

Original articles

Research article

<https://doi.org/10.17308/kcmf.2022.24/9052>**Formation of a solvate of manganese(III) acetylacetonate with chloroform**

V. P. Zlomanov✉, R. S. Eshmakov, I. V. Prolubshchikov

*Lomonosov Moscow State University,
1 Leninskie Gory, Moscow 119991, Russian Federation***Abstract**

Metal acetylacetonates are coordination compounds consisting of the acetylacetonate anion ($\text{CH}_3\text{COCHCOCH}_3$, indicated as acac) and metal ions. Typically, both oxygen atoms of the anion bind with the metal and form a six-membered chelate ring. The simplest complexes have the formulas $\text{M}(\text{acac})_3$ and $\text{M}(\text{acac})_2$. Many complexes are soluble in organic solvents, and such solutions are used for the synthesis of catalysts. The processes of formation of solvates of acetylacetonates of various metals have not been studied properly. It should be noted that the determination of the composition and properties of solvates is important for understanding the peculiarities of the extraction processes of metal acetylacetonates. Manganese(III) acetylacetonate $\text{Mn}(\text{acac})_3$, for example, is also widely used. The recrystallisation of the complex is most commonly conducted from solutions in chloroform, and in this case, the corresponding solvates may be formed, which can affect the structure and properties of $\text{Mn}(\text{acac})_3$. There are no data on the synthesis conditions and the composition of the solvates of manganese(III) acetylacetonate with chloroform. Therefore, the purpose of this work is to study the possibilities of its formation and to establish the composition of such solvates.

The formation of the solvate in solution was established using Fourier IR spectroscopy by the shift of the absorption band of the C-H chloroform bond. The composition of the $\text{Mn}(\text{acac})_3 \cdot 2\text{CHCl}_3$ solvate was determined using gravimetric analysis.

Keywords: Manganese, Acetylacetonate, Solvate, Gravimetric analysis, IR spectroscopy

For citation: Zlomanov V. P., Eshmakov R. S., Prolubshchikov I. V. Formation of a solvate of manganese(III) acetylacetonate and chloroform. *Kondensirovannye sredy i mezhfaznye granitsy = Condensed Matter and Interphases*. 2022;24(1): 29–32. <https://doi.org/10.17308/kcmf.2022.24/0000> <https://doi.org/10.17308/kcmf.2022.24/9052>

Для цитирования: Зломанов В. П., Эшмаков Р. С., Пролубщикова И. В. Образование сольвата ацетилацетоната марганца(III) с хлороформом. *Конденсированные среды и межфазные границы*. 2022;24(1): 29–32. <https://doi.org/10.17308/kcmf.2022.24/9052>

✉ Vladimir P. Zlomanov, e-mail: zlomanov1@mail.ru
© Zlomanov V. P., Eshmakov R. S., Prolubshchikov I. V., 2022



The content is available under Creative Commons Attribution 4.0 License.

1. Introduction

Manganese(III) acetylacetonate – $[\text{Mn}(\text{C}_5\text{H}_7\text{O}_2)_3]$ – is used as the source material for the synthesis of electrolytes [1] and catalysts [2–8]. Regardless of the synthesis method, $\text{Mn}(\text{acac})_3$ is most frequently recrystallised from solutions in chloroform. In this case, the corresponding solvates may be formed, which can affect the structure and properties of $\text{Mn}(\text{acac})_3$. The processes of formation of solvates of acetylacetonates of various metals have not been studied properly. There are some data on the formation of solvates of acetylacetonates of trivalent chromium, iron, and scandium with chloroform [9, 10]. However, there are no such data for $\text{Mn}(\text{acac})_3$. The purpose of this work was to study the possibilities of formation of solvates of manganese(III) acetylacetonates with chloroform using gravimetry and Fourier IR spectroscopy.

