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Volatile Single-Source Molecular Precursor for the Lithium Ion Battery Cathode

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Supporting Information

ABSTRACT: The first single-source molecular precursor for a lithium−manganese cathode material is reported. Heterometallic *β*-diketonate $LiMn_2(thd)_5$ (**1**, thd = 2,2,6,6-tetramethyl-3,5-heptanedionate) was obtained in high yield by simple one-step solid-state reactions employing commercially available reagents. Substantial scale-up preparation of **1** was achieved using a solution approach. The crystal structure of the precursor contains discrete Li:Mn = 1:2 trinuclear molecules held together by bridging diketonate ligands. The complex is relatively stable in open air, highly volatile, and soluble in all common solvents. It was confirmed to retain its heterometallic structure in solutions of non-coordinating solvents. The heterometallic diketonate **1** was shown to exhibit clean, low-temperature decomposition in air/oxygen that results in nanosized particles of spinel-type oxide $LiMn_2O_4$, one of the leading cathode materials for lithium ion batteries.

Among the various available storage technologies,[1] rechargeable lithium ion batteries are the fastest growing and the most promising systems, offering high energy density, flexible lightweight design, and longer lifespan than comparable battery technologies.[2] One of the most important active materials for the positive electrode of lithium ion batteries[3] is lithium−manganese oxide, $LiMn_2O_4$.[4] This cathode material has a spinel-type structure that can release Li^+ ions upon oxidation of its transition metal centers. Abundant Mn resources, low toxicity, high electronic and lithium ion conductivity, as well as an excellent rate capacity have made $LiMn_2O_4$ a leading candidate for vehicle battery applications.[5]

Development of lithium ion batteries is largely attributed to the growing demand for smaller, more sophisticated, and portable devices.[6] Thin-film batteries,[7] composed of solid-state materials that are only nanometers or micrometers thick, represent an improvement of the common rechargeable lithium ion battery technology in terms of safety, temperature stability, flexibility, and charge density. Because of their small size and unique features, thin-film batteries have a wide range of applications as power sources for consumer products as well as in medicine, semiconductor industry, oil drilling, and space exploration.

For thin-film batteries, a number of methods can be employed to deposit a thin-film cathode material onto the current collector.[8] The majority of these techniques involve the application of metal complexes with organic ligands, which are easily hydrolytically or thermally decomposable substances usually referred to as molecular precursors.[9] The interest in materials that incorporate more than one type of metal atoms has brought a great need for single-source precursors (SSPs)—molecules containing all the necessary elements in the proper ratio and decomposable in a controllable manner under mild conditions to yield phase-pure compounds.[10] Once developed, these heterometallic precursors may be exploited for thin-film growth as well as for other applications such as preparation of nanocrystals with an appropriate size that exhibit fundamental modifications in electrochemical behavior of oxide materials.

The SSP approach to lithium−transition metal oxides is relatively undeveloped. Only a handful of heterometallic compounds have been reported recently,[11,12] starting with the pioneering work by Boyle.[11] Notably, all of the previous reports deal with nonvolatile Li−Co(Ni) compounds. In fact, most of the known precursors are insoluble coordination polymers suitable for bulk decomposition only. Since stable Li-containing compounds with transition metals tend to crystallize as coordination polymers or ionic frameworks, the preparation of discrete heterometallic molecules with an appropriate Li:M ratio and ligands that can be removed cleanly under relatively mild conditions is a difficult task. Even more challenging is to synthesize lithium-containing compounds that are volatile and retain their heterometallic structures upon sublimation. To the best of our knowledge, there are no reports on molecular precursors for the $LiMn_2O_4$ spinel cathode material. While several dozen Li−Mn heterometallic compounds are known, none of those can be used as a SSP.

