

THE DEHYDRATION OF $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ AND $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$

G. RABBERING, J. WANROOY AND A. SCHUIJFF

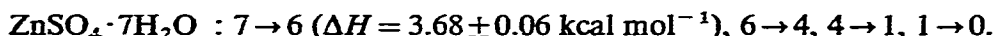
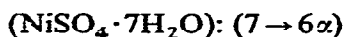
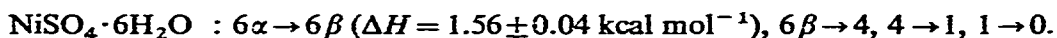
*Laboratorium voor Algemene Chemie, Afdeling Chemische Thermodynamica,
Rijksuniversiteit Utrecht, Padualaan 8, Utrecht (The Netherlands)*

(Received 13 December 1974)

ABSTRACT

Using differential scanning calorimetry (DSC) in combination with effluent analysis, differential thermal analysis (DTA), thermogravimetric analysis (TG) and X-ray analysis, the dehydration of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ was investigated and a few transition enthalpies were measured. The dehydration of both compounds showed a great analogy. For $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ the α - β phase transition was studied.

The dehydration scheme of both hydrates can be given as follows:



INTRODUCTION

There is a good deal of literature about the dehydration of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$; in spite of several applied methods, viz. DTA and TG, the interpretations of the dehydration course are contradictory.

For $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ Vallet and Bassière¹ have found the hexahydrate and tetrahydrate as intermediates between hepta- and monohydrate by calculations on TG-curves; these intermediates were also shown, while the possibility of the existence of tri- or dihydrate was not excluded. Pannetier et al.² have found similar results. Using thermal analysis methods Demassieux and Fedoroff³ have found hepta-, hexa- and monohydrate. On the basis of crystallization data Rohmer⁴ has arrived at the conclusion that there are three stable (hepta-, hexa- and monohydrate) and two instable hydrates (tetra- and dihydrate).

Between hexa- and monohydrate Frost et al.⁵ have found amorphous intermediates. This has also been given by Chihara and Seki⁶, who have described the dehydration of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ as: $7 \rightarrow 6$, $6 \rightarrow 6$ (phase transition of the hexahydrate), $6 \rightarrow 1$ and $1 \rightarrow 0$. Murgulescu and Segal⁷ assume an intermediate tetrahydrate and Fruchart⁸ gives the dehydration course as: $7 \rightarrow 6\beta$, $6\beta \rightarrow 6\alpha$, $6\alpha \rightarrow 5$, $5 \rightarrow 1$, $1 \rightarrow 0.75$, $0.75 \rightarrow 0$.

Finally, Berg and Pribylov⁹ give hepta-, hexa-, di- and monohydrate as intermediates in the dehydration. Besides they give some transition enthalpies.

Analogous to zinc sulphate, Demassieux and Fedoroff¹⁰ have found for nickel sulphate only the hepta-, hexa- and monohydrate, although they mention amorphous intermediates between hexa- and monohydrate. Chihara and Seki⁶ give the following dehydration course: $7 \rightarrow 6\beta$, $6\beta \rightarrow 6\alpha$ (spontaneously), $6\alpha \rightarrow 6\gamma$ or $6\gamma'$ (below or above 100°C , respectively), 6γ or $6\gamma' \rightarrow 4$, $4 \rightarrow 1$, $1 \rightarrow 0$; they note that 6γ and $6\gamma'$ may be the same. Lendormy¹¹ has found hepta- and monohydrate, Caillère and Pobeguín¹² give the dehydration as follows: $7 \rightarrow 6$, $6 \rightarrow 6$ (phase transition of the hexahydrate), $6 \rightarrow 4$, $4 \rightarrow 1$ (possibly via tri- or dihydrate), $1 \rightarrow 0$, while Pannetier et al.¹³ confirm the conclusions of Caillère and Pobeguín.

On the basis of the contradictory literary data it seemed very interesting to investigate the dehydration of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ by an alternative method and consequently to investigate whether or not the hexahydrate of nickel sulphate shows a phase transition (crystal transition) during the dehydration.

EXPERIMENTAL

Materials

$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and TiNO_3 were obtained from Merck; only p.a. reagentia were used. $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ was obtained by crystallization from an aqueous solution of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ at room temperature.

