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PAPER

Mechanochemical and solution synthesis, and crystal structures and IR and solid-state (CPMAS) NMR spectroscopy of some bis(triphenylphosphine) silver(I) mono- and di-hydrogencitrate systems†

Graham A. Bowmaker,*[a] John V. Hanna,*[b] Brian W. Skelton[c] and Allan H. White[c]

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The complex $[(Ph_3P)_2Ag(H_2cit)]\cdot EtOH$ (**1**; H_2cit^- = dihydrogencitrate = $C_6H_7O_7^-$) contains $[(Ph_3P)_2Ag(H_2cit)]$ molecules in which the silver atom is coordinated to two PPh_3 molecules and the two oxygen atoms of one of the 'terminal'/1-carboxylate groups of the dihydrogencitrate group. The molecules form centrosymmetric hydrogen-bonded dimers in the solid. In $[\{(Ph_3P)_2Ag\}_2(Hcit)]$, (**2**), unsymmetrical deprotonation of the citrate grouping is found, from the 1- and 3- (*i.e.* terminal and central) carboxylates: $[(Ph_3P)_2Ag(O_2CCH_2C(OH)(CH_2COOH)CO_2)Ag(PPh_3)_2]$. The above complexes, as well as $[(Ph_3P)_3Ag(H_2cit)]$ (**3**) were prepared *via* conventional solution methods, involving the reaction of trisilver(I) citrate, citric acid and triphenylphosphine, and by a mechanochemical method involving the reaction of silver(I) oxide, citric acid and triphenylphosphine. IR studies of **1–3** show the presence of coordinated carboxylate and free carboxylic acid groups in the mono- and di-hydrogencitrate ligands, and the formation of **2** from **1** shows that dihydrogencitrate deprotonation can occur upon dissolution of **1** in protic solvents. High-field (9.40 T) ^{31}P CPMAS NMR spectra were recorded and analysed, yielding heteronuclear $^1J(^{107/109}Ag,^{31}P)$ and homonuclear $^2J(^{31}P,^{31}P)$ spin–spin coupling constants.

Introduction

The many crystallographic studies of complexes of silver(I) that have been reported demonstrate its structural versatility in its coordination chemistry.[1,2] Many of these complexes involve anionic ligands such as halides, pseudohalides and oxyanions. Some types of oxyanion complex, such as those involving carboxylate ligands, have long been known,[3,4] and we have previously characterized a number of examples involving formate, the simplest possible carboxylate ligand, by crystal structure and spectroscopic methods.[5,6] Silver–carboxylate systems are of considerable interest in a number of different areas of chemistry, such as the synthesis and mechanism of action of silver metal catalysts,[7–9] the preparation of silver colloids, coatings, nanoparticles and nanowires,[9–17] and as antibacterial agents.[18,19] Silver(I) is known to deactivate cellular enzymes and DNA by coordinating to electron-donating groups such as carboxylates.[20] While many structural studies have been reported on silver(I) mono-carboxylate complexes,[1,21–26] there is a paucity of data on those of familiar oligo-/poly-carboxylates. For example, a number of the interesting applications of silver–carboxylate systems involve the tribasic acid citric acid ($C_6H_8O_7$ = 'H_3cit') and its various deprotonated forms, referred to collectively as 'citrate',[10–16,18] with structures available in ref. 27 and 28. However, there has been no systematic study of families of silver(I) complexes involving citrate ligands, complexes of which are sometimes difficult to crystallize and, while there are references in the patent literature to 'silver dihydrogen citrate' and its antimicrobial action,[18] there have been no reports of a proper characterization of this compound or any complexes thereof. The compound 'silver citrate hydrate' ($C_6H_5O_7Ag_3$ = Ag_3cit)·(xH_2O) 'trisilver citrate' is commercially available (*e.g.* Aldrich 361259), but its structure is not known and results of a recent solid-state ^{109}Ag CPMAS NMR study suggest that the silver coordination in this compound is quite different from that in silver(I) carboxylates involving monobasic carboxylic acids.[29]

In the present work we undertook a study of complexes of silver(I) mono- and di-hydrogencitrate with triphenylphosphine. Use of the triphenylphosphine ligand PPh_3 allows the isolation of silver carboxylate units, which might otherwise form polymeric structures,[28] and provides an NMR probe by way of the ^{31}P nucleus. ^{31}P CPMAS NMR spectra were acquired with the aim of measuring the heteronuclear $^1J(^{107/109}Ag,^{31}P)$ and homonuclear $^2J(^{31}P,^{31}P)$ spin–spin coupling constants, which provide information about the metal–ligand bonding in the complexes. Infrared spectroscopy was also applied to provide evidence concerning the nature of the citrate ligand present and its mode of bonding to the silver atom. X-ray crystal structures were determined where possible to provide more detailed structural

[a]*School of Chemical Sciences, University of Auckland, Private Bag 92019, Auckland, New Zealand. E-mail: ga.bowmaker@auckland.ac.nz*
[b]*Department of Physics, University of Warwick, Coventry, CV4 7AL, UK*
[c]*School of Chemistry and Biochemistry M313, The University of Western Australia, Crawley 6009, Western Australia*

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information and geometric parameters for correlation with the NMR data.

The ready accessibility of a number of novel species and/or forms by way of mechanochemical synthesis[30–50] has encouraged us to explore some triphenylphosphine–silver(I) mono- and di-hydrogencitrate systems in this manner. We chose to use silver(I) oxide Ag_2O as the source of silver(I) in these reactions. Most of the mechanochemical syntheses of metal complexes reported to date use metal salts or other metal complexes as the source of the metal ion,[30–37,46–50] but some recent reports demonstrate the possibility of using metal oxides, particularly those of groups 2 and 12,[42–45] and the present work shows that this approach may be extended to the Group 11 metal oxide Ag_2O.

Experimental

Chemicals

Silver(I) oxide (BDH), triphenylphosphine (RdH), citric acid monohydrate (Merk) and sodium dihydrogencitrate (Sigma) were used as received. Trisilver(I) citrate was prepared by mechanochemical reaction of silver(I) oxide (0.9 mmol) and citric acid (0.6 mmol) as described below.

Preparation of compounds

$[(Ph_3P)_2Ag(H_2cit)]\cdot$EtOH, 1. *Method 1*. A mixture of trisilver(I) citrate ($Ag_3cit \equiv Ag_3C_6H_5O_7$) (0.51 g, 1.0 mmol), citric acid monohydrate (0.84 g, 4.0 mmol) and PPh_3 (1.6 g, 6.0 mmol) and ethanol (20 ml) was heated with stirring. The resulting solution was filtered while hot and allowed to cool slowly in a hot water bath. The colourless crystalline product was collected and washed with ice-cold ethanol. Yield 2.2 g (84%). Found: C 61.5, H 5.0%; calcd for $C_{44}H_{43}AgO_8P_2$: C 60.8, H 5.0%.

Method 2. Silver(I) oxide (0.070 g; 0.3 mmol) and citric acid monohydrate (0.126 g, 0.6 mmol) were ground together in a mortar and pestle to form a homogeneous mixture and then water (0.04 g) was added and grinding was continued to produce an off-white powder. To this was added triphenylphosphine (0.315 g, 1.2 mmol) with grinding followed by addition of ethanol (0.06 g). Upon further grinding the mixture changed to a viscous oil, which suddenly stiffened to produce an off-white paste. This was ground further, following addition of further ethanol (0.06 g) and the mixture was allowed to dry by standing in a fume cupboard. The resulting solid mass was broken up by grinding and placed in a 50 °C oven for 30 m. The IR spectrum of this product was identical to that of the product **1** prepared by Method 1 above. Heating for a longer period (50 °C oven for 2 d) resulted in loss of EtOH, as indicated by disappearance of the EtOH ν(OH) band at 3497 cm^{-1}) and formation of the desolvated complex **$[(Ph_3P)_2Ag(H_2cit)]$**, **1b**. The EtOH solvate **1** was regenerated by grinding the desolvated product with EtOH (0.1 g) followed by air-drying under ambient conditions.

