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Liquid Coordination Complexes

Liquid Coordination Complexes Formed by the Heterolytic Cleavage of Metal Halides**

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Liquids containing very high metal concentrations are of value for a number of applications: from electrochemistry and Lewis acidic catalysis through to metals refining and inorganic materials syntheses. In the ideal case, such liquids should have well-controlled and tunable metal coordination, leading to adjustable physical properties (i.e. viscosity modifiable from mobile liquid to glass). Some of these requirements have been met by concentrated aqueous or acetonitrile solutions,[1] molten metals/alloys, molten salts,[2] ionic liquids,[3] or deep eutectic solvents.[4] However, each approach has some drawbacks, such as high cost, solubility limits, corrosiveness, or limited control over the metal coordination environment; consequently, the ideal system remains elusive.

Herein, we describe a synthetic route to liquid coordination complexes (LCCs, shown in Figure 1), identify the metal coordination environment referring to in such systems, and present LCCs as a promising addition to the 'metals in the liquid state' toolbox.

A large number of ligands were reported to induce asymmetric splitting of the "M_2Cl_6" unit, where $M = Al^{III}$ or Ga^{III}, leading to the formation of an ionic compound of formula $[MCl_2L_2][MCl_4]$.[5] These were investigated primarily within two distinct disciplines, coordination chemistry and electrochemistry. The traditional methodology of a coordination chemist involves allowing a metal halide and ligand to react in a solvent, using excess or equimolar amount of ligand, followed by the isolation of a crystalline product, and its analysis by single-crystal X-ray diffraction. Hence, inevitably, the majority of reported products of asymmetric cleavage are crystalline solids. For example, Richard and Beavers[6] recently described four crystal structures of coordination compounds based on Group 13 metal halides, only briefly mentioned the formation of '*an oil that could not be crystallized and NMR spectroscopy suggested a complex mixture of products*'. From another perspective, extremely concentrated solutions of metal halides in various coordinating solvents have been studied as electrolytes. The ionic nature of such liquids was inferred from their high conductivities, but the identity of the ionic species often remained speculation.[7] Recently the electrodeposition of aluminum,[8] as well as antimony, tellurium and their alloys,[9] from mixtures of urea or acetamide with the respective metal chlorides was reported. The identity of the product was only proposed for the Al^{III}-based system;[8] the material was postulated to be an ionic liquid, $[AlCl_2(n\text{Amide})][AlCl_4]$ ($n = 1$ or 2). However, this assignment was based mainly on mass spectrometry, which has been demonstrated to produce erroneous results when used for the identification of chlorometallate anions[10] and coordination compounds.[11] Furthermore, this characterization requires the existence of tricoordinate ions, $[AlCl_2L]^+$, which have not been reported to date. In summary, LCCs have been encountered sporadically over decades, but their significance as soft materials in their own right has not been recognized. Moreover, the absence of detailed characterization has halted their design and use.

In this work, the reaction of neat $AlCl_3$ or $GaCl_3$ with substoichiometric amounts of simple donor molecules (reactants ratio is expressed as the molar ratio of metal chloride, χ_{MCl_3}) was studied. Donors included: O-donors (urea, Ur, acetamide, AcA, dimethylacetamide, DMA, and trioctylphosphine oxide, $P_{8\,8\,8}O$), an S-donor (thiourea, SUr) and a P-donor (trioctylphosphine, $P_{8\,8\,8}$). Low-viscosity liquids (Figure 1) were formed for excess metal chloride. For Al^{III}-based systems, liquids were typically obtained for $\chi_{AlCl_3} = 0.60$ (i.e. 3 mole of $AlCl_3$ per 2 mole of donor); most $\chi_{AlCl_3} = 0.50$ and 0.67 samples contained white powder suspended in a liquid. For Ga^{III}-based LCCs, all $\chi_{GaCl_3} = 0.67$ and 0.75 samples were mobile liquids (see Table 1-SI in the Supporting Information).

