

## Halide Ligands: Anchors for Metal Clusters on Gold Surfaces

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Many chemically modified metal surfaces have been prepared by covalent adsorbate–surface interactions.<sup>1</sup> Most of this work has centered around organo–sulfur, chlorosilane, and alkoxy silane compounds, which provide a direct and simple route for the creation of well-ordered monolayers on coinage metal and metal oxide surfaces. Control of both the micro- and macroscopic surface properties is achieved by a judicious choice of the organic moiety. By contrast few purely inorganic molecules are adaptable to these methods, and little work has been done toward the development of versatile inorganic adsorbates for the generation of monolayers. Recent work with silicotungstates on silver surfaces<sup>2</sup> indicates that a significant range of surface–adsorbate interactions remain unexplored.

In this communication we describe the interaction of redox active metal halide clusters  $[\text{Bu}_4\text{N}]_3[\text{Nb}_6\text{Cl}_{12}\text{X}_6]$  ( $\text{X} = \text{Cl}, \text{Br}, \text{or I}$ ) with silver and gold surfaces. Halide ligands coordinate strongly to a variety of early transition metal ions in positive oxidation states. For example  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$  form ordered arrays on  $\text{Ag}(111)$ <sup>3</sup> and  $\text{Au}(111)$ ,<sup>4</sup> and both  $\text{Br}^-$  and  $\text{I}^-$  have been shown to covalently interact with gold surfaces.<sup>5</sup> The significant ionic character of halide ligands attached to early transition metal clusters suggested that halide ligands may retain their affinity for gold and silver and thereby serve as bridges between the metal cluster and the noble metal surface.

The cluster systems chosen for the present research,  $[\text{Nb}_6\text{Cl}_{12}\text{X}_6]^{3-}$ , consist of an octahedron of six niobium atoms with 12 “inner” chloride ligands bridging the metal–metal bonds. A set of six “outer” or axial halides is terminally bound, to the six niobium atoms (Figure 1). The mixed halide clusters where  $\text{X} = \text{Br}$  or  $\text{I}$  are easily synthesized<sup>6</sup> by the reaction of  $[\text{Bu}_4\text{N}]_3[\text{Nb}_6\text{Cl}_{12}(\text{OSO}_2\text{CF}_3)_6]$ <sup>7</sup> with  $[\text{Bu}_4\text{N}]\text{X}$ , and the all-chloro clus-

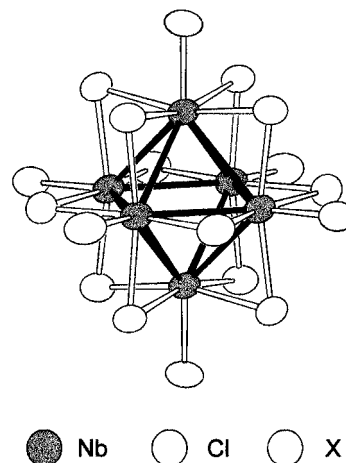


Figure 1. Structure of  $[\text{Nb}_6\text{Cl}_{12}\text{X}_6]^{3-}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ).

ter is readily available.<sup>8</sup> The  $\text{Nb}_6\text{Cl}_{12}^{n+}$  core remains intact over a range of oxidation states that are electrochemically accessible in solution. One-electron oxidation and reduction of  $[\text{Nb}_6\text{Cl}_{12}\text{Cl}_6]^{3-}$  generates  $[\text{Nb}_6\text{Cl}_{12}\text{Cl}_6]^{2-}$  and  $[\text{Nb}_6\text{Cl}_{12}\text{Cl}_6]^{4-}$ , respectively.<sup>9</sup> This redox activity provides a useful means of characterizing the cluster attached to a noble metal substrate.