$[\{(Ph_3P)_2Ag\}_2(Hcit)]$, 2. *Method 1*. $[(Ph_3P)_2Ag(H_2cit)]\cdot$EtOH, **1** (0.9695 g) was dissolved in boiling EtOH (12 ml) and the resulting solution decanted from a small amount of undissolved white solid and allowed to cool slowly in a warm water bath. The colourless crystalline product that deposited upon cooling was filtered and washed with a little ice-cold EtOH. Yield 0.715 g (83.5%). Found: C 63.3, H 4.9%; calcd for $C_{78}H_{66}Ag_2O_7P_4$: C 64.4, H 4.6%.

Method 2. Silver(I) oxide (0.070 g; 0.3 mmol) and citric acid monohydrate (0.063 g, 0.3 mmol) were ground together in a mortar and pestle to form a homogeneous mixture and then water (0.08 g) was added and grinding was continued to produce an off-white paste. This was allowed to partially dry by evaporation, then triphenylphosphine (0.315 g, 1.2 mmol) was added with grinding followed by addition of ethanol (0.07 g). Upon further grinding the mixture changed to a viscous oil, which suddenly stiffened to produce an off-white paste. This was ground further, following addition of further ethanol (0.06 g) and the mixture was allowed to dry by standing in a fume cupboard; the latter procedure was repeated following the addition of further ethanol (0.4 g). The IR spectrum of this product was identical to that of the product **2** prepared by Method 1 above.

$[(Ph_3P)_3Ag(H_2cit)]$, 3. *Method 1*. A mixture of trisilver(I) citrate (0.51 g, 1.0 mmol), citric acid (0.4 g, 2.1 mmol) and PPh_3 (2.5 g, 9.5 mmol) and ethanol (20 ml) was heated with stirring. The resulting solution was filtered while hot and the filter was washed several times with hot EtOH to dissolve solid product which had separated in the filter. The filtrate deposited a colourless microcrystalline product that was collected and washed with ice-cold ethanol. Yield 1.4 g (42%). Found: C 67.2, H 5.2%; calcd for $C_{60}H_{52}AgO_7P_3$: C 66.4, H 4.8%.

Method 2. Silver(I) oxide (0.056 g; 0.23 mmol) and citric acid monohydrate (0.097 g, 0.46 mmol) were ground together in a mortar and pestle to form a homogeneous mixture and water (0.04 g) was then added and grinding was continued to produce an off-white powder. To this was added triphenylphosphine (0.362 g, 1.38 mmol) with grinding followed by addition of ethanol (0.09 g). Upon further grinding the mixture changed to a viscous oil, which suddenly stiffened to produce an off-white paste. This was ground following addition of further ethanol (0.3 g) and the mixture was allowed to dry by standing in a fume cupboard. The latter process was repeated twice but the IR spectrum of the product was not the same as that of the product **3** above. The dry product was placed in a glass tube, ethanol (0.4 g) was added, and the tube was sealed and placed in a 60 °C oven for 2 h. The resulting mixture was dried in an open tube at 60 °C to yield a white product. The IR spectrum of the product was identical to that of the product **3** prepared by Method 1 above.

Mechanochemical reactions between Ag_2O and citric acid. These were carried out in order to compare the products of such reactions with those carried out in the presence of triphenylphosphine: silver(I) oxide (0.3, 0.6, or 0.9 mmol) and citric acid monohydrate (0.6 mmol) were ground together dry in a mortar and pestle and then water (0.1 g) was added and the grinding was continued to produce an off-white paste. The products were dried in the air under ambient conditions.

Structure determinations

Full spheres of CCD area-detector diffractometer data were measured at *ca.* 100 K yielding $N_{t(otal)}$ reflections, these merging

Table 1 A selection of crystallographically established P_2AgO_2C discrete silver(I) atom environments

Anion/silver	Ag–P/Å	Ag–O/Å	P–Ag–P/°	O–Ag–O/°	P–Ag–O/°
H_2citrate (**1**)/1	2.3904(5) 2.4417(5)	2.4355(13) 2.4615(12)	129.203(16)	53.73(4)	98.43(4) −125.82(4)
Hcitrate (**2**)/1	2.403(3) 2.421(3)	2.409(11) 2.455(11)	131.95(8)	54.9(4)	101.3(3) −115.6(3)
Hcitrate (**2**)/2	2.413(4) 2.424(5)	2.501(15) 2.528(11)	136.78(17)	51.8(4)	104.3(4) −111.8(3)
O_2CCH_3/1[a] (anhydrate)	2.4332(8) 2.4483(8)	2.420(2) 2.438(2)	129.62(3)	53.33(7)	106.03(7) −114.83(7)
O_2CCH_3/2	2.4264(8) 2.4608(8)	2.379(3) 2.510(3)	124.13(3)	52.3(1)	102.0(1) −125.61(8)
$(\frac{1}{2}H_2O{\cdot}\frac{3}{4}EtOH)$/1[b]	2.4461(8) 2.4490(8)	2.438(2) 2.451(3)	127.72(3)	52.8(1)	110.75(8) −115.28(7)
$(\frac{1}{2}H_2O{\cdot}\frac{3}{4}EtOH)$/2	2.4063(8) 2.4582(8)	2.431(2) 2.449(3)	127.96(3)	53.5(1)	103.10(9) −122.50(7)
O_2CCF_3/1[c]	2.423(1) 2.445(1)	2.526(3) 2.542(4)	142.18(4)	51.6(1)	97.13(9) −112.41(9)
$O_2CC(OH)CH_3$/1[d]	2.4345(9) 2.4671(9)	2.425(3) 2.508(4)	126.15(3)	51.3(1)	104.7(1) −126.5(1)

[a] Ref. 21(redetermination, *cf.* ref. 25). [b] Ref. 23 (redetermination of material recorded as a 'sesquihydrate' in ref. 21). [c] Ref. 22. [d] Ref. 24.

to N unique after 'empirical'/multiscan absorption correction (R_{int} cited) which were used in the full matrix least squares refinements on F^2, refining anisotropic displacement parameter forms for the non-hydrogen atoms, hydrogen atom treatment following a riding model (reflection weights: $(\sigma^2(F_o^2) + (aP)^2)^{-1}$ ($P = (F_o^2 + F_c^2)/3)$); N_o with $I > 2\sigma(I)$ were considered 'observed'. Neutral atom complex scattering factors were employed within the SHELXL 97 program.[51] Pertinent results are given below and in Table 1 and the figures, the latter depicting the non-hydrogen atoms with 50% probability amplitude displacement envelopes, hydrogen atoms, where shown, having arbitrary radii of 0.1 Å.

Crystal/refinement data

$[(Ph_3P)_2Ag(O_2CCH_2C(OH)(CO_2H)CH_2COOH)]\cdot C_2H_5OH$, $[(Ph_3P)_2Ag(H_2cit)]\cdot EtOH$ 1. $C_{44}H_{43}AgO_8P_2$, M = 869.6. Triclinic, space group $P\bar{1}$, a = 12.2314(5), b = 12.8542(5), c = 14.4510(4) Å, α = 82.679(2), β = 87.727(3), γ = 64.362(4)°, V = 2031.4(2) Å^3. D_c (Z = 2) = 1.42_2 g cm^{-3}. Monochromatic Mo Kα radiation, λ = 0.7107_3 Å. μ_{Mo} = 0.63 mm^{-1}; specimen: = 0.41 × 0.28 × 0.25 mm; $T_{min/max}$ = 0.99. $2\theta_{max}$ = 65°; N_t = 37387, N = 14 800 (R_{int} = 0.039), N_o = 9552. R_1 = 0.036, wR_2 = 0.073 (a = 0.030); S = 0.90.

