mg^{2+}-Al^{3+}-NO_3^- ions were studied by infrared and Mössbauer spectroscopy. The reduction of ferrate(III) ions and ligand-exchange were both found to take place during the intercalation process.

MATERIALS AND METHODS

A hydrotalcite-like material containing Mg^{2+}-Al^{3+}-NO_3^- ions (I) was synthesized at 65°C by the method described by Miyata (1975), using aqueous solutions of $Mg(NO_3)_2\cdot6H_2O$, $Al(NO_3)_3\cdot9H_2O$, and NaOH. The amount of Mg^{2+} and Al^{3+} in the material (I) thus synthesized was determined by the chelate titration of the sample dissolved in dilute hydrochloric acid (Miyata, 1975). The anion-exchange capacity was determined to be 3.25 meq/g. Three grams of this material (9.75 meq anion-exchange capacity) was suspended with stirring in 300 cm^3 of decarbonated water containing $K_3Fe(CN)_6$, $K_4Fe(CN)_6\cdot3H_2O$, or $Na_2Fe(CN)_5NO\cdot2H_2O$ (58.5 meq of ferrate ions) under a nitrogen atmosphere at 60°C for 2 hr. The solid was filtered, washed with decarbonated water, and dried in vacuo or in air at 110°C for 12 hr. All reagents were obtained from Kanto Chemical Co., Inc.

Infrared (IR) spectra were recorded on a Shimadzu IR-460 spectrophotometer in an air atmosphere by the KBr pellet method. The 12-mm-diameter pellets were obtained by pressing in air at 600 kg/cm² for 1 min a powder mixture containing 49 mg of KBr and 0.74 mg of hydrotalcite-like materials. X-ray powder diffraction (XRD) patterns of samples were recorded on a Philips
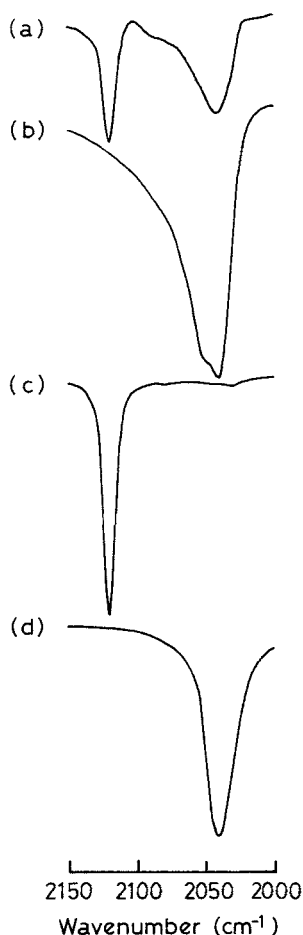
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Figure 1. Infrared spectra for the hydrotalcite-like materials anion-exchanged in aqueous solutions of (a) $K_3Fe(CN)_6$ and (b) $K_4Fe(CN)_6 \cdot 3H_2O$ and for (c) pure $K_3Fe(CN)_6$ and (d) $K_4Fe(CN)_6 \cdot 3H_2O$.

PW 1700 diffractometer using monochromatic CuKα radiation, operating at 40 kV and 30 mA. Mössbauer spectra were taken in air with a constant acceleration spectrometer (Elron Electronics), using a 512 channel analyzer. Ten millicuries of ^{57}Co in a Rh matrix was used as a source, and the samples were prepared by mixing an adhesive with hydrotalcite-like materials in air. Isomer shifts were determined relative to $Na_2Fe(CN)_5NO \cdot 2H_2O$. Specific surface areas were determined by a nitrogen adsorption method using a conventional static adsorption apparatus.

RESULTS AND DISCUSSION

Anion exchange with $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$

The degree of anion exchange with $Fe(CN)_6^{3-}$ was determined to be 84% from the decrease in the intensity of IR absorption band at 1380 cm^{-1} characteristic of NO_3^- interlayer anion. The XRD patterns indicated

the presence of two sets of solid phases having different interlayer spacings. One phase had the same non-expanded basal spacing (8.2 Å) as the original material (I), and the other had an expanded spacing of 10.7 Å. Assuming a layer thickness of 4.8 Å (Miyata, 1975), the interlayer spacing of the expanded phase was estimated to be 5.9 Å, in accord with that reported in earlier studies on the intercalation of $Fe(CN)_6^{3-}$ (Cavalcanti et al., 1987), $Fe(CN)_6^{4-}$ (Kikkawa and Koizumi, 1982), and $Co(CN)_6^{3-}$ (Suzuki et al., 1989). This spacing indicates that the complexes were located in the interlayer sites and had their three-fold symmetry axes perpendicular to the host layer. The expansion of the interlayer spacing was confirmed by an increase in the specific surface area from 13 to 380 m²/g upon the anion exchange.

