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International Journal of Mass Spectrometry 244 (2005) 144–147

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Identification of the short-lived $Au(N_3)_4{}^{2-}$ dianion from its Coulomb explosion products

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Received 21 April 2005; received in revised form 8 June 2005; accepted 9 June 2005

Abstract

In high-energy collisions between $Au(N_3)_4{}^-$ anions and sodium vapor, electron transfer occurred to produce $Au(N_3)_4{}^{2-}$ dianions. These were short-lived (sub microsecond) and Coulomb exploded into $Au(N_3)_3{}^-$ and $N_3{}^-$ with a kinetic energy release of 2.6 ± 0.5 eV. In the product ion spectra, peaks correspond to fragment ions formed from collisionally activated $Au(N_3)_4{}^-$ parent anions. Loss of one or more $N_3{}^\bullet$ or N_2 produced $AuN_n{}^-$ complexes ($n = 1$–4, 6, 9–10) whereas complexes with $n = 5$, 7, and 8 were not detected. These ions can be assigned to gold–nitride–azide complexes $Au(N)_x(N_3)_y{}^-$ ($x = 0$–2 and $y = 0$–4). Cationic complexes were measured for $n = 1$–4 and 6. Sodium vapor collision experiments were also performed for $Au(N_3)_2{}^-$, which is generated in situ by the spontaneous reduction of $Au(N_3)_4{}^{2-}$ and concurrent azide dissociation. In this case there was no clear signature indicative of the formation of a dianion. The formation of dianions cannot be excluded, however, since such ions may decay by electron emission instead of dissociation into two singly charged fragment ions.

Keywords: Molecular dianions; Coulomb explosion; Kinetic energy release; Metal ion complexes; Electron transfer

1. Introduction

Molecular dianions have attracted much attention and several reviews on their fascinating chemistry and physics have been published in recent years [1–6]. Dianions are interesting species since the two extra electrons have to correlate their motion in order to minimize their mutual repulsion. Electron correlation is difficult to describe in quantum chemical models, and approximations to the Schrödinger equation are obviously necessary. To test current ab initio and density functional theory models and reveal their strengths and weaknesses, experimental data on dianions are useful. Thus, a model that properly describes small dianions is likely to be successful for the description of electron correlation in other systems.

In recent papers we have described the successful preparation of molecular dianions in high-energy, typical 50 keV, collisions between monoanions and sodium vapor [7–10]. For example, we have produced the $Cr(SCN)_4{}^{2-}$ dianion that has a lifetime of a few microseconds with respect to Coulomb explosion into $Cr(SCN)_3{}^-$ and SCN^- [7]. Such delicate dianions are too short-lived to survive the traveling time in the accelerator mass spectrometer, about 100 μs, from the ion source to the field-free region where their metastable decay is measured. The sodium collision technique has the advantage that it overcomes this problem as long as we can prepare a long-lived monoanion precursor. Collision experiments can also be used to generate dianions from larger dianions by loss of neutral fragments as demonstrated for $Pt(CN)_6{}^{2-}$ [11]. In this continuation of our previous work on metal ion complexes in the gas phase we have studied $Au(N_3)_4{}^-$ and $Au(N_3)_2{}^-$ complexes and investigated the possible existence of dianionic derivatives. The $Au(N_3)_4{}^-$ ion was chosen for this study because of the feasibility of N_2 loss under colli-

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doi:10.1016/j.ijms.2005.06.002

sional activation and thus the possibility of generating gas phase nitrides.

2. Experiments

2.1. Mass spectrometry

Experiments were performed with an accelerator mass spectrometer equipped with an electrospray ion source [12,13]. The $Au(N_3)_4^-$ and $Au(N_3)_2^-$ anions were formed by electrospray ionization of the $[P(C_6H_5)_4][Au(N_3)_4]$ salt dissolved in methanol. All ions were accelerated to an energy of 50 keV followed by mass selection of the $Au(N_3)_4^-$ ions (*m*/*z* 365) or $Au(N_3)_2^-$ ions (*m*/*z* 281) by a magnet with unit mass resolution. These ions were then collided with sodium vapor in a 4 cm long collision cell at a pressure of 6.5×10^{-4} Torr (single-collision conditions), and the product ions were analyzed with a hemispherical electrostatic analyzer that scanned the kinetic energy of the fragment ions. The obtained spectra are denoted mass-analyzed ion kinetic energy (MIKE) spectra. In the collision the anion becomes vibrationally excited and/or an electron is transferred from the sodium donor to the anion acceptor. In other experiments helium was used as collision gas instead of sodium in which case only collision-induced dissociation took place.

