Anionic Clays with Variable Valence Cations: Synthesis and Characterization of $[Co_{1-x}Al_x(OH)_2](CO_3)_{x/2}\cdot nH_2O$

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The synthesis of hydrotalcite-like compounds containing cobalt(II) ions in the layer lattice is described. Hydrothermal treatment of freshly precipitated materials, which is normally carried out to improve crystallinity, leads to a partial oxidation of Co(II) to Co(III) species, with simultaneous formation of a well dispersed Co_3O_4 spinel phase. Formation of this compound seems to be responsible for the low thermal stability observed for the Co(II)–Al(III)–CO_3^{2-} hydroxytalcite.

Introduction

Hydrotalcite-like compounds (HT), so-called "anionic clays", are layered double hydroxides with general formula $[M_{1-x}M'_x(OH)_2]^{x+}(X)_{x/m}\cdot nH_2O$, where M = Mg(II), Zn(II), Ni(II), ..., M′ = Al(III), Fe(III), ..., and X = CO_3^{2-}, NO_3^-, SO_4^{2-}, ... Their structure consists of brucite-like layers, [MM′(OH)$_2$], positively charged because of substitution by trivalent cations, with the interlayer space filled with anions and water molecules.[1-3] These materials exhibit anion-exchange properties,[4] and the interlayer space can be changed depending on the size of the intercalated anions.[5,6] Upon thermal decomposition, they lead to mixed oxides.[7,8] Both HT and heat-treated HT compounds find applications as anion scavangers from aqueous solutions and as catalysts or catalysts supports.[9-11]

Most of the papers reported in the literature on these compounds deal with main-group elements or transition elements with only a single stable oxidation state, and when cations with more than one stable oxidation state exist, they are usually in the most stable form (i.e., Fe(III) instead of Fe(II)). In this paper we report the synthesis and characterization of a Co,Al–hydroxycarbonate compound containing Co(II) cations with a hydrotalcite structure. Synthesis of this type of materials has been previously reported by Reichle,[12] but he has not reported the interesting features of these samples and their behavior upon ageing, say, Co(II)/Co(III) oxidation, according to the experimental conditions used during its synthesis.

Experimental Section

The preparation of the compounds studied here has been carried out following one of the methods described in the literature to prepare hydrotalcite materials.[12] Briefly, an aqueous solution of Co(II) and Al(III) ions is added with vigorous stirring to an aqueous solution of NaOH–Na_2CO_3 at room temperature. The final pH was 12.2. The molar NaOH:Co ratio was 2:1, and the carbonate content was 3 times that corresponding to the stoichiometric value. The gel thus obtained was aged for 48 h at room temperature, leading to a brownish-pink solid (sample M1) that changes to deep brown (almost black) after hydrothermal ageing at 343 K for 36 h (sample M2). All chemicals used were from Merck.

The Co/Al ratio was determined in a Philips PSEM 500 microscope coupled to an energy-dispersive X-ray EDAX International analysis system. This system was equipped with an ECON IV detection unit and a PV9900 data processor; the value calculated was close to Co:Al = 2.2:1 in both samples. X-ray diffraction patterns were recorded on a Philips PW 1130 instrument, using Co Kα radiation, at a scanning speed of 1° (2θ) min^{-1}. Transmission electron micrographs (TEM) were obtained on a JEOL 200CX microscope. The visible–ultraviolet/diffuse reflectance (visible–UV/DR) spectra were recorded on a Shimadzu UV-240 instrument with a diffuse reflectance accessory, using a slit of 5 nm and MgO as a reference. DTA and TG and DTG profiles were recorded in Perkin-Elmer DTA 1700 and TGS-2 instruments, respectively, using air or nitrogen (60 mL/min in both cases) at a heating rate of 12 K/min. Specific surface area measurements were carried out in a Micromeritics Flowsorb II 2300 apparatus.