Apparatus and procedures

Measurements were carried out by means of DSC-1B of Perkin-Elmer. Effusing crystal water was detected by a katharometer (effluent analysis). The pulverized samples (5–15 mg) were placed in small aluminum pans. Experiments were done both with closed sample pans and with sample pans with a pin-hole of approximately $10\text{--}20\ \mu\text{m}$ in diameter. X-ray photographs of powders of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ were made with a high temperature Guinier camera and a Debye-Scherrer camera. TG and DTA-scans were made of the powdered hydrates.

RESULTS

DSC

Figures 1 and 2 show DSC-scans of the dehydration of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ in closed sample pans as well as in sample pans with a pin-hole. Effluent analysis graphs are also drawn in these figures. From the fact that peaks 4 and 11 do not appear in scans with closed sample pans it was concluded that they are to be ascribed to the evaporization of liberated crystal water:



Enthalpy changes (or in the case of closed sample pans, strictly speaking, heats of

dehydration) were measured for peaks 1 and 9. For other peaks no reliable values can be given because of complicating circumstances, inherent to the technique used, viz., solving the solid hydrate in liberated crystal water.

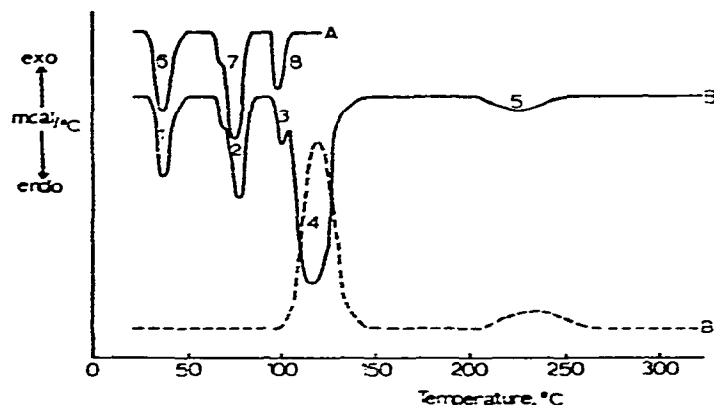


Fig. 1. DSC-scan of the dehydration of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ in a closed sample pan (A) and in a sample pan with a pin-hole in combination with effluent analysis (B); 1, 6 = $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}(\text{s}) \rightarrow \text{ZnSO}_4 \cdot 6\text{H}_2\text{O}(\text{s}) + \text{H}_2\text{O}(\text{l})$; 2, 7 = $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}(\text{s}) \rightarrow \text{ZnSO}_4 \cdot 4\text{H}_2\text{O}(\text{s}) + 2\text{H}_2\text{O}(\text{l})$; 3, 8 = $\text{ZnSO}_4 \cdot 4\text{H}_2\text{O}(\text{s}) \rightarrow \text{ZnSO}_4 \cdot \text{H}_2\text{O}(\text{s}) + 3\text{H}_2\text{O}(\text{l})$; 4 = $6\text{H}_2\text{O}(\text{l}) \rightarrow 6\text{H}_2\text{O}(\text{g})$; 5 = $\text{ZnSO}_4 \cdot \text{H}_2\text{O}(\text{s}) \rightarrow \text{ZnSO}_4(\text{s}) + \text{H}_2\text{O}(\text{g})$.

