Volume 30
Number 15
July 24, 1991

Inorganic Chemistry

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Communications

Gas-Phase Copper Chalcogenide Cluster Ions, Formed by Laser Ablation

Few metal chalcogenide species in the gas phase have been characterized.[1] Being cognizant of the plethora and variety of metal chalcogenide clusters characterized in the condensed phases[2] and of their significance for semiconductor material science,[3] redox devices,[4] and biology,[5] we are investigating the formation and properties of metal chalcogenide clusters in the gas phase.[6] We report that copper chalcogenide anions are readily formed by laser ablation (LA) of various solid compounds and from mixtures of elements. A single pulse from a Nd YAG laser (1064 nm) was used at various powers (150–1600 MW cm^{-2}), focused onto disks of pressed solid samples. The ablated ions were observed with a Spectrospin CMS-47 (FT-ICR) spectrometer[7] equipped with a cylindrical ICR cell and a 4.7-T superconducting magnet.[8] The samples investigated were CuS, Cu_2S, KCu_4S_3,[9] $Cu_{2-\delta}Se$, Cu + Se mixtures, Cu_2Te, and Cu + Te mixtures.

Table I. Assignments of the Negative-Ion Fourier Transform Ion Cyclotron Resonance Mass Spectra of Laser-Ablated KCu_4S_3, Cu_2Se, Cu + Se, Cu_2Te, and Cu + Te

	m/z^c (intensity)				
ion	KCu_4S_3	Cu_2Se	Cu + Se[a]	Cu_2Te	Cu + Te[b]
$[CuE]^-$	95 (35)[d]	143 (19)	(11)[d]	193 (8)[d]	(45)[d]
$[CuE_2]^-$	127 (100)[d]	223 (26)	(37)	321 (6)	(6)
$[CuE_3]^-$	159 (40)[d]	301 (10)	(25)	449 (6)	(5)
$[Cu_2E_2]^-$	190 (50)	286 (58)	(15)	384 (10)	(9)
$[Cu_2E_3]^-$	224 (40)	366 (15)	(11)	512 (3)	(3)
$[Cu_3E_2]^-$	255 (22)	349 (20)	(<5)		
$[Cu_3E_3]^-$	287 (88)	429 (53)	(34)	575 (6)	(5)
$[Cu_4E_3]^-$	350 (44)	492 (53)	(31)	639 (3)	(5)
$[Cu_4E_4]^-$	382 (15)	571 (25)	(15)	767 (<3)	(3)
$[Cu_5E_4]^-$	445 (50)	634 (45)	(26)	830 (<3)	(6)
$[Cu_6E_4]^-$	509 (90)	697 (100)	(39)	893 (<3)	(7)
$[Cu_6E_5]^-$	541 (8)				
$[Cu_7E_4]^-$		762 (22)	(10)	956 (<3)	(8)
$[Cu_7E_5]^-$	604 (15)	840 (20)	(8)		
$[Cu_8E_5]^-$	667 (35)	905 (55)	(25)		
$[Cu_9E_5]^-$	732 (45)	968 (83)	(30)	1212 (<3)	(20)
$[Cu_{10}E_6]^-$	827 (19)				
$[Cu_{11}E_6]^-$	890 (43)	1174 (22)	(22)	1466 (<3)	(22)
$[Cu_{12}E_7]^-$	987 (27)	1317 (<5)	(14)		
$[Cu_{13}E_7]^-$	1050 (35)	1380 (22)	(26)	1721[e] (<3)	(22)
$[Cu_{15}E_8]^-$	1210 (45)	1585 (17)	(37)	1975[e] (<3)	(21)
$[Cu_{17}E_9]^-$	1367 (40)	1791[e] (13)	(40)	2231[e] (<3)	(14)
$[Cu_{19}E_{10}]^-$	1527 (40)			2485[e] (<3)	(27)
$[Cu_{21}E_{11}]^-$	1687[e] (25)				
	[f]				

[a] 2:1 w/w mixture of Cu and Se (ions to Cu_9Se_5), 10:1 w/w mixture of Cu and Se (ions larger than Cu_9Se_5). [b] 2:1 w/w mixture of Cu and Te (ions to Cu_7Te_4), 10:1 w/w mixture of Cu and Te (ions larger than Cu_7Te_4). [c] m/z of the most intense isotopomer. [d] $(E_y)^-$ ions, not listed, have intensity 100. [e] Composition not yet confirmed by high-resolution narrow-band spectra. [f] Higher mass ions from KCu_4S_3 (see Figure 1) not included.

