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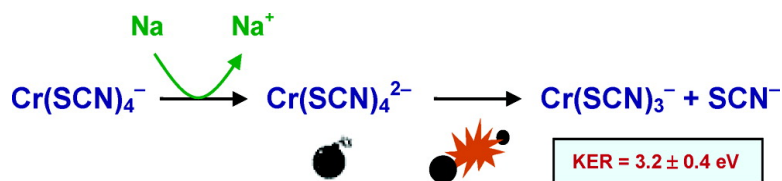
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Coulomb Explosion upon Electron Attachment to a Four-Coordinate Monoanionic Metal Complex

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The stability of small multiply charged anions without a surrounding solvent shell is a topic of high current interest.[1-3] When an unsolvated molecular dianion becomes too small, it will stabilize itself by spontaneous emission of an electron (autodetachment) or dissociate into two singly charged fragment ions (charge dissociation) with the release of kinetic energy into translational energy of the fragments. Several kinetic energy release (KER) values have been reported for charge dissociation (Coulomb explosion) of molecular dications. However, to our knowledge, the only KER measured for a dianion is that recently published by Friedrich et al.[4] for the dissociation of $IrBr_6^{2-}$ into $IrBr_5^- + Br^-$ after photoexcitation. Hence, the description of charge dissociation processes of dianions has largely been limited to theoretical calculations of barrier heights.[5-7] In this work, we report the formation of the $Cr(SCN)_4^{2-}$ dianion in a high-energy collision between $Cr(SCN)_4^-$ and sodium vapor and demonstrate that the dianion Coulomb explodes into $Cr(SCN)_3^-$ and SCN^- with a kinetic energy release of 3.2 ± 0.4 eV.

The experimental layout is described elsewhere.[8] Briefly, the $Cr(SCN)_4^-$ anions were formed by electrospray ionization of $NH_4[Cr(NH_3)_2(SCN)_4]$, dissolved in methanol, under harsh ion source conditions to remove ammonia from the initial $Cr(NH_3)_2(SCN)_4^-$ complex. No $Cr(SCN)_4^{2-}$ dianions were produced from the source in any detectable yield. All ions were accelerated to an energy of 50 keV followed by mass selection of the $Cr(SCN)_4^-$ ions (m/z 284) by a magnet with unit mass resolution. These ions were then collided with sodium vapor in a collision cell at a pressure of 4.7×10^{-4} Torr (single-collision conditions), and the product ions were analyzed with a hemispherical electrostatic analyzer that scans the kinetic energy of the fragment ions. In the collision, the anion becomes vibrationally excited and an electron is transferred from the sodium donor to the anion acceptor. The high translational energy of the anions is important for the efficiency of the electron-transfer process according to the Massey criterion, and sodium was chosen as the collision gas instead of gases such as Xe or CH_4 to reduce the energy defect.[9] The mass-analyzed ion kinetic energy (MIKE) spectrum obtained is shown in Figure 1B. A spectrum for collisions with molecular oxygen is included for comparison (Figure 1A). Peaks corresponding to fragment ions are seen in both spectra: $Cr(CN)(SCN)_3^-$ (m/z 252), $Cr(N)(SCN)_3^-$ (m/z 240), $Cr(SCN)_3^-$ (m/z 226), $Cr(CN)(SCN)_2^-$ (m/z 194), $Cr(SCN)_2^-$ (m/z 168), $Cr(CN)_2(SCN)^-$ (m/z 162), $Cr(CN)(SCN)^-$ (m/z 136), $Cr(CN)_2^-$ (m/z 104), and SCN^- (m/z 58). Interestingly, however, a peak at m/z 142, one-half the m/z value of the parent ion, appears when sodium is used as the collision gas but is absent when O_2 is used. In dissociation processes, kinetic energy is released with the result of broad peaks in MIKE spectra. The width of the peak at m/z 142 is narrower than that of other peaks, which implies that the corresponding ion is not a fragment ion but instead a dianion, $Cr(SCN)_4^{2-}$, formed by electron capture to $Cr(SCN)_4^-$. The charge-transfer cross section is 5 ± 2 Å^2. If we
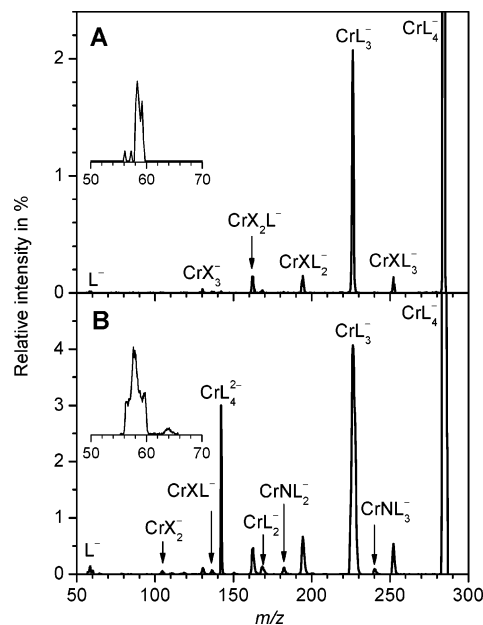