$[(Ph_3P)_2Ag(O_2CCH_2C(OH)(CH_2COOH)CO_2)Ag(PPh_3)_2]$, $[\{(Ph_3P)_2Ag\}_2(Hcit)]$ 2. $C_{78}H_{66}Ag_2O_7P_4$, M = 1454.9. Monoclinic, space group $P2_1/c$, a = 24.568(2), b = 12.4749(7), c = 23.1076(10) Å, β = 106.704(6)°, V = 6783.2(8) Å^3. D_c (Z = 4) = 1.42_5 g cm^{-3}. Monochromatic Cu Kα radiation, λ = 1.5418_3 Å. μ_{Cu} = 6.0 mm^{-1}; specimen: = 0.13 × 0.12 × 0.04 mm; $T_{min/max}$ = 0.75. $2\theta_{max}$ = 125°; N_t = 25 678, N = 10 450 (R_{int} = 0.061), N_o = 5353. R_1 = 0.13, wR_2 = 0.35 (a = 0.20); S = 1.11.

Variata. Data were weak and limited and measured using a monochromatic Cu Kα radiation source. In the refinement, one of the phenyl rings in triphenylphosphine ligand 3 and all in ligand 4 were modelled as disordered over pairs of sites of equal occupancy with isotropic displacement parameter forms and constrained geometries.

Spectroscopy

Infrared spectra were recorded at 4 cm^{-1} resolution on samples suspended in KBr using a Nicolet 8700 FTIR spectrometer, or on dry powders using a Perkin Elmer Spectrum 400 FT-IR spectrometer equipped with a Universal ATR sampling accessory. The ATR spectra were converted to conventional absorbance spectra using OMNIC software.

Solid-state ^{31}P CPMAS NMR data were obtained at ambient temperature on Bruker DSX-400 (9.40 T) spectrometer operating at a ^{31}P Larmor frequency of 161.92 MHz. Conventional cross-polarization[52] and magic-angle-spinning[53] techniques, coupled with spin temperature alternation[54] to eliminate spectral artefacts, were implemented using a Bruker 3.2 mm double-air-bearing probe in which MAS frequencies of ~10–12 kHz were achieved. An initial ^{1}H π/2 pulse width of 3 μs, recycle delay of 15–30 s, Hartmann–Hahn contact period of 2–5 ms and a ^{1}H decoupling field of 80–85 kHz (during acquisition) were used in these ^{31}P experiments. The reported ^{31}P chemical shifts were externally referenced to the IUPAC standard of 85% H_3PO_4 *via* a secondary solid reference of ammonium dihydrogen phosphate ($(NH_4)(H_2PO_4)$) which exhibits a shift at δ 1.0 ppm; this secondary

reference material was also used to set the Hartmann–Hahn condition. The 2D ^{31}P CPCOSY experiment was implemented with the TPPI (time proportional phase incrementation) method[55–57] for acquisition of phase-sensitive data in both the F1 and F2 dimensions. The application of this technique has been discussed in detail elsewhere.[58,59] The recycle delay, contact period, ^{1}H $\pi/2$ pulse width and MAS rate were the same as those implemented in the above 1D ^{31}P CPMAS experiments. A total of 256 F1 increments were acquired into 256 word blocks, with both dimensions zero-filled to 1 K words and weighted with Gaussian multiplication prior to Fourier transformation.

Results and discussion

In principle the dihydrogencitrate complex **1** can be prepared by addition of the stoichiometrically required amount of citric acid to a 1 : 6 mixture of trisilver(I) citrate, Ag_3cit and PPh_3:

$$Ag_3cit + 2H_3cit + 6PPh_3 \rightarrow 3[(Ph_3P)_2Ag(H_2cit)] \quad (1)$$

However, the product of this reaction when carried out in EtOH solution consisted of a mixture of **1** and the monohydrogen citrate complex **2**, indicating that deprotonation of the dihydrogencitrate to monohydrogencitrate occurs under these conditions with the formation of the binuclear complex **2**:

$$2[(Ph_3P)_2Ag(H_2cit)] \rightarrow [(Ph_3P)_2Ag_2(Hcit)] + H_3cit \quad (2)$$

Indeed, it was subsequently found that attempted recrystallization of the pure dihydrogencitrate complex **1** from EtOH produced the pure monohydrogencitrate complex **2**. In order to prepare pure **1** from EtOH solution it was necessary to add excess citric acid to the reaction mixture in order to suppress the dissociation reaction (2) (see Experimental above and Crystal structures below). In the presence of excess PPh_3 the reaction analogous to (1) yielded the 1 : 3 complex **3**:

$$Ag_3cit + 2H_3cit + 9PPh_3 \rightarrow 3[(Ph_3P)_3Ag(H_2cit)] \quad (3)$$

The above complexes were more cleanly prepared by solvent-assisted mechanochemical synthesis in a two-step process using Ag_2O, citric acid and PPh_3 as starting materials, *e.g.* For complex **1**:

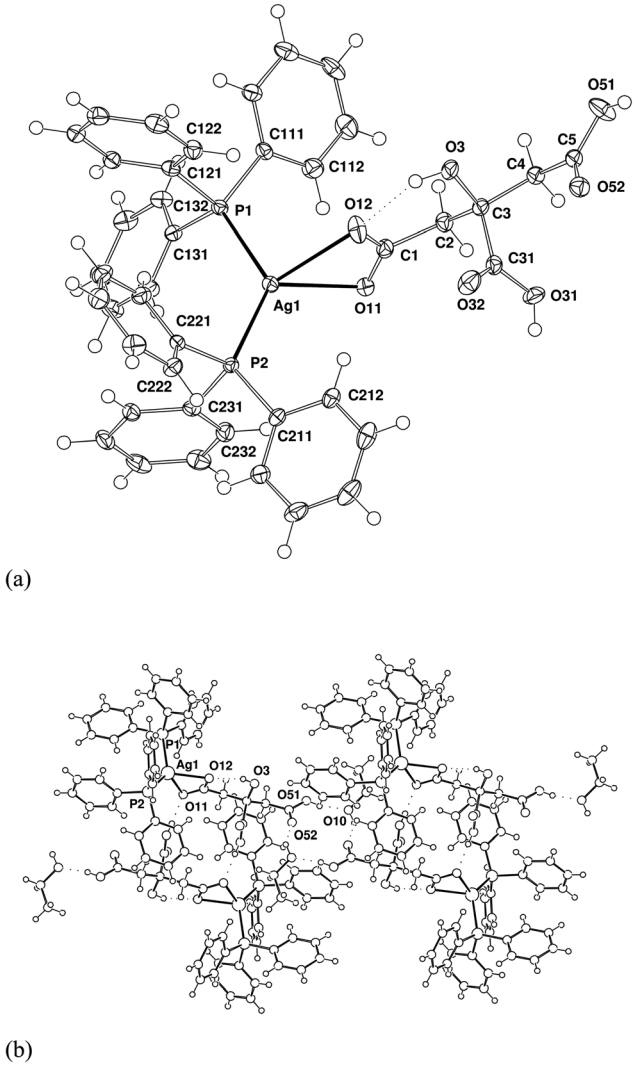
$$3Ag_2O + 6H_3cit + 12PPh_3 \rightarrow 6[(Ph_3P)_2Ag(H_2cit)] + 3H_2O \quad (4)$$