2.2. Synthesis of $[P(C_6H_5)_4][Au(N_3)_4]$

$HAuCl_4$ (35 mg, 0.10 mmol) and sodium azide (53 mg, 0.81 mmol) were dissolved in 2 mL water. Tetraphenylphosphonium chloride (45 mg, 0.12 mmol) was added and the product precipitated in a 48% yield. Anal. Cald. for $C_{24}H_{20}N_{12}PAu$: C, 40.92; H, 2.86; N, 23.86. Found: C, 41.64; H, 2.70; N, 22.87.

3. Results and discussions

The spectra obtained from collisions between $Au(N_3)_4^-$ and He and Na are shown in Fig. 1. In both spectra, peaks can be assigned to the following fragment ions, N_3^- (*m*/*z* 42), Au^- (*m*/*z* 197), AuN^- (*m*/*z* 211), AuN_2^- (*m*/*z* 225), AuN_3^- (*m*/*z* 239), AuN_4^- (*m*/*z* 253), AuN_6^- (*m*/*z* 281), AuN_9^- (*m*/*z* 323), and AuN_{10}^- (*m*/*z* 337). Interestingly, the complexes AuN_5^- (*m*/*z* 267), AuN_7^- (*m*/*z* 295), and AuN_8^- (*m*/*z* 309) were not observed. A very weak signal might be assignable to AuN_{11}^-.

At half the mass to charge ratio of the parent ion there was no measurable signal in the sodium spectrum. However, there is indirect evidence for the formation of dianions since there are two wings on the N_3^- peak, and the $Au(N_3)_3^-$ peak is considerably broadened compared to that in the helium spectrum. These findings indicate that N_3^- and $Au(N_3)_3^-$ ions are formed in a Coulomb explosion process after electron transfer to $Au(N_3)_4^-$ from Na. To verify this, we carried out collision experiments at two other acceleration voltages, 25 and 80 kV, and made narrow scans in the regions of the N_3^- and $Au(N_3)_3^-$ peaks (Figs. 2 and 3). Indeed the width of each peak decreases with acceleration voltage as expected when potential energy is released into translational energy. Hence the formation of two singly charged ions is competitive with electron autodetachment. The middle peak (most clear for N_3^-) is the result of dissociation of vibrationally excited ions as was the case in helium.

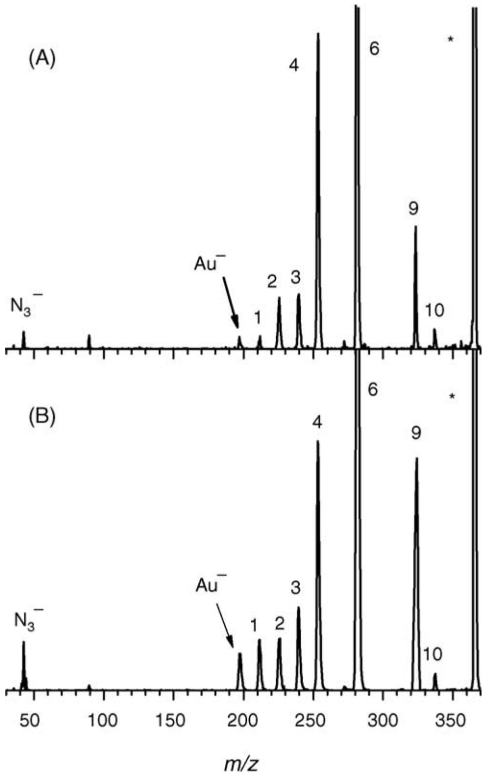

Fig. 1. Spectra obtained from collisions between $Au(N_3)_4^-$ and helium (A) and sodium (B). The parent ion is indicated by '*'. The numbers refer to the number of nitrogen in the gold complexes. The peak at *m*/*z* 90 is unassigned and is likely due to an ion impurity.

The kinetic energy release of the dissociation process was calculated from this expression [16]:

$$\mathrm{KER} = eV_{\mathrm{acc}}\Delta m_2^2/(16 m_2 m_3),$$

where V_{acc} is the acceleration voltage, m_2 and m_3 masses of the two fragments ions, and Δm_2 is the width of one of the fragment peaks. We found that the kinetic energy released is 2.6 ± 0.5 eV, which is similar to that found for the dissociation of $Cr(SCN)_4^{2-}$, 3.2 ± 0.4 eV [7] and for the photodissociation of $IrBr_6^{2-}$, 2.2 ± 0.2 eV [17]. To a first approximation, the KER can be assumed equal to the barrier height for the opposite reaction where the two singly charged fragments approach each other and form a dianion. Typical calculated values for barrier heights of similar systems range between 2 and 4 eV [18–20] in good agreement with the experimental values. Also we have earlier used a simple model based on electrostatics to predict the barrier height for loss of CN^-