Gold surfaces<sup>10</sup> were immersed in 0.1 mM  $\text{CH}_2\text{Cl}_2$  solutions of  $[\text{Bu}_4\text{N}]_3[\text{Nb}_6\text{Cl}_{12}\text{X}_6]$  ( $\text{X} = \text{Cl}, \text{Br}, \text{or I}$ ) for 12 h, rinsed with clean solvent, and dried under  $\text{N}_2$ . With this procedure only  $[\text{Bu}_4\text{N}]_3[\text{Nb}_6\text{Cl}_{12}\text{Br}_6]$  produced a monolayer of the cluster. X-ray photoelectron spectra<sup>11</sup> of gold surfaces treated with  $[\text{Bu}_4\text{N}]_3[\text{Nb}_6\text{Cl}_{12}\text{Br}_6]$  reveal the expected binding energies for the presence of Nb (3d) 205.4, Cl (2p) 200.0, Br (3d) 68.8, N (1s) 401.2, and C (1s) 285.7 eV with peak intensities in the ratios expected for the intact cluster. Films of  $[\text{Bu}_4\text{N}]_3[\text{Nb}_6\text{Cl}_{12}\text{Br}_6]$  on gold are stable for days in air. By contrast no sign of niobium or chlorine is observed in the XPS spectrum of gold surfaces that were exposed to  $[\text{Bu}_4\text{N}]_3[\text{Nb}_6\text{Cl}_{12}\text{Cl}_6]$ . At the other extreme, solutions of  $[\text{Bu}_4\text{N}]_3[\text{Nb}_6\text{Cl}_{12}\text{I}_6]$  completely dissolve 100 nm thick gold layers after 12 h, but shorter reaction times produce a strongly absorbed layer of  $[\text{Bu}_4\text{N}]_3[\text{Nb}_6\text{Cl}_{12}\text{I}_6]$  which was detected with cyclic voltammetry and XPS. The increased reactivity of the clusters with the heavier halides parallels the interaction of gold with the free halide ions where  $\text{Cl}^-$  absorbs the weakest and  $\text{I}^-$  the strongest.<sup>5</sup>

(1) (a) Murray, R. W. *Acc. Chem. Res.* **1980**, *13*, 135. (b) Abruña, H. D. *Coord. Chem. Rev.* **1988**, *86*, 135. (c) Tredgold, R. H. *Order in Thin Organic Films*; Cambridge University Press: Cambridge, 1994. (d) Finklea, H. O. In *Electroanalytical Chemistry*; Bard, A. J., Rubinstein, I., Eds.; Marcel Dekker: New York, 1996; Vol. 19, pp 110–335.

(2) Ge, M.; Zhong, B.; Klemperer, W. G.; Gewirth, A. A. *J. Am. Chem. Soc.* **1996**, *118*, 5812.

(3) (a) Schott, J. H.; White, H. S. *J. Phys. Chem.* **1994**, *98*, 291. (b) Schott, J. H.; White, H. S. *Langmuir* **1994**, *10*, 486. (c) Kawasaki, M.; Ishii, H. *Langmuir* **1995**, *11*, 832.

(4) McCarley, R. L.; Bard, A. J. *J. Phys. Chem.* **1991**, *95*, 9618.

(5) Deakin, M. R.; Li, T. T.; Melroy, O. R. *J. Electroanal. Chem.* **1988**, *243*, 343.

(6) Under prepurified  $\text{N}_2$  a solution of 0.48 mmol of  $[\text{Bu}_4\text{N}]\text{X}$  in 10 mL of  $\text{CH}_2\text{Cl}_2$  was added to 0.06 mmol of  $[\text{Bu}_4\text{N}]_3[\text{Nb}_6\text{Cl}_{12}(\text{OSO}_2\text{CF}_3)_6]$  in 10 mL of  $\text{CH}_2\text{Cl}_2$ . After stirring for 18 h, the brown solution is concentrated to 2 mL and layered with 10 mL of diethyl ether. The brown precipitate was collected by filtration and dried under vacuum.