In the first step the appropriate amounts of Ag_2O and citric acid were reacted together in a single water-assisted mechanochemical treatment. The product of this reaction was then reacted with PPh_3 in an ethanol-assisted mechanochemical reaction. In the case of compounds **1** and **2**, the second reaction was complete after only one or two mechanochemical treatments. For compound **3**, monitoring of the product by IR spectroscopy showed that the reaction was not complete after three mechanochemical treatments, so the method of solvent-assisted solid-state synthesis was applied,[36] treating the reaction mixture with a small amount of ethanol and heating in a closed tube at 60 °C. Recent reports have demonstrated the use of Group 2 and Group 12 metal oxides as reactants in mechanochemical synthesis,[42–45] and the present examples extend this to the case of the Group 11 metal oxide Ag_2O. Also, previous studies have demonstrated the possibility of carrying out solvent-assisted mechanochemical synthesis involving more than two reactants, but these syntheses have been carried out using a single solvent.[37,45] The present study addresses the situation of a three-component reaction A + B + C → product, where a solvent that is appropriate for assisting the reaction A + B is not appropriate for C. In the present case the reaction between Ag_2O and citric acid is best assisted by the solvent water, in which the citric acid is readily soluble, but water is not an appropriate solvent for PPh_3. We therefore carried out the reactions in two steps, using water for the solvent-assisted reaction between Ag_2O and citric acid, and ethanol for the solvent-assisted reaction of PPh_3 with the product of the first reaction. Using this approach, the number of cycles of mechanochemical treatment required to form pure product was reduced to a minimum. An additional feature of the mechanochemical synthesis as applied to the present system is that the reaction to produce **1** produced a pure product using the stoichiometric amounts of the three reactants as shown in eqn (1), whereas the solution reaction required an excess of citric acid to suppress the dissociation reaction (2). The reason for this difference is that in the mechanochemical reaction there is insufficient solvent present to accommodate the citric acid produced in the dissociation, so the dissociation is suppressed in this case by the very nature of the solvent-assisted mechanochemical reaction!

Crystal structures

In many carboxylate structures, the potentially oligodentate carboxylate ligand functionalities serve to bridge metal atoms to yield oligo- or polymeric forms (the complexes of silver being no exception),[1] a common motif being the $Ag(O{\cdot}CX{\cdot}O)_2Ag$ eight-membered ring, as found in the structure of the parent silver acetate,[60] possibly augmented by bridges further afield from the oxygen atoms. However, in the present structurally characterised species, it is evident that the stratagem of occupying coordination sites about the silver atom with multiple PPh_3 donors has been effective in assisting to thwart such multiple interactions, and all carboxylate–silver interactions are cleanly bidentate chelate in CO_2AgP_2 environments in arrays which are discrete neutral mono- and bi-nuclear.

In the solvated complex **1**, the 1-carboxylate group of citric acid is deprotonated (as in the structure of sodium dihydrogencitrate),[61] and supplanted by *O,O′*-complexation with a silver atom, the complex being $[(Ph_3P)_2Ag(O_2CCH_2C(OH)(COOH)CH_2COOH)]$, one molecule, together with a molecule of ethanol, comprising the asymmetric unit of the structure. The silver atom environment (Table 1) is similar to those found in other silver(I) monocarboxylate phosphine complexes;[21–25] there is a pronounced asymmetry (0.03 Å) in the Ag–O distances, the oxygen atom associated with the shorter being hydrogen-bonded intramolecularly by the 3-hydroxyl group (Fig. 1(a)) (O,H···O 2.660(2), 1.95 Å). The hydrogen atom of the associated 3-carboxylate group hydrogen-bonds to the other coordinated oxygen atom of an inversion-related molecule so that a centrosymmetric dimer is formed (O,H···O 2.638(2), 1.82 Å). Hydrogen-bonds between the uncoordinated terminal 5-carboxylate group and the ethanol solvent molecule knit the dimers into a one-dimensional chain (Fig. 1(b)) (O,H(51)···O(10) 2.584(2), 1.76; O,H(10)···O(52) $(2 - x, \bar{y}, 1 - z)$ 2.821(2), 2.09 Å).



(a)

(b)

Fig. 1 (a) Molecular projection of $[(Ph_3P)_2Ag(H_2cit)]\cdot(EtOH)$, **1**. (b) The extended one-dimensional hydrogen-bonded array.

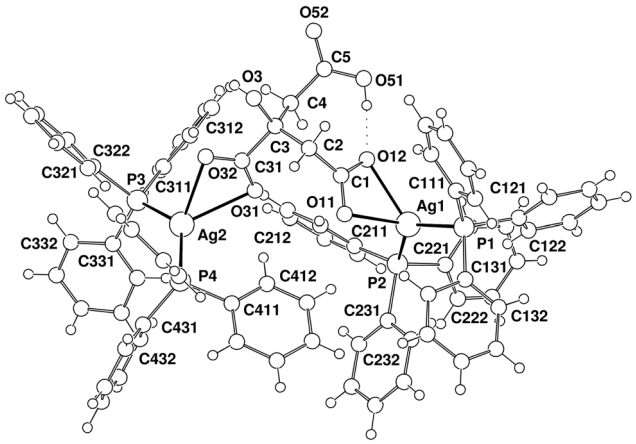
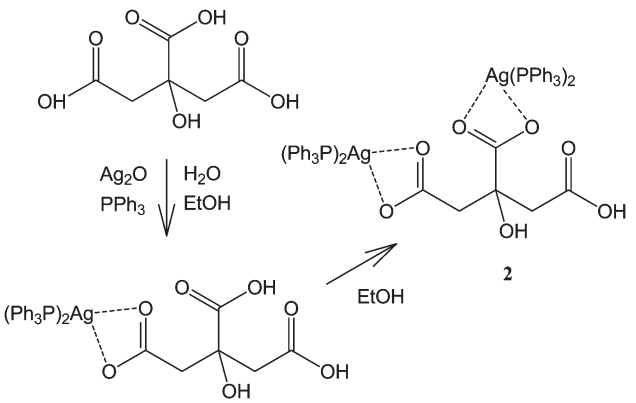


Fig. 2 Molecular projection of $[\{(Ph_3P)_2Ag\}_2(Hcit)]$, **2**.



Scheme 1

The other structurally characterized silver(I)/citrate compound is a complex of the $Hcit^{2-}$ anion, $[\{(Ph_3P)_2Ag\}_2(Hcit)] \equiv [(Ph_3P)_2Ag(O_2CCH_2C(OH)(CH_2COOH)CO_2)Ag(PPh_3)_2]$, **2**, unsolvated, and with a single molecule comprising the asymmetric unit of the structure (Fig. 2). Although the determination is of inferior precision, it establishes clearly that, rather than both of the ('terminal') 1,5-carboxylates being symmetrically deprotonated (or, for that matter, the alcohol OH), one terminal and the central 3-carboxylates are those which chelate the two silver atoms; the data of Table 1 suggest that the interaction of the 3-carboxylate may be the weaker of the two, indicative of significantly different basicity. An internal intraligand hydrogen-bond is found between the carboxylic hydrogen and the more strongly coordinated oxygen atom of the more distant chelating deprotonated group (O,H(51)···O(12) 2.54(2), 1.70 Å).

Based on the above structures, an overall scheme for the formation of **1** and **2** is shown in Scheme 1, where the mechanochemical reaction is represented in the formation of **1** and the solution reaction is represented in the formation of **2**.

