(CrCl₃)₃@2[C₄mim][OMe]—Molecular Cluster-Type Chromium(III) Chloride Stabilized in a Salt Matrix

Bert Mallick
Harald Kierspel
Anja V. Mudring

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As an innovative class of solvents ionic liquids have received substantial attention in recent years. They often exhibit properties like negligible vapor pressures, wide liquidus ranges, good thermal stabilities, considerable electric conductivities, and wide electrochemical windows which are advantageous for a large number of applications. However, as solvents they are used predominantly in organic syntheses. Only a few examples are known where they have been used for inorganic syntheses, although traditional molten salts are widely used as flux materials in solid state syntheses.

Here we report on using ionic liquids for the synthesis and stabilization of a “new modification” of molecular chromium trichloride. While cuprous chloride has been extensively studied as a salt matrix to stabilize unconventional polymorphs of phosphorus and other group 15 and 16 compounds, little attention has been paid to the growing class of ionic liquids in this respect. It has only recently been noted that ionic liquids can be used as matrices to trap unusual metal coordination environments. However, we were able to stabilize a molecular trimeric CrCl₃ in a matrix of [C₄mim][OMe] (C₄mim = 1-butyl-3-methylimidazolium, OMe = methoxy). This novel compound of the composition [C₄mim][CrCl₃][OMe] shows unprecedented structural and bonding features within the CrCl₃ unit. It can be synthesized in high yields by reacting the ionic liquid [C₄mim]Cl with CrCl₃ in the presence of CrCl₂ in methanol.

Surprisingly, crystal structure analysis of I reveals the molecular unit, Cr₃Cl₆, embedded in a matrix of [C₄mim][OMe] (Figure 1). The structural subunit can be viewed as a new modification of CrCl₃ whose structural and bonding features have never been observed for the known bulk CrCl₃. The formula of I can be rewritten as (CrCl₃)₂@2[C₄mim][OMe] to stress the fact that [C₄mim][OMe] indeed provides an ionic host matrix for molecular (CrCl₃)₃ (cf. Figure 1). The neutral Cr³⁺ cluster is formed by three edge sharing tetrahedra. The mean Cr–Cl distance of 2.314 Å in I is slightly shorter than observed for CrCl₃ where Cr³⁺ is surrounded octahedrally by Cl (d_{octa}(Cr–Cl) = 2.348 Å). However, taking into account the lower coordination number of Cr³⁺ in I the distance lies well in the expected range. The interatomic Cr³⁺–Cl distances in I are slightly larger for the bridging chloride ions (2.367 Å) than for the terminal ones (2.263 Å). Interestingly, in the triangular (CrCl₃)₃ unit each Cr³⁺ has two other metal neighbors at short distances of 2.943 and 2.952 Å, respectively. The observed mean Cr–Cr distance is slightly longer than in the heterocubane tetrakis(µ₂-oxo)-µ₃-cyclopentadienytrichromium(III)⁸ and tris(µ₂-chloro)-tris(µ²-µ³-cyclopentadieny)(µ₃-methyleneidenetricromium(III)).⁹ The Cr–Cr distance in I is quite similar to the more electron rich compound bis(tetraethylammonium)bis(µ₂-selenido)-deca-carbonyl-trichromium (0,1) where 16 electrons can be attributed to the triangular d electron system.¹⁰