The positive-ion measurements yielded only Cu^+ and a series of chalcogenide ions E_n^+ (n = 1–6), but the negative-ion spectra were rich with interesting species, extending in some cases to very high mass. Most of the ions up to m/z ca. 1600 were observed under high-resolution narrow-band conditions and could be identified unambiguously by simulation of their isotopomer patterns:[10] they are listed in Table I. The negative-ion spectra of CuS, Cu_2S (synthetic chalcocite), and KCu_4S_3 were all similar and gave ions $[Cu_xS_y]^-$ up to m/z 3600. A representative broad-band spectrum is shown in Figure 1. Ions up to $[Cu_{19}S_{10}]^-$, m/z 1527.4, have been unambiguously identified, but the unfortunate mass coincidence[10] for copper and sulfur and the increasing difficulty of obtaining good narrow-band spectra at higher mass complicate unambiguous assignment of the higher mass ions. Nevertheless, the spectra clearly reveal that there exist series of ions that progress by addition of Cu_2S. The most intense series probably contains the ions of general formula $[Cu_{2n-1}S_n]^-$, with an intensity maximum at $[Cu_{29}S_{15}]^-$, up to $[Cu_{45}S_{23}]^-$. There is

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(10) Copper isotopes ^{63}Cu (69%) and ^{65}Cu (31%) contribute mass very close to two ^{32}S. The small differences between the masses of the ion with compositions $\pm n(CuS_{-2})$, e.g. $Cu_{27}S_{14}$ and $Cu_{25}S_{18}$, defy the resolution obtainable for the ions at higher mass and lower abundance. Similar difficulties arise with Cu_xTe_y ions, where the isotopes ^{126}Te (18.7%), ^{128}Te (31.8%), and ^{130}Te (34.5%) are almost mass-equivalent to two Cu atoms.

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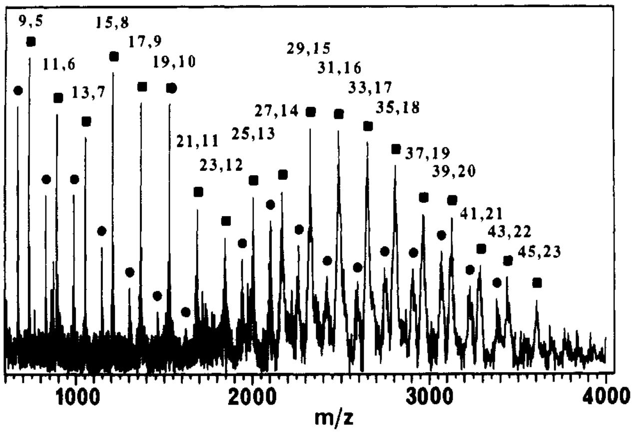

Figure 1. Part of the negative-ion FT-ICR broad-band mass spectrum of laser-ablated KCu_4S_3. Peak labels are *x*,*y* for ions $[Cu_xS_y]^-$. Peaks above *m*/*z* 1600 have not been unambiguously identified (see text) but are labeled as probable extensions of the low-mass series: ■, $x = 2y - 1$; ●, $x = 2y - 2$.

a lower intensity series of ions $[Cu_{2n-2}S_n]^-$, confirmed up to $n = 10$.

Samples of $Cu_{2-\delta}Se$ (synthetic Berzelianite) and of various mixtures of copper and selenium powders gave similar negative-ion spectra, but with different relative intensity patterns. Samples of both types gave significant amounts of the polyselenide ions Se_n^- (n = 1, 2, 3, 4, 5, 8). The negative-ion spectra of Cu_2Te (synthetic Weissite) and of mixtures of copper and tellurium powders were dominated by Te^-, which diminished the relative intensities of the $[Cu_xTe_y]^-$. Both sample types gave similar ions, but mixtures of copper and tellurium gave larger mass ions that cannot yet be unambiguously identified.[10]

There are two significant general conclusions about the cluster formation processes in these experiments. (i) The fact that the pattern of ions observed is largely independent of the composition of the sample ablated by the laser pulse suggests that reactions in the plasma during and immediately after ablation are the principal cluster formation processes. This is observed also for nickel chalcogenides[6a] and tantalum carbides.[11] It is established that high-power laser pulses cause immense heating of the sample, but the fact that the ions observed are present within milliseconds of the laser pulse causes us to believe that they are not formed by reactions of the molten elements. (ii) Combination of result i with the observation that the pattern of compositions of the negative ions $[Cu_xE_y]^-$ is largely independent of the chalcogen E (=S, Se, Te) indicates that this distribution of ions reflects the ion stabilities. Differences in relative intensities are presumably due to some differences in the plasma dynamics.