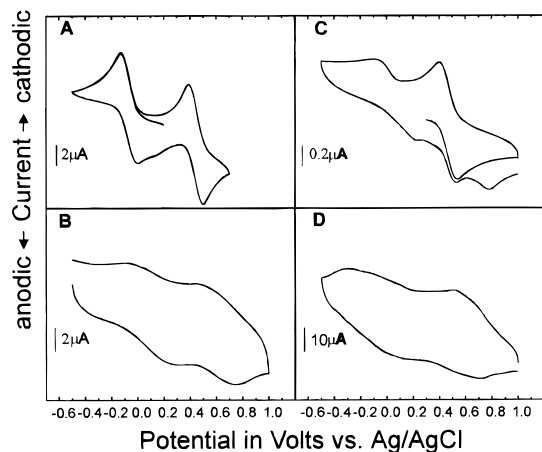
(7) (a) Kennedy, V. O.; Stern, C. L.; Shriver, D. F. *Inorg. Chem.* **1994**, *33*, 5967. (b) Johnston, D. H.; Gaswick, D. C.; Lonergan, M. C.; Stern, C. L.; Shriver, D. F. *Inorg. Chem.* **1992**, *31*, 1869.

(8) Fleming, P. B.; Dougherty, T. A.; McCarley, R. E. *J. Am. Chem. Soc.* **1967**, *89*, 159.

(9) Quigley, R.; Barnard, P. A.; Hussey, C. L.; Seddon, K. R. *Inorg. Chem.* **1992**, *31*, 1255.

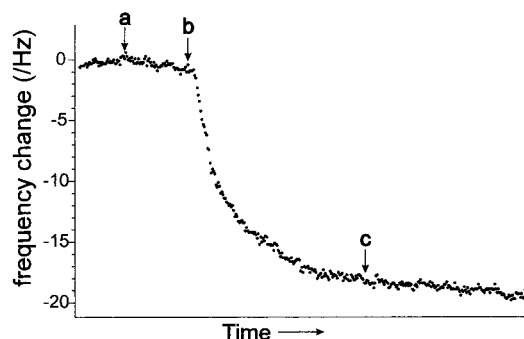
(10) Gold and silver surfaces were prepared by thermal evaporation of the metal on to freshly cleaved mica substrates in a Veeco VE400 thermal evaporator operating at a base pressure of  $10^{-6}$  Torr. AFM on the gold substrates reveals surface features consistent with published micrographs of thermally evaporated gold on unannealed mica (Caldwell, W. B.; Chen, K. M.; Herr, B. R.; Mirkin, C. A.; Hulteen, J. C.; Vanduyne, R. P. *Langmuir* **1994**, *10*, 4109). No obvious changes in the surface morphology or aggregates are observed by AFM after adsorption of  $[\text{Bu}_4\text{N}]_3[\text{Nb}_6\text{Cl}_{12}\text{Br}_6]$ .

(11) XPS spectra were collected on a VG Scientific ESCALAB MKII X-ray photoelectron spectrometer. All binding energies are referenced to the Au 4f peak at 84.7 eV.



**Figure 2.** Cyclic voltammograms of  $[\text{Bu}_4\text{N}]_3[\text{Nb}_6\text{Cl}_{12}\text{Br}_6]$  and  $[\text{Bu}_4\text{N}]_3[\text{Nb}_6\text{Cl}_{12}\text{I}_6]$  in solution (A and C) and adsorbed to gold (B and D). All CVs were obtained using 0.1 M  $[\text{Bu}_4\text{N}]\text{BF}_4$   $\text{CH}_2\text{Cl}_2$  electrolyte with Pt counter electrodes and scan rates of 100 mV/s. Pt working electrodes were used in A and C.

