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Synthesis of Mono-coordinate Iron(II)-phen Complex via a Solid State Ligand Exchange Process from Iron(II) Oxalate Dihydrate at Room Temperature under Mechanical Stressing

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Mono-coordinate iron(II)-1,10-phenanthroline (phen) complex was obtained in a solid state ligand exchange reaction under mechanical stressing by starting from a mixture of iron(II) oxalate dihydrate (FeC₂O₄·2H₂O) and phen, which was not available via a thermal route or from iron(II) chloride tetra hydrate (FeCl₂·4H₂O).

Keywords Iron(II) complex, ligand field distortion, mechanical stressing, solid state ligand exchange, spin crossover

INTRODUCTION

In a solid state, a ligand exchange reaction exhibits a unique feature (Fernández-Bertrán et al., 1999; Ohshita et al., 2002; Paneque et al., 2001), particularly when a molecular crystal is subjected to anisotropic deformation, inducing disproportionation of the ligand field. We reported that the coordination compound $\text{Fe}^{II}(\text{phen})_3$ was obtained from iron(II) chloride and phen in an almost quantitative yield when we exert mechanical shear stress on the powder mixture comprising $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and phen (Ohshita et al., 2002). Emphasis was laid on the role of ligand field distortion under mechanical stress (Ohshita et al., 2002, 2004; Tsuchiya et al., 1996, 2000, 2001).

As we extended our study to change the starting materials, we found another peculiarity of a solid state ligand exchange reaction. We focus here on the sequence and mechanisms of mono-, di- and tri-coordination of phen to a ferrous ion in a solid state. Two comparisons are made here, i.e., those between the starting ferrous materials and between the thermal and mechanochemical processes.

EXPERIMENTAL

Powders of iron(II) oxalate dihydrate (FeC₂O₄ · 2H₂O, Fe-Ox) (Kanto Chem., >99.0%) and 1,10-phenanthroline (phen) (Aldrich, >99.0%) were mixed in the stoichiometric ratio Fe-Ox/phen = 1/1, 1/2 or 1/3. The mixture was subjected to mechanical stressing by grinding in a planetary ball-mill (AGO-II, URF, modified by Nara Machinery) at 300 rpm for 3 h in a water-cooled alumina-lined cylindrical vessel together with 10 mm zirconia balls in Ar atmosphere. We also examined the effects of grinding Fe-Ox alone. Heating was carried out at temperatures between 333 K and 353 K for 5 h in an Ar-sealed glass tube.

RESULTS

Effects of Grinding

As shown in Figure 1, the intensity of the broad MLCT absorption band at around 500 nm was significantly increased by grinding a mixture of Fe-Ox and phen (Madeja and König, 1963). This indicates the coordination of phen to Fe^{II} by grinding. We have observed similar kinds of mechanochemical ligand exchange reactions from different combinations, e.g., FeCl₂·4H₂O-phen as well (Ohshita et al., 2002).

The unique feature of the system Fe-Ox-phen becomes obvious, however, when we change the stoichiometry of the starting mixture. Far-IR spectra, shown in Figure 2, reveals the signal specific to the ring vibration of free phen around 244 cm^{-1} and 411 cm^{-1} when we start from the mixture Fe-Ox/phen = 1/2 and 1/3 in molar basis (Hutchinson et al., 1970). We do not observe any bands attributable to di-coordinated phen compounds, typically those at around 280 cm^{-1} (Adams et al., 1982; Takemoto and Hutchinson, 1972, 1973). The bands from free phen disappear when we start from an

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FIG. 1. UV-VIS diffuse reflectance spectra of (*a*) as-mixed and (*b*) 3 h milled mixture of FeC₂O₄ · 2H₂O and phen with the molar ratio 1/2.

equimolar mixture of Fe-Ox and phen, as shown in Figure 2, curve (d).

These spectroscopic features consistently suggest the formation of a mono-coordinated phen complex in a solid-state under mechanical stressing, i.e., via a mechanochemical route, as shown in Scheme 1(*a*). A unique band at around 272 cm^{-1} from the milled mixture, curves (*b*), (*c*) and (*d*) in



FIG. 2. Far-infrared absorption spectra of the mixture in the molar ratio of Fe-Ox to phen, 1/2 before grinding (*a*), and those after grinding a mixture of the molar ratio 1/3 (*b*), 1/2 (c) and 1/1 (*d*).



SCH. 1. Solid state synthesis on (a) mechanochemical and (b) thermal processes.

Figure 2, is most likely ascribed to the mono-coordinated phen compound, although we do not find any literature support, since the mono-coordinated phen compound was rarely studied. Charron et al. (1983) has synthesized $Fe(phen)Cl_2$ by Broomhead-Dwyer synthesis. Their study was restricted, however, to the magnetic properties by Mössbauer spectroscopy. Conversely, the present mechanochemical route does not bring about the di- or tris-coordinated phen complex even when we gave abundant amount of phen into the starting mixture.