2. Experimental

2.1. Synthesis

To evaluate the possibility of the formation of solvates, we used chloroform as a solvent since it dissolves manganese(III) acetylacetonate well. A saturated solution of $\text{Mn}(\text{acac})_3$ in chloroform was prepared at room temperature. The solution was filtered and left in air until a crystal haze formed. After that, the crystals were separated by decantation. Oversaturation was created through evaporation of chloroform, which allowed regulating the rate of formation and growth of nuclei of new phases, including possible solvates. The crystallisation took from one to several days. Upon cooling, big shiny black crystals of the $\text{Mn}(\text{acac})_3$ solvate with chloroform were isolated at first and then decomposed after drying (for more than 24 hours) in air, which manifested in surface clouding and the transformation of crystals into powder.

2.2. Gravimetric determination of the composition of a $\text{Mn}(\text{acac})_3$ solvate with chloroform

The composition of the $\text{Mn}(\text{acac})_3 \cdot n\text{CHCl}_3$ solvate obtained through the recrystallisation of $\text{Mn}(\text{acac})_3$ from chloroform was determined using gravimetry. To do that, we poured the saturated solution of manganese(III) acetylacetonate in

chloroform into a weighed 50-ml flask and left it in air. Once the free solvent evaporated and signs of decomposition (loss of shine, colour changed from black to dirty green) of the first few crystals appeared, we recorded the weight of the flask and calculated the weight of the solvate. Two weeks later, when the decomposition of the solvate was almost complete (the weight stopped changing), we heated the flask with the substance up to 100 °C for 10 minutes using a heat gun in order to remove the last traces of solvent. After that, the weight was recorded again. The flasks were weighed on scales with an accuracy of 0.01 g. Over the whole period of the experiment the substance in the open flask was kept in a dark and dry place with almost fixed temperature (23 ± 1 °C).

The weight of the flask with the substance at the beginning of decomposition, in other words, the weight of the flask with the solvate, was $M = 34.17 \pm 0.01$ g. At the end of decomposition, after being heated with a heat gun the weight of the flask with crystals (manganese(III) acetylacetonate without chloroform) was $m = 31.45 \pm 0.01$ g. The weight of the empty flask is $m_F = 27.48 \pm 0.01$ g. If we express the composition of the solvate by the formula $\text{Mn}(\text{acac})_3 \cdot n\text{CHCl}_3$, then, using the obtained data, we can calculate the number n of chloroform molecules in the solvate as follows:

$$\begin{aligned} n &= \frac{(M - m) * M(\text{Mn}(\text{acac})_3)}{(m - m_F) * M(\text{CHCl}_3)} = \\ &= \frac{(34.17 - 31.45) * 352.265}{(31.45 - 27.48) * 119.378} = 2.022, \\ \Delta n &= \left(\frac{\Delta M + \Delta m}{M - m} + \frac{\Delta m + \Delta m_F}{m - m_F} \right) * n = \\ &= \left(\frac{0.01 + 0.01}{34.17 - 31.45} + \frac{0.01 + 0.01}{31.45 - 27.48} \right) * 2.022 \pm 0.03, \end{aligned}$$

that is, $n = 2.02 \pm 0.03$, while the composition of the solvate, therefore, can be expressed by the formula $\text{Mn}(\text{acac})_3 \cdot 2\text{CHCl}_3$, in other words, trivalent manganese acetylacetonate forms solvates with chloroform with the ratio of 1:2 as well as the corresponding derivatives of iron(III), chromium(III), and scandium (III).

2.3. Fourier IR spectroscopy

To establish the possibility of the formation of solvates, we analysed the IR spectra of

solutions using Perkin Elmer Frontier FT-IR. The transmission spectrum of the $\text{Mn}(\text{acac})_3$ solution in chloroform was recorded in a potassium bromide cuvette. The device was calibrated using a cuvette with pure chloroform.

A bright band was observed at $\sim 3000\text{ cm}^{-1}$ in the IR transmission spectrum of the $\text{Mn}(\text{acac})_3$ solution in chloroform relative to chloroform (Fig. 1). It corresponds to the vibrations of the C-H bond in CHCl_3 [11]. Its intensity should not be considered significant, since it should be subtracted from the background when recording the spectrum. $\text{Mn}(\text{acac})_3$ does not have such intense absorption bands in this region [12–14]. The considered band is also shifted in relation to the spectrum of pure chloroform. The observed band is associated with the interaction of chloroform molecules with $\text{Mn}(\text{acac})_3$ molecules, in other words, it indicates the formation of $\text{Mn}(\text{acac})_3$ solvates with CHCl_3 .