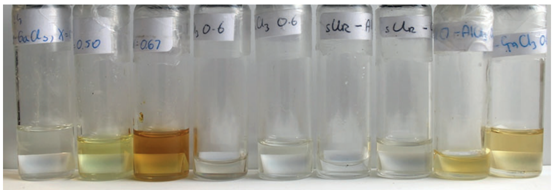

Figure 1. Selected LCCs, based on $AlCl_3$ or $GaCl_3$ and a range of ligands, where $\chi_{MCl_3} = 0.50$ to 0.75.

Decomposition temperatures of the liquid samples of Ga^{III}-based LCCs (see Table 1) were measured using thermogravimetric analysis (TGA). TGA curves are presented in the Supporting Information (Figure 1-SI).

The decomposition onset temperatures suggest good thermal stability and very low vapor pressure near ambient

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Table 1: Decomposition temperatures (T_d/°C) of LCCs.

Donor molecule	T_d [°C]			
	χ_{GaCl_3} 0.50	0.60	0.67	0.75[a]
Ur	–	230	237	238
AcA	–	235	223	200
DMA	–	220	245	226
$P_{8\,8\,8}O$	315	280	314	441
$P_{8\,8\,8}$	296	322	322	322
SUr	–	286	259	243

[a] Typically, a slow, gradual mass loss was observed for χ_{GaCl_3} =0.75 samples before the thermal decomposition onset temperature was reached.

conditions. The decomposition onset temperatures were found to be good indicators of thermal stability for χ_{GaCl_3} =0.50 to 0.67 samples. However, some of the χ_{GaCl_3} =0.75 compositions were slowly losing mass at lower temperatures, before reaching decomposition temperature (see Figure 1-SI). These compositions appear to be metastable, most likely decomposing to release $GaCl_3$ even at near-ambient temperatures. Al^{III}-based LCCs hydrolyzed rapidly even within the short time required to place the sample on a sample pan and insert into the TGA oven, hence these samples were not measured.

Characterization of LCCs was by multinuclear NMR and Raman spectroscopy. ^{27}Al or ^{71}Ga NMR spectra were recorded (neat) for all liquid samples; suspended solids were removed by filtration. ^{71}Ga NMR spectra brought no conclusive information, as the signals were too broad to be separated from the baseline. In contrast, ^{27}Al NMR spectra (Figure 2) were very informative; well-pronounced signals were obtained for all χ_{AlCl_3} =0.50 and 0.60 samples, and for χ_{AlCl_3} =0.67 compositions based on $P_{8\,8\,8}O$ and $P_{8\,8\,8}$ ligands (for chemical shifts see Table 1-SI).

For χ_{AlCl_3} =0.50, systems based on O-donors were characterized by remarkably similar ^{27}Al NMR spectra, with three intense peaks of roughly 1:2:1 area (Figure 2, right), and a fourth small signal, visible in the magnified spectrum of the AcA-$AlCl_3$ system (Figure 2, bottom left).

The most downfield and narrow signal (at $\delta = 101 \pm 1$ ppm) was assigned to the symmetrical, tetrahedral $[AlCl_4]^-$ ion, in very good agreement with the literature values.[12] The upfield-shifted, broader peaks were assigned to complexes where chlorides were replaced with neutra*l* *O*-donor ligands: $[AlCl_3L]$, $[AlCl_3L_2]$, and $[AlCl_2L_2]^+$.[13] The spectrum for SUr-$AlCl_3$ (χ_{AlCl_3} =0.50) contained a peak corresponding to $[AlCl_4]^-$, and a broad, downfield shifted signal at $\delta = 109.3$ ppm, which after close examination revealed a well-marked shoulder at around $\delta = 119$ ppm. These were assigned to $[AlCl_3SUr]$ and $[AlCl_2SUr_2]^+$ complexes, respectively; S-donors cause downfield shift of the ^{27}Al NMR signal.[13] Finally, the spectrum recorded for $P_{8\,8\,8}$-$AlCl_3$ (χ_{AlCl_3} =0.50) featured a very weak signal corresponding to $[AlCl_4]^-$ (at ca. $\delta = 100$ ppm), with the dominant signals at $\delta =$ 121, 117 and 74 ppm. The downfield shifted (relatively sharp) peaks may be assigned to $[AlCl_3P_{8\cdot8\cdot8}]$ and $[AlCl_2(P_{8\cdot8\cdot8})_2]^+$ complexes;[13] however, the origin of the upfield-shifted broad peak is yet to be explained.