The goal of our research was to create a Li−Mn heterometallic compound that meets certain requirements for an ideal SSP attractive to industrial applications:

(1) to contain discrete molecules with a proper 1:2 lithium to manganese metal ratio;
(2) to be a volatile compound that sublimes congruently (composition in the gas phase corresponds to that in the solid state);
(3) to be soluble in common solvents and to retain the heterometallic structure in solution;
(4) to be readily available via a simple reaction procedure on a large scale with high yield;
(5) to have an overall low cost of preparation, preferably through one-pot synthesis using commercially available starting reagents or compounds that can be conveniently obtained from commercial sources;

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(6) to exhibit low moisture- and air-sensitivity, so it can be handled outside the glovebox;
(7) to demonstrate clean, low-temperature decomposition leading to the phase-pure $LiMn_2O_4$ oxide.

Herein we report preparation, characterization, and decomposition study of the first volatile heterometallic molecular precursor that has a proper Li:Mn ratio for the corresponding lithium ion battery cathode material. We also discuss in detail how the title compound fits the criteria for an ideal SSP.

Heterometallic β-diketonate $LiMn_2(thd)_5$ (**1**) (thd = 2,2,6,6-tetramethyl-3,5-heptanedionate) has been obtained in a sealed evacuated ampule at 110 °C by stoichiometric solid-state redox reaction of reagents that are both commercially available:

$$2Li + 2Mn(thd)_3 \rightarrow LiMn_2(thd)_5 + Li(thd) \qquad (1)$$

Yellow crystals of **1** can be conveniently collected with ca. 70% yield after 5 days in the cold end of the ampule, where the temperature was kept ca. 5 °C lower. The second product, Li(thd), is volatile only after 160 °C and thus remains in the hot end of the container during the course of reaction and mass-transfer. Heterometallic diketonate can be additionally recrystallized by sublimation at 90−100 °C, if needed. Purity of the bulk product **1** has been confirmed by elemental analysis as well as by X-ray powder diffraction through comparison of the experimental spectrum with the theoretical pattern calculated from the single-crystal data (Figure 1).

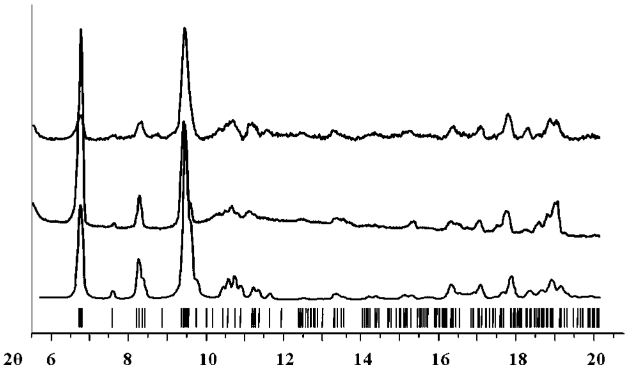

Figure 1. X-ray powder diffraction patterns of $LiMn_2(thd)_5$ (**1**) bulk products synthesized by solution (top) and solid-state (middle) methods and their comparison with the simulated pattern (bottom) calculated from the single-crystal data.

An even better yield of **1** (85%) was obtained in another solid-state reaction between lithium diketonate and anhydrous manganese(II) chloride:

$$5Li(thd) + 2MnCl_2 \rightarrow LiMn_2(thd)_5 + 4LiCl \qquad (2)$$

While this reaction is a bit slower than reaction 1, it does not involve the use of metallic lithium as a reactant and employs a much cheaper Mn source. The second product, lithium chloride, is not volatile and does not interfere with heterometallic product **1** which is collected in the cold zone of the ampule. The process also employs commercially available reactants, though we used Li(thd) that was freshly prepared from lithium hydroxide.

We confirmed that reactions 1 and 2 can also be run in solution to provide a fast preparation of heterometallic precursor **1** on a gram scale. In both procedures, the yellow amorphous powder initially obtained can be either annealed or resublimed to yield microcrystalline material that is identical to $LiMn_2(thd)_5$ (**1**) obtained by the solid-state/gas-phase technique (Figure 1).