Figure 1. Spectra obtained from collisions between CrL_4^- and molecular oxygen (A) and sodium (B), L = SCN and X = CN. The insets show the peaks corresponding to the SCN^- ion.

assume that the anion interacts with sodium over a distance of 5 Å, the interaction time is 3 fs (time of passage). This time is shorter than the time of any vibrational period, and the electron transfer is therefore assumed to be vertical. In the spectrum obtained with sodium as the collision gas, the widths of the peaks corresponding to SCN^- and $Cr(SCN)_3^-$ are significantly larger than those of the other fragment peaks, which is indicative of a Coulomb explosion of the dianion into $Cr(SCN)_3^-$ and SCN^- with release of kinetic energy. The SCN^- peak shape is composed of a broad peak with a narrow peak in the center. The broad peak corresponds to SCN^- formed from $Cr(SCN)_4^{2-}$, whereas the narrow peak corresponds to SCN^- formed from collisionally excited $Cr(SCN)_4^-$. To obtain a similar peak shape for $Cr(SCN)_3^-$, we had to reduce the slit width before the electrostatic analyzer (Figure 2). On the basis of the widths of the broad peaks, we estimate the KER to be 3.2 ± 0.4 eV.[10] The lifetime of the dianion is in the order of microseconds as the flight time from the collision region to the detector is 5 μs.