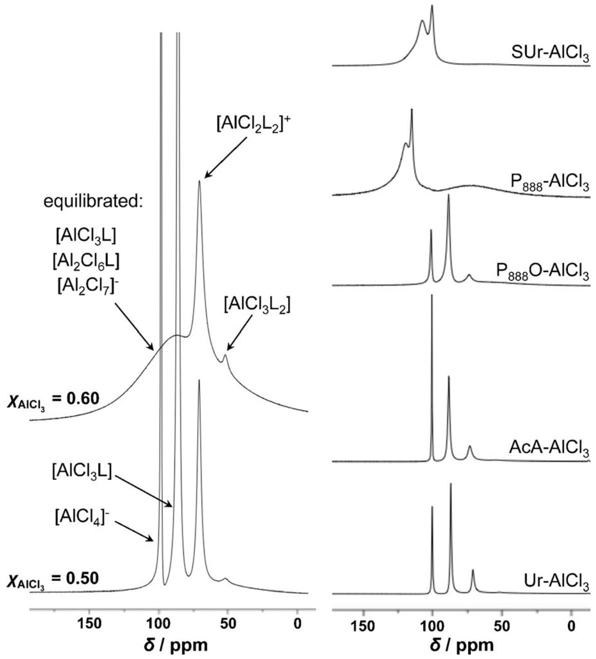


Figure 2. ^{27}Al NMR spectra (130.36 MHz, 27 °C, neat, DMSO lock) of: AcA-$AlCl_3$ system of two different compositions (left) and LCCs based on various ligands, at χ_{AlCl_3} =0.50 composition (right).

When an excess of $AlCl_3$ was used (χ_{AlCl_3} =0.60), ^{27}Al NMR spectra of systems based on O-donors featured sharp peaks corresponding to $[AlCl_2L_2]^+$ and $[AlCl_3L_2]$, partially obscured by a broad signal which replaced the two sharp signals corresponding to $[AlCl_4]^-$ and $[AlCl_3L]$ (Figure 2, top left). It is most likely that these remain in dynamic equilibria with dimeric species, $[Al_2Cl_7]^-$ and $[Al_2Cl_6L]$. An analogous equilibrium between $[AlCl_4]^-$ and $[Al_2Cl_7]^-$ ions, described for neat chloroaluminate(III) ionic liquids (with chloride as the only ligand) also manifests itself in a dramatic broadening of the ^{27}Al NMR signal for χ_{AlCl_3} >0.50 compositions, without significant change in chemical shifts.[12] For LCCs based on $P_{8\,8\,8}$ or SUr, broad peaks indicating the presence of dimers obscured all other signals.

Raman spectra, recorded for both Al^{III}- and Ga^{III}-based LCCs, are shown in Figure 3.

Bands corresponding to M–Cl and M–L vibrations fall within 500–100 cm^{-1} (see Table 2-SI).[14] The strongest signals in this range corresponded to M–Cl$_{terminal}$ stretching frequencies in $[MCl_4]^-$ and/or $[M_2Cl_7]^-$, all in very good agreement with the literature values.[14–16] In comparison with Raman spectra of the analogous chlorometallate(III) ionic liquids, equilibria in LCCs appeared to be shifted towards the formation of oligomeric species. In ionic liquids, for χ_{MCl_3} =0.50, only monomeric $[MCl_4]^-$ ions were detected,[15,16] whereas for LCCs, pronounced bands for dimeric species were found (Figure 3, right). Furthermore, in chlorogallate(III) ionic liquids, a band at 392 cm^{-1}, indicating the presence of the trimer, $[Ga_3Cl_{10}]^-$, was found only for very high excess of $GaCl_3$ (χ_{GaCl_3} =0.71).[15] In contrast, for $GaCl_3$-based LCCs, a shoulder corresponding to $[Ga_3Cl_{10}]^-$ was unexpectedly found for some χ_{GaCl_3} =0.60 samples, and evolved into