3. Conclusions

As a result of our work, through the use of Fourier IR spectroscopy, it was found that manganese(III) acetylacetonate forms a solvate with chloroform in solution, and it was also found through the use of gravimetry that the composition of the crystal solvate is expressed by the formula $\text{Mn}(\text{acac})_3 \cdot 2\text{CHCl}_3$. The obtained results are the first steps in the study of the solvation of manganese(III) acetylacetonate. For a more extended picture and a better understanding of the influence of the processes occurring in the solution on the structure of the complex, its solvates should be studied with a number of other solvents, and not only their composition, but also the structure should be established.

The latter task is very difficult, but it is highly interesting as part of the studied issue.

Author contributions

All authors made an equivalent contribution to the preparation of the publication.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

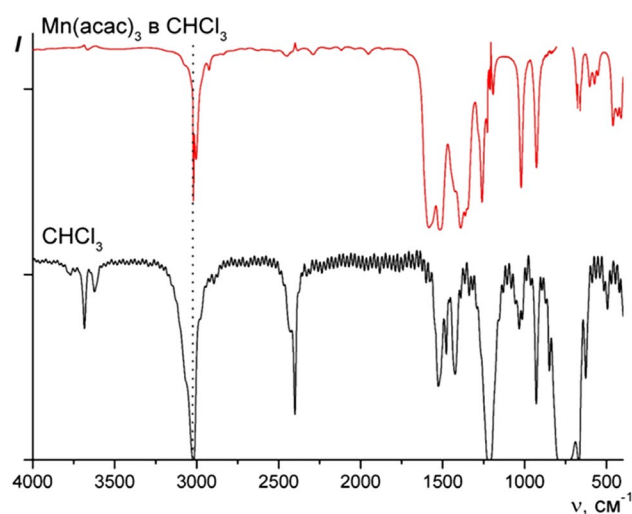


Fig. 1. IR transmission spectra of pure chloroform (relative to air) and a solution of $\text{Mn}(\text{acac})_3$ in chloroform (relative to chloroform). The intensities of the spectra are normalised

References

1. Sleightholme A. E. S., Shinkle A. A., Liu Q., Li Y., Monroe C. W., Thompson L. T. Non-aqueous manganese acetylacetonate electrolyte for redox flow batteries. *Journal of Power Sources*. 2011;196(13): 5742–5745. <https://doi.org/10.1016/j.jpowsour.2011.02.020>
2. Hirano M., Yakabe S., Clark J. H., Morimoto T. Synthesis of sulfoxides by the oxidation of sulfides with sodium chlorite catalysed by manganese(III) acetylacetonate in acetone in the presence of alumina. *Journal of the Chemical Society, Perkin Transactions 1*. 1996;22: 2693–2698. <https://doi.org/10.1039/P19960002693>
3. Dewar M. J. S., Nakaya T. Oxidative coupling of phenols. *Journal of the American Chemical Society*. 1968;90(25): 7134–7135. <https://doi.org/10.1021/ja01027a051>
4. Van Gorkum R., Bouwman E., Reedijk J. Fast Autoxidation of ethyl linoleate catalyzed by $[\text{Mn}(\text{acac})_3]$ and bipyridine: A possible drying catalyst for alkyd paints. *Inorganic Chemistry*. 2004;43(8): 2456–2458. <https://doi.org/10.1021/ic0354217>
5. Sharma R. K., Yadav M., Monga Y., Gaur R., Adholeya A., Zboril R., Varma R. S., Gawande M. B. Silica-based magnetic manganese nanocatalyst – Applications in the oxidation of organic halides and alcohols. *ACS Sustainable Chemistry & Engineering*. 2016;4(3): 1123–1130. <https://doi.org/10.1021/acsuschemeng.5b01183>
6. Ban H. T., Kase T., Murata M. Manganese-based transition metal complexes as new catalysts for olefin polymerizations. *Journal of Polymer Science, Part A:*