Infrared spectroscopy

The mid-range IR spectra (4000–1500 cm^{-1}) of the citrate complexes **1**, **2**, **3** are shown in Fig. 3. These contain bands due to the coordinated citrate anion, together with some bands (not labelled) due to the triphenylphosphine ligand. A broad ν(OH) band derivative of the carboxylic acid groups occurs in the range 2500–3500 cm^{-1}, similar to the range observed in citric acid itself (Fig. 4(a)). The large width and complex structure of the ν(OH) band is probably the result of extensive hydrogen-bonding, which is evident in the structures of compounds **1** and **2** (see Crystal structures, above).

The asymmetric CO stretches ν_a(CO) of the carboxylic acid and carboxylate groups occur at *ca.* 1720 and 1560 cm^{-1} respectively in complexes **1**, **2** and **3** (Fig. 3(a), (c), (d)). These values are in good agreement with those found in related systems.[6,62,63] In the spectrum of complex **1** the ν_a(CO) bands occur at 1746, 1719 and 1561 cm^{-1}, consistent with the presence of two carboxylic acid groups and one carboxylate group in this dihydrogencitrate complex. Upon conversion to the monohydrogencitrate complex **2**, the absorption intensity in the 1560 cm^{-1} region increases at the expense of that in the 1720 cm^{-1} region, consistent with the deprotonation of the dihydrogencitrate to monohydrogencitrate upon formation of **2** from **1**. Although no

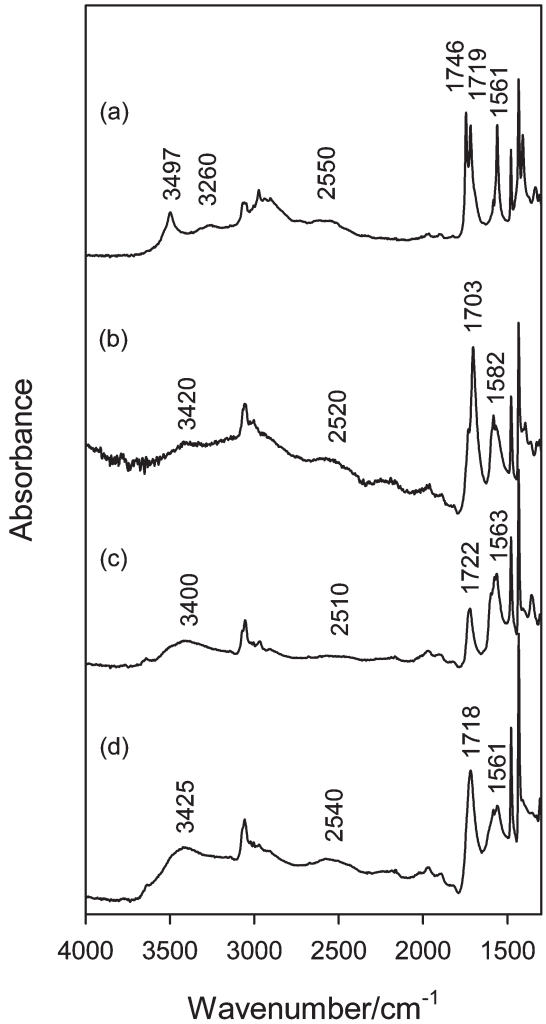


Fig. 3 Mid-range IR spectra of (a) $[(Ph_3P)_2Ag(H_2cit)]\cdot EtOH$, **1**. (b) $[(Ph_3P)_2Ag(H_2cit)]$, **1b**. (c) $[\{(Ph_3P)_2Ag\}_2(Hcit)]$, **2**. (d) $[(Ph_3P)_3Ag(H_2cit)]$, **3**.

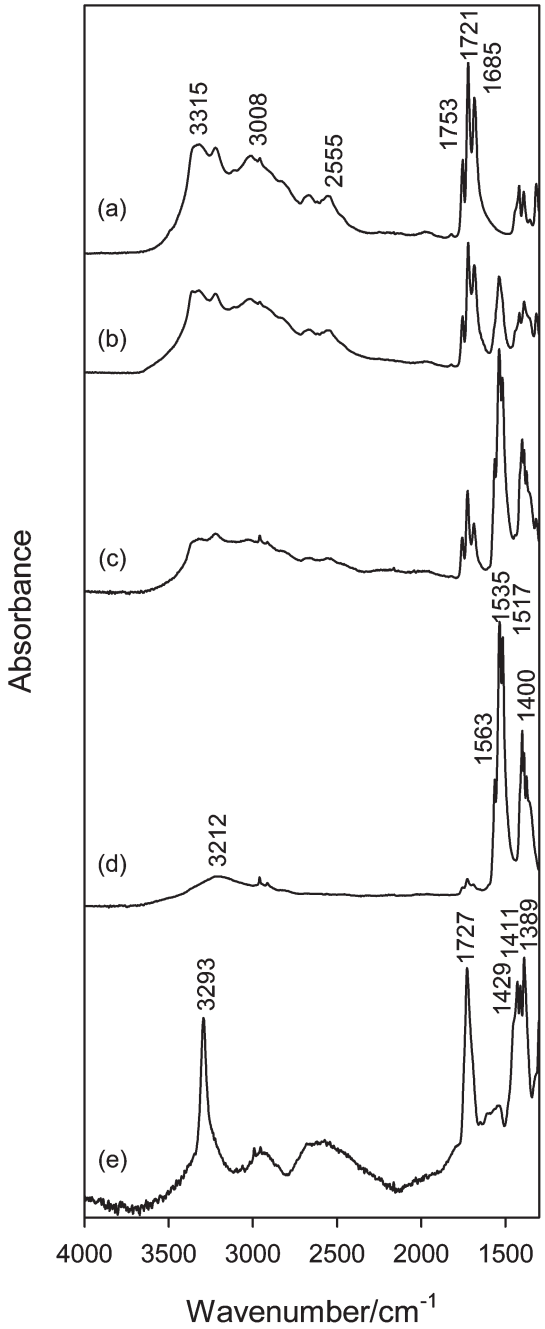


Fig. 4 Mid-range IR spectra of (a) citric acid monohydrate, $H_3cit\cdot H_2O$, and of the products of H_2O assisted mechanochemical reactions of nAg_2O: $H_3cit\cdot H_2O$ for (b) $n = 0.5$, (c) $n = 1$, (d) $n = 1.5$; the spectrum of NaH_2cit (e) is included for comparison (see text).

crystal structure has been accessible for complex **3**, the relative intensities of the ν_a(CO) bands at 1718, 1561 cm^{-1} are consistent with the proposed formulation $[(Ph_3P)_3Ag(H_2cit)]$, these bands being assigned to two carboxylic acid and one coordinated carboxylate group respectively.

The IR spectrum of complex **1** also contains a ν(OH) band at 3497 cm^{-1} ascribed to the lattice EtOH present in the solvated structure (Fig. 3(a)). This band disappears when the complex is desolvated by heating it to 50 °C (Fig. 3(b); see Experimental). The desolvation has an unexpectedly large effect on the ν_a(CO) bands of the carboxylic acid and carboxylate groups, which appear at 1703, 1582 cm^{-1} respectively. The shifts in these bands upon desolvation are greater than those caused by a change in the state of deprotonation of the citric acid (*cf.* **1** and **2**; Fig. 3(a) and (c)) and by a change in the number of coordinated PPh_3 ligands (*cf.* **1** and **3**; Fig. 3(a) and (d)), which is consistent with loss of the lattice EtOH causing a change in the structure of the complex. This is consistent with the ^{31}P CP MAS NMR spectra of the solvated form **1** and the desolvated form **1b** (see below). Nevertheless, the process is completely reversible; grinding the desolvated **1** with EtOH under ambient conditions results in the reformation of the EtOH solvate, as evidenced by its IR spectrum, which is identical to that of the initial solvated complex (Fig. 3(a)). Reversible structural changes associated with solvation–desolvation of a complex solvate have been reported previously.[35]