A cyclic voltammogram of a gold electrode modified with  $[\text{Bu}_4\text{N}]_3[\text{Nb}_6\text{Cl}_{12}\text{Br}_6]$  is shown in Figure 2B. For comparison, a voltammogram of the cluster in solution (Figure 2A) exhibits a reversible one-electron oxidation at 0.44 V and an irreversible one-electron reduction at  $-0.06$  V vs Ag/AgCl corresponding to the generation of  $[\text{Nb}_6\text{Cl}_{12}\text{Br}_6]^{2-}$  and  $[\text{Nb}_6\text{Cl}_{12}\text{Br}_6]^{4-}$ , respectively. The redox couples for the surface-bound cluster are anodically shifted by 0.15 V, consistent with the expected transfer of electron density from the bromide ligands to the gold surface upon adsorption. The linear plots of current versus sweep rate are characteristic of surface confined redox couples. The  $[\text{Nb}_6\text{Cl}_{12}\text{Br}_6]^{2-}/[\text{Nb}_6\text{Cl}_{12}\text{Br}_6]^{3-}$  couple is reversible for the cluster in solution with gold, platinum, and carbon working electrodes, but the surface-bound cluster exhibits large peak separations,  $\Delta E_p$ . For the two redox couples  $\Delta E_p$  are 0.28 and 0.31 V at scan rates of 100 mV/s. These values are much larger than the 0 V separation expected for a reversible electron transfer of surface species. Lowering the sweep rate to 10 mV/s results in  $\Delta E_p$  values of 0.20–0.21 V. The decrease in  $\Delta E_p$  of 0.08–0.11 V with a decade change in scan rate is reasonably close to the value of 0.12 V expected for a slow electron-transfer process.<sup>12</sup> By contrast fast “inner sphere” electron transfer has been observed for a series of Co(III) halide complexes in solution.<sup>13</sup> In the present work with gold electrodes it is likely that the substantial  $\Delta E_p$  values arise from restricted movement of overlapping  $[\text{Bu}_4\text{N}]^+$  ions because films of the metal halide cluster compounds must include countercations to maintain charge neutrality. In the present case, up to four tetrabutylammonium ions are required per cluster. Since the size of the  $[\text{Bu}_4\text{N}]^+$  ion is comparable to that of the metal halide cluster,<sup>14</sup> the tetrabutylammonium ions comprise a majority of the adsorbed film. Presumably these cations constitute a second layer on top of the anionic cluster layer which is directly adsorbed to the gold surface. Reduction and



**Figure 3.** In situ QCM measurement of frequency change due to adsorption of  $[\text{Bu}_4\text{N}]_3[\text{Nb}_6\text{Cl}_{12}\text{Br}_6]$  on a gold surface: (a) injection of pure  $\text{CH}_2\text{Cl}_2$ , (b) injection of  $[\text{Bu}_4\text{N}]_3[\text{Nb}_6\text{Cl}_{12}\text{Br}_6]$  dissolved in  $\text{CH}_2\text{Cl}_2$ , and (c) second injection of  $[\text{Bu}_4\text{N}]_3[\text{Nb}_6\text{Cl}_{12}\text{Br}_6]$ . The curvature most likely results from kinetic and diffusion limitations on the adsorption process.

oxidation of the cluster layer will be accompanied by adsorption/desorption of these counterions to maintain local electrical neutrality. Hindrance to the movement of these ions in and out of the highly charged and sterically crowded surface may limit the rate of electron transfer and thereby account for the irreversibility. Films of  $[\text{Bu}_4\text{N}]_3[\text{Nb}_6\text{Cl}_{12}\text{Br}_6]$  are quite stable to multiple redox cycles when a 0.1 M  $[\text{Bu}_4\text{N}]\text{BF}_4$  methylene chloride electrolyte is employed. No decrease in current is observed after 40 min of cycling at 100 mV/s. In a more polar solvent, acetonitrile, the cluster quickly desorbs after a single cycle of the potential from  $-0.60$  to 1.00 V. It is unclear whether desorption is due to solubility differences or reactivity of the cluster with acetonitrile.<sup>15</sup>