Results and Discussion

The electron micrographs of the samples show that they have similar morphologies (Figure 1) with a hexagonal lamellar shape and are slightly larger for sample M2 than for sample M1. The particles form stacks that can be seen parallel or perpendicular to the observation direction. The fact that the shape and size of the particles do not change too much upon ageing is somewhat unexpected, as previous studies that we have carried out on several hydroxycarbonates subjected to similar hydrothermal treatments[13] have shown a very appreciable increase in the particle size

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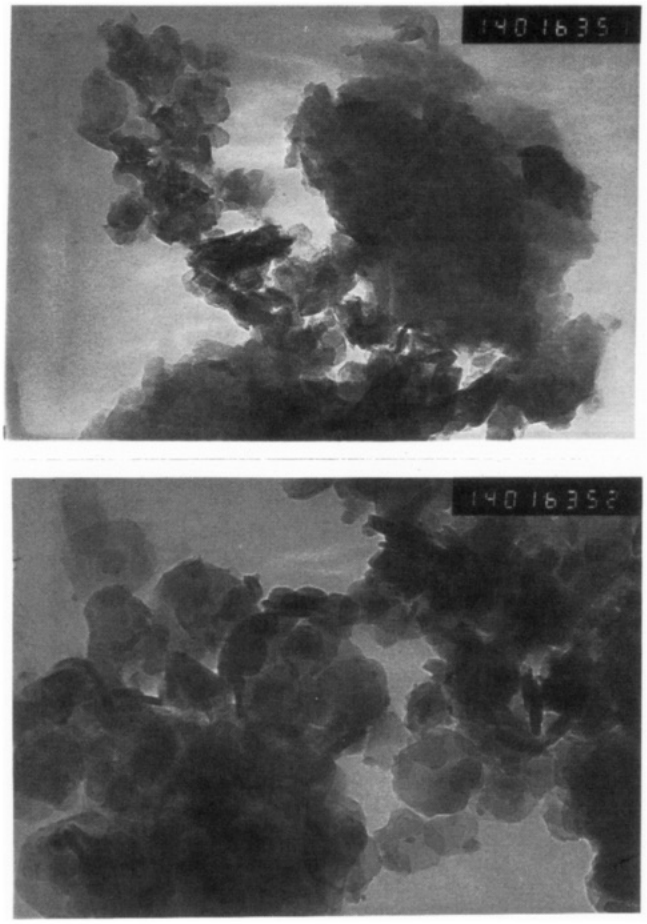

Figure 1. Transmission electron micrographs of samples M1 and M2 (×99 500).

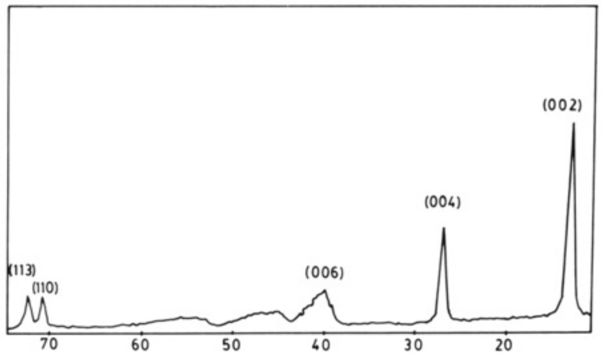

Figure 2. X-ray diffraction pattern of sample M2.

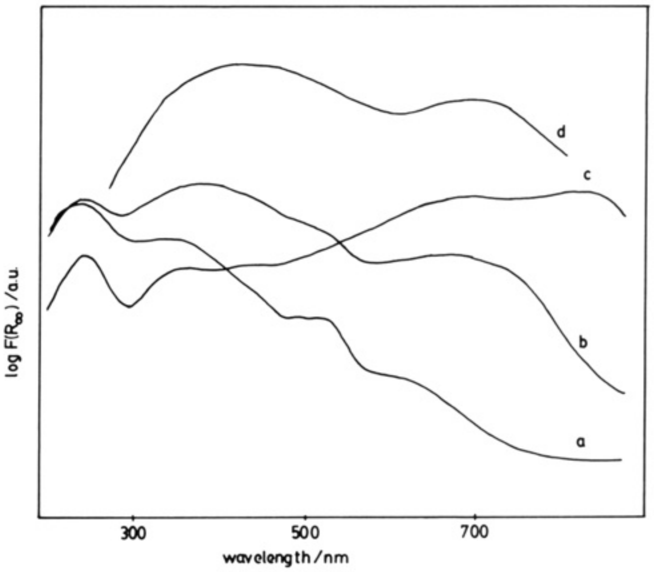

Figure 3. Visible–ultraviolet/diffuse reflectance spectra of samples (a) M1, (b) M2, (c) after hydrothermal treatment at 400 K for 8 days, and (d) Co_3O_4. Reference: MgO.