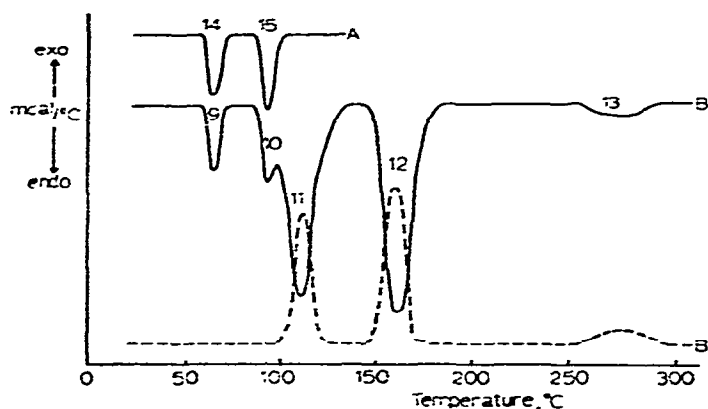


Fig. 2. DSC-scan of the dehydration of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ in a closed sample pan (A) and in a sample pan with a pin-hole in combination with effluent analysis (B); 9, 14 = $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}(\text{s}, \alpha) \rightarrow \text{NiSO}_4 \cdot 6\text{H}_2\text{O}(\text{s}, \beta)$; 10, 15 = $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}(\text{s}, \beta) \rightarrow \text{NiSO}_4 \cdot 4\text{H}_2\text{O}(\text{s}) + 2\text{H}_2\text{O}(\text{l})$; 11 = $2\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{H}_2\text{O}(\text{g})$; 12 = $\text{NiSO}_4 \cdot 4\text{H}_2\text{O}(\text{s}) \rightarrow \text{NiSO}_4(\text{s}) + 3\text{H}_2\text{O}(\text{g})$; 13 = $\text{NiSO}_4 \cdot \text{H}_2\text{O}(\text{s}) \rightarrow \text{NiSO}_4(\text{s}) + \text{H}_2\text{O}(\text{g})$.

For the reaction at peak 1: $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}(\text{s}) \rightarrow \text{ZnSO}_4 \cdot 6\text{H}_2\text{O}(\text{s}) + \text{H}_2\text{O}(\text{l})$, an enthalpy increase was found of $3.68 \pm 0.06 \text{ kcal mol}^{-1}$ ($3.737 \text{ kcal mol}^{-1}$ (ref. 14)).

Peak 9, which, as will be shown, is caused by the phase transition $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}(\text{s}, \alpha) \rightarrow \text{NiSO}_4 \cdot 6\text{H}_2\text{O}(\text{s}, \beta)$, gives a ΔH -value of $1.56 \pm 0.04 \text{ kcal mol}^{-1}$.

Determination of the quantity of crystal water

In order to determine whether the experiments had been started with $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, respectively, accurately weighed quantities of both materials were heated up to 400°C , then cooled down quickly and weighed immediately afterwards. The number of molecules of crystal water per molecule $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ were found to be 5.98 and 6.86, respectively.

Effluent analysis

Figures 1 and 2 show DSC-scans of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ together with effluent analysis. For $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ the ratio of both effluent analysis peaks was 6:1; the three peaks of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ were in the proportion of 2:3:1.

Stability of $\text{ZnSO}_4 \cdot 4\text{H}_2\text{O}$

It appeared that $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, when exposed to air for a longer period, changes into $\text{ZnSO}_4 \cdot 4\text{H}_2\text{O}$. This was shown by DSC in combination with effluent analysis and by the determination of the quantity of crystal water (Fig. 3).

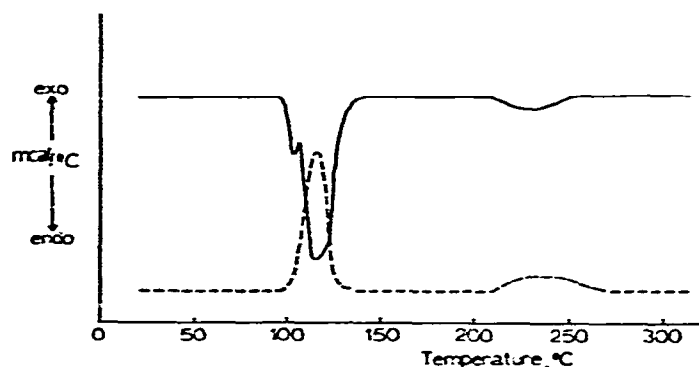


Fig. 3. DSC-scan of $\text{ZnSO}_4 \cdot 4\text{H}_2\text{O}$ in a sample pan with a pin-hole (solid curve) in combination with effluent analysis (dotted curve).

The ratio of the effluent analysis peaks was 3:1 in accordance with the supposition that $\text{ZnSO}_4 \cdot 4\text{H}_2\text{O}$ was present. Determination of the quantity of crystal water confirmed this.

Identification of peaks 9 and 10 (see Fig. 2)

The identification of peaks 9 and 10 gave rise to difficulties. In the literature^{18,21}, the existence of two different crystal modifications of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ is known: $\alpha\text{-NiSO}_4 \cdot 6\text{H}_2\text{O}$, which is tetragonal and $\beta\text{-NiSO}_4 \cdot 6\text{H}_2\text{O}$, which is monoclinic. Further experimental work was done in order to confirm that the peaks are to be ascribed to:



The main difficulty was the coincidence of peaks 10 and 11 under various thermodynamic circumstances. In the following the results are stated briefly.