The KER for the $Cr(SCN)_4^{2-} \rightarrow Cr(SCN)_3^- + SCN^-$ reaction is to a good approximation equal to the barrier height for the opposite reaction: $Cr(SCN)_3^- + SCN^- \rightarrow Cr(SCN)_4^{2-}$. Barrier heights for the reactions $PtCl_3^- + Cl^- \rightarrow PtCl_4^{2-}$, $BeF_3^- + F^- \rightarrow BeF_4^{2-}$, and $CaF_3^- + F^- \rightarrow CaF_4^{2-}$ have been calculated to be 2.3,[6] 3.5,[5] and 2 eV,[5] respectively. For $Pt(CN)_3^- + CN^- \rightarrow Pt(CN)_4^{2-}$, the barrier height is estimated to be between 1.5 and 3.5 eV.[11] In general, a more ionic bonding character results in a smaller barrier height. Thus, the KER measurement in this study
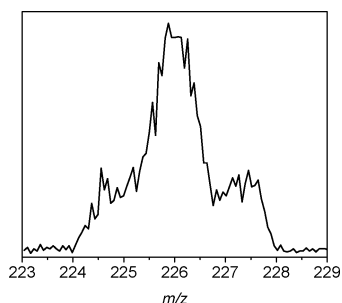
Figure 2. Narrow scan in the region around the $Cr(SCN)_3^-$ fragment ion. The peak in the center corresponds to $Cr(SCN)_3^-$ formed from $Cr(SCN)_4^-$, and the two wings are due to charge dissociation of $Cr(SCN)_4^{2-}$ into $Cr(SCN)_3^-$ and SCN^- with the release of kinetic energy. The spectrum was recorded with a 0.5-mm hole diameter of the slit that is positioned before the electrostatic analyzer. There is discrimination against ions that are not scattered in the backward or forward direction, that is, with a nonzero angle relative to the beam direction. The discrimination is larger on the low-mass side (low forward kinetic energy) than on the high-mass side (high forward kinetic energy).
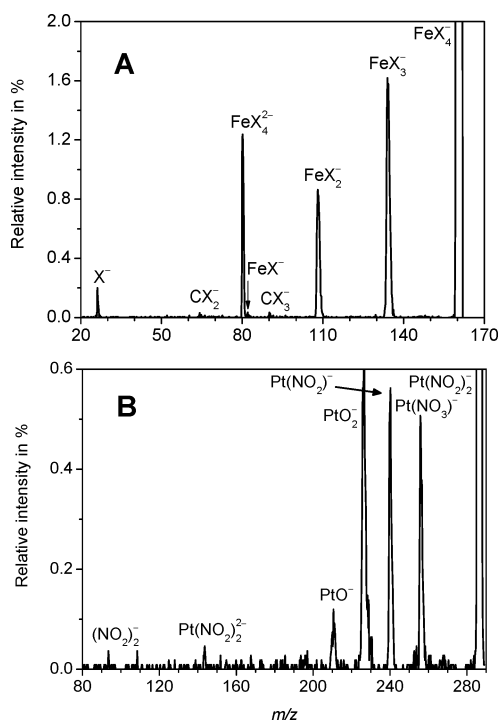

Figure 3. Spectra obtained from collisions between FeX_4^- (X = CN) and sodium (A) and $Pt(NO_2)_2^-$ and sodium (B).

of 3.2 eV is comparable to the calculations on similar systems composed of a metal and four ligands. The KER for charge dissociation of the six-coordinate dianion complex $IrBr_6^{2-}$ into $IrBr_5^-$ and Br^- was measured to 2.2 ± 0.2 eV[4] which is similar to the values for four-coordinate complexes.

The experimental data reveal that $Cr(SCN)_4^{2-} \rightarrow Cr(SCN)_3^- + SCN^-$ is the dominant Coulomb explosion channel. The $(SCN)_2^-$ ion was not detected, and hence dissociation into $Cr(SCN)_2^-$ and $(SCN)_2^-$ does not occur. For comparison, the energetically favored fragmentation channel in the case of BeC_4^{2-} is $BeC_4^{2-} \rightarrow BeC_2^- + C_2^-$ based on theoretical calculations.[7]

In another experiment, we subjected $Fe(CN)_4^-$ (m/z 160) to collisions with sodium, and again a dianion, $Fe(CN)_4^{2-}$ (m/z 80),

was observed (Figure 3A) in addition to fragment ions: $Fe(CN)_3^-$ (m/z 134), $Fe(CN)_2^-$ (m/z 108), $C(CN)_3^-$ (m/z 90), $Fe(CN)^-$ (m/z 82), $C(CN)_2^-$ (m/z 64), and CN^- (m/z 26). However, the widths of the CN^- and $Fe(CN)_3^-$ peaks are similar to those of the other fragment ion peaks. This finding is in agreement with previous collision experiments on metal-cyanide dianions that showed that electron emission occurs and not dissociation into two singly charged fragment ions.[11] Because of the much smaller mass of the electron, the electron will carry nearly all of the kinetic energy released. In similar experiments on $Pt(NO_2)_2^-$ (m/z 286) and $Pt(C_2O_4)_2^-$ (m/z 370), the dianions $Pt(NO_2)_2^{2-}$ (m/z 143) (Figure 3B) and $Pt(C_2O_4)_2^{2-}$ (m/z 185) (spectrum not shown) were formed, but there was no clear indication of Coulomb explosion processes. The $Pt(NO_2)_2^{2-}$ is a rather small dianion containing only seven atoms, and its formation by electron capture to $Pt(NO_2)_2^-$ demonstrates the strength of this experimental technique. The difference between dianion complexes of thiocyanate and other ligands with respect to charge dissociation must be due to a difference in electron binding energy in the dianion. The electron is likely more positively bound in the $Cr(SCN)_4^{2-}$ complex, and charge dissociation therefore takes over or becomes competitive with electron emission.