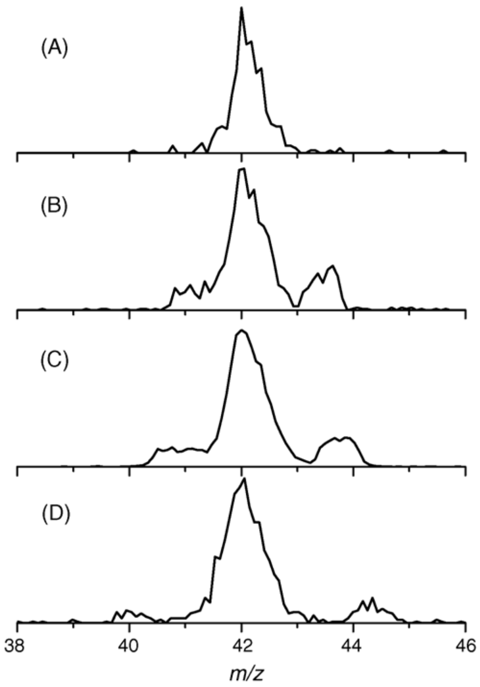

Fig. 2. Narrow scan spectra in the region around the N_3^- fragment ion as a function of the collision gas and acceleration voltage: (A) He, 50 kV; (B) Na, 80 kV; (C) Na, 50 kV; (D) Na, 25 kV. The middle peak is from dissociation of vibrationally excited $Au(N_3)_4^-$ ions whereas the two wings arise from the dissociation of $Au(N_3)_4^{2-}$ dianions. Because of a high release of potential energy into translational energy of the fragments, there is a discrimination of ions that are not scattered exactly in the backward and forward direction, i.e., with a non-zero angle relative to the beam direction. This discrimination is most pronounced for backward scattered ions.

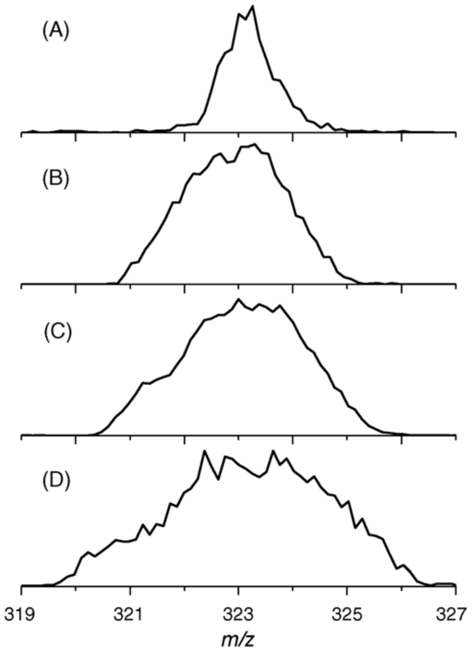

Fig. 3. Narrow scan spectra in the region around the $Au(N_3)_3^-$ fragment ion as a function of the collision gas and acceleration voltage: (A) He, 50 kV; (B) Na, 80 kV; (C) Na, 50 kV; (D) Na, 25 kV.

Table 1
Assignment of AuN_n^- ions

Ion	*m*/*z*	Possible formulation with ‘formal’ Au oxidation state	Fragment loss from $[Au^{III}(N_3)_4]^-$
Au^-	197	Au^-	$4N_3^{\bullet}$
AuN^-	211	$Au^{II}N^-$	N_2, $3N_3^{\bullet}$
AuN_2^-	225	$[Au^{V}(N)_2]^-$	$2N_2$, $2N_3^{\bullet}$
AuN_3^-	239	$[Au^{0}(N_3)]^-$	$3N_3^{\bullet}$
AuN_4^-	253	$[Au^{III}(N)(N_3)]^-$	N_2, $2N_3^{\bullet}$
AuN_6^-	281	$[Au^{I}(N_3)_2]^-$	$2N_3^{\bullet}$
AuN_9^-	323	$[Au^{II}(N_3)_3]^-$	$N_3^{\bullet}$
AuN_{10}^-	337	$[Au^{V}(N)(N_3)_3]^-$	N_2, $N_3^{\bullet}$
AuN_{12}^-	365	$[Au^{III}(N_3)_4]^-$	

from $Pt(CN)_4^{2-}$ to be between 1.5 and 3 eV, dependent on the ionic and covalent character of the bonds.

The geometry of the gold atom in the $[Au(N_3)_4]^{2-}$ dianion is likely to be a square planar. The starting $[Au(N_3)_4]^-$ anion is shown by crystal structure analysis of the tetraphenylarsonium salt [14,15] to have a square planar geometry, as would be expected for a low spin four coordinate d^8 metal ion. In one limiting electronic assignment, the formal metal oxidation state in the $[Au(N_3)_4]^{2-}$ is Au^{II} (d^9). In this oxidation state gold is likewise anticipated to show a square planar geometry. Thus no major structural rearrangement should be needed in the reduction of $[Au(N_3)_4]^-$. Apart from typically showing four coordinate square planar geometry Au^{II} complexes in condensed phases are often dinuclear and contain an Au–Au bond. This is due to the propensity of the radical Au^{II} ions to dimerise.