X-ray analysis

Powder photographs taken with a high temperature Guinier camera gave no definite results, mainly because of the instability of the supposed β -modification. However, there were some indications that the dehydration of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ proceeds via the 6α - and 6β -modifications and the tetrahydrate.

Reversibility

A way of determining whether peak 9 is caused by a crystal transition or by a dehydration would be to investigate the reversibility of the process. Therefore DSC-scans were made in sample pans with a pin-hole combined with the procedure of weighing the sample. It appeared that there was a loss of weight under isothermal circumstances near the transition temperature. No conclusion can be drawn from this experiment, as the assumption holds for both a dehydration and the instability of $\beta\text{-NiSO}_4 \cdot 6\text{H}_2\text{O}$.

DTA and TG

In these experiments peaks 9, 10 and 11 of the DSC-scans were found to coincide. Therefore it was concluded that the DTA-peak is caused by the overall reaction:



The assumed instability of $\beta\text{-NiSO}_4 \cdot 6\text{H}_2\text{O}$ can account for this.

Dehydration of $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$

Figure 4 shows a DSC-scan of the dehydration of $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ in a closed sample pan. Comparison with the dehydration of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ in a closed sample

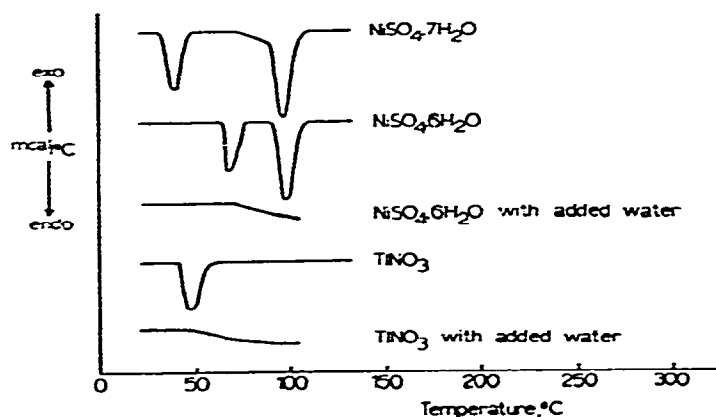


Fig. 4. DSC-scan of $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and TiNO_3 in closed sample pans, showing the influence of added (liberated) water on the crystal transition.

pan clearly shows that crystal water, liberated from the transition $7 \rightarrow 6$ very strongly influences peak 9. The latter is deformed and shifted to a higher temperature, so that it partially coincides with peak 10. This experimental fact was used to distinguish between a crystal transition and a dehydration.

TiNO₃ and NiSO₄·6H₂O with water

It is known¹⁵ that TiNO₃ shows a crystal transition at about 43°C. A DSC-scan of this transition is shown in Fig. 4. In the same figure the DSC-scans of TiNO₃ with water, of NiSO₄·6H₂O (with and without water) and of NiSO₄·7H₂O (all in closed sample pans) are given. Solubility data being known¹⁵, the quantities of water, added to TiNO₃ and NiSO₄·6H₂O, were comparable. For practical reasons it was impossible to add an amount of water comparable to the quantity of crystal water that effuses at the transition $7 \rightarrow 6$ of NiSO₄·7H₂O.

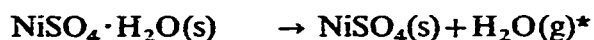
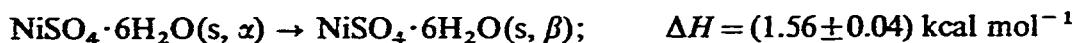
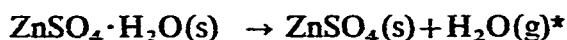
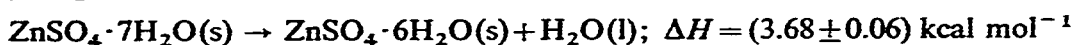
However, it is clear from Fig. 4 that addition of water has the same effect on peak 9 of NiSO₄·6H₂O as on the phase transition of TiNO₃. This gives strong evidence for a phase transition of NiSO₄·6H₂O.

ZnSO₄·7H₂O

From Fig. 2 it can be seen that the dehydration peaks $6 \rightarrow 4$ and $4 \rightarrow 1$ are not influenced by crystal water, liberated during a previous dehydration ($7 \rightarrow 6$).

