Mechanochemical synthesis and thermal property investigation of metallomesogens and transition metal complexes

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Dialkyl 2,2′-bipyridyl-4,4′-dicarboxylate ($L\beta_n$, where $\beta_n$ refers to the number of carbons in $\beta$-substituted alkyl chain) complexes including $\text{Pt}L\beta_{16}\text{Cl}_2$, $\text{Cd}L\beta_{16}\text{Cl}_2$, $[\text{Ag}L\beta_{n}\text{NO}_3]$ and the dodecylsulfate salt $[\text{Ag}L\beta_{n}2\text{(DOS)}]$ were produced at reduced cost and in shorter times, compared to traditional solvent-based methods, by mechanochemical reaction in the absence of solvent. $\text{Pt}L\beta_{16}\text{Cl}_2$ and the $[\text{Ag}L\beta_{n}2\text{(DOS)}]$ complexes are the first mesogenic transition metal complexes to be produced via ball milling. The effectiveness of a simple ligand modification, $\beta$- versus $\alpha$-attachment of the alkyl functionalities to the ligand, is presented as a highly effective method for increasing the stable temperature range of a variety of metallomesogens and for producing sub-room-temperature liquid crystals.

**Keywords:** metallomesogen; liquid crystal; room-temperature liquid crystal; ball mill; mechanochemical; mechanochemistry

1. Introduction
Mechanochemical synthesis or mechanochemistry refers to the use of mechanical energy (generally in the form of grinding or shaking) to drive reactions. Mechanochemical synthesis is generally thought of as a solid-state synthetic method, although liquid reagents and small amounts of solvent can be used during synthesis, as has been reviewed.[1–6] There are three general types of mechanochemical apparatuses: (1) the mortar and pestle, (2) the vibratory ball mill and (3) the planetary ball mill. In a vibratory ball mill and (3) the planetary ball mill, such as the one utilised in this research, reagents and milling balls are shaken inside a milling vial.

The main advantages of mechanochemical methods over traditional solvent-based syntheses are: (1) reduced/eliminated solvent waste, (2) reduced reaction time and/or (3) improved yield.[3] While not all of these benefits are realised for all reactions, the net effect of any one of these benefits reduced reaction cost, once the expense for the change in reaction equipment is recouped. At many smaller institutions, however, the initial outlay presents a considerable barrier to attempting mechanochemical synthesis. While reactions can sometimes be carried out using a mortar and pestle,[7] the manual labour involved makes this unappealing and often impractical. The syntheses discussed herein demonstrate that efficient, labour-saving mechanochemical reactions do not require purpose-built mechanochemical reactors or high-powered planetary ball mills. The reactions presented here were completed using a Spex 5100 Mixer Miller (Spex, Metuchen, NJ, USA), a vibratory mill more commonly utilised to prepare finely ground samples for infrared (IR) spectroscopic analysis of KBr pellets and a device that many institutions already have access to.

Beyond the initial differences in reaction conditions, mechanochemical synthesis can be remarkably similar to solvent-based methods once the purification stage is reached. Although the reactions themselves are solvent free, product purification can be essentially unchanged from the process utilised after wet synthesis, a situation that needs to be avoided to maximise the benefits of utilising an alternative energy addition method. Purification of mechanochemically derived products has recently been reviewed.[3] The ideal reaction for mechanochemical synthesis is one in which a single product is produced, a so-called atom-conserved reaction. Atom-conserved, and therefore by-product-free, mechanochemical reactions are rare.[1,2] The research presented herein adds to the number of these reactions.

Mechanochemistry is only just beginning to be utilised for the production of transition metal complexes. A few nonmesogenic platinum complexes have been prepared,[8–12] but few monomeric transition metal complexes of any kind have been prepared via mechanochemistry.[3,13–18] To the authors’ knowledge, this is the first time metallomesogenic complexes have been prepared by mechanochemical methods.

Synthesis, whether mechanochemical or solvent based, is simply a means to an end in preparing
compounds with improved liquid crystalline properties. In addition to presenting a generalisable method for preparing transition metal complexes via mechanochemical synthesis, herein is also presented a simple ligand modification that produces liquid crystalline complexes stable over a wider temperature range that includes room temperature. As shown in Figure 1, this modification involves changing the attachment of the long alkyl chains on the ligand from $\alpha$ to $\beta$.