While the physical mixture of FeOx and phen with its stoichiometry 1 to 2 is diamagnetic solely due to an intrinsic property of FeOx (Wrobleski and Brown, 1979), paramagnetic behavior at high spin states appeared after grinding the mixture, as shown in Figure 3. This indicates that a tri-coordinated phen complex at low spin states was not formed, and



FIG. 3. Temperature dependence of $\chi_{\rm M}$ under the external field, 500 mT, for (*a*) as-mixed and (*b*) 3 h milled mixture of FeC₂O₄ · 2H₂O and phen.

unreacted FeOx was absent. We therefore suggest that the mono-coordinated phen complex is predominantly formed via a mechanochemical route.

Products From a Thermal Process

After heating a mixture of Fe-Ox and phen with a stoichiometry 1 to 2 at temperatures at 353 K for 3 h, IR bands from free phen at 411 cm^{-1} disappeared, as shown in Figure 4(*d*). Instead, we observe a new band at 282 cm^{-1} to be assigned to the ring vibration of di-coordinated phen (Adams et al., 1982; Takemoto and Hutchinson, 1972, 1973). Thus, the di-coordinated phen compounds, never obtained mechanochemically, were easily obtained by simply heating a stoichiometric mixture at 353 K. Note that we did not observe IR bands at 272 cm^{-1} attributable to the mono-coordinated phen from any of the samples obtained by heating. This indicates that the di-coordinated compound was formed by heating without halting at the stage of the mono-coordinated state, as shown in Scheme 1(*b*).

We observe spin crossover behavior from the above-mentioned mixture after heating at 353 K, as shown in Figure 5. This makes a contrast to the diamagnetic behavior of the intact mixture. According to the literature (Balasubramanian, 1999), the di-coordinated phen compounds behave as spin crossover complex compounds. Thus, formation of the di-coordinated phen complex upon heating is obvious, not only from the Far-IR spectra but also from the change in the magnetic properties.



FIG. 4. Far-infrared absorption spectra of the mixture in the molar ratio of Fe-Ox to phen, 1/2 before grinding (*a*), and after heating at 343 K (*b*), 348 K (*c*), 353 K (d) for 5 h.



FIG. 5. Temperature dependence of effective magnetic moment, μ_{eff} , under the external field, 500 mT, for (*a*) as-mixed and (*b*) heated at 353 K mixture of FeC₂O₄ · 2H₂O and phen.

DISCUSSION

As shown in Figure 6(a), the binding energy of O_{1s} orbital of intact FeC₂O₄ · 2H₂O peaks at 532.1 eV and 530.3 eV with its intensity ratio being about 2 to 1. The peak at the higher binding energy is attributed to the oxygen atom in the oxalate ion and the lower one to that of H₂O.

Upon grinding Fe-Ox for 3 h, the lower energy peak decreased its intensity to 11% from ca 33% of the intact state, with a simultaneous chemical shift to the lower energy side by 0.8 eV. This implies the dehydration with simultaneous weakening of the Fe^{II}- H₂O coordination bonds as a



FIG. 6. X-ray photoelectron spectra of O_{1s} orbital of (a) intact and (b) 3 h-milled $FeC_2O_4 \cdot 2H_2O$.

consequence of grinding, while keeping the Fe-Ox bond strength eventually unchanged (Avvakumov et al., 1994). This serves as evidence of preferential substitution of H_2O by phen upon grinding the mixture of Fe-Ox and phen.

This kind of anisotropic change in the bond strength is less likely by heating. Based on the scale of the spectrochemical series, the bond strengths of Fe-O(H₂O) and Fe-O(Ox²⁻) are quite similar and weaker than that of phen (Huheey et al., 1993). This results in the formation of di-coordination complex, being thermodynamically more stable, by heating the 1:2 molar ratio mixture.

We previously reported the formation of the tri-coordination phen complex upon grinding a mixture comprising $FeCl_2 \cdot 4H_2O$ and phen. In $FeCl_2 \cdot 4H_2O$, there is no such an anisotropy. Note that the anisotropy in Fe-Ox is attributed to the existence of the 2-D coplanar networking of Fe-Ox bonds (Wrobleski and Brown, 1979).

CONCLUSION

The mono-coordinated phen complex was formed from the powdered mixture of $FeC_2O_4 \cdot 2H_2O$ and 1,10-phenanthroline only by grinding, even when we started from the mixture in excess stoichiometry of phen. This makes a contrast with our previous observation to form the tri-coordinated phen complex from $FeCl_2 \cdot 4H_2O$ and phen. The 2-D network structure, due to chelate bridging bonds, causes anisotropy in crystallographical and mechanical properties of the oxalate. The anisotropy, in turn, results in the unusual preference to the ligand exchange of phen with H_2O under mechanical stressing. This explains the unique feature of the mono-coordinated phen complex formation by grinding. This kind of anisotropy-induced phenomenon does not occur in a conventional thermal process.

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