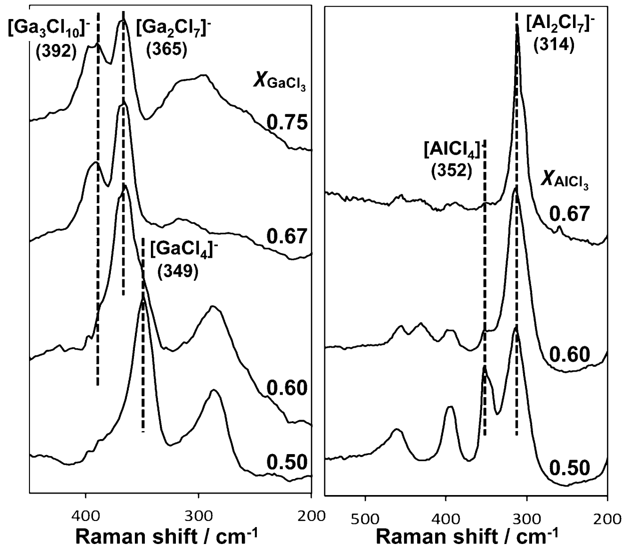
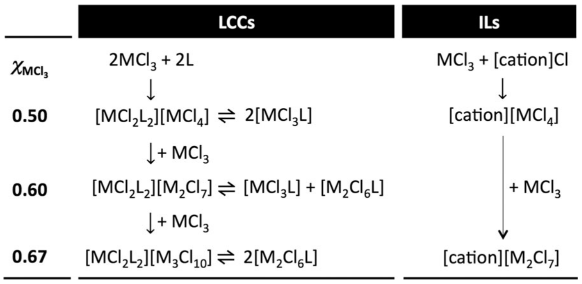


Figure 3. Sections of the Raman spectra (ambient temperature) of the SUr-MCl_3 (M = Al or Ga) systems, corresponding to M–Cl and M–S vibrations, with dominant bands for M–Cl stretching frequencies assigned to chlorometallate anions.

a strong band for χ_{GaCl_3} =0.67 and 0.75 compositions (Figure 3, left).

Inferring from spectroscopic studies, LCCs contain a complex mixture of statistically distributed anionic, neutral, and cationic species (e.g. 1:2:1 peak area in ^{27}Al NMR spectra), in which chloride is replaced to various degrees with a neutral ligand. Equilibria found for the key compositions of LCCs are presented in Scheme 1, and compared to equilibria in analogous chlorometallate ionic liquids.



Scheme 1. Main equilibria in LCCs, inferred from spectroscopic studies for the key compositions, and compared to equilibria in chlorometallate ionic liquids (ILs); M = Al^{III} or Ga^{III}.

Based on Scheme 1, it may be assumed that, at χ_{MCl_3} =0.50, LCCs were solid or contained precipitation arising from the crystallization of neutral $[MCl_3L]$ or ionic $[MCl_2L_2][MCl_4]$. In contrast, at χ_{MCl_3} =0.60, the dominant $[M_2Cl_7]^-$ ion, characterized by lower symmetry and dispersed charge, promoted the formation of liquids.[17] At χ_{MCl_3} =0.67, Ga^{III}-based systems formed homogenous liquids, Al^{III}-based LCCs contain suspended white powder. This situation is easily explained by the ability of Ga^{III} to form oligomeric chlorogallate(III) anions, such as $[Ga_3Cl_{10}]^-$,[15,18] whereas homogenous chloroaluminate(III) ionic liquids based on $[Al_3Cl_{10}]^-$ ions are not known;[19] it is most likely that the white suspended powder is residual aluminum(III) chloride.