after such a treatment of the samples. This increase in the particle size is generally related to a sintering of the crystallites during the hydrothermal treatment. The fact that in the present work the particle size increases only slightly when the sample is hydrothermally treated, whereas the color changes appreciably, suggests that the sample does not simply sinter, but that a chemical transformation may occur. On the basis of the results shown below, we suspect that some cobalt spinel (Co_3O_4) is formed.

The XRD diagrams do not show any appreciable difference for the samples before and after hydrothermal treatment with regard to the existing phases and their degree of crystallinity; for example, the results for sample M2 are shown in Figure 2. The spacing corresponding to the unit layer thickness (d_{002}) is of the same order as for other HT materials with carbonate anions and water molecules in the interlayer space,[3,14] thus confirming that the interlayer spacing is mainly controlled by the size of the anion and not by the nature of the cations existing in the brucite-like layers. However, some minor differences can be observed in the position of the main diffraction lines. Peaks due to the (00*l*) planes are recorded at 7.96 and 7.50 Å (002) (1 Å = 100 pm), 3.88 and 3.80 Å (004), and 2.61 and 2.59 Å (006) for samples M1 and M2, respectively. These results indicate that the hydrothermal treatment has led to a small but observable decrease in the interlayer spacing. With Mg(II) and Al(III) ions in the brucite-like layers, however, the interlayer spacing slightly *increases* upon thermal treatment of the samples.[15] In both cases, carbonate ions exist in the interlayer space, and so the decrease observed in the interlayer space for sample M2 upon hydrothermal treatment should be related to the chemical changes taking place during such a treatment, probably because of the presence of oxidizable ions in the present case.

Neither electron microscopy nor XRD show important differences between the samples, but the color change from pink to blackish brown upon thermal treatment suggests a partial oxidation of Co(II) species to Co(III) similar to the reported oxidation of $Co(OH)_2$ while exposed to air in an aqueous solution.[16] To check this assumption, the visible–UV/DR spectra shown in Figure 3 were recorded. For comparison purposes, the spectrum of bulk Co_3O_4, obtained by decomposition in air of $CoCO_3$, is also included in this figure. For sample M2 a broad band centered at 800–600 nm, probably due to Co(III) species and absent in the spectrum of sample M1, is observed, suggesting that the thermal treatment at 343 K partially oxidizes Co(II) species to Co(III) ones, but leading to very well dispersed moieties, as the XRD diagram does not show any line that could be ascribed to the presence of crystallized Co_3O_4 particles. Moreover, when the sample is treated hydrothermally at ca. 400 K or for a prolonged period of time at room temperature, its XRD diagram very clearly shows (and almost exclusively) the diffraction lines of Co_3O_4, and the visible–UV spectrum of this sample shows an almost

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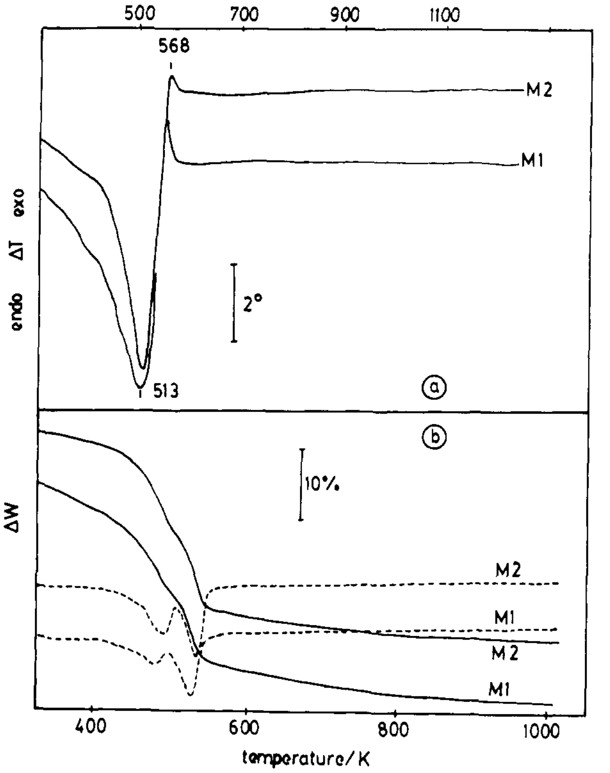