Integration of the redox waves in the cyclic voltammograms reveals a surface coverage,  $\Gamma$ , of  $1.3 \times 10^{-10}$  mol/cm<sup>2</sup> of  $[\text{Nb}_6\text{Cl}_{12}\text{Br}_6]^{3-}$ , which is somewhat less than the  $2.0 \times 10^{-10}$  mol/cm<sup>2</sup> expected for a full monolayer composed only of the cluster.<sup>16</sup> In situ quartz crystal microbalance (QCM) experiments<sup>17</sup> for the adsorption of  $[\text{Bu}_4\text{N}]_3[\text{Nb}_6\text{Cl}_{12}\text{Br}_6]$  on gold electrodes reveals a total mass change corresponding to  $2.1 \times 10^{-10}$  mol/cm<sup>2</sup> of cluster (Figure 3). The increase in mass is attributed to adsorption of anionic metal cluster only and is independent of changes in cation mass from 130 to 538 amu corresponding to  $[\text{Et}_4\text{N}]^+$  and  $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{N}^+$ . Surface coverage determined by the QCM experiments is very close to the value expected for a full monolayer of cluster,  $2.0 \times 10^{-10}$  mol/cm<sup>2</sup>. Cyclic voltammograms obtained on the gold electrodes used in the QCM experiments indicate a surface coverage of  $1.3 \times 10^{-10}$  mol/cm<sup>2</sup>, the same value for the films on the gold/mica substrates. The apparent  $\Gamma$  calculated from the cyclic voltammetry experiments reflects only the absorbed cluster that is electrochemically active. Monolayers of redox couples can be rendered completely inactive by

(15) Hussey, C. L.; Quigley, R.; Seddon, K. R. *Inorg. Chem.* **1995**, *34*, 370.

(16) The estimate of the maximum theoretical surface coverage is based on the structure of the analogous  $[\text{Nb}_6\text{Br}_{12}\text{Br}_6]^{4-}$  (Ueno, F.; Simon, A. *Acta Cryst. Sect. C* **1985**, *41*, 308) assuming a closest packing of these ions.

(17) A QCM cell designed to maintain a constant solution volume during addition of adsorbate was employed for the in situ experiments. Quartz crystals with thermally evaporated gold or silver electrodes operating at their fundamental frequency of about 5 MHz were obtained from International Crystal Manufacture. The oscillator circuit is that of D. A. Buttry described in: *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker, Inc.: New York, 1992; Vol. 17, pp 1–83.

(12) Gileadi, E.; Kirova-Eisner, E.; Penciner, J. *Interfacial Electrochemistry*; Addison-Wesley Publishing Company, Inc.: Reading, MA, 1975; pp 370–375.

(13) Barr, S. W.; Weaver, M. J. *Inorg. Chem.* **1984**, *23*, 1657.

(14) The ratio of van der Waals radii for  $[\text{Bu}_4\text{N}]^+ / [\text{Nb}_6\text{Br}_{12}\text{Br}_6]^{4-}$  is 0.94.

poor ion migration inside an adsorbed film,<sup>18</sup> and low counterion mobility has been invoked to explain the electrochemical passivation of polymolybdate films on glassy carbon electrodes.<sup>19</sup> Similarly, in the present system the bulky cations may partially shield the cluster layer and account for the discrepancy between the QCM and CV measurements of surface coverage.

The large peak widths of the redox waves for the surface-confined cluster (full width at half-maximum greater than 250 mV) provide evidence for large repulsive interactions between the highly charged surface-confined clusters.<sup>20</sup> Ineffective shielding of adsorbates by counterions coupled with the close proximity of neighboring clusters may lead to the observed peak broadening. Broadening might also result from inhomogeneity in the binding sites of the clusters. Taken collectively, the voltammetry and QCM data support a model consisting of a layer of  $[\text{Nb}_6\text{Cl}_{12}\text{Br}_6]^{3-}$  closest to the gold surface and a second layer of cations lying on top of the clusters.

Figure 2D,C show the cyclic voltammograms for  $[\text{Bu}_4\text{N}]_3[\text{Nb}_6\text{Cl}_{12}\text{I}_6]$  adsorbed to a gold surface and dissolved in electrolyte solution, respectively. The peak shifts and peak widths are similar to those for the surface-confined  $[\text{Nb}_6\text{Cl}_{12}\text{Br}_6]^{3-}$ . Integration of the voltammogram of the monolayer of  $[\text{Nb}_6\text{Cl}_{12}\text{I}_6]^{3-}$  adsorbed to gold also reveals a submonolayer coverage,  $1.4 \times 10^{-10}$  mol/cm<sup>2</sup>. Solutions of  $[\text{Bu}_4\text{N}]_3[\text{Nb}_6\text{Cl}_{12}\text{I}_6]$  exhibit a quasi-reversible oxidation at 0.46 V and a chemically irreversible reduction at 0.06 V. This chemical irrevers-

