



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

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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, 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

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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 Ω (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 μs 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 ($M/\Delta M$) 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 $Al_2Cl_7^-$ 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_2Cl_6 , it is not surprising that $AlCl_4^-$ and $Al_2Cl_7^-$ 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 $Al_3Cl_{10}^-$. The actual structure of these aluminum-chlorine compounds needs to be determined from either ab initio calculations or spectroscopy studies,

Table 1
Experimentally observed transition metal-chlorine ions and their relative intensity

Titanium	Chromium	Iron	Cobalt	Nickel	Copper	Zinc	Aluminium
TiCl ₂ ⁻	62 CrCl ₃ ⁻	100 FeCl ₃ ⁻	37 CoCl ₂ ⁻	8 NiCl ₂ ⁻	11 CuCl ₂ ⁻	100 ZnCl ₃ ⁻	100 AlCl ₄ ⁻
TiCl ₃ ⁻	44 CrCl ₄ ⁻	61 FeCl ₄ ⁻	100 CoCl ₃ ⁻	100 NiCl ₃ ⁻	75 CuCl ₃ ⁻	7 Zn ₂ Cl ₅ ⁻	99 Al ₂ Cl ₇ ⁻
TiCl ₄ ⁻	100 CrCl ₅ ⁻	4 Fe ₂ Cl ₅ ⁻	12 CoCl ₄ ⁻	15 NiCl ₄ ⁻	6 Cu ₂ Cl ₅ ⁻	69 Zn ₃ Cl ₇ ⁻	16 Al ₃ Cl ₁₀ ⁻
TiCl ₅ ⁻	7 CrCl ₆ ⁺	100 Fe ₂ Cl ₆ ⁻	49 Co ₂ Cl ₅ ⁻	36 Ni ₂ Cl ₅ ⁻	100 Cu ₂ Cl ₄ ⁻	4 Zn ₄ Cl ₉ ⁻	
		36 Fe ₂ Cl ₇ ⁻	53 Co ₂ Cl ₆ ⁻	6 Ni ₂ Cl ₆ ⁻	6 Cu ₃ Cl ₄ ⁻	4	100 Al ⁺
TiCl ₂ ⁺	100 CrCl ₇ ⁺	16 Fe ₃ Cl ₈ ⁻	4 Co ₃ Cl ₇ ⁻	2 Ni ₃ Cl ₇ ⁻	5 Cu ⁺	Zn ⁺	100 AlCl ⁺
TiCl ₂ ⁺	69 CrCl ₈ ⁺	7 Fe ₃ Cl ₉ ⁻	7 Co ₃ Cl ₈ ⁻	6 Ni ₄ Cl ₉ ⁻	5 CuCl ⁺	ZnCl ⁺	15 Al ₃ Cl ⁺
TiCl ₃ ⁺	27 CrCl ₉ ⁺	17 Fe ₃ Cl ₁₀ ⁻	17 Co ₃ Cl ₈ ⁻	6 Ni ₄ Cl ₉ ⁻	5 CuCl ⁺	<1	3 Al ₃ Cl ₂ ⁺
		4 Fe ₄ Cl ₁₁ ⁻	4 Co ⁺	9 Ni ⁺	100 Cu ₂ Cl ⁺	100	28 Al ₃ Cl ₂ ⁺
			4 CoCl ⁺	71 NiCl ⁺	48 Cu ₂ Cl ₂ ⁺	4	3 Al ₄ Cl ⁺
		36 Fe ⁺	36 CoCl ₂ ⁺	3 Ni ₂ Cl ₂ ⁺	17 Cu ₃ Cl ₂ ⁺	45	
		100 FeCl ⁺	100 Co ₂ Cl ⁺	100 Ni ₂ Cl ₃ ⁺	4 Cu ₃ Cl ₃ ⁺	21	
		44 FeCl ₂ ⁺	44 Co ₂ Cl ₂ ⁺	4 Ni ₃ Cl ₃	5		
			9 Co ₂ Cl ₃ ⁺				

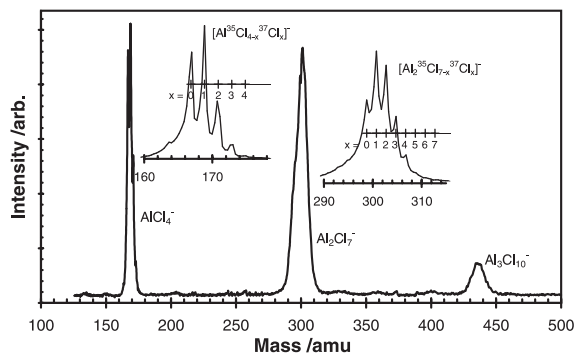


Fig. 1. Time-of-flight mass spectrum of aluminum-chlorine anions.

however, chemical intuition suggests the structures displayed in Fig. 2. $\text{Al}_3\text{Cl}_{10}^-$ can adopt a linear configuration or form a ring structure by rotation. This ring-like structure may be stabilized by forming a pseudo $[\text{Al}_2\text{Cl}_6][\text{AlCl}_4]^-$ 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 complexes 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. FeCl_2 and FeCl_3 are both stable, commercially available compounds. Addition of a Cl^- ion produces FeCl_3^- and FeCl_4^- , the only monoiron-chlorine anions observed. Further additions of FeCl_2 or FeCl_3 building blocks produces all of the iron-chlorine clusters we see¹. 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

¹ Dimeric FeCl_3 is found in the gas phase, where the structure is assumed to be two tetrahedra sharing an edge, as in Al_2Cl_6 .