Features of the ion compositions are the excess of metal atoms ($x > y$) in all but the smallest ions (this occurs also for $[Ni_xS_y]^-$ ions on laser ablation of Ni_3S_2[6a]) and the series of ions $[Cu_{2n-1}E_n]^-$ that progress by addition of Cu_2E where nine or more Cu atoms are present. Experiments using samples with larger E:Cu ratios increase the proportions of $[E_y]^-$ ions, without changing the compositions of the $[Cu_xE_y]^-$ ions. $[Cu_6E_4]^-$ has large relative intensity, which bears comparison with the [*cuboctahedro*-Cu_{12}-*hexahedro*-$S_8]^{4-}$ ion characterized in the condensed phase.[12] The high Cu:E ratio may be contrasted to the composition of the [*tetrahedro*-Cu_4-*octahedro*-$(ER)_6$] clusters prevalent with chalcogenolate ligands.[13] The element ratios in the ion series $[Cu_{2n-1}E_n]^-$ (observed also for silver[6b]) resemble those of the core compositions of the copper selenide clusters $[Cu_{29}Se_{15}(PPr^i_3)_{12}]$, $[Cu_{30}Se_{15}(PPr^i_3)_{12}]$, and $[Cu_{36}Se_{18}(PBu^t_3)_{12}]$ recently reported by Fenske.[14] We note that the probable assignment of the most intense peak (*m*/*z* 2322) in the higher mass envelope in Figure 1 is $[Cu_{29}S_{15}]^-$, the same as the core composition of $[Cu_{29}Se_{15}(PPr^i_3)_{12}]$.[14] Freiser has recently reported that laser ablation of copper oxide, CuO, gives different results.[15] The positive ions include the series $[Cu_{2n}O_n]^+$, n = 1–6, as well as some ions $[Cu_{2n+1}O_n]^+$, $[Cu_{2n-1}O_n]^+$, and $[Cu_{2n-2}O_n]^+$, while the negative ions fall in several series $[Cu_{2n-m}O_n]^-$, m = 2–5.

Metal chalcogenides are notoriously nonmolecular in structure, and yet the phenomena and applications cited in the introduction relate to molecular clusters, nanocrystallites, and to the control of structural molecularity. A standard method for avoiding or regulating the condensation of molecular clusters is the use of obstructive terminal ligands in designed syntheses.[14,16] However, complexes such as $[Cu_{29}Se_{15}(PPr^i_3)_{12}]$, $[Cu_{30}Se_{15}(PPr^i_3)_{12}]$, $[Cu_{36}Se_{18}(PBu^t_3)_{12}]$, and $[Ni_{20}Te_{18}(PEt_3)_{12}]$[16] are thermally unstable relative to the nonmolecular binary metal chalcogenides.[14,16] Our experiments, which allow preservation of the molecular metal chalcogenide ions in the gas phase, provide an alternative entry to examination of their fundamental chemistry. We are currently investigating the reactivities of these ions by collisional activation and ion–molecule reactions.

Acknowledgment. This research was supported by the Australian Research Council. K.J.F. acknowledges the award of an Australian National Research Fellowship.

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Received December 28, 1990

An Isostructural Series of Molecular Metamagnets: The Organometallic Charge-Transfer Salts Decamethylmanganocenium Bis[bis(trifluoromethyl)ethylenedithiolato]nickelate, -palladate, and -platinate

Despite substantial efforts,[1] the search for ferromagnetically ordered molecular charge-transfer salts has yielded only two such compounds: $[Fe(Cp^*{}_2)][TCNE]$[2,3] and $[Mn(Cp^*)_2][TCNQ]$.[4] In addition, $[Fe(Cp^*)_2][TCNQ]$ is a metamagnet,[5] a compound

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(2) Abbreviations: $Cp^* = [C_5(CH_3)_5]^-$; TCNQ = 7,7,8,8-tetracyanoquinodimethanide; TCNE = tetracyanoethyleneide; tfd = bis(trifluoromethyl)ethylenedithiolate.

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