Figure 1a shows an IR spectrum of the original material (I) anion-exchanged in aqueous solution containing $Fe(CN)_6^{3-}$ and dried in vacuo. The material gave absorption bands at 2120 and 2040 cm^{-1} in the C≡N stretching region. Figures 1c and 1d show the C≡N stretching bands for pure $K_3Fe(CN)_6$ and $K_4Fe(CN)_6 \cdot 3H_2O$, respectively. Note the strong absorption bands at 2120 and 2040 cm^{-1}, respectively. In general, the frequency of the C≡N stretching in cyanoferrate complexes is sensitive to the oxidation state of the iron in the complex (Tosi and Danon, 1964). The C≡N stretching bands are in the range 2050–2070 cm^{-1} for Fe(II) complexes of $Fe(CN)_5X$ and in the range 2115–2125 cm^{-1} for Fe(III) complexes of the same type. Thus, the absorption band at 2120 cm^{-1} can be assigned to the C≡N stretching of the intercalated hexacyanoferrate(III) ions. The existence of the band at 2040 cm^{-1} for the material anion-exchanged in an aqueous solution of $Fe(CN)_6^{3-}$ suggests that the Fe(III) complex was reduced to a Fe(II) complex upon intercalation. A simple ligand exchange cannot explain the large band shift of 80 cm^{-1}.

The IR spectrum of the hydrotalcite-like material (I) anion-exchanged in an aqueous solution of $Fe(CN)_6^{4-}$ and dried in vacuo is shown in Figure 1b. The C≡N stretching band is at 2040 cm^{-1}, as expected. On the other hand, if the material (I) was subjected to an anion exchange in a solution of $Fe(CN)_6^{4-}$ and kept in air or dried in air at 110°C, a new band appeared at 2120 cm^{-1}, indicating the oxidation of Fe(II) to Fe(III). The oxidation of $Fe(CN)_6^{4-}$ to $Fe(CN)_6^{3-}$ was reported by Cavalcanti et al. (1987). Itaya et al. (1987) also reported that a redox cycle of hexacyanoferrate ion in interlayer sites of a hydrotalcite-like material can be achieved by an electrochemical method, suggesting strongly that the redox cycle occurs without change in ligands. Actually, hexacyanoferrate ions are known to be an outer-sphere electron-transfer reductant or oxidant (Gordon et al., 1961; Pelizzetti et al., 1976).

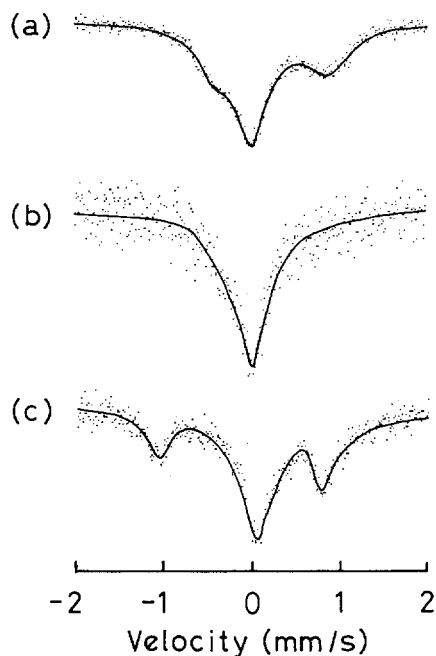Ferrate(III) ions can be reduced to ferrate(II) ions under pressure for many compounds (Champion and

Figure 2. Mössbauer spectra for the hydrotalcite-like materials anion-exchanged in aqueous solutions of (a) $K_3Fe(CN)_6$, (b) $K_4Fe(CN)_6 \cdot 3H_2O$, and (c) $Na_2Fe(CN)_5NO \cdot 2H_2O$.