The mechanochemical syntheses of complexes **1**, **2**, and **3** were carried out in two steps, the first being a water-assisted reaction between Ag_2O and citric acid, and the second an EtOH-assisted reaction between the product of the first reaction and an appropriate amount of PPh_3. It was therefore of interest to

investigate the nature of the first reaction, and this was achieved by carrying out an IR study of the products of the following water-assisted mechanochemical reactions

$$n\mathrm{Ag_2O} + \mathrm{H_3cit} \rightarrow \text{product} \quad (5)$$

for n = 0.5, 1, 1.5 (see Experimental). Possible products of these reactions are AgH_2cit, Ag_2Hcit and Ag_3cit respectively. The IR spectra of citric acid and the products of the above reactions are shown in Fig. 4. From these it is clear that the reactions for n = 0.5, 1 produce a mixture of citric acid (ν_a(CO) = 1753, 1721, 1685 cm^{-1}); *cf.* Fig. 4(a)) and a product with ν_a(CO) = 1563, 1535, 1517 cm^{-1}. This latter product is the only one produced for the n = 1.5 case, indicating that the product is Ag_3cit. Thus the products of the n = 0.5, 1 reactions are mixtures of Ag_3cit and citric acid. Therefore, although the PPh_3 complexes **1** and **2** formally contain AgH_2cit and Ag_2Hcit respectively, the initial mechanochemical reactions using the appropriate proportions of Ag_2O and citric acid do not produce these latter two compounds. Rather, the PPh_3 complexes of AgH_2cit and Ag_2Hcit form only after reaction of the initially formed mixture of Ag_3cit and citric acid with PPh_3. The above results cast some doubt on the existence of compounds such as AgH_2cit and Ag_2Hcit, despite references in the patent literature to 'silver dihydrogen citrate' and its antimicrobial action.[18] This is rather surprising, as the monosodium salt of citric acid, NaH_2cit exists,[61] and its IR spectrum is shown in Fig. 4(e). From this it is clear that mono-deprotonation of citric acid results in substantial changes in the IR spectrum, so that if the product of the reaction whose spectrum is shown in Fig. 4(b) had been AgH_2cit, then it would not contain bands with exactly the same wavenumbers and relative intensities as citric acid.

Solid-state NMR spectroscopy

The solid-state ^{31}P CPMAS NMR spectra of complexes **1**, **2**, and **3** are shown in Fig. 5 and an expansion and simulation of the spectrum of complex **1** is shown in Fig. 6. The derived NMR parameters are listed in Table 2. In general, the spectra of the silver complexes are expected to consist of partially resolved multiplets due to the individual ^{31}P chemical shifts resulting from the chemically inequivalent P nuclei bound to each Ag centre. Each resonance displays $^1J(^{107,109}Ag,^{31}P)$ scalar coupling between the ^{31}P (I = 1/2) and $^{107,109}Ag$ nuclei (I = 1/2), and further splitting of these doublets can occur *via* $^2J(^{31}P,^{31}P)$ coupling.[64] For the present compounds, this is well illustrated by compound **1**, which contains two inequivalent P atoms bound to the same Ag atom, resulting in an ABX spin system (A, B = ^{31}P; X = $^{107,109}Ag$) for each Ag isotope. The ^{31}P spectrum shows the AB part of the ABX spectrum, which in general consists of two overlapping sets of AB quartets,[65] the separate patterns for coupling to the $^{107,109}Ag$ isotopes sometimes remaining unresolved. In the case of **1** the spectrum consists of two overlapping, nearly identical AB quartets, in which the $^{107,109}Ag$ isotopic splitting is partially resolved (Fig. 5(a), Fig. 6). The relative intensities of the peaks (as well as correlation peaks in the 2D ^{31}P CPCOSY spectrum, not shown) allow unambiguous assignment of the two AB sub-spectra, from which the parameters in Table 2 are obtained. The spectrum of the desolvated complex **1b** (Fig. 5(b))

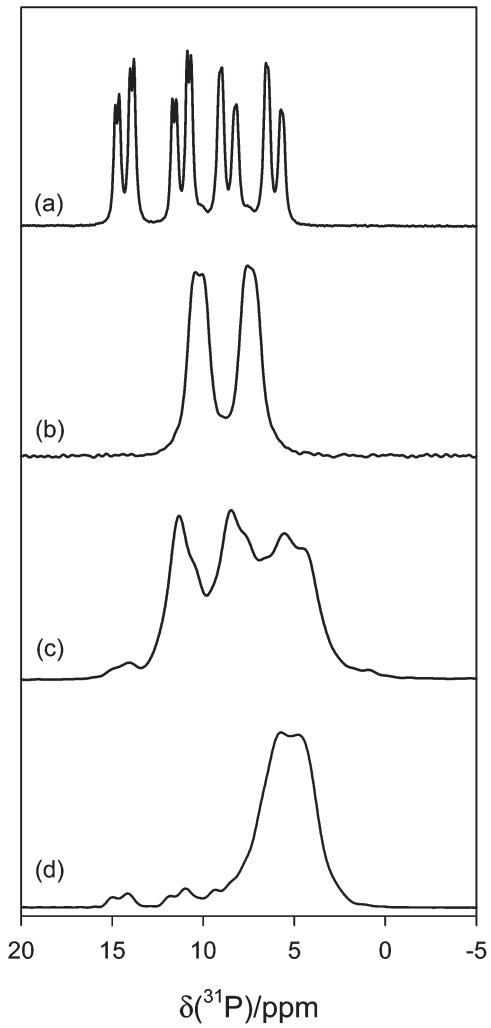


Fig. 5 Solid-state ^{31}P CPMAS NMR spectra acquired at 9.40 T of (a) $[(Ph_3P)_2Ag(H_2cit)]\cdot EtOH$, **1**. (b) $[(Ph_3P)_2Ag(H_2cit)]$, **1b**. (c) $[\{(Ph_3P)_2Ag\}_2(Hcit)]$, **2**. (d) $[(Ph_3P)_3Ag(H_2cit)]$, **3**.

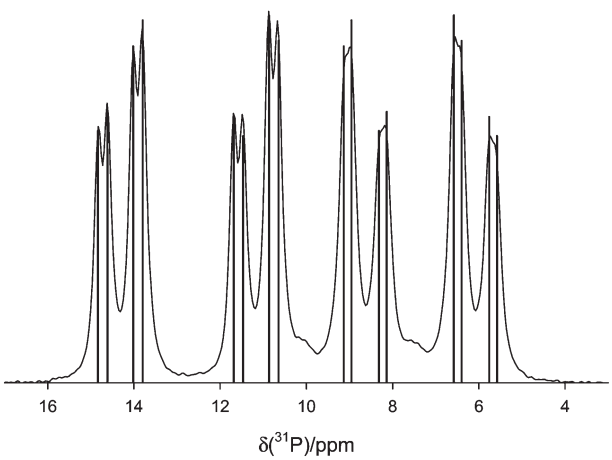


Fig. 6 Expansion of the ^{31}P CP MAS NMR spectrum of $[(Ph_3P)_2Ag(H_2cit)]\cdot EtOH$, **1** and stick diagram of the spectrum simulated as the AB part of an ABX system with δ_A = 7.39, δ_B = 12.71, J_{AX}^{107} = 384 Hz, J_{AX}^{109} = 442 Hz, J_{BX}^{107} = 475 Hz, J_{BX}^{109} = 546 Hz, J_{AB} = 132 Hz.