Heterometallic diketonate **1** in crystalline form was found to be relatively stable in moist air and can be handled outside the glovebox in a course of decomposition studies. Air-sensitivity of the complex was tested by continuous recording of its powder diffraction pattern (SI, Figure S1). The latter revealed that the complex remains intact for at least 24 h, after which time some structural changes started to occur. Heterometallic diketonate is highly volatile at temperatures of ≥100 °C, while the sublimation process is likely of a congruent character. Indirect proof for the latter comes from two observations: (i) the compound can be resublimed quantitatively, and (ii) the mass-transfer of **1** in vapor phase can be achieved at temperatures as low as 90 °C, at which one of its possible dissociation products, Li(thd), is not volatile.

Single-crystal X-ray analysis (SI, Table S1) revealed that heterometallic diketonate **1** contains discrete trinuclear molecules $LiMn_2(thd)_5$ (Figure 2a) with a proper 1:2 metal ratio for the desired decomposition product. The compound crystallizes in the centrosymmetric triclinic unit cell with two crystallographically independent molecules. One of those is highly disordered, but it can be perfectly refined (even with anisotropic displacement parameters for the core atoms) as a superposition of two enantiomers (SI, Figure S2). The lithium atom exhibits distorted tetrahedral coordination of four diketonate oxygens. The manganese atoms maintain distorted octahedral geometry that was previously observed[13−16] in all Mn-containing homo- and heterometallic β-diketonate complexes. The molecular formula suggests that Li atom is in +1 and Mn atoms are in +2 oxidation states. Two of the five diketonate groups are chelating to Mn atoms, the third group is chelating to Li/bridging to Mn, and the remaining two ligands are acting in an unusual (though not entirely unknown[17]) manner of bridging metal atoms (none of those are located in diketonate plane) through both of the oxygens (SI, Figure S3). Sterically bulky thd ligands provide coordinative saturation of metal atoms in complex **1** as well as protection of the trinuclear unit, as can be seen from the space-filling diagram of $LiMn_2(thd)_5$ (Figure 2b). The latter ensures the absence of metal-based intermolecular contacts and prevents polymerization of the metal units so typical for lithium compounds with small monoanionic oxo-donor ligands. It also explains the

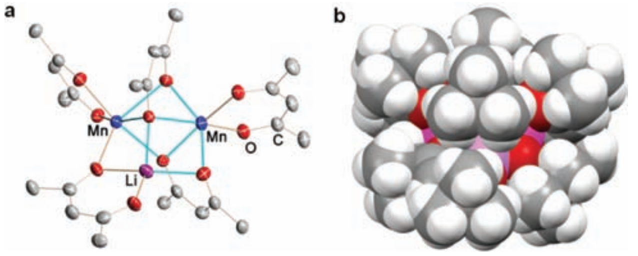

Figure 2. Molecular structure of $LiMn_2(thd)_5$ (**1**). (a) View of trinuclear heterometallic diketonate complex drawn with thermal ellipsoids at the 40% probability level. Metal−oxygen bonds to diketonate ligands involved in bridging interactions are shown in blue. Hydrogen atoms and *tert*-butyl groups are omitted for clarity. Selected bond distances and angles are listed in SI, Table S2. (b) Space-filling representation. The view is similar to that depicted in part (a), with all *tert*-butyl groups added.

relatively low air- and moisture-sensitivity of the heterometallic complex.

Heterometallic diketonate **1** is readily soluble in all common solvents, including hexanes. Solutions of **1** in non-coordinating solvents are NMR (^{1}H, ^{13}C, and ^{7}Li) silent, as we have already noted for other manganese(II)-containing diketonates $MMn_2(\beta\text{-dik})_6$ (M = Mn,[13] Pb,[15] Cd,[16] and Hg_2[16]) that also exhibit discrete molecular structures. Importantly, the absence of NMR signals in non-coordinating solvents (hexanes, toluene, chloroform) indicates that the heterometallic molecules $LiMn_2(thd)_5$ remain intact in these solutions. In contrast, in coordinating solvents (DMSO, THF) the molecule dissociates into $Mn(thd)_2(sol)_2$ (NMR silent) and $Li(thd)(sol)_2$ adducts, for which ^{1}H and ^{7}Li signals instantly appear in NMR spectra (SI, Figures S4−S7). Additional information on the solution structure can be obtained by comparison of the solid-state and solution IR spectra of **1** that are identical for non-coordinating solvents (SI, Figure S8) but different for coordinating ones.