To summarize, we have presented a new scheme for the generation of small molecular dianions in the gas phase by electron capture to mononanions in high-energy collisions with sodium. In this way, we prepared $Cr(SCN)_4^{2-}$, $Fe(CN)_4^{2-}$, $Pt(NO_2)_2^{2-}$, and $Pt(C_2O_4)_2^{2-}$. The measurement of KER when $Cr(SCN)_4^{2-}$ Coulomb explodes into $Cr(SCN)_3^-$ and SCN^- provides the first experimental value for a charge dissociation process of a four-coordinate dianionic metal complex. The scheme provides a means to study dianions that have too short lifetimes with respect to charge dissociation to survive from the ion source; here, the dianion is not made until we are ready to take a snapshot of its dissociation dynamics.

References

(1) For reviews, see: (a) Dreuw, A.; Cederbaum, L. S. *Chem. Rev.* **2002**, *102*, 181. (b) Boldyrev, A. I.; Gutowski, M.; Simons, J. *Acc. Chem. Res.* **1996**, *29*, 497. (c) Schröder, D.; Schwarz, H. *J. Phys. Chem. A* **1999**, *103*, 7385. (d) Scheller, M. K.; Compton, R. N.; Cederbaum, L. S. *Science* **1995**, *270*, 1160.

(2) Wang, X.-B.; Wang, L.-S. *Nature* **1999**, *400*, 245.

(3) Middleton, R.; Klein, J. *Phys. Rev. A* **1999**, *60*, 3515.

(4) Friedrich, J.; Gilb, S.; Ehrler, O. T.; Behrendt, A.; Kappes, M. M. *J. Chem. Phys.* **2002**, *117*, 2635.

(5) Weikert, H.-G.; Cederbaum, L. S. *J. Chem. Phys.* **1993**, *99*, 8877.

(6) Weis, P.; Hampe, O.; Gilb, S.; Kappes, M. M. *Chem. Phys. Lett.* **2000**, *321*, 426.

(7) Shi, Q.; Kais, S. *J. Am. Chem. Soc.* **2002**, *124*, 11723−11729.

(8) (a) Boltalina, O. V.; Hvelplund, P.; Jørgensen, T. J. D.; Larsen, M. C.; Larsson, M. O.; Sharoitchenko, D. A. *Phys. Rev. A* **2000**, *62*, 023202. (b) Larsson, M. O.; Hvelplund, P.; Larsen, M. C.; Shen, H.; Cederquist, H.; Schmidt, H. T. *Int. J. Mass Spectrom. Ion Processes* **1998**, *177*, 51.

(9) (a) Boltalina, O. V.; Hvelplund, P.; Larsen, M. C.; Larsson, M. O. *Phys. Rev. Lett.* **1998**, *80*, 5101. (b) Tuinman, A. A.; Compton, R. N. *Phys. Rev. A* **2002**, *65*, 052724.

(10) KER = 50 keV $\Delta m_2^2/(16 m_2 m_3)$, where m_2 and m_3 are the masses of the two daughter fragments (58 and 226 amu), and Δm_2 is the peak width of one of the daughter ions (3.7 amu) [Cooks, R. G.; Beynon, J. H.; Caprioli, R. M.; Lester, G. R. *Metastable Ions*; Elsevier: Amsterdam, 1973].

(11) Bojesen, G.; Hvelplund, P.; Jørgensen, T. J. D.; Nielsen, S. B. *J. Chem. Phys.* **2000**, *113*, 6607.

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