Figure 4. (a) DTA profiles of samples M1 and M2 recorded in air. (b) TG profiles of samples M1 and M2 recorded in air. Dotted lines: DTG profiles.

continuous absorption above 500 nm (Figure 3c), very similar to that shown by Co_3O_4. The shoulder recorded around 500 nm in the spectrum of sample M1 (where crystalline Co_3O_4 seems to be absent), formed by two or three component bands, probably arises from Co(II) species in an octahedral environment, [CoO_6], in the layer of the hydroxide, as its position and relatively low intensity, if compared to that of the bands shown by Co_3O_4, are similar to those of the bands recorded in the visible–UV spectrum of coordination compounds of Co(II) octahedrally coordinated by weak-field ligands,[17] such as $[Co(H_2O)_6]^{2+}$.

The DTA diagrams for these samples, recorded in air, are shown in Figure 4a. An intense endothermic peak centered at 513 K is observed in both cases with a weak, but detectable, exothermic peak at 568 K, the latter being appreciably less intense for sample M2. The endothermic peak for sample M1 is broader than that for sample M2 and shows a series of shoulders, indicating that several peaks are overlapped in this temperature range. The total weight loss takes place mainly at around 520 K in two overlapped steps and corresponds, as determined from the TG profiles in Figure 4b, to 33% for sample M1 and 30% for sample M2. About 25% of weight is lost below 540 K, and above this temperature the TG curves exhibit an almost horizontal *plateau*. Taking into account the similar thermal decomposition patterns of hydrotalcite materials containing Mg and Al,[15] the weight loss and the endothermic effect at 513 K should correspond to removal of interlayer water molecules, CO_2 (from carbonate ions), and water (from condensation of hydroxyl groups). Thermal decomposition of brucite through removal of hydroxyl groups as water molecules[18] takes place between 600 and 800 K, and so the small weight loss above 540 K should be ascribed to elimination of residual hydroxyl groups from the brucite-like sheets, which withdrawal is probable hindered by diffusion at a lower temperature. Taking into account the fact that the amounts of sample used to perform these analyses were almost identical, it should be noted that the exothermic effect is about 4–5 times more intense for sample M1 than for sample M2. As this exothermic effect is recorded at the same temperature for both samples, it should correspond to the same physicochemical change taking place in both samples. In such a case, the amount of species reacted (i.e., giving rise to this effect) in sample M2 is about 4–5 times lower than in sample M1. We will discuss this further later.

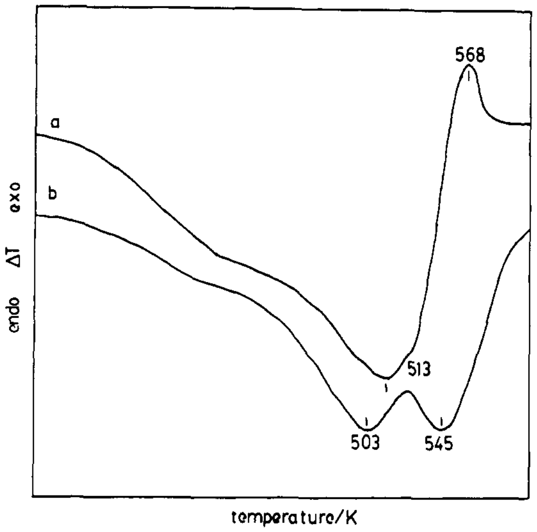

Figure 5. DTA profiles of sample M1 recorded in (a) air and (b) nitrogen.

The thermal behavior of these samples is fairly similar to that of HT-like compounds such as $[Al_2Li(OH)_6]_2(CO_3)\cdot nH_2O$ that decompose below 570 K also in single step.[19,20] The relatively low stability of these samples is, however, quite different from that shown by other HT-like compounds with nonoxidizable cations in the layers, where decomposition takes place in two or three steps: Loss of interlayer water takes place at around 470 K, leading to a decrease in the crystallographic *c* parameter, while the layered structure collapses at 770 K or even above.[3,20,21] This lower stability appears to be related to the existence of cations that are oxidizable in the samples studied here.