To confirm the existence of dynamic equilibria, the Al^{III}-based LCC, DMA-$AlCl_3$, χ_{AlCl_3} =0.60, was studied using ^{27}Al NMR spectroscopy at 30, 40, 60, and 80 °C. If multiple Al^{III}-containing species were to remain in a dynamic equilibrium with each other, NMR signals are expected to broaden and merge at higher temperatures as a result of increased exchange rates. In contrast, if the Al^{III}-containing species are not exchanging, the peaks are anticipated to narrow and become better defined at higher temperatures because of the reduced viscosity of the liquid. As shown in Figure 4, the peaks merged and became less defined with increasing temperature, furthermore their relative areas changed with temperature, which is indicative of a sequence of dynamic equilibria.

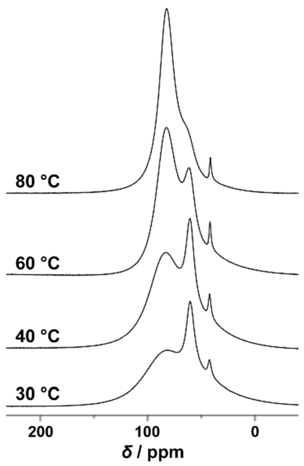


Figure 4. ^{27}Al NMR spectra (130.36 MHz, neat with external DMSO lock) of DMA-$AlCl_3$, χ_{AlCl_3} =0.60, recorded at different temperatures.

Based on the proposed characterization, it was concluded that LCCs may offer the same advantages as analogous chlorometallate ionic liquids: high Lewis acidity through the presence of oligomeric species and good ionic conductivity, opening routes to new media for electrochemistry. Two systems: DMA-$AlCl_3$, χ_{AlCl_3} =0.60 and DMA-$GaCl_3$, χ_{GaCl_3} =0.60, were selected for a screening study of these properties in LCCs.

Lewis acidity can be quantified by the Gutmann acceptor number (AN), which is directly proportional to the ^{31}P NMR chemical shift of a basic probe molecule, triethylphosphine oxide (tepo), dissolved in the neat liquid. AN values have been determined for a number of conventional Brønsted and Lewis acids,[20] and for a wide range of ionic liquids.[10,21,22] The chloroaluminate(III) ionic liquid based on the 1-octyl-3-methylimidazolium cation, χ_{AlCl_3} =0.60, is characterized by AN = 93; its chlorogallate(III) analogue has AN = 95.[21] We found, DMA-$GaCl_3$, χ_{GaCl_3} =0.60, has AN as high as 103. For the Al^{III}-based analogue, several ^{31}P NMR signals were recorded (corresponding to different Al^{III} species detected by the probe), and the calculating AN values were between 96 and 103. These high AN values are very encouraging, making

LCCs promising candidates for application in Lewis acidic catalysis.

The electrochemical properties, such as, conductivity, electrochemical window, and electrodeposition of metal from LCCs, were investigated. The DMA-$AlCl_3$, χ_{AlCl_3} =0.60, system had conductivity of 1.114 mS cm^{-1} (24.6 °C) and kinematic viscosity of 63.3 cSt (25 °C). Its Ga^{III}-based analogue had a slightly higher conductivity of 1.396 mS cm^{-1} (24.9 °C), combined with kinematic viscosity of 53.1 cSt. Dynamic viscosities at 25 °C were very similar for both systems, 87.6 and 90.5 cP, respectively. Conductivities for LCCs were lower than those for ionic liquids of similar viscosities, where values of approximately 2.5 mS cm^{-1} would be expected.[23] This is consistent with the proposed characterization of LCCs, in which neutral species coexist with the ionic ones.

Subsequently, electrodeposition of aluminum from DMA-$AlCl_3$, χ_{AlCl_3} =0.60, was investigated. Cyclic voltammograms (Figure 2-SI) showed that the electrochemical window was extended towards the cathodic direction compared to chloroaluminate(III) ionic liquids.[24] Metallic aluminum was electrodeposited at a more negative potential compared to conventional chloroaluminate(III) ionic liquids, with a smaller deposition current (Figure 3-SI). This may result from monomeric cationic species being reduced (as opposed to $[Al_2Cl_7]^-$) and/or from the lower availability (concentration) of these ionic species due to their "dilution" with neutral components. A photograph of aluminum deposited on a gold substrate, along with a scanning electron microscope (SEM) image and X-ray energy dispersive analysis (EDX) of the deposit are shown in Figure 5.