Figure 3. Infrared spectra for the hydrotalcite-like materials anion-exchanged in aqueous solution of (a–d) $Na_2Fe(CN)_5NO \cdot 2H_2O$ and (e) the pure $Na_2Fe(CN)_5NO \cdot 2H_2O$. The materials before the anion exchange had been obtained at pHs of (a) 8.5, (b) 10.0, (c) 11.0, and (d) 13.0 in their preparation stages.

Drickamer, 1967; Drickamer et al., 1969; Larsen and Drickamer, 1957). The ferrate(III) ion is probably not reduced to ferrate(II) ion during the preparation of pellets under pressure, because the reduction was observed also in IR spectra for samples prepared by dispersing powder of the anion-exchanged materials (I) onto a KBr plate. The extent of reduction observed for the samples prepared by different methods was the same. In addition, as will be described below, Mössbauer spectroscopic studies of samples prepared under no pressure also revealed the reduction of ferrate(III) ions.

The information on the oxidation states of the ion complexes was obtained also by Mössbauer spectroscopy. Figures 2a and 2b show the Mössbauer spectra of the hydrotalcite-like material (I) subjected to anion exchange in an aqueous solution of $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$, respectively.

The spectrum for the material anion-exchanged with $Fe(CN)_6^{3-}$ suggests the presence of two kinds of iron species. One species shows a doublet having an isomer shift of $\delta = 0.25$ mm/s (with respect to $Na_2Fe(CN)_5NO \cdot 2H_2O$) and a quadrupole splitting of $\Delta E = 1.26$ mm/s. The other species shows a single absorption with $\delta = 0.00$ mm/s without an apparent quadrupole splitting.

The former species is probably $Fe(CN)_6^{3-}$, because the values of the isomer shift and the quadrupole splitting are in the range of the metal salts of hexacyano-

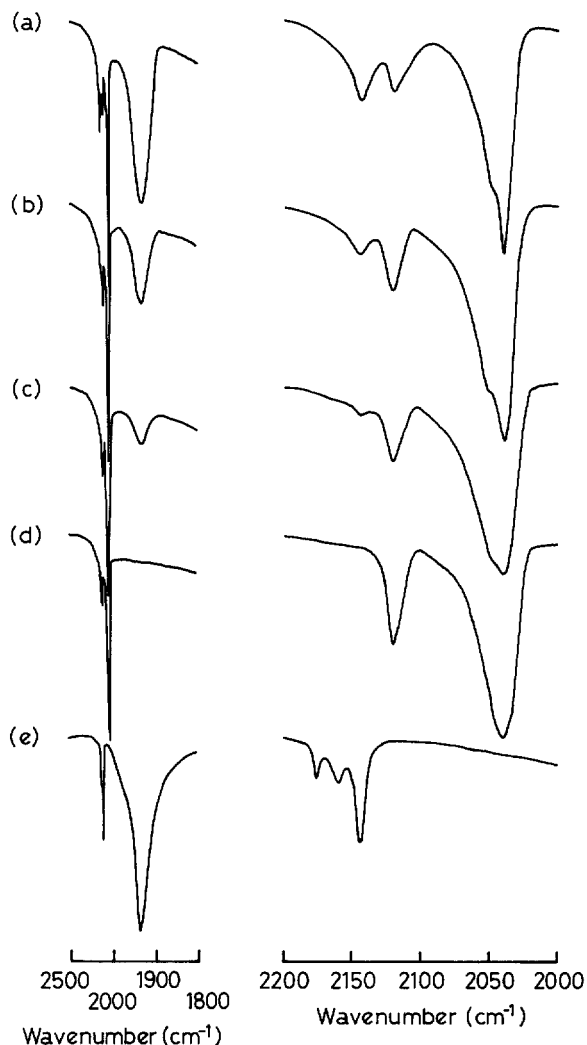ferrate(III), although both values are close to the upper ends of the groups (Fluck et al., 1963).

The rather large value of the quadrupole splitting indicates that ferrate ions in intercalated hexacyanoferrate(III) complex were not in an octahedral environment. The large complex ions in the interlayers must have had to contend with high stress from the host layers in order to maintain the expanded interlayer distance. Then, the $Fe(CN)_6^{3-}$ ions were probably distorted in the direction of the three-fold symmetry axis, inasmuch as the interlayer spacing of 5.9 Å indicates that the complex was located with its three-fold symmetry axis perpendicular to the host layers. This orientation may have caused an uneven population of

electrons among t_{2g} orbitals. The rather large isomer shift also indicates a partial electron transfer from the complex to the host layers through C≡N ligands, resulting in a decrease in the number of 3d electrons in the iron atom.