The exothermic effect recorded at 568 K, which is absent in the DTA patterns of other HT-like compounds without oxidizable cations, can be ascribed to a Co(II) → Co(III) oxidation process, as it is not observed when the analysis is carried out in nitrogen, as shown in Figure 5 for sample M1; instead, the exothermic peak splits into two minima at 503 and 545 K. Probably, elimination of water and carbonate anions, without the change of oxidation of Co(II) species, gives rise to a different decomposition pattern. As mentioned above, the exothermic peak is less intense for sample M2 than for sample M1 (Figure 4a) as the former sample should have already become partially oxidized during the hydrothermal treatment, as confirmed by the fact that its visible–UV/DR spectrum already shows bands

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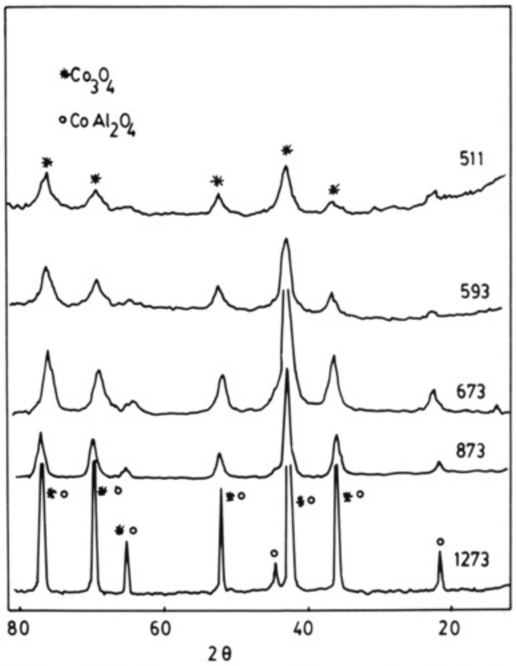

Figure 6. X-ray diffraction patterns of the samples obtained upon calcination of sample M1 at the indicated temperatures (K).

that can be ascribed to the presence of Co_3O_4-like species. It should be noted that Co_3O_4 is more stable than CoO in the presence of oxygen below 1200 K.[22]

HT-like materials are sometimes used as precursors of high specific surface area mixed oxides. Usually, due to the simultaneous presence of M(II) and M(III) cations, spinel structures are formed together with the oxide of the metal present above the stoichiometric value to form AB_2O_4 species.[23-26] We have checked the phases existing after calcination at increasing temperatures (those leading to formation of new phases, according to the DTA profiles) that have been identified by XRD (Figure 6). The XRD profiles of the sample calcined in air at 511 and 593 K (just before and after the exothermic effect) clearly show the presence of Co_3O_4 as the only crystalline phase, in agreement with the visible–UV/DR data shown above (Figure 3c). As the calcination temperature is increased (673, 873 K), the crystallinity of the spinel is improved, while the ratio between the intensities of the peaks due to Co_3O_4 is maintained. After heating at 1273 K, the diagrams are more complicated, with peaks that can be ascribed to Co_3O_4, $CoAl_2O_4$, and/or Co_2AlO_4. However, from the intensity ratio of the peaks recorded close to $2\theta = 22$ and 45°, it can be concluded that the compounds existing after heating at 1273 K are a mixture of Co_3O_4 and $CoAl_2O_4$.