DISCUSSION

On the basis of the experimental results, the dehydration of ZnSO₄·7H₂O and NiSO₄·6H₂O was established as follows:



When starting from NiSO₄·7H₂O, the following transition is also present:



*These transitions only occur when starting with sample pans with a pin-hole.

The dehydration course of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ agrees with the findings of Pannetier et al.². The transition of $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$ to $\text{ZnSO}_4 \cdot 4\text{H}_2\text{O}$ shows a shoulder peak (Fig. 1), giving some indication for a crystal transition, analogous to $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$. However, this could not be confirmed.

The dehydration of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ has also been given by Caillère and Pobeguïn¹² and by Pannetier et al.¹³. No indications have been found of other crystal modifications of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ as given by Chihara and Seki⁶.

Of major importance for all experiments with DSC were the thermodynamic circumstances. As soon as the experimental circumstances were changed, as for example was the case with DTA, TG and X-ray analysis, the dehydration course was different from that established by DSC and effluent analysis.

This was most evident in the transition $6\alpha \rightarrow 6\beta$ for $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$. This peak coincided with the dehydration $6 \rightarrow 4$ because of the instability of $\beta\text{-NiSO}_4 \cdot 6\text{H}_2\text{O}$.

The strong resemblance in dehydration between $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ is striking; the transition temperatures of the dehydrations, which are higher for nickel sulphate, constitute the main difference. It is known that hepta-, tetra- and monohydrate of nickel- and zincsulphate are isomorphous^{13,16-18}. It is equally well known that the hydrates $\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{MnSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{CoSO}_4 \cdot 6\text{H}_2\text{O}$ etc., are isomorphous with those of nickel- and zincsulphate¹⁶⁻²⁰. It is reasonable to suppose that these hydrates will show a behaviour, analogous to the dehydration of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$.

REFERENCES

- 1 P. Valiet and M. Bassière, *Bull. Soc. Chim. Fr.*, 5 (1938) 546.
- 2 G. Pannetier, A. Michel, J.-M. Brégeault and G. Djega-Mariadassou, *Bull. Soc. Chim. Fr.*, (1963) 1204.
- 3 N. Demassieux and B. Fedoroff, *C.R. Acad. Sci.*, 205 (1937) 457.
- 4 R. Rohmer, *C.R. Acad. Sci.*, 210 (1940) 669.
- 5 G. Frost, K. Moon and E. Tompkins, *Can. J. Chem.*, 29 (1951) 604.
- 6 H. Chihara and S. Seki, *J. Chem. Soc. Japan*, 26 (1953) 88.
- 7 I. Murgulescu and E. Segal, *Anal. Univ. Bucarest*, 22 (1959) 75.
- 8 E. Fruchart, *Thesis*, Lille, 1959.
- 9 G. Berg and K. Pribylov, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 7 (1964) 535; and 9 (1966) 6.
- 10 N. Demassieux and B. Fedoroff, *C.R. Acad. Sci.*, 206 (1938) 1649.
- 11 N. Lendormy, *Chim. Anal.*, 44 (1962) 255.
- 12 S. Caillère and Th. Pobeguïn, *Bull. Soc. Chim. Fr., Miner. Crist.*, 85 (1962) 48.
- 13 G. Pannetier, J.-M. Brégeault, C. Lecouturier and G. Djega-Mariadassou, *Bull. Soc. Chim. Fr.*, (1964) 3141.
- 14 R. Barieau and W. Giauque, *J. Am. Chem. Soc.*, 72 (1950) 5676.
- 15 *Handbook of Physics and Chemistry*, Chem. Rubber Publishing Co., Cleveland, 52nd ed., 1971/1972.
- 16 Y. le Fur, J. Coing-Boyot and G. Bassi, *C.R. Acad. Sci., Ser. C*, 262 (1966) 632.
- 17 G. Pannetier, J.-M. Brégeault and M. Tardy, *Bull. Soc. Chim. Fr.*, (1966) 324.
- 18 R. Wijckoff, *Crystal Structures*, Vol. 3, Interscience Publishers, New York, 1965.
- 19 H. Oswald, *Helv. Chim. Acta*, 48 (1965) 590.
- 20 B. O'Connor and D. Dale, *Acta Crystallogr.*, 21 (1966) 705.
- 21 D. Sutor, *Acta Crystallogr.*, 12 (1959) 72.