2. Results and discussion

2.1 Syntheses

The utility of $\beta$-substituted bipyridine ligands in producing near-room-temperature liquid crystalline compounds was recently demonstrated by our group; however, due to the cost of platinum starting materials and a modest yield of 72% for the PtL$_{\beta16}$Cl$_2$ using toluene,[19] the applicability of ball milling to the reaction was investigated with the goal of determining a more cost-effective method for producing systems in which metallophilic interactions [20] could be studied. This reaction will be discussed in detail, but the procedures utilised to optimise the synthetic conditions are applicable to all the complexes discussed herein. The L$_{\beta n}$ reactions discussed here give quantitative yields of the desired product, as determined by nuclear magnetic resonance (NMR) spectroscopy, and the values given here and in the Supplemental data are the isolated recoveries. Specific synthetic details and characterisation information for all compounds may be found in the Supplemental data.

Initially, PtL$_{\beta16}$Cl$_2$ synthesis was attempted by grinding PtCl$_2$ with L$_{\beta16}$ in a 1:1 mol ratio using a glass mortar and pestle for 15 minutes, as certain reactions can be accomplished with this simple method.[7] While there was no visible colour change in the sample, upon dissolution in CDCl$_3$ and centrifugation a pale orange colour was observed. Analysis of the sample by $^1$H NMR spectroscopy showed a minute quantity of the desired platinum complex was produced. A concern in this analysis would be that the reaction actually occurred in the NMR solvent rather than during the course of ball milling; however, PtCl$_2$ is insoluble in chloroform and does not react with L$_{\beta16}$ upon stirring at room temperature even over long time periods.

Based on this promising result, a 1:1 reaction mixture was milled to determine the complete conversion time; however, conversion peaked at 86% after 2 hours and could not be increased with additional milling time. To counteract this, the reaction was performed again using a 50% excess of PtCl$_2$, and PtL$_{\beta16}$Cl$_2$ was obtained in quantitative yield after 2 hours of milling. Proton NMR spectroscopy (Figure 2) confirmed the absence of unbound ligand, and the product spectrum was in agreement with the results from the solution-synthesised product.[19] In Figure 2, the aromatic region is shown because of the large alteration in the positions of the aromatic regions upon complexation of the metal centre. The alkyl protons, being farther removed from the metal centre, are largely unchanged upon coordinating the platinum centre.

The advantages of using mechanochemistry for this reaction are numerous. By eliminating the solvent incompatibilities of the reagents, the product was obtained in a higher yield (100% vs 72%) and in less time (2 hours compared to 18 hours). The purification of the product was also simplified: dissolution and filtration to remove excess PtCl$_2$ compared to column chromatography to remove unreacted ligand,[19] and there is a difference in solvent usage of approximately 2 litres over the course of the entire synthesis and purification.

In the process of developing the mechanochemical reaction, improvements were also made in the solution synthesis of PtL$_{\beta16}$Cl$_2$.[19] This reaction also benefits from the addition of excess PtCl$_2$, and 1.9 equivalents of the reagent will result in quantitative yield after overnight reaction under a nitrogen atmosphere. However, precise temperature is of vital importance in optimising the solution preparation. Refluxing the reaction mixture or performing the
synthesis above 100°C results in significant production of Pt(0), limiting yields. Lower temperatures are insufficient to fully dissolve the platinum starting material in toluene and also result in reduced yields and drastically increased reaction times.

The mechanochemical methodology can also be easily modified for different metal centres. The solution synthesis of the α-substituted dodecysulfate salt [AgL{α}_{16}^2](DOS) has already been reported as liquid crystalline.[21] [AgL{β}_{16}^2](DOS) was synthesised by ball-milling Ag(DOS) with L{β}_{16} in a 1:2 mol ratio using a polystyrene grinding jar. The starting material Ag(DOS) was synthesised according to the literature procedure[22] and stored in a dark location to avoid any possible photodecomposition. During ball milling, a polystyrene vial had to be used instead of a steel vial as Ag(DOS) decomposes upon milling in a steel vial. [AgL{β}_{16}^2](DOS) was obtained in 97.9% recovery after 4 hours compared to 82% yield in 24 hours for the solution synthesis of the α-substituted derivative in dichloromethane.[21] Interestingly, the ball mill synthesis does not need to be carried out under an inert atmosphere, unlike the solution-based preparation.[21] Proton NMR analysis of [AgL{α}_{16}^2](DOS) was not reported in the literature.[21] so comparisons cannot be made; however, the shift in aromatic resonances is in keeping with what is observed for other silver complexes with pyridine-derived ligands.[23–25] [AgL{β}_{16}^2](DOS) can similarly be prepared in high yield.