Chromium–chromium metal-to-metal bonds have received considerable attention ever since the discovery of metal-to-metal quadruple bonds.¹¹ Recently, even compounds with Cr–Cr quintuple bonds were synthesized.¹² Examples of metal-to-metal single bonds are abundant among the transition metals. Especially the temperature dependent interaction of d-electrons of reduced early transition metal halides such as for example, d¹-TiI₃ or d²-TiI₂ has been the focus of research. However, examples for Cr–Cr interactions with a bond order less than four have been comparatively little studied. Generally, interatomic Cr–Cr distances of 2.65–2.97 Å are regarded as indicative for Cr–Cr single bonds.¹³ Antiferromagnetic coupling of the d-electrons has been observed with respect to the d-electron system of I isoelectronic, tris(µ₂-chloro)-tris(µ²-µ³-cyclopentadieny)(µ₃-methyleneidenetricromium(III))⁹ and for the structurally similar eight-d-electron cluster compound bis(µ₁-sulfido)-tris(µ₂-sulfido)-(tris(bis(1,2-dimethylphosphino)-ethane-P,P')trichromium, in which a Cr–Cr interatomic distance of 2.558 Å is found, Cr–Cr bonds have been discussed.¹⁶ Thus, for I the question whether Cr–Cr bonds are present in the trinuclear Cr³⁺ cluster has to be addressed.

Magnetic measurements show an antiferromagnetic coupling of the electrons (Figure 2, left). From extrapolation of the high temperature region a Tₑ of 55.3 K can be estimated. At temperatures below 50 K the susceptibility grows and ferromagnetic contributions are observed. The effective magnetic moment of 3.54 µB per Cr³⁺

Figure 1. [C₄mim][CrCl₃][OMe]: View of the crystal structure along b (left); molecular [CrCl₃] unit (right).

Figure 2. [C₄mim][CrCl₃][OMe]: Temperature dependence of the reciprocal molar susceptibility (left) and the effective magnetic moment (right).
until it reaches a final value of 1.88 μB. The CrCl₃ unit of [C₄mim][CrCl₃][OMe]₂ shows significant Cr-contributions with some Cl-p admixture right below the Fermi level (Figure 3). With falling temperature the effective magnetic moment drops - Cr interactions are, from lower to higher Cr bonding, then slightly antibonding. B which corresponds well to B). At high temperatures is slightly reduced when compared to the expected spin-only value for three d electrons (3.88 μB). With falling temperature the effective magnetic moment drops until it reaches a final value of 1.88 μB which corresponds well to the expected value for one unpaired electron per Cr₃Cl₉ unit (Figure 2, right). The temperature dependence of the effective magnetic moment can be interpreted with an increasing d-electron interaction, hence, localization of electrons in metal-to-metal bonds of the CrCl₃ unit. At last, at low temperatures all of the nine d-electrons get paired in bonds except for one remaining electron.

This observation can be backed by theoretical calculations. Analysis of the density of states (DOS) and Cr-d as well as Cl-p PDOS (projected DOS) obtained by extended-Hückel calculations shows significant Cr-contributions with some Cl-p admixture right below the Fermi level (Figure 3).

However, the Cr–Cr interactions are, from lower to higher energies, first strongly Cr–Cr bonding, then slightly antibonding. The SOMO (singly occupied molecular orbital) is again somewhat metal-to-metal bonding. Figure 4 gives a graphical representation of the five occupied frontier orbitals in the Cr₃Cl₉ unit. All orbitals are predominantly of Cr-d character and stretch over the chromium triangle. Thus Cr–Cr interactions at low temperatures arise from the localization of electrons in 3c–2e bonds.

[Cr₃mim][CrCl₃][OMe]₂ is a novel compound where a trinuclear chromium cluster of the composition (CrCl₃)₃ which can be grasped as molecular trimeric chromium(III)chloride is embedded in a salt matrix of [Cr₃mim][OMe]. According to our experimental and theoretical investigations the trivalent chromium cations interact with their nine d electrons. With decreasing temperature the antiferromagnetic coupling of the d electrons increases until all electrons but the remaining last one are paired in 3c–2e chromium–chromium bonds.

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Supporting Information Available: Experimental procedures, details on the structure analysis, powder XRD, vibrational spectroscopy (MIR), thermal investigations, and further crystallographic information ( cif). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) For a recent review on the topic see: Plechkova, N. V.; Seddon, K. R. Chem. Soc. Rev. 2008, 37, 123.