Table 2 ^{31}P CPMAS NMR parameters

Compound	$\delta(^{31}P)$/ppm	$^{1}J(^{107,109}Ag,^{31}P)$/Hz
$[(Ph_3P)_2Ag(H_2cit)]\cdot EtOH$, **1**	7.6, 12.9	412, 501 (^{2}J(PP) = 134 Hz)
$[(Ph_3P)_2Ag(H_2cit)]$, **1b**	8.8	450
$[\{(Ph_3P)_2Ag\}_2(Hcit)]$, **2**	*ca.* 7.9	*ca.* 465
$[(Ph_3P)_3Ag(H_2cit)]$, **3**	5.25	160

is much simpler, being effectively a simple doublet, indicating that loss of the lattice EtOH causes a significant change in the structure of the complex, such that the two Ag–P bonds become nearly equivalent.

The spectrum of **2** consists of an unresolved multiplet that has not been analysed in detail, although peak separations comparable in magnitude to $^{1}J(^{107,109}Ag,^{31}P)$ in **1** are evident. The complex spectrum is not surprising because the compound contains two inequivalent $Ag(PPh_3)_2$ groups that would give rise to two ABX spin systems, with a total of sixteen lines in the ^{31}P spectrum. These are clearly not all resolved, possibly because of broadening of the lines that might be the result of the disorder observed in the crystal structure of this complex (see Experimental). There is also a very weak shoulder in the spectrum at about 15 ppm that is probably due to the presence of a small amount of **1** present as an impurity.

The spectrum of **3** consists of a dominant peak at *ca.* 5 ppm that is assigned to the 1 : 3 complex $[(Ph_3P)_3Ag(H_2cit)]$, with a number of weaker peaks at lower field that can readily be assigned to the EtOH-solvated 1 : 2 complex **1**. The dominant peak is a strongly overlapped doublet with a splitting that is assigned to $^{1}J(^{107,109}Ag,^{31}P)$ coupling (Table 2).

The ^{1}J(Ag,P) coupling constants in Table 2 are consistent with the structures of **1** and **2** and with the proposed structure of **3**. It has previously been shown that one of the factors that determines the magnitude of ^{1}J(M,P) coupling constants in metal-phosphine complexes is the number of phosphine ligands coordinated to the metal atom M, a reduction in magnitude occurring with an increase in the number of phosphine ligands.[66–68] In particular, the values are similar to those reported previously for other silver complexes containing an oxyanion and two or three coordinated PPh_3 ligands.[5,6,66] In the case of the formate complexes $[(Ph_3P)_nAg(O_2CH)]$, ^{1}J(Ag,P) reduces from *ca.* 430 (n = 2) to *ca.* 230 Hz (n = 3) with increasing phosphine ligand coordination, which is similar to the change observed for the corresponding dihydrogencitrate complexes **1** and **3** (Table 2).

Conclusion

The complexes $[(Ph_3P)_2Ag(H_2cit)]\cdot EtOH$ (**1**), $[\{(Ph_3P)_2Ag\}_2(Hcit)]$, (**2**) and $[(Ph_3P)_3Ag(H_2cit)]$ (**3**) were prepared by conventional solution methods, involving the reaction of trisilver(I) citrate, citric acid and triphenylphosphine, and also by a mechanochemical method involving the reaction of silver(I) oxide, citric acid and triphenylphosphine. Complexes **1** and **2** have been structurally defined by single crystal X-ray studies as the neutral mononuclear $[(Ph_3P)_2Ag(O_2CCH_2C(OH)(COOH)CH_2COOH)]$ and binuclear $[(Ph_3P)_2Ag(O_2CCH_2C(OH)(CH_2COOH)CO_2)Ag(PPh_3)_2]$ molecular species respectively, the carboxylate groups being cleanly bidentate chelate in CO_2AgP_2 coordination environments. The mechanochemical synthetic method provides another example of the recently demonstrated use of metal oxides in such syntheses and, further, it demonstrates the application of two-step solvent-assisted mechanochemical synthesis in which different solvents are used for the two reaction steps, the solvents being chosen on the basis of the solubility of a component or components of the reaction in the solvent concerned. The above complexes may be regarded as adducts of $Ag(H_2cit)$ or $Ag_2(Hcit)$ with two or three molecules of PPh_3 per Ag atom, but mechanochemical studies showed that neither $Ag(H_2cit)$ nor $Ag_2(Hcit)$ can be prepared as distinct compounds, despite the existence in the literature of references to compounds such as 'silver dihydrogen citrate'. The present work shows that the only stable product of the reaction between silver oxide and citric acid is trisilver citrate, Ag_3cit. IR studies of **1–3** show the presence of coordinated carboxylate and free carboxylic acid groups in the mono- and di-hydrogencitrate ligands, and the formation of **2** from **1** shows that dihydrogencitrate deprotonation can occur upon dissolution of **1** in protic solvents. In such cases, the present work shows that mechanochemical synthesis can proceed to a unique product using stoichiometric quantities of reactants, whereas solution synthesis requires an excess of the acid to prevent unwanted deprotonation reactions.

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References

1 (*a*) R. J. Lancashire, in *Comprehensive Coordination Chemistry*, ed. G. Wilkinson, R. D. Gillard, J. A. McCleverty, Pergamon, Oxford, 1987, vol. 5, p. 775; (*b*) M. C. Gimeno and A. Laguna, in *Comprehensive Coordination Chemistry II*, eds-in-chief, J. A. McCleverty and T. J. Meyer, Elsevier Pergamon, 2004, vol. 6, ed. D. E. Fenton, p. 911.
2 C. E. Holloway, M. Melnik, W. A. Nevin and W. Liu, *J. Coord. Chem.*, 1995, **35**, 85.
3 A. Angel and A. V. Harcourt, *J. Chem. Soc. Trans.*, 1902, **81**, 1385.
4 A. Angel, *J. Chem. Soc. Trans.*, 1906, **89**, 345.
5 G. A. Bowmaker, Effendy, J. V. Hanna, P. C. Healy, G. J. Millar, B. W. Skelton and A. H. White, *J. Phys. Chem.*, 1995, **99**, 3909.
6 G. A. Bowmaker, Effendy, J. V. Hanna, P. C. Healy, J. C. Reid, C. E. F. Rickard and A. H. White, *J. Chem. Soc., Dalton Trans.*, 2000, 753.
7 J. Shibata, K.-I. Shimizu, S. Satokawa, A. Satsuma and T. Hattori, *Phys. Chem. Chem. Phys.*, 2003, **5**, 2154.
8 K. Vehlow, K. Köhler, S. Blechert, S. Dechert and F. Meyer, *Eur. J. Inorg. Chem.*, 2005, 2727.
9 L. Jiang, Z. Wu, D. Wu, W. Yang and R. Jin, *Nanotechnology*, 2007, **18**, 185603.
10 Z. S. Pillai and P. V. Kamat, *J. Phys. Chem. B*, 2004, **108**, 945.
11 O. Siiman, L. A. Bumm, R. Callaghan, C. G. Blatchford and M. Kerker, *J. Phys. Chem.*, 1983, **87**, 1014.
12 J. Clarkson, C. Campbell, B. N. Rospendowski and W. E. Smith, *J. Raman Spectrosc.*, 1991, **22**, 771.
13 C. H. Munro, W. E. Smith, M. Garner, J. Clarkson and P. C. White, *Langmuir*, 1995, **11**, 3712.