Following this success, the ability of branching to induce mesomorphic behaviour in a compound whose α-substituted derivative is not liquid crystalline was investigated. To test this, the [AgL{β}_{16}NO_3] and Cd{β}_{16}Cl_2 were chosen, as similar α-substituted derivatives have been previously reported as nonliquid crystalline [19,26]; however, the overall structure of the compounds, with their disc-like ‘heads’ and long alkyl chains, is similar to that of the liquid crystalline platinum complexes already discussed. Although the compounds were successfully synthesised in high recovery via mechanochemistry, as is discussed further in the section on Thermal Properties, it was determined that neither of these compounds is mesogenic. [AgL{β}_{16}NO_3] was synthesised in 97.9% recovery in 4 hours and is a liquid at room temperature. During workup, hexane was used to help remove the product from the ball milling vial. Initial elemental analysis results showed half a hexane molecule was incorporated into the material for each metal centre. This solvent can easily be removed upon heating under vacuum. [AgL{β}_{16}NO_3] was similarly prepared.

### 2.2 Thermal properties

A summary of the thermal properties of the newly synthesised complexes is shown in Table 1. In the case of the liquid crystalline complexes, data on the corresponding α-substituted derivatives are presented for comparison. Previous comparison of PtL{α}_{16}Cl_2 and PtL{β}_{16}Cl_2 showed that modification to a branched alkyl chain system dramatically improved the liquid crystalline range for the compound while maintaining the smectic structure and metallophilic interactions of the mesophase.[19] This work endeavoured to determine whether this benefit would be realised at shorter chain lengths.

The α-substituted derivative [AgL{α}_{16}](DOS), previously reported,[21] contains a crystal-to-crystal transition not observed for the newly synthesised β-derivative. The α-substituted derivative’s onset temperature is 73°C higher than that of the β-derivative.
Table 1. Thermal properties of CdL\textsuperscript{β16}Cl\textsubscript{2}, [AgL\textsuperscript{β16}](DOS), [AgL\textsuperscript{β16}(NO\textsubscript{3})\textsubscript{2}] (\textit{n} = 10, 16) and [AgL\textsuperscript{β10}](DOS).\textsuperscript{a}

| Species (decomposition, °C) | Transition | Temperature (°C) | ΔH (kJ/mol) | Ref. |
|-----------------------------|------------|------------------|-------------|------|
| CdL\textsuperscript{β16}Cl\textsubscript{2} | Cr to I | 152.2 | 27.7 | b |
| (278.4) | I to Cr | 133.5 | 26.4 |
| [AgL\textsuperscript{β16}(NO\textsubscript{3})\textsubscript{2}] | glass to I | -17.7 |
| (240.6) | I to glass | -23.1 |
| [AgL\textsuperscript{β16}(NO\textsubscript{3})\textsubscript{2}] | Cr to I | 10.7 | 23.9 | b |
| (230.8) | I to Cr | -0.1 | 20.6 |
| [AgL\textsuperscript{β10}](DOS) | FLC to LC | -17 | c | b |
| (269.3) | LC to I | 46.8 | 3.9 |
| | I to LC | 40.0 | 3.4 |
| | LC to FLC | -20 | c |
| [AgL\textsuperscript{β16}](DOS) | Cr to LC | 7.9 | 67.7 | b |
| (251.0) | LC to I | 39.7 | 4.3 |
| | I to LC | 30.8 | 4.9 |
| | LC to Cr | 0.4 | 59.8 |
| [AgL\textsuperscript{β16}](DOS) | Cr1 to Cr2 | 77 | 16.8 | [21] |
| d | Cr2 to LC | 81 | 98.5 |
| | LC to I | 85 | 62.2 |
| | I to LC | 64 | 41.2 |
| | LC to Cr1 | 48°C | 39.3 |

Notes: \textsuperscript{a}Transition temperatures for liquid crystalline compounds from differential scanning calorimetry (DSC) maxima/minima during second heat/cool, melting temperatures determined by melting point apparatus, decomposition temperatures from thermogravimetric analysis (TGA) first mass loss inflection points; crystalline phase, Cr; liquid crystalline phase, LC; isotropic liquid, I; frozen liquid crystalline phase, FLC. \textsuperscript{b}This work. \textsuperscript{c}This transition occurs without endotherm or exotherm or distinct \textit{T}\textsubscript{c}. \textsuperscript{d}Not reported.

and similarly the \textit{α}-substituted derivative’s clearing temperature is 45°C higher than that of the \textit{β}-derivative. Besides the improvement in the onset temperature, the liquid crystalline temperature range increased from 4°C to 32°C going from the \textit{α}- to \textit{β}-substitution of the alkyl chains. Since the \textit{β}-branching decreases the onset temperature more than the clearing temperature, this leads to a dramatic increase in the liquid crystalline range.