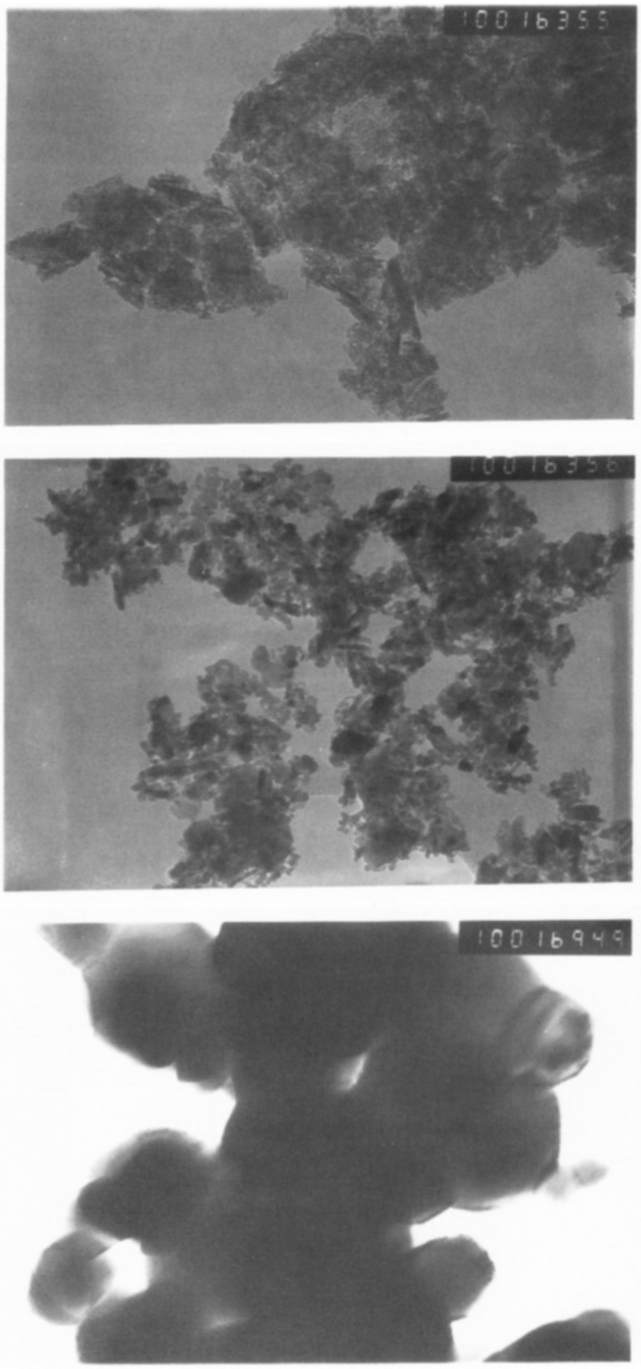

Figure 7. Transmission electron micrographs of sample M1 submitted to calcination at (a) 573 K, (b) 873 K, and (c) 1273 K (×70 000).

These changes in the crystallinity of the samples take place together with an increase in the specific surface area (SSA) of the solids and a further sintering when the spinel phase is formed. So, while sample M1 shows a SSA value of 49 $m^2\ g^{-1}$, after the hydrothermal treatment to obtain sample M2 and leading to the partial collapsing of the structure, the SSA increases up to 62 $m^2\ g^{-1}$, as is usually observed with hydrotalcite-like compounds,[13,25,27] because of the changes taking place in the size of the crystallites (see electron micrographs). Upon calcination at 673 K a further increase is observed, up to 97 $m^2\ g^{-1}$; formation of well-defined spinel phases leads to a decrease of the SSA to 66 $m^2\ g^{-1}$ for sample calcined at 873 K. Changes in the morphology of the samples as a result of these treatments can be inferred from the transmission electron micrographs in Figure 7. After calcination at 673 K, small particles with a bimodal shape distribution are observed. The same is true for the sample calcined at 873 K, although the average particle size has increased and the particles are now spherical and sticklike shaped. Finally, calcination at 1273 K leads to a sharp sintering, with formation of

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extremely large particles and accordingly very low specific surface area, which could not be even measured.

Thus, it can be concluded that materials for which a synthesis is reported here have a hydrotalcite-like structure, although its thermal stability is much lower than those of Ni–Al, Mg–Al, or Mg–Fe compounds with the same structure,[3,20,21] where no collapsing of the layered structure is observed below 523 and 573 K. It can be tentatively argued that this behavior is due to the presence of cations that can become oxidized during the hydrothermal treatment. Simultaneously, migration of the M(II) and/or M(III) cations from octahedral to tetrahedral sites of the lattice, leading to formation of spinel, may help the collapse of the HT-like structure. In fact, the Co(II) ions in spinel Co_3O_4 occupy tetrahedral sites and in its environment as $[CoO_4]$ species will give rise to electronic absorption bands around 400 nm, thus accounting for the increase in absorbance observed in the visible–UV/DR spectrum of sample M2 (Figure 3b).

