Transition metal-chlorine anions and cations: monomers, clusters, and periodic trends

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Received 17 July 2000; in final form 26 September 2000

Abstract
Laser ablation and time-of-flight mass spectrometry have been used to generate and characterize aluminum-chlorine and transition metal-chlorine ionic species. Many new complexes have been observed. The structures of the monometal-chlorine species are discussed. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Material science has been an important branch of science in the past millennium and will be more critical in the new millennium. Generally speaking, there are three main building blocks of solid materials, i.e., cations/anions, neutral atoms and individual molecules, and correspondingly three main types of materials, ionic crystals, network solids and molecular solids [1]. In the past several decades, we have witnessed a tremendous growth in both pure and applied research in material science that challenges and changes our vision about materials. One of the most significant developments in recent years is the discovery of new carbon related materials, from fullerenes to nanotubes [2]. These new carbon compounds lie between the traditional network solids and molecular solids. Another important type of material is organic polymers [3], also in between the old classifications of network and molecular solids. Metal clusters can also be viewed as new materials and, due to their important role in heterogeneous catalysis, have attracted significant attention. In contrast to well studied simple neutral clusters, binary neutral clusters, ionic clusters, and radical clusters (ionic or neutral) have received much less attention. In the material world, however, they are the building blocks of a majority of solids. Several recent studies indicate an increasing interest in this field (see, for example, [4–8]).

Many monometal–metal chloride species have been characterized in solution and solid phase inorganic chemistry [9]. However, no ionic clusters composed only of a transition metal and chlorine seem to have been reported in the gas phase. Binary aluminum-chlorine clusters, neutral and ionic, and radical clusters (ionic or neutral) have received considerable attention [10–12]. On the other hand, transition metal-chlorine clusters have not received as much attention, possibly due to difficulties in preparation, separation, and isolation. Only recently have iron-chlorine neutral and ionic clusters been observed in...
melts [12] and theoretically investigated [13,14]. The main focus of other publications is MCl$_2$ (M = Cr, Mn, Fe, Co, Ni, Cu). The structure of MCl$_2$ (linear vs. bent) has been debated theoretically [15–19] and experimentally [8,20–26]. The current consensus is that MCl$_2$ is linear, contrary to several bonding models (Lewis, VSEPR, ligand field theory, crystal field theory, some semi-empirical, and ab initio methods).

2. Experimental setup

The experimental setup is typical for laser ablation experiments. It consists of a vaporization laser, a molecular beam source, two differentially-pumped vacuum chambers, a switched time-of-flight mass spectrometer (TOF-MS), and a computer data acquisition system.

The vaporization laser radiation used was the 355 nm 3rd harmonic of a Nd:YAG laser (Continuum NY-61), operating at 10 Hz and typically tens of millijoules per pulse. The molecular beam source was the same as that used in the production of transition metal radicals for spectroscopic studies and has been described in detail previously [27]; a brief description specific to the present experiment is given here. The source consists of a rotating metal rod (5.0 mm diameter, 3.0 cm long), a 20 mm expansion channel, and an in-house constructed molecular beam valve. A gas mixture of 5% Cl$_2$ in helium at 3 atm total pressure was injected at 10 Hz. The forward edge of the molecular beam coincided with the vaporization laser pulse on the metal rod.

The laser generates a plasma consisting of electrons and cations, anions, and neutral species. The pressure in this source chamber was maintained at 10$^{-4}$ Torr during the experiment. This plasma propagates through a field free region into the mass spectrometer chamber maintained at 10$^{-6}$ Torr. In the mass spectrometer chamber, a high voltage switch extracts anions or cations orthogonally in a Wiley–McLaren TOF-MS [28]. The distance between the source and the extraction region is 76 cm. The TOF drift region is 90 cm. A microchannel plate (MCP) detector consisting of two microchannel plates, impedance matched to 50 $\Omega$ (Galileo TOF-2003), was used to detect the ions.

The data acquisition system includes a 386, 25 MHz computer, a Tektronix 2440 digital oscilloscope (350 MHz; 500 MS/s), a digital counter card, an A/D and D/A interface card, and an EG & G 9650 digital delay generator.

In our experiments, we observed that the anions appeared in the TOF extraction region about 50 $\mu$s before the cations. Appropriate polarity high voltage pulses (Behlke HTS 31) were used to extract either the anions or cations in separate experiments. To detect positive ions, a standard voltage setup was used with the oscilloscope placed at near ground potential. For anion detection, the MCP signal was capacitatively coupled to the oscilloscope. The intrinsic mass resolution (M/DM) of the TOF-MS was determined on neutral clusters to be 800, however, in the present study, space charge effects limit the mass resolution to approximately 150.

3. Results and discussion

We used eight different metal rods, available in our lab from other experiments: Al and the 3d transition metals Ti, Cr, Fe, Co, Ni, Cu, Zn. Table 1 lists all the observed anions and cations for the metals studied together with the relative intensities extracted from the mass spectra.