The lack of the quadrupole splitting for the absorption at $\delta = 0.00$ mm/s indicates that the second species was hexacyanoferrate(II) ions formed by the reduction of the corresponding ferrate(III). These data confirm the result obtained by IR. Ferrate(III) ions can also be reduced to ferrate(II) ions under pressure for many compounds (Champion and Drickamer, 1967; Drickamer *et al.*, 1969; Larsen and Drickamer, 1957).

The complexes in the interlayer sites of the material may have been subjected to large stress from the host layers and may have been compressed, as described above. Actually, hexacyanoferrate(II) ion has a smaller effective radius (4.33 Å) than the corresponding ferrate(III) ion (4.45 Å) (Brown and Shriver, 1969), which may relieve the stress on the complex. Fukushima and Kamigaito (1984) estimated that the stress on intercalated molecules is about 500 kg/cm², if interlayer spacing of the host materials is expanded by about 20%.

The value of the isomer shift ($\delta = 0.00$ mm/s) also supports this idea. The iron atom in most of metal salts of hexacyanoferrate(II) shows an isomer shift of 0.10–0.35 mm/s, which is much larger than that for the complex ion in the interlayers. Champion and Drickamer (1967) reported that the isomer shift for Fe in potassium hexacyanoferrate(III) decreases by 0.20 mm/s under pressure of 200 kg/cm². Thus, the smaller value of the isomer shift of the complex may be explained by the high stress which the host layers exert on the complex ions in the interlayer sites.

The hydrotalcite-like material (I) anion-exchanged in an aqueous solution of $Fe(CN)_6^{4-}$ gave the Mössbauer spectrum shown in Figure 2b. The single absorption at $\delta = 0.00$ mm/s is in accord with the second species found in the material anion-exchanged with hexacyanoferrate(III), also supporting the conclusion on the electronic state of the ferrate(II) ion in the interlayer sites.

The mechanism for reduction of $Fe(CN)_6^{3-}$ upon intercalation is not clear at this moment. Larsen and Drickamer (1957) supposed an equation,

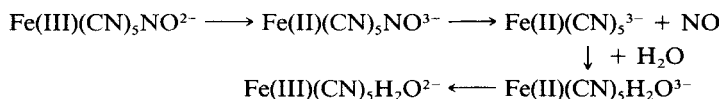$$4\ K_3Fe(CN)_6 \rightarrow 3\ K_4Fe(CN)_6 + Fe + 6/x\ (CN)_x,$$
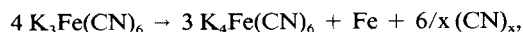
for the reduction of ferrate(III) to ferrate(II) ion observed in a plastic deformation of $K_3Fe(CN)_6$ at high pressure. We speculate that the reduction in the inter-

calation process proceeded in the same manner as supposed by Larsen and Drickamer. Thus, the reduction involved the transfer of electrons from one anion to three others; the release of negative charge would decrease the size of the anion. Inasmuch as the hexacyanoferrate(II) ion formed in this way was more stable than hexacyanoferrate(III) ions, the electron deficient anion had no means of regaining its lost electron. Instead, it probably released two other electrons and split off cyanide radicals to form paracyanogen, $(CN)_x$, and iron, Fe.

Anion exchange with $Fe(CN)_5NO^{2-}$

Hydrotalcite-like materials (I) were prepared at four different pHs. The XRD patterns of these four materials show that each had the structure of hydrotalcite, but that the crystallinity of the material was greater if it had been prepared at the higher pH. These materials were subjected to anion exchange in an aqueous solution of sodium nitrosylpentacyanoferrate(III). The interlayer spacing was expanded to 5.7 Å by the intercalation. Figure 3 shows the IR spectra of the four materials and pure sodium nitrosylpentacyanoferrate(III). In addition to the absorption band due to a N≡O stretching (1940 cm⁻¹) (Bor, 1961), four bands are present in the C≡N stretching region (2040–2143 cm⁻¹). The intensity ratio of bands due to N≡O and C≡N stretching observed for the materials is much smaller than that observed for sodium nitrosylpentacyanoferrate(III), indicating that most of the N≡O ligand was eliminated during the anion-exchange process. The intensity of the N≡O stretching is smaller for the ferrate ion if this ion had been intercalated in the material prepared at the higher pH. The intensity of the C≡N stretching band at 2143 cm⁻¹, which occurs also in the IR spectrum of $Na_2(CN)_5NO \cdot 2H_2O$, similarly decreased and, thus, can be assigned to C≡N groups in $Fe(CN)_5NO^{2-}$ in the interlayer sites. The intensities of the other three bands at 2120, 2050, and 2040 cm⁻¹ increased with an increase in the pH at which the materials had been prepared. As discussed above, the band at 2120 cm⁻¹ may be due to C≡N stretching in the hexacyanoferrate(III), and the bands at 2040 and 2050 cm⁻¹ may be due to those in the hexacyanoferrate(II) complex. The appearance of a band at 580 cm⁻¹ for the M–C≡N bending also indicates the presence of ferrate(II) species (Brown, 1971).