The AuN_n^- ions observed correspond to chemically reasonable formulations involving nitride and azide ligands and the formal oxidation states recognized for gold (Table 1). Although Au^{V} is rare, it is known for AuF_6^- and AuF_5 [21–24]. Its stabilization by a nitride ligand is feasible in the assignment $[Au^{V}(N)(N_3)_3]^-$ for AuN_{10}^-, since nitrides are well known to stabilize high oxidation states for several metal ions. Indeed the $Au(N_3)_4^-$ ion was originally chosen for this study because of the feasibility of N_2 loss under collisional activation and thus the possibility of generating gas phase nitrides. To our knowledge simple molecular gold nitrides are not known. Photoemission spectroscopy has been used to demonstrate the formation of a surface gold nitride upon irradiation of an Au(1 1 0) surface with 500 eV nitrogen ions at room temperature [25]. However to the best of knowledge simple molecular gold nitrides are yet not known.

We have also measured the positive ions formed in helium collisions by reversing the polarity of the electrostatic analyzer. The charge-reversal spectrum is shown in Fig. 4, and peaks can be assigned to gold–nitrogen complexes, AuN^+, AuN_2^+, AuN_3^+, AuN_4^+, and AuN_6^+. These ions are formed after collisional detachment of at least two electrons. As for the series of AuN_n^- ions the intensities of the AuN_n^+ ions do not follow a linear relationship with respect to the value of n. The implication is again that the product ions contain specific combinations of nitride and azide ligands. Proposed

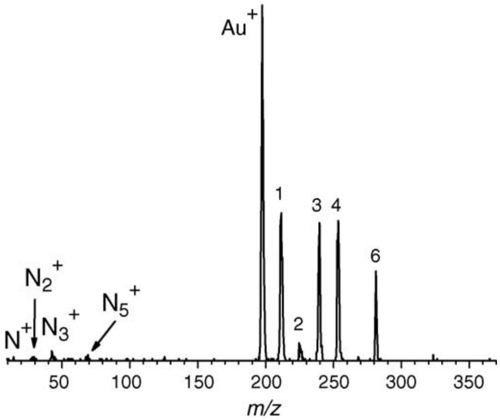

Fig. 4. Charge-reversal, $^{-}$CR^{+}, spectrum obtained from collisions between $Au(N_3)_4^-$ and He. The numbers refer to the number of nitrogen in the gold complexes.

Table 2
Assignment of AuN_n^+ ions

Ion	m/z	Possible formulation with ‘formal’ Au oxidation state
AuN^+	211	$Au^{IV}N^+$
AuN_2^+	225	$[Au^{VII}(N)_2]^+$
AuN_3^+	239	$[Au^{II}(N_3)]^+$
AuN_4^+	253	$[Au^{V}(N)(N_3)]^+$
AuN_6^+	281	$[Au^{III}(N_3)_2]^+$

formulations are listed in Table 2. Notably the intensity of AuN_2^+ ions is markedly less than the others (i.e. one tenth of those for AuN^+ and AuN_3^+ occurring at ±14 *m/z*). To this ion the formal very high oxidation state of Au^{VII} is assigned. Thus the intensities of the ions in fact reflect relative expected stabilities.

$Au(N_3)_2^-$ anions were also subjected to collision experiments. Again AuN_n^- was measured for $n = 1–4$. There are no peaks in the sodium spectrum that can be assigned to dianions, and there is no clear indication of any Coulomb explosion processes from a peak broadening. If Coulomb explosion took place for $Au(N_3)_2^{2-}$, an even larger KER than that observed for $Au(N_3)_4^{2-}$ is expected because of its smaller size. However, it is possible that the $Au(N_3)_2^{2-}$ dianion is formed but then it decays by electron emission, a process that we cannot identify. Because of its low mass, the electron will carry nearly all of the kinetic energy released.

4. Conclusions

We have shown that the $Au(N_3)_4^{2-}$ dianion exists but that it is unstable with respect to dissociation into two singly charged ions on a sub microsecond timescale since the flight time from the collision cell to the detector is about 5 μs. Electron autodetachment may be another decay pathway but cannot be identified with the present setup. The $Au(N_3)_4^{2-}$ dianion presents an interesting case of a dianion for which metal–ligand bond breakage competes with electron tunneling through the Coulomb barrier to recover the parent monoanion. In addition our study has revealed the existence of several monoanionic and cationic gold complexes with nitrogen-containing ligands for which formulations are consistent with combinations of nitride and azide ligands appropriate to the assignable formal Au oxidation states.

Acknowledgement

S.B.N. gratefully acknowledges a Steno grant from the Danish Natural Science Research Council (# 21-02-0129).

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