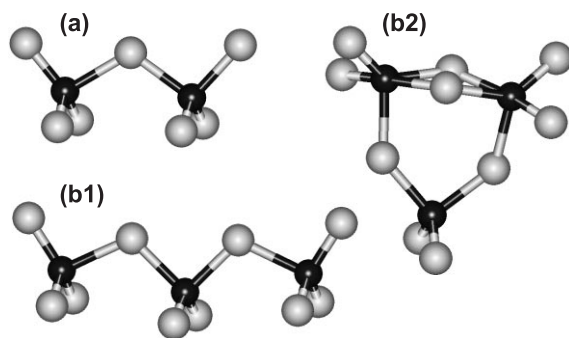


Fig. 2. Possible structures of Al₂Cl₇⁻ (a) and Al₃Cl₁₀⁻ (b1, b2).

observation may be important to the development of new nanoscopic ionic clusters.

A few species fall outside of these general expectations and deserve mention. CoCl₂⁻ and NiCl₂⁻ 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., FeCl₄⁻, NiCl₄⁻, CuCl₃⁻, and ZnCl₃⁻.

(iii) *Molecular orbital considerations.* Several stable anions with large relative yields are observed: TiCl₄⁻, CrCl₃⁻, CrCl₄⁻, FeCl₄⁻, CoCl₃⁻, NiCl₃⁻, CuCl₂⁻, and ZnCl₃⁻. 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 CuCl₂⁻ 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 CuCl₂⁻ anion has a closed shell configuration with electrons filling the bonding and non-bonding MOs. We therefore expect CuCl₂⁻ to be stable. The lowest unoccupied molecular orbital (LUMO) is expected to be significantly antibonding, and the yield of CuCl₃⁻ under identical conditions is expected to be low, as is found. We also notice that CuCl₂⁻ is a common

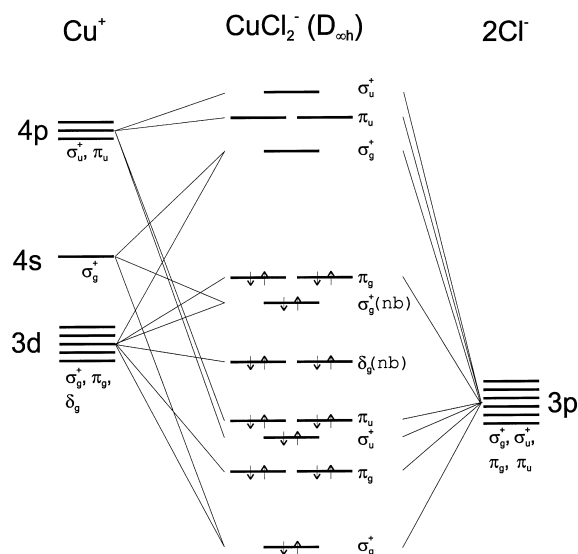


Fig. 3. Qualitative molecular orbital diagram for linear CuCl₂⁻ (D_{∞h} symmetry).

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 CuCl₂ indicate a mixed ²Σ_g⁺ and ²Π_g ground state [16,18,19] which is in agreement with the current MO model. In radical systems like CuCl₂, 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 MCl₂ neutral species are linear. The additional electron in MCl₂⁻ 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 CuCl₂⁻ is expected to be delocalized predominantly onto the chlorine atoms.

The structure of CrCl₃⁻ 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 $\dots(e'')^4$. 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_3^- is significantly lower than CuCl_2^- (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_2^- , 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–monochlorine 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,

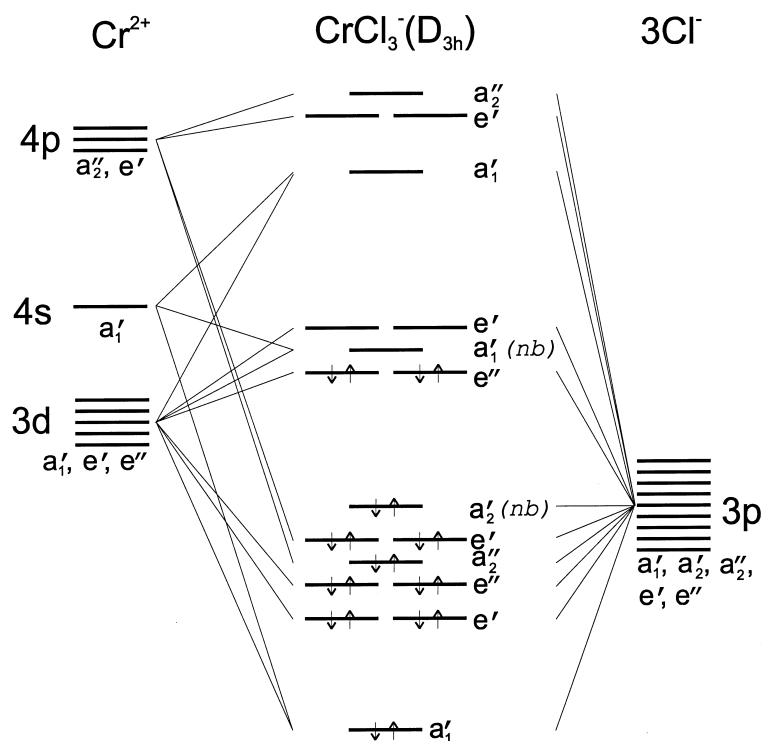


Fig. 4. Qualitative molecular orbital diagram for planar CrCl_3^- (D_{3h} symmetry).

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 1 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, isomorphous 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 chlorine, 12.97 eV. In this respect, the MCl_n^+ 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_2Cl^+ and Co_2Cl^+ 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.

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