The ferrate(III) ions may have been reduced under the stress of the host layers, inducing the elimination of neutral N≡O ligand and resulting in the ligand exchange in the presence of water as follows:

$$Fe(III)(CN)_5NO^{2-} \longrightarrow Fe(II)(CN)_5NO^{3-} \longrightarrow Fe(II)(CN)_5^{3-} + NO$$
$$\downarrow + H_2O$$
$$Fe(III)(CN)_5H_2O^{2-} \longleftarrow Fe(II)(CN)_5H_2O^{3-}$$

Thus, the bands at 2120 cm^{-1} and 2040–2050 cm^{-1} are probably assignable to $Fe(CN)_5H_2O^{2-}$ and $Fe(CN)_5H_2O^{3-}$, respectively. In fact, $Fe(CN)_5H_2O^{2-}$ and $Fe(CN)_5H_2O^{3-}$ give strong C≡N stretching bands at 2132 and 2045 cm^{-1}, respectively (Tosi and Danon, 1964). The reason why, for the material (I) prepared at the higher pH, the electronic state of iron complex on intercalation changed easily is not understood at this moment.

Carrado *et al.* (1988) also concluded from ESR data that the pentacyanonitrosyl moiety is decomposed in the interlayer sites of a hydrotalcite-like material. The electronic state of iron in the hydrotalcite-like material (I) prepared at pH 10 and anion-exchanged in aqueous solution of $Fe(CN)_5NO^{2-}$ was confirmed by Mössbauer spectroscopy. As shown in Figure 2c, three kinds of species were present. One shows an isomer shift of $\delta = -0.11$ mm/s and a quadrupole splitting of $\Delta E = 1.83$ mm/s, suggesting that the species responsible is $Fe(CN)_5X^{2-}$ (X = H_2O or NO), where X = H_2O is more probable (Brown, 1971; Costa *et al.*, 1962). The reported values of the Mössbauer parameters for $Fe(CN)_5H_2O$ are $\delta = 0.12$ mm/s and $\Delta E = 1.82$ mm/s. A second species has parameters of $\delta = 0.42$ mm/s and $\Delta E = 0.82$ mm/s, which may be attributed to $Fe(CN)_5X^{3-}$, judging from the size of the quadrupole splitting (Brown, 1971; Costa *et al.*, 1962). A third species shows a single peak at $\delta = 0.06$ mm/s, the origin of which is not clear at this moment.

ACKNOWLEDGMENTS

REFERENCES

Allmann, R. (1970) Doppelschichtstrukturen mit brucitähnlichen Schichtionen $[Me(II)_{1-x}Me(III)_x(OH)_2]^{x+}$: *Chimia* **24**, 99–108.

Bor, G. (1961) High-resolution infra-red spectrum of the $[Fe(CN)_5NO]^{2-}$ ion: *J. Inorg. Nucl. Chem.* **17**, 174–175.

Brown, D. B. (1971) On the effective charge of iron in nitroprusside: *Inorg. Chim. Acta.* **5**, 314–316.

Brown, D. B. and Shriver, D. F. (1969) Structures and solid-state reactions of prussian blue analogs containing chromium, manganese, iron, and cobalt: *Inorg. Chem.* **8**, 37–42.

Carrado, K. A., Kostapapas, A., and Suib, S. L. (1988) Layered double hydroxides (LDHs): *Solid State Ionics* **26**, 77–86.