Polymer Chemistry. 2001;39(21): 3733–3738. <https://doi.org/10.1002/pola.10021>

7. Park Y. J., Kim J. G., Kim M. K., Chung H. T., Kim H. G. Preparation of LiMn_2O_4 thin films by a sol-gel method. *Solid State Ionics*. 2000;130(3-4): 203–214. [https://doi.org/10.1016/S0167-2738\(00\)00551-8](https://doi.org/10.1016/S0167-2738(00)00551-8)

8. Shimizu Y., Murata T. Sol-gel synthesis of perovskite-type lanthanum manganite thin films and fine powders using metal acetylacetonate and poly(vinyl alcohol). *Journal of the American Ceramic Society*. 1997;80(10): 2702–2704. <https://doi.org/10.1111/j.1151-2916.1997.tb03178.x>

9. Steinbach J. F., Burns J. H. Chloroform-bearing chelates. *Journal of the American Chemical Society*. 1958;80(8): 1839–1841. <https://doi.org/10.1021/ja01541a018>

10. Clarke F. R., Steinbach J. F., Wagner W. F. Halomethane solvates of trivalent acetylacetonates. *Journal of Inorganic and Nuclear Chemistry*. 1964;26(7): 1311–1316. [https://doi.org/10.1016/0022-1902\(64\)80215-3](https://doi.org/10.1016/0022-1902(64)80215-3)

11. Grinvald I. I., Kalagaev I. Yu., Petukhov A. N., Grushevskaya A. I., Kapustin R. V., Vorotyntsev I. V. Association of haloforms in condensed and gas phases. Ir spectroscopy and Dft calculations. *Journal of Structural Chemistry*. 2018;59(2): 313–320. <https://doi.org/10.1134/S0022476618020087>

12. Pinchas S., Silver B. L., Laulich I. Infrared absorption spectra of the ^{18}O -labeled acetylacetonates of Cr(III) and Mn(III). *Journal of Chemical Physics*. 1967;46(4): 1506–1510. <https://doi.org/10.1063/1.1840881>

13. Lawson K. E. The infrared absorption spectra of metal acetylacetonates. *Spectrochimica Acta*. 1961;17(3): 248–258. [https://doi.org/10.1016/0371-1951\(61\)80071-4](https://doi.org/10.1016/0371-1951(61)80071-4)

14. Diaz-Acosta I., Baker J., Hinton J. F., Pulay P. Calculated and experimental geometries and infrared spectra of metal tris-acetylacetonates: vibrational spectroscopy as a probe of molecular structure for ionic complexes. Part II. *Spectrochimica Acta, Part A*. 2003;59(2): 363–377. [https://doi.org/10.1016/S1386-1425\(02\)00166-X](https://doi.org/10.1016/S1386-1425(02)00166-X)

Information about the authors

Vladimir P. Zlomanov, DSc in Chemistry, Professor at the Department of Inorganic Chemistry of the Faculty of Chemistry, Lomonosov Moscow State University (Moscow, Russian Federation).

<https://orcid.org/0000-0002-0327-4715>
zlomanov1@mail.ru

Rodion S. Eshmakov, 6th year student of the Faculty of Chemistry, Lomonosov Moscow State University (Moscow, Russian Federation).

<https://orcid.org/0000-0002-6002-6515>
rodion.eshmakov@chemistry.msu.ru

Igor V. Prolubshchikov, 4th year student of the Faculty of Chemistry, Lomonosov Moscow State University (Moscow, Russian Federation).

<https://orcid.org/0000-0003-0735-1658>
prolubshikoviv@gmail.com

Received November 15, 2021; approved after reviewing December 10, 2021; accepted February 15, 2022; published online March 25, 2022.

Translated by Marina Strepetova

Edited and proofread by Simon Cox