3.1. Anions

(i) Aluminum. In Fig. 1, the negative ion mass spectrum from aluminum is shown. The inserts display the fine structure of the AlCl$_4^-$ and Al$_2$Cl$_7^-$ peaks due to $^{35}$Cl and $^{37}$Cl isotopes. From Fig. 1, it is evident that the basic building blocks for the aluminum-chlorine clusters are AlCl$_4^-$ and AlCl$_3$. Given that the neutral species is dimeric in the vapor, Al$_2$Cl$_6$, it is not surprising that AlCl$_4^-$ and Al$_2$Cl$_7^-$ are the dominant species we observe. Both of these anions occur in molten AlCl$_3$/NaCl [10]. A minor peak in our spectrum can be attributed to Al$_3$Cl$_{10}^-$. The actual structure of these aluminum-chlorine compounds needs to be determined from either ab initio calculations or spectroscopy studies,
however, chemical intuition suggests the structures
displayed in Fig. 2. Al₃Cl₁₀ can adopt a linear
configuration or form a ring structure by rotation.
This ring-like structure may be stabilized by
forming a pseudo [Al₂Cl₆][AlCl₄] structure as
shown. Additionally, the added stability associated
with ring formation may preclude the growth of
larger clusters.

(ii) Transition metals. As shown in Table 1,
negative ions of transition metal/chlorine com-
plexes were also observed in our experiments. The
idea of basic building blocks for the formation of
clusters can be applied to the transition metal-
chlorine molecules and clusters. While aluminum
is stable only in the +3 oxidation state, iron is
found in both the +2 and +3 oxidation states.
FeCl₂ and FeCl₃ are both stable, commercially
available compounds. Addition of a Cl⁻ ion pro-
duces FeCl⁻³ and FeCl⁻⁴, the only monoiron-chlo-
rine anions observed. Further additions of FeCl₂
or FeCl₃ building blocks produces all of the iron-
chlorine clusters we see. Similar arguments can
be used to explain essentially all the anionic
transition metal-chlorine clusters experimentally
observed. The ‘building block’ approach to the
formation of the aluminum and the transition
metal-chlorine clusters appears to be followed for
most of the anionic clusters in Table 1. This

Table 1

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1 Dimeric FeCl₃ is found in the gas phase, where the structure
is assumed to be two tetrahedra sharing an edge, as in Al₂Cl₆.
observation may be important to the development of new nanoscopic ionic clusters.

A few species fall outside of these general expectations and deserve mention. CoCl$_2^-$ and NiCl$_2^-$ were observed yet they do not represent stable oxidation states of the metal. They are not the dominant monometallic species. For transition metal complexes, the metal p orbitals are required to achieve high coordination numbers, e.g., FeCl$_4^-$, NiCl$_4^-$, CuCl$_4^-$, and ZnCl$_4^-$. 

(iii) Molecular orbital considerations. Several stable anions with large relative yields are observed: TiCl$_4^-$, CrCl$_3^-$, CrCl$_4^-$, FeCl$_4^-$, CoCl$_2^-$, NiCl$_3^-$, CuCl$_2^-$, and ZnCl$_3^-$. In the following paragraphs, we consider the structures of these anions with the aid of simple molecular orbital models. The reader must be cautioned that this discussion is aimed at a qualitative interpretation of the experimental results. A more accurate analysis must await high-resolution spectroscopy studies and/or accurate ab initio calculations.

In Fig. 3, a molecular orbital (MO) diagram for linear CuCl$_2^-$ is presented. In this MO diagram, we have omitted the 3s orbital on chlorine, which we believe will have minimal effect on the qualitative picture presented herein.

Within this picture, the CuCl$_2^-$ anion has a closed shell configuration with electrons filling the bonding and non-bonding MOs. We therefore expect CuCl$_2^-$ to be stable. The lowest unoccupied molecular orbital (LUMO) is expected to be significantly antibonding, and the yield of CuCl$_2^-$ under identical conditions is expected to be low, as is found. We also notice that CuCl$_2^-$ is a common linear anion in solution phase chemistry [29,30]. An interesting, isovalent, neutral species, ArCuCl, was recently characterized as linear by laser ablation Fourier transform microwave spectroscopy [31]. Recent ab initio calculations on CuCl$_2$ indicate a mixed $^2\Sigma_g^+$ and $^2\Pi_g$ ground state [16,18,19] which is in agreement with the current MO model. In radical systems like CuCl$_2$, there are two opposing forces that determine its geometry. On the one hand, Renner–Teller effects (i.e., vibronic interaction) will tend to reduce the symmetry [16,27] and favor a bent geometry whereas electrostatic forces due to the negatively charged chlorine atoms will tend to stretch the radical leading to a linear geometry. As was discussed previously [8,16–27], many of the MCl$_2$ neutral species are linear. The additional electron in MCl$_2^-$ will reinforce the linear structure. The Cl$^-$ anion is a good Lewis base since the electron affinity of Cl is only 3.61 eV whereas ionization energies of copper and chlorine atoms are 7.73 and 12.97 eV, respectively. Based on these considerations and symmetry, the negative charge on CuCl$_2^-$ is expected to be delocalized predominantly onto the chlorine atoms.