[AgL\textsuperscript{β16}](DOS) does not behave quite as cleanly as its longer chained counterpart. Upon heating from \textdegree{}80°C, the material gradually softens until it takes on a fluid, liquid crystalline phase at approximately \textdegree{}20°C. This change is not marked by an endotherm in the differential scanning calorimetry (DSC) trace, nor does it show a sharp glass transition. Based on the birefringence of the low-temperature phase, it is likely that at lower temperatures the material forms a frozen liquid crystalline phase that retains the ordering from the liquid crystalline phase. Above approximately \textdegree{}20°C, the material behaves as a typical liquid crystalline phase and its clearing temperature is 46.8°C. The reverse behaviour is observed upon cooling.

Polarised optical microscopy of PtL\textsuperscript{β16}Cl\textsubscript{2} demonstrated that the material had a very similar texture to PtL\textsuperscript{β10}Cl\textsubscript{2},\textsuperscript{[19,27]} and the complexes were determined by variable-temperature X-ray diffraction to be structurally similar as well.\textsuperscript{[19,28]} Likewise [AgL\textsuperscript{β16}](DOS) and [AgL\textsuperscript{β10}](DOS) demonstrate similar textures under cross-polarisation to each other. No evidence of Maltese crosses, like those observed for [AgL\textsuperscript{α16}](DOS),\textsuperscript{[21]} was observed upon cooling. Textures for the \textit{β}-substituted compounds are given in Figure 3. These textures are obtained upon cooling the compounds from the isotropic melt and shearing the samples.

The remaining complexes were not liquid crystalline as determined through a combination of optical analysis and DSC. DSC analysis of [AgL\textsuperscript{β16}NO\textsubscript{3}] showed only one transition, which occurs at 10.7°C. Polarised optical microscopy reveals that below 10.7°C the compound is a solid, while above it is an isotropic liquid. [AgL\textsuperscript{β16}NO\textsubscript{3}] is a pale yellow solid at room temperature with a melting point of 93°C. This drastic decrease in the melting point is similar to the 73°C decrease in the onset temperature for [AgL\textsuperscript{β16}](DOS) and could be extended to other nonliquid crystalline materials to fine-tune their thermal properties. Shortening the alkyl chain, as in [AgL\textsuperscript{β10}NO\textsubscript{3}], decreases the melting point compared to [AgL\textsuperscript{β16}NO\textsubscript{3}] but does not induce mesomorphism.

Figure 3. (colour online) Micrographs of the liquid crystalline phases of [AgL\textsuperscript{β16}](DOS) (left) and [AgL\textsuperscript{β16}](DOS) (right) under cross-polarised light.
Interestingly, the low-temperature phase of [AgL$^{16}$NO$_3$] is highly crystalline, as evidenced by the sharp endotherms and exotherms on heating and cooling and the relatively large changes in enthalpy. [AgL$^{10}$NO$_3$] undergoes a glass transition upon cooling leading to the conclusion that the high degree of crystallinity in [AgL$^{10}$NO$_3$] is afforded due to the packing of the longer alkyl chains. From this, it can be concluded, at least in this case, that $\beta$-substitution will not induce mesomorphism in a compound whose $\alpha$-substituted version is not already liquid crystalline. While $\beta$-substitution did not affect the ability to form a liquid crystalline phase, it did alter the melting point properties of the compounds.

3. Conclusions
Mechanochemical synthesis has been shown to be effective for preparing metallomesogenic compounds for the first time. The synthetic technique was shown to be general for preparation of a variety of complexes, while it greatly reduced reaction time, solvent use and improved yields when compared to solvent-based methods. While modification of the alkyl chain attachment on dialkyl 2,2′-bipyridyld-4,4′-dicarboxylate ligands from $\alpha$ to $\beta$ is effective in decreasing the onset temperatures for liquid crystalline temperatures and broadening the stable temperature range of [AgL$^{\beta}$](DOS) derivatives, it was not effective in preparing mesogenic complexes in the cases of [AgL$^{\beta}$NO$_3$] and CdL$^{16}$Cl$_2$.

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Supplemental data
Supplemental data for this article can be accessed here.

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