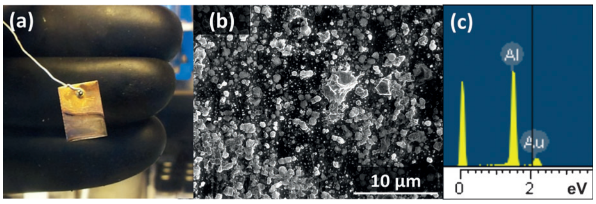


Figure 5. Photograph of aluminum electrodeposited on a gold plate at 23 °C from DMA-$AlCl_3$, χ_{AlCl_3} =0.60 (a), along with SEM image (b) and EDX analysis of the deposit (c).

Parallels between the strategies used to suppress melting point in ionic liquids[17] and in LCCs can be drawn. The presence of oligomeric anions with delocalized charge is the key factor, as is the presence of multiple species, remaining in dynamic equilibria (Scheme 1). Also the introduction of long alkyl chains, known to decrease melting points in ionic liquids, appears to have the same effect in LCCs (c.f. solid trimethylphosphine oxide-$AlCl_3$ system vs. the liquid analogue based on $P_{888}O$). Based on these conclusions, a general synthetic route to access new libraries of LCCs may be proposed. To validate this postulate, LCCs based on $SnCl_2$, $SnCl_4$, $ZnCl_2$, and $FeCl_3$ were prepared using P_{888} and $P_{888}O$ as ligands. Systems based on $P_{888}O$-$SnCl_4$, P_{888}-$SnCl_2$, $P_{888}O$-$SnCl_2$, and $P_{888}O$-$FeCl_3$ were mobile liquids, whilst the $P_{888}O$-$ZnCl_2$ system had a higher viscosity, most likely a result of the presence of doubly charged chlorozincate(II) anions (Figure 4-SI).

LCCs have the potential to offer all the major benefits of chlorometallate ionic liquids: low vapor pressure, high conductivity, and Lewis acidity. In addition, metal coordination in LCCs can be manipulated not only by changing the composition (χ_{MCl_3}), but also the ligand, leading to a much wider spectrum of accessible species. This opens up routes to wide ranges of Lewis acidities and redox potentials, available uniquely in LCCs. Higher metal concentrations, achievable by avoiding "dead load" of the organic cation, result in dense liquids of presumably high heat capacities and refractive indices. Finally, in terms of cost and ease of preparation, LCCs are superior to traditional chlorometallate ionic liquids.

Experimental Section

LCCs were prepared by mixing donor molecules with anhydrous metal(III) chloride in a glovebox (30–80 °C, 1–6 h, solventless). Raman spectra were recorded neat, 40 × 2 s scans were acquired. NMR spectra were recorded neat, with sealed DMSO capillaries as a lock. 1.1 m solutions of $M(NO_3)_3$ in D_2O were used as a reference for ^{27}Al and ^{71}Ga NMR spectroscopy, neat 85 % H_3PO_4 was used as a reference in ^{31}P NMR spectroscopy (for AN measurements). AN values were derived as described elsewhere.[21] TGA data were acquired using TA Instruments Q50 thermogravimetric analyzer. The samples were measured in platinum pans, at a heating rate of 10 °C min^{-1}, under a nitrogen atmosphere. Cyclic voltammograms were recorded with a PC-controlled Autolab Type III Potentiostat. Electrodeposition experiments were carried out on a gold substrate. All electrochemical experiments were conducted inside the glovebox at 23 °C. The SEM studies on the electrodeposits were carried out using a JEOL 6500F Field Emission Scanning Electron Microscope, and the EDX analysis were carried out using Oxford Instruments INCA systems. Conductivities were measured using Mettler Toledo conductivity meter with a platinum electrode.

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