The structure of CrCl$_3^-$ can be qualitatively understood with the aid of Fig. 4, a MO diagram constructed for D$_{3h}$ symmetry. It is predicted that
CrCl$_3$ has a closed shell configuration with an electron configuration of \( \ldots (e')^3 \). It is also clear that the unoccupied \( a'_1 \) and \( e' \) orbitals are low lying and can participate in further bonding. This may explain why, in the case of chromium, the relative intensity of CrCl$_4^-$ is comparable with CrCl$_3^-$ (61:100), whereas the intensity of CuCl$_4^-$ is significantly lower than CuCl$_3^-$ (7:100). The negative charge in CrCl$_3^-$ is expected to be delocalized similar to CuCl$_2^-$. Electrostatic repulsion considerations suggest that MCl$_3^-$ anions will take D$_{3h}$ symmetry irrespective of the number of electrons around the central atom [21,22]. The partially charged chlorine atoms are large, and will protect the central metal atom from further coordination. This may explain the stability of NiCl$_3^-$ and ZnCl$_3^-$.

The structures of TiCl$_4^-$, CrCl$_4^-$, FeCl$_4^-$, and CoCl$_3$ are much more difficult to predict. A MO diagram similar to Fig. 4, when applied to CoCl$_3^-$, suggests a radical with three unpaired electrons. Simple electron counting for TiCl$_4^-$ and FeCl$_4^-$ implies at least one unpaired electron in each case. Interestingly, these species are amongst the most abundant. MO considerations (Jahn–Teller effect) predict a C$_{4v}$ symmetry. Electrostatic considerations, similar to those applied to MCl$_4^-$, lead to a tetrahedral geometry and stability of the MCl$_4^-$ radical anions. FeCl$_4^-$ is slightly tetragonally distorted from tetrahedral in the solid phase [32–34].

Titanium and chromium were not observed to form species with more than one metal atom. In bonding with chlorine, the early metals lose all of their d electrons and are thus unable to form metal–metal bonds. The late metals still retain electrons in their d orbitals and are able to form metal–metal bonds.

It is interesting to note in Table 1 that no metal mono-chlorine anions were observed. The reason behind this observation is believed to be the following: since the electron affinity for the chlorine atom is only 3.61 eV, the MCl$^-$ anion is very reactive and will behave as a Lewis base in most situations with the Cl atom being a good Lewis acid. When combined with a single metal atom,

![Image](https://via.placeholder.com/150)

**Fig. 4.** Qualitative molecular orbital diagram for planar CrCl$_3^-$ (D$_{3h}$ symmetry).
which normally would act as a base, there is little added stability by forming the metal-monochloride. Further, the orbitals of Cl$^{-}$ are significantly larger than the metal orbitals, resulting in poor overlaps. Upon the formation of larger MCl$_x^{-}$ anions ($x > 1$), however, delocalization of electron density results in smaller chlorine orbitals and better overlaps with the metal center.

3.2. Cations

The building block approach introduced for anions does not work as well for cations. For the middle and late transition metals, atomic cations were observed, corresponding to greater shielding by the other valence electrons across the period. The number of Cl atoms bonded to each transition metal is systematically less for all metals, comparing cations to anions. The removal of 2Cl$^{-}$ ions maintains the same oxidation state of the transition metal and is common in Table I but the removal of additional Cl atoms is evident in Co, Ni, and Al. Changes in orbital energies and bonding must be responsible for these observations.

In contrast to anions, isomorphic cations are more electronegative and therefore have smaller orbitals. As an example, TiCl$^+$ can be considered formed by combining Ti$^+$ and Cl. The second ionization potential of Ti is 13.57 eV, slightly higher than the first ionization of chloride, 12.97 eV. In this respect, the MCl$_x^+$ are similar to small molecules consisting of only non-metallic elements. We believe this is the reason that fewer clusters were observed in comparison with the anions.

It is interesting to observe that Cu$_2$Cl$^+$ and Co$_2$Cl$^+$ have high intensities in the mass spectrum. It is almost certain that metal–metal multiple bonds are present in these and other cationic clusters.

4. Summary

A systematic survey of the transition metal-chlorine complexes was conducted. Trends were evident in the formation of anionic complexes that can be explained by a simple building block model. To a lesser extent, the building block model can be applied to cationic complexes but metal–metal interactions in the cations is not accounted for. Cluster formation was observed in the middle and late transition metal complexes. Cationic complexes had fewer Cl atoms than similar anionic complexes. These experiments provide sufficient densities of small cationic and anionic clusters to make spectroscopic characterization possible.

Acknowledgements

The authors are grateful for financial assistance in terms of operating and student grants from the University of Victoria and the Natural Sciences and Engineering Research Council of Canada.

References