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Synthesis and Physical Studies of a New Organic Donor: 2,3-Dimethyl-5,6:11,12-bis(dithio)tetracene[1,2]

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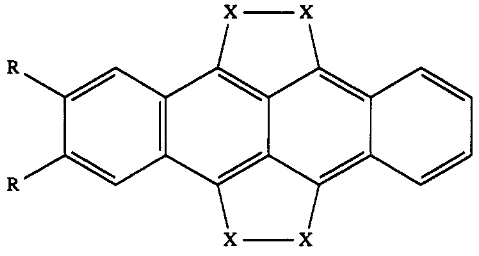
A new organic donor, 2,3-dimethyl-5,6:11,12-bis(dithio)tetracene (2,3-dimethyl-5,6,11,12-tetrathiotetracene, DMTTT), has been synthesized. Cyclic voltammetry of DMTTT in benzonitrile shows two reversible one-electron-transfer steps at 0.18 and 0.60 V vs the Ag/AgCl reference electrode. The electron spin resonance of $DMTTT^+$, generated in THF solution with trifluoroacetic acid, exhibits an 11-line hyperfine splitting spectrum with $g = 2.0078$. A single-crystal X-ray structure determination was carried out using crystals grown from chlorobenzene solution. The compound, $C_{20}H_{12}S_4\cdot[C_6H_5Cl]_{0.5}$, crystallizes in the triclinic space group $P\bar{1}$: $a = 7.635$ (1) Å, $b = 9.834$ (1) Å, $c = 13.214$ (2) Å, $\alpha = 100.39$ (1)°, $\beta = 101.46$ (1)°, $\gamma = 93.58$ (1)°, $V = 951.5$ (2) Å^3, and $Z = 2$. The structure involves linear chains of DMTTT molecules stacked along the a axis, and the crystal lattice contains one solvent molecule per unit cell. Preliminary studies indicate the related donor DMTSeT can be prepared by using the reported synthetic scheme for DMTTT and that conducting charge-transfer salts of DMTTT can be prepared.

Introduction

At room temperature, the electron donor 5,6,11,12-tetrathiotetracene (TTT, **1a**) and its selenium analogue (TSeT, **1b**) form charge-transfer salts that possess some of the highest electrical conductivities of any known synthetic metal.[3,4] A conductivity of ca. 10^3 S/cm is observed for $(TTT)_2I_3$ at room temperature.[3] As the temperature of this salt is decreased, the conductivity increases, as does that of a metal, until ca. 35 K. At that point, it undergoes a metal-to-insulator (M–I) transition.



1a TTT: X = S, R = H

1b TSeT: X = Se, R = H

2 DMTTT: X = S, R = CH_3

The introduction of a substituent or substituents into otherwise very symmetrical donors and acceptors (e.g., with original symmetry, D_{2h}) is known to suppress the temperature at which M–I transitions occur. A case in point is that of 2-fluorotetraselenotetracene (FTSeT), wherein the conductivity of the salt, $(FTSeT)_2Br$, increases smoothly from room temperature to 4.2 K.[5] Although the room-temperature conductivity of this salt is comparable to the other salts discussed above and the conductivity increases as the temperature is decreased, this salt never becomes superconducting.

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(1) Preliminary accounts of portions of this work have been presented at the March American Physical Society Meeting in St. Louis, MO, 20–24 Mar 1989 (*Bull. Am. Phys. Soc.* **1989**, *34*, 452), at the NATO Advanced Study Institute in Spetses Island, Greece, 21–23 June 1989 (*Lower Dimensional Systems and Molecular Devices*; Metzger, R. M., Day, P., Papavassiliou, G. C., Eds.; NATO ASI Series B: Physics; Plenum Publishing Co.: New York, 1991; p 205, in press), and at the Materials Research Society Meeting in Boston, MA, 27 Nov–2 Dec 1989 (*Electrical, Optical, and Magnetic Properties of Organic Solid State Materials*; Chiang, L. Y., Chaikin, P. M., Cowan, D. O., Eds.; Fall 1989, Materials Research Society Proceedings: Pittsburgh, 1990; Vol. 173, p 149).

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