Cavalcanti, F. A. P., Schutz, A., and Biloen, P. (1987) Interlayer accessibility in layered double-metal hydroxides: in *Preparation of Catalysts IV*, B. Delmon, P. Grange, P. A. Jacobs, and G. Poncelet, eds., Elsevier, Amsterdam, 165–174.

Costa, N. L., Danon, J., and Xavier, R. M. (1962) Measurement of nuclear quadrupole interaction in iron complexes using the Mössbauer effect: *J. Phys. Chem. Solids* **23**, 1783–1785.

Champion, A. R. and Drickamer, H. G. (1967) Effect of pressure on the Mössbauer resonance in potassium ferrocyanide, potassium ferricyanide, and insoluble prussian blue: *J. Chem. Phys.* **47**, 2591–2594.

Drickamer, H. G., Lewis, G. K., Jr., and Fung, S. C. (1969) The oxidation state of iron at high pressure: *Science* **163**, 885–890.

Fluck, E., Kerler, W., and Neuwirth, W. (1963) The Mössbauer effect and its significance in chemistry: *Angew. Chem., Int. Ed. Engl.* **2**, 277–287.

Frondel, C. (1941) Constitution and polymorphism of the pyroaurite and sjogrenite groups: *Amer. Miner.* **26**, 295–315.

Fukushima, Y. and Kamigaito, O. (1984) Layered oxide compounds—Reactions in the intercalated compounds and its applications: *Seramikkusu* **19**, 109–113.

Gordon, B. M., Williams, L. L., and Sutin, N. (1961) The kinetics of the oxidation of iron(II) ions and of coordination complexes: *J. Amer. Chem. Soc.* **83**, 2061–2064.

Itaya, K., Chang, H.-C., and Uchida, I. (1987) Anion-exchanged hydrotalcite-like-clay-modified electrodes: *Inorg. Chem.* **26**, 624–626.

Kikkawa, S. and Koizumi, M. (1982) Ferrocyanide anion bearing Mg,Al hydroxide: *Mat. Res. Bull.* **17**, 191–198.

Larsen, H. A. and Drickamer, H. G. (1957) Chemical effects of plastic deformation at high pressure: *J. Phys. Chem.* **61**, 1249–1252.

Miyata, S. (1975) The synthesis of hydrotalcite-like compounds and their structures and physico-chemical properties-I. The systems $Mg^{2+}-Al^{3+}-NO_3^-$, $Mg^{2+}-Al^{3+}-Cl^-$, $Mg^{2+}-Al^{3+}-ClO_4^-$, $Ni^{2+}-Al^{3+}-Cl^-$, and $Zn^{2+}-Al^{3+}-Cl^-$: *Clays & Clay Minerals* **23**, 369–375.

Miyata, S. (1980) Physico-chemical properties of synthetic hydrotalcites in relation to composition: *Clays & Clay Minerals* **28**, 50–55.

Miyata, S. (1983) Anion-exchange properties of hydrotalcite-like compounds: *Clays & Clay Minerals* **31**, 305–311.

Miyata, S. and Hirose, T. (1978) Adsorption of N_2, O_2, CO_2, and H_2 on hydrotalcite-like system. $Mg^{2+}-Al^{3+}-(Fe(CN)_6)^{4-}$: *Clays & Clay Minerals* **26**, 441–447.

Miyata, S. and Kumura, T. (1973) Synthesis of new hydrotalcite-like compounds and their physico-chemical properties: *Chem. Lett.*, 843–848.

Miyata, S. and Okada, A. (1977) Synthesis of hydrotalcite-like compounds and their physico-chemical properties—The systems $Mg^{2+}-Al^{3+}-SO_4^{2-}$ and $Mg^{2+}-Al^{3+}-CrO_4^{2-}$: *Clays & Clay Minerals* **25**, 14–18.

Pelizzetti, E., Mentasti, E., and Baiocchi, C. (1976) Kinetics and mechanism of oxidation of quinols by hexachloroiridate(IV) in aqueous acidic perchlorate media: *J. Phys. Chem.* **80**, 2979–2982.

Suzuki, E., Idemura, S., and Ono, Y. (1989) Properties of hexacyanocobaltate(III)-exchanged hydrotalcite-like minerals: *Clays & Clay Minerals* **37**, 173–178.

Tosi, L. and Danon, J. (1964) Infrared spectral evidence of π-bonding in the $Fe(CN)_5NO^{2-}$ ion: *Inorg. Chem.* **3**, 150–151.