According to the thermogravimetric analysis data, heterometallic diketonate **1** exhibits clean, low-temperature decomposition that occurs in a single step between 145 and 220 °C. X-ray powder diffraction analysis of decomposition traces confirmed the presence of a $LiMn_2O_4$ oxide phase. The weight of the decomposition residue (18.0%) corresponds well with the theoretical value (17.5%) that was calculated on the basis of metal content, assuming it is pure $LiMn_2O_4$ oxide (SI, Figures S9 and S10).

Thermal decomposition of $LiMn_2(thd)_5$ (**1**) precursor obtained by both solid-state and solution methods has been carried out at 600 °C in an oxygen atmosphere oven using high-alumina crucibles. Analysis of decomposition products by X-ray powder diffraction revealed the presence of a phase-pure $LiMn_2O_4$ (Figure 3). Elemental analysis indicates no appreciable carbon content in the oxide material. The appearance of spinel phase can be detected after just a few minutes. Initially, the diffraction peaks are noticeably broad, but the crystallinity of the oxide can be significantly increased by annealing the sample for an additional time. SEM images (SI, Figure S11) confirmed that the oxide phase appears as nanosized particles measured at 20−30 nm that grow to 80−90 nm upon annealing.

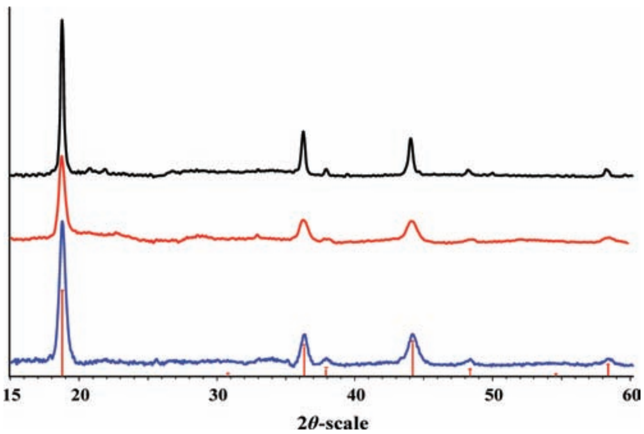

Figure 3. X-ray powder diffraction patterns of $LiMn_2O_4$ spinel obtained by decomposition at 600 °C of $LiMn_2(thd)_5$ (**1**) samples prepared by solution (blue) and solid-state methods (annealing times of 2 h (red) and 24 h (black)). The powder diffraction patterns correspond to $LiMn_2O_4$ that is shown as a peak diagram.

In conclusion, the first molecular precursor for a lithium−manganese cathode material reported in this work exhibits several characteristics of an ideal single-source precursor. The isolation of heterometallic diketonate $LiMn_2(thd)_5$ was a result of a long, systematic search for appropriate ligands and starting materials that allow one to obtain the target product with discrete molecular structure and a proper metal ratio. The complex is highly volatile, and as such it can be broadly used to obtain thin films, nanocrystals, or single crystals of $LiMn_2O_4$ cathode material. The retention of heterometallic structure in solution of non-coordinating solvents opens unique opportunities for application of the title precursor in direct liquid injection chemical vapor deposition techniques for thin-film growth. Synthetic approaches developed in this work for the preparation of compound **1** should help to design a new generation of volatile molecular precursors for the lithium (sodium)−transition metal oxide, fluoride, and silicate cathode materials.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Full synthetic and characterization details, TGA plots and traces of thermal decomposition, IR and NMR spectra, powder X-ray diffraction patterns, additional details on interatomic distances and angles in the structure of **1**, and X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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