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Note

The dehydration of aquohalobis(dimethylglyoximato)cobalt(III) monohydrate complexes

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We recently prepared and characterized three halo complexes of the type $[Co(DMG)_2(H_2O)X]\cdot H_2O$ where X = Cl, Br or I and DMG is the dimethyl glyoximate anion[1]. We became interested in comparing the dehydration behavior of these compounds because they are isostructural with one another. This feature provides an opportunity to investigate differences in the solid-phase dehydration brought by the chemical differences within the series.

EXPERIMENTAL

The preparation and characterization of the title complexes is reported elsewhere[1]. Kinetic studies were performed by computer evaluation of nonisothermal DSC traces[2]. The compounds were heated in the low-temperature operation mode of a Perkin-Elmer DSC-1B differential scanning calorimeter. Heating rates of 5°C min^{-1} and N_2 flows of 20–30 ml min^{-1} were employed. Diphenyl ether was used as the calibrant[3]. Isothermal mass-loss studies were performed on each compound at 40°C to aid in choosing an appropriate rate law. All other instruments and procedures are described elsewhere[4].

The main *d*-spacings for $[Co(DMG)_2(H_2O)Cl]\cdot H_2O$ were at 6.92 Å (vs), 5.04 Å (s), 4.70 Å (s), 3.97 Å (w), 3.68 Å (vs), 3.16 Å (vs), 2.93 Å (vs) and 2.59 Å (s). For $[Co(DMG)_2(H_2O)Br]\cdot H_2O$ the main reflections correspond to *d*-spacings of 6.97 Å (vs), 5.08 Å (s), 4.75 Å (w), 3.97 Å (m), 3.69 Å (vs), 3.19 Å (vs), 2.88 Å (m) and 2.60 Å (s). For the anhydrous complex $[Co(DMG)_2(H_2O)Cl]$ the main reflections were for 6.97 Å (vs), 6.28 Å (vs), 5.68 Å (s), 5.28 Å (w), 4.10 Å (m), 3.53 Å (w), 3.12 Å (m) and 2.82 Å (w). For $[Co(DMG)_2(H_2O)Br]$ the main reflections were for 7.02 Å (vs), 6.61 Å (vs), 6.11 Å (s), 5.75 Å (s), 5.47 Å (m), 4.11 Å (w), 3.56 Å (s), 3.11 Å (w) and 2.85 Å (m). The hydrated complexes are isostructural. The dehydrated complexes have lattices that are different from those of the parent hydrates. The lattices of the dehydrated complexes appear to be similar, but not strictly isostructural, with one another.

RESULTS AND DISCUSSION

All three compounds, $[Co(DMG)_2(H_2O)X]\cdot H_2O$ ($X = Cl$, Br, or I), undergo a two-step dehydration, losing lattice water beginning at about 40°C and ending at about 70°C. The chloro and bromo complexes lose coordinated water beginning at 160–170°C. This dehydration is accompanied by extensive decomposition of the complex. The iodo complex begins the second mass loss at 125°C. The lower temperature is probably associated with electron-transfer between iodide and cobalt(III).

The contracting-square rate law, $(1-\alpha)^{1/2} = 1-kt$, where α is the fraction of dehydration, k is the rate constant and t is time, gave the best curve fit for the isothermal loss of lattice water. The particle size of the compounds was too small to verify this model using optical microscopy with our equipment. However, the complex has one quite unique axis, the axis on which H_2O and X are bound to the cobalt center. It would not be surprising if the complexes stacked through the solid, so that one direction was very much unique while the other two were similar to each other. The contracting-square rate law is often observed for solid-phase reactions in such crystals, particularly those characterized by a lamellar or layered lattice. The contracting-square rate law was also the one giving the best curve-fit to the Arrhenius line for the DSC results.

The Arrhenius activation energies for each complex, as obtained from DSC studied using the contracting-square rate law, are shown in Table 1.

TABLE 1

RESULTS OBTAINED FROM ANALYSIS OF DSC CURVES FOR DEHYDRATION OF $[Co(DMG)_2\text{-}(H_2O)X]\cdot H_2O$ TYPE COMPLEXES

X	*α-Range*[a]	*Peak range* (*K*)	*Peak maximum* (*K*)	*E*[a] *kcal mol*$^{-1}$[b]	*ΔH* (*kcal mol*$^{-1}$)[b]
Cl	0.3–0.8	304–352	342	20.2±0.2	11.0±0.8
Br	0.3–0.8	307–353	344	21.1±0.8	14.7±0.5
I	0.2–0.7	318–380	354	19.5±1.0	18.6±0.4
	0.3–0.8	318–380	354	19.0±0.7	18.6±0.4

[a] This is the range of α values over which the kinetic analysis was made. [b] Error limits are deviations from the mean for 2–5 runs in each case.

The poorest fit to the Arrhenius line was found for the iodo complex. This compound was also the most sensitive to the α-range selected for kinetic analysis of the data and showed the most scatter in E_a values among the individual runs. The E_a values and their associated error limits overlap at about 20.3 kcal mol^{-1}. This makes it difficult to judge whether differences in the activation energies within the series are due to random errors or reflect real differences in the kinetic processes involved. Partly because the activation energies show no trend, we are inclined to believe that the differences are due to random errors and that the activation energies are equal. Thus the mechanism of dehydration is apparently unaffected by the identity of the halide. This is consistent with the fact that the lattices of the starting complexes are isostructural. Apparently, the chemical differences within the series are too slight to be reflected in differences in E_a.

While the activation energies are apparently equal, the enthalpy changes increase uniformly in magnitude through the series, as shown in Table 1. In fact, ΔH is linearly correlated with the molecular weight of the respective complexes. This could reflect the fact that the product lattices are not strictly isostructural with each other. The results indicate that the chloro complex is best able to rearrange from the transition-state into a more stable product lattice, while the iodo complex is least able to rearrange. This difference could be due to the respective masses of the complexes. For the iodo complex, ΔH and E_a are nearly equal, indicating little rearrangement from transition-state to final product.

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