14 C. Rodger, W. E. Smith, G. Dent and M. Edmondson, *J. Chem. Soc., Dalton Trans.*, 1996, 791.
15 K. K. Caswell, C. M. Bender and C. J. Murphy, *Nano Lett.*, 2003, **3**, 667.
16 F.-K. Liu, P.-W. Huang, Y.-C. Chang, F.-H. Ko and T.-C. Chu, *J. Mater. Res.*, 2011, **19**, 469.
17 A. Jakob, T. Rüffer, H. Schmidt, P. Djiele, K. Körbitz, P. Ecorchard, T. Haase, K. Kohse-Höinghaus, S. Frühauf, T. Wächtler, S. Schulz, T. Gessner and H. Lang, *Eur. J. Inorg. Chem.*, 2010, 2975.
18 A. B. Arata, *US Patent Pat*, 20060100273, 2006.
19 J. Adaskaveg, H. Foerster, B. A. Holtz, E. Hoffman, D. Gubler and E. Erickson, *Acta Hortic. (ISHS)*, 2006, **704**, 277.
20 V. Sambhy, M. M. MacBride, B. R. Peterson and A. Sen, *J. Am. Chem. Soc.*, 2006, **128**, 9798.
21 S. W. Ng and A. H. Othman, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1997, **53**, 1396.
22 S. W. Ng, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1998, **54**, 743.
23 J. V. Hanna and S. W. Ng, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1999, **55**, IUC9900031.
24 J. V. Hanna and S. W. Ng, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 2000, **56**, 24.
25 B. Femi-Onadenko, *Z. Kristallogr.*, 1980, **152**, 159.
26 Y. Zhao, P. Zhang, B. Li, X. Meng and T. Zhang, *Inorg. Chem.*, 2011, **50**, 9097.
27 D. W. Hartley, G. Smith, D. S. Sagatys and C. H. L. Kennard, *J. Chem. Soc., Dalton Trans.*, 1991, 2735.
28 D. S. Sagatys, G. Smith, R. C. Bott, D. E. Lynch and C. H. L. Kennard, *Polyhedron*, 1993, **12**, 709. (ref. 27 and 28 record two of the three (only) structural characterisations available for silver(I)/citrate complexes. The third is a more complex form entailing borate as well as citrate as the complexing anionic species (I. I. Zviedre, V. K. Bel'sky and E. M. Shvarts, *Latv. Khim. Z.*, 1998, 99 (CCDC: 159197 (LUQHIO)), which is less helpful).
29 G. H. Penner and W. Li, *Inorg. Chem.*, 2004, **43**, 5588.
30 G. A. Bowmaker, N. Chaichit, C. Pakawatchai, B. W. Skelton and A. H. White, *Dalton Trans.*, 2008, 2926.
31 G. A. Bowmaker, N. Chaichit, C. Pakawatchai, B. W. Skelton and A. H. White, *Can. J. Chem.*, 2009, **87**, 161.
32 G. A. Bowmaker, B. W. Skelton and A. H. White, *Inorg. Chem.*, 2009, **48**, 3185.
33 G. A. Bowmaker, C. Pakawatchai, S. Saithong, B. W. Skelton and A. H. White, *Dalton Trans.*, 2009, 2588.
34 G. A. Bowmaker, C. Pakawatchai, S. Saithong, B. W. Skelton and A. H. White, *Dalton Trans.*, 2010, **39**, 4391.
35 G. A. Bowmaker, J. V. Hanna, B. W. Skelton and A. H. White, *Dalton Trans.*, 2009, 5447.
36 G. A. Bowmaker, J. V. Hanna, B. W. Skelton and A. H. White, *Chem. Commun.*, 2009, 2168.
37 G. A. Bowmaker, C. Di Nicola, C. Pettinari, B. W. Skelton, N. Somers and A. H. White, *Dalton Trans.*, 2011, **40**, 5102.
38 G. A. Bowmaker, Effendy, J. V. Hanna, P. C. Healy, S. P. King, C. Pettinari, B. W. Skelton and A. H. White, *Dalton Trans.*, 2011, **40**, 7210.
39 T. Friscic and W. Jones, *Cryst. Growth Des.*, 2009, **9**, 1621.
40 T. Friscic, A. V. Trask, W. Jones and W. D. S. Motherwell, *Angew. Chem., Int. Ed.*, 2006, **45**, 7546.
41 A. N. Swinburne and J. W. Steed, *CrystEngComm*, 2009, **11**, 433.
42 T. Friscic and L. Fabian, *CrystEngComm*, 2009, **11**, 743.
43 E. H. H. Chow, F. C. Strobridge and T. Friscic, *Chem. Commun.*, 2010, **46**, 6368.
44 F. C. Strobridge, N. Judas and T. Friscic, *CrystEngComm*, 2010, **12**, 2409.
45 T. Friscic, *J. Mater. Chem.*, 2010, **20**, 7599.
46 C. J. Adams, H. M. Colquhoun, P. C. Crawford, M. Lusi and A. G. Orpen, *Angew. Chem., Int. Ed.*, 2007, **46**, 1124.
47 D. Braga, S. L. Giaffreda, F. Grepioni, A. Pettersen, L. Maini, M. Curzi and M. Polito, *Dalton Trans.*, 2006, 1249.
48 D. Braga, M. Curzi, A. Johansson, M. Polito, K. Rubini and F. Grepioni, *Angew. Chem., Int. Ed.*, 2006, **45**, 142.
49 L.-F. Yang, M.-L. Cao, Y. Cui, J.-J. Wu and B.-H. Ye, *Cryst. Growth Des.*, 2010, **10**, 1263.
50 V. Strukil, L. Fabian, D. G. Reid, M. J. Duer, G. J. Jackson, M. Eckert-Maksic and T. Friscic, *Chem. Commun.*, 2010, **46**, 9191.
51 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2007, **64**, 112.
52 A. Pines, M. G. Gibby and J. S. Waugh, *J. Chem. Phys.*, 1973, **59**, 569.
53 E. R. Andrew, A. Bradbury and R. Eades, *Nature*, 1958, **182**, 1659.
54 E. O. Stejskal and J. Schaefer, *J. Magn. Reson.*, 1975, **18**, 560.
55 G. Bodenhausen, R. L. Vold and R. R. Vold, *J. Magn. Reson.*, 1980, **37**, 93.
56 D. Marion and K. Wuethrich, *Biochem. Biophys. Res. Commun.*, 1983, **113**, 967.
57 T. Allman, *J. Magn. Reson.*, 1989, **83**, 637.
58 J. V. Hanna, M. E. Smith, S. N. Stuart and P. C. Healy, *J. Phys. Chem.*, 1992, **96**, 7560.
59 J. V. Hanna, R. D. Hart, P. C. Healy, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1998, 2321.
60 L. P. Olson, D. R. Whitcomb, M. Rajeswaran, T. N. Blanton and B. J. Swertka, *Chem. Mater.*, 2006, **18**, 1667.
61 J. P. Glusker, D. van der Helm, W. E. Love, M. L. Dornberg, J. A. Minkin, C. K. Johnson and A. L. Patterson, *Acta Crystallogr.*, 1965, **19**, 561.
62 D. L. Pavia, G. M. Lampman and G. S. Kriz, *Introduction to Spectroscopy*, Brooks/Cole, 2001, pp. 60–62.
63 K. Nakamoto, John Wiley & Sons, Inc., New York, 5th edn, 1997, pp. 59–62.
64 G. A. Bowmaker, J. V. Hanna, C. E. F. Rickard and A. S. Lipton, *J. Chem. Soc., Dalton Trans.*, 2001, 20.
65 R. K. Harris, *Nuclear Magnetic Resonance Spectroscopy*, Longman, London, 1986, pp. 54–57.
66 L. J. Baker, G. A. Bowmaker, D. Camp, Effendy, P. C. Healy, H. Schmidbaur, O. Steigelmann and A. H. White, *Inorg. Chem.*, 1992, **31**, 3656.
67 E. C. Alyea, J. Malito and J. H. Nelson, *Inorg. Chem.*, 1987, **26**, 4294.
68 E. L. Muetterties and C. W. Alegranti, *J. Am. Chem. Soc.*, 1972, **94**, 6386.