Thermochimica Acta, 31 (1979) 391–394

Note

Dehydration of copper(II) sulfate and its double salts: comparison with the dehydration of cobalt(II) sulfate

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(Received 7 August 1978)

In a recent paper[1], the authors reported the results of spectrophotometric and TG–DTA studies on the dehydration of copper(II) sulfate and its double salts. The comparison of these data with those on the dehydration of cobalt(II) sulfate leads to some comments, which may be of interest especially in connection with the spectral and structural changes of $Co_2Cu(SO_4)_3 \cdot 18H_2O$.

EXPERIMENTAL

Use was made of the same spectrophotometric and TG–DTA techniques as those in the foregoing paper[1].

The crystals of $CoSO_4 \cdot 6H_2O$ used were obtained from a saturated solution at 50–55 °C according to the literature[2] and its water content was checked by TG measurement.

RESULTS AND DISCUSSION

The TG–DTA curves of $CoSO_4 \cdot 6H_2O$ (Fig. 1) show the occurrence of the following changes

$CoSO_4 \cdot 6H_2O \rightarrow CoSO_4 \cdot H_2O \rightarrow CoSO_4$

The powder reflection spectra of the three salts (Fig. 2) show that the *d–d* band at 19 800 cm^{-1} of $CoSO_4 \cdot 6H_2O$, which is very similar to that of $[Co(H_2O)_6]^{2+}$ in aqueous solution, is displaced slightly to the red in the first step of dehydration, and then splits into several components in the second.

As pointed out briefly in the foregoing paper, these spectral changes are nearly the same as those observed in the *d–d* band of $Co_2Cu(SO_4) \cdot 18H_2O$ at 19 900 cm^{-1}

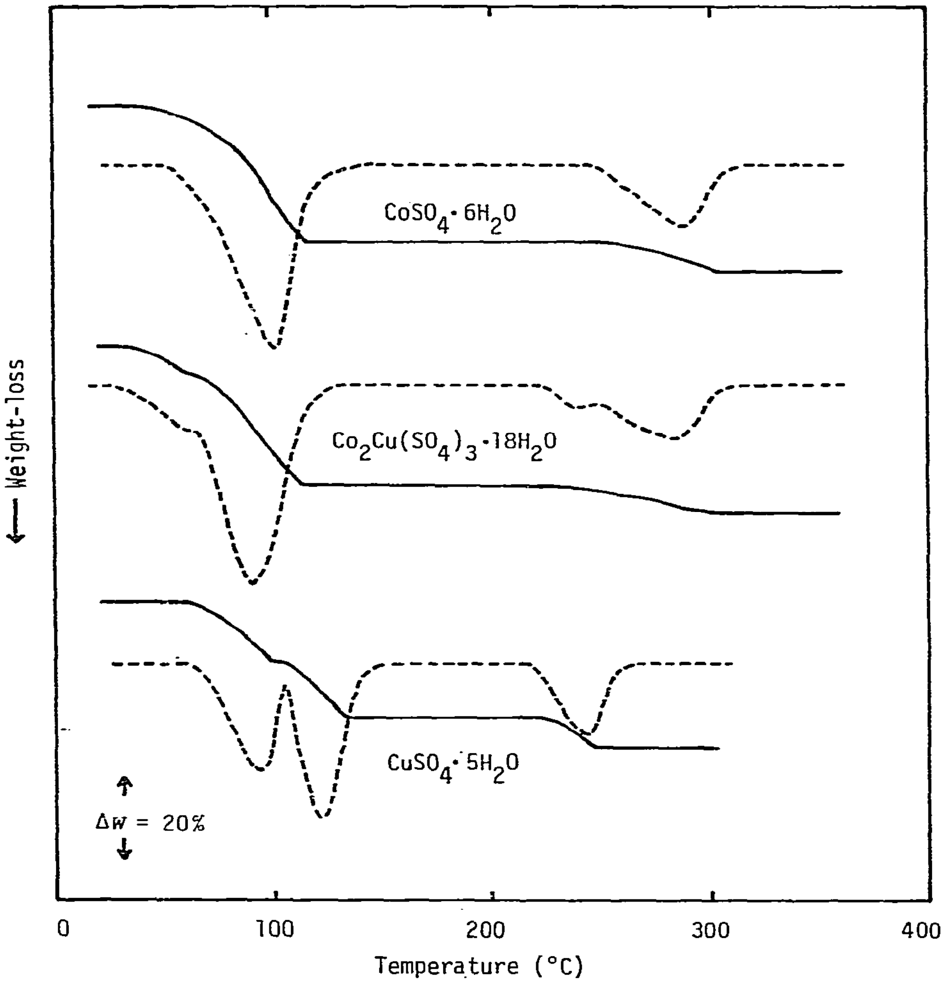

Fig. 1. TG–DTA curves of Co(II), Cu(II)–Co(II) and Cu(II) sulfates.

in the course of dehydration. Table 1 summarizes the peak positions of all these spectra[1].

Now all the three Co(II) sulfates in Fig. 2 are, very probably, essentially octahedral complexes. The hexahydrate can naturally be formulated as $[Co(H_2O)_6]SO_4$, and the Co–O distances in the two sets of $[Co(H_2O)_6]^{2+}$ in it were found to lie between 2.05 and 2.14 Å (and, for the most part, 2.11 and 2.14 Å), showing that their octahedrons are quite regular[2]. In $CoSO_4 \cdot H_2O$, a Co^{2+} ion is surrounded by four sulfate oxygens on the x–y plane and two water molecules on the z-axis, each of the latter bridging two Co^{2+} ions together (Co–O: 2.04–2.17 Å)[3]. The situation in $CoSO_4$ is complicated by the existence of three modifications A, B and C, but it was reported that they are closely related to one another, and the Co–O lengths in the form B, which is isomorphous with $CuSO_4$, were found to be 2.00 Å(×2), 2.10 Å (×2) and 2.29 Å (×2)[4].

These data show that the CoO_6 octahedrons in the hexahydrate are gradually deformed in the course of dehydration, and the relatively large deformation in the

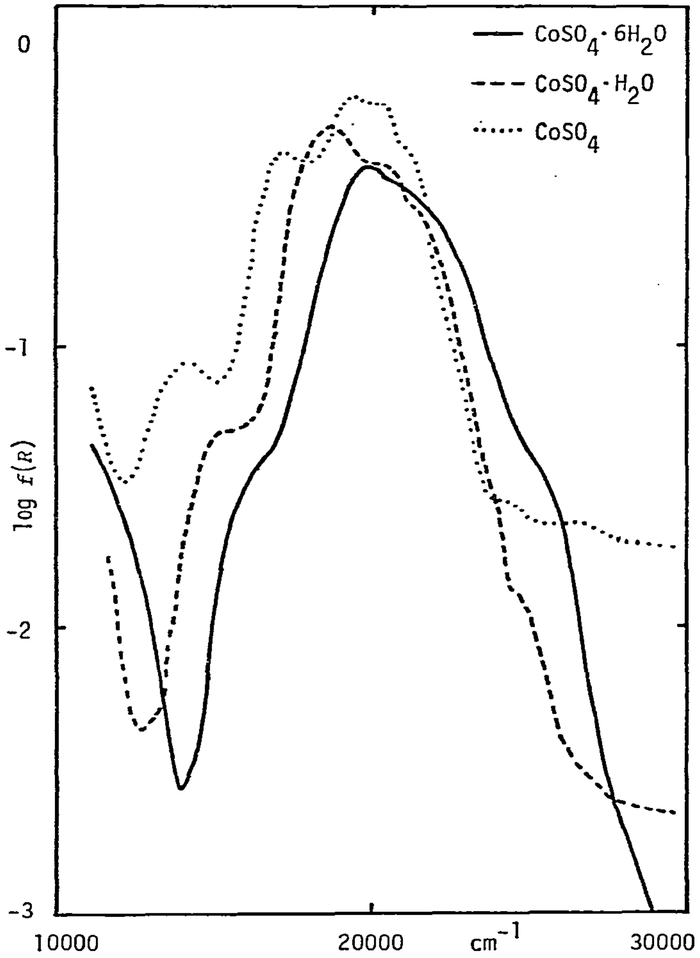

Fig. 2. Reflectance spectra of Co(II) sulfates.

TABLE 1

COLORS AND $\tilde{\nu}_{max}$ VALUES OF CO(II) AND CU(II)–CO(II) SULFATES

Compound	*Color*	ν^{*}_{max}
$CoSO_4 \cdot 6H_2O$	Reddish pink	16600 sh, 19800, 20800 sh
$CoSO_4 \cdot H_2O$	Pink	15400 sh, 18600, 20400 sh
$CoSO_4$	Violet	14000, 17100, 19400, 20400 sh, 21100 sh
$Co_2Cu(SO_4)_3 \cdot 18H_2O$	Dark pink	13200, 19900, 20800 sh
$Co_2Cu(SO_4)_3 \cdot 3H_2O$	Pink	11800, 18900, 20200 sh
$Co_2Cu(SO_4)_3$	Violet	12100, 17200, 18900, 20500, 21400

* *d–d* bands of Cu(II) are underlined.

last step is probably the reason for the notable splitting of the *d–d* band observed. However, compared with the data on $CuSO_4$[1], it can be said that the degree of deformation (tetragonality) in $CoSO_4$ is much smaller; if the tetragonality T is defined by the ratio R_S/R_L, where R_L is the longest M–O length and R_S the mean of the shorter ones[5], the T values for $CuSO_4$ and $CoSO_4$ are 0.82 and 0.90, respectively.

So it seems to be plausible that, in the lattices of $Co_2Cu(SO_4)_3 \cdot 3H_2O$ and $Co_2Cu(SO_4)_3$, where Cu^{2+} and Co^{2+} ions share SO_4^{2-} ions as ligands, the geometry of Cu^{2+} ions is influenced by that of Co^{2+} ions which are double in number, becoming sensibly more octahedral than in the lattice of $CuSO_4$. This may be the reason for the particularly large shift of the *d–d* band of Cu(II) toward lower frequency observed in the dehydration of $Co_2Cu(SO_4)_3 \cdot 18H_2O$.

Owing to this shift, the dark pink color of $Co_2Cu(SO_4)_3 \cdot 18H_2O$ which is apparently a superposition of "blue" (Cu^{2+}) and "red" (Co^{2+}), changes into pink (trihydrate) and then violet (anhydrous salt). That is to say, the "blue" part of the color disappears with dehydration, just as in the case of $CuSO_4 \cdot 5H_2O$, and the colors which are very similar to those of $CoSO_4 \cdot H_2O$ and $CoSO_4$ remain. This may be taken as an interesting example of the thermochromism of metallic complexes, where the color of one of the components disappears by heating, leaving the color of the other component which also changes by heating.

From all these results, it can be concluded that, although the disappearance of the blue color of $CuSO_4 \cdot 5H_2O$ by dehydration can be related to the decrease of ligand field strength, the spectral shift which is purely due to this effect is rather small, and the modes of coordination of SO_4^{2-} ions (and, in particular, the tetragonality of the coordination sphere formed by them) have a large influence on the position of the *d–d* band in it and related compounds, just as in the case of many other Cu(II) complexes.

REFERENCES

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