ibility most likely corresponds to loss of an iodide ligand, which presumably is replaced by a  $\text{BF}_4^-$  from the electrolyte.<sup>21</sup> There is no loss of an iodide ligand upon reduction, and the surface-bound cluster is stable with respect to changes in electrochemical potentials with no loss or change in current after repeated cycling. The surface-confined  $[\text{Nb}_6\text{Cl}_{12}\text{I}_6]^{3-}$  does not exhibit the chemical irreversibility that is observed for the cluster in solution. The shift of electron density from the cluster to the gold may stabilize the reduction product,  $[\text{Nb}_6\text{Cl}_{12}\text{I}_6]^{4-}$ .

Both  $[\text{Bu}_4\text{N}]_3[\text{Nb}_6\text{Cl}_{12}\text{I}_6]$  and  $[\text{Bu}_4\text{N}]_3[\text{Nb}_6\text{Cl}_{12}\text{Br}_6]$  dissolved 100 nm thick films of Ag after only 6 h in 0.1 mM cluster solutions; however,  $[\text{Bu}_4\text{N}]_3[\text{Nb}_6\text{Cl}_{12}\text{Cl}_6]$  showed no signs of eroding silver and appears to adsorb in monolayer fashion. The surface coverage, determined from QCM,  $1.9 \times 10^{-10}$  mol/cm<sup>2</sup>, is very close to the value expected for a monolayer<sup>22</sup> of adsorbed cluster,  $2.2 \times 10^{-10}$  mol/cm<sup>2</sup>. Unlike SAMs of polytungstate clusters on silver electrodes,<sup>2</sup> no electrochemical passivation of the surface is observed with  $[\text{Bu}_4\text{N}]_3[\text{Nb}_6\text{Cl}_{12}\text{Cl}_6]$  and the cluster is quickly desorbed from the surface upon changing the potential. The range of interaction exhibited by  $[\text{Bu}_4\text{N}]_3[\text{Nb}_6\text{Cl}_{12}\text{X}_6]$  (X = Cl, Br, and I) with silver and gold clearly demonstrates that halide and pseudohalide ligands should be versatile anchors for immobilizing many types of Werner complexes to metal surfaces.

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(18) (a) De Long, H. C.; Buttry, D. A. *Langmuir*. **1990**, *6*, 1319. (b) Creager, S. E.; Rowe, G. K. *Anal. Chim. Acta* **1991**, *246*, 233. (c) Herr, B. R.; Mirkin, C. A. *J. Am. Chem. Soc.* **1994**, *116*, 1157. (d) Shi, X.; Caldwell, W. B.; Chen, K.; Mirkin, C. A. *J. Am. Chem. Soc.* **1994**, *116*, 11598. (e) Caldwell, W. B.; Campbell, D. J.; Chen, K.; Herr, B. R.; Mirkin, C. A.; Malik, A.; Durbin, M. K.; Dutta, P.; Huang, K. G. *J. Am. Chem. Soc.* **1995**, *117*, 6071. (f) Campbell, D. J.; Herr, B. R.; Hulteen, J. C.; Van Duyne, R. P.; Mirkin, C. A. *J. Am. Chem. Soc.* **1996**, *118*, 10211.

(19) Ingersoll, D.; Kulesza, P. J.; Faulkner, L. R. *J. Electrochem. Soc.* **1994**, *141*, 140.

(20) Chidsey, C. E. D.; Bertozzi, C. R.; Putvinski, T. M.; Muijsce, A. M. *J. Am. Chem. Soc.* **1990**, *112*, 4301.

(21) Oxidation of the free iodide is observed at 0.78 V. A similar EC mechanism is observed upon homogeneous electrochemical generation of  $[\text{Ta}_6\text{Cl}_{12}\text{Cl}_6]^{4-}$  and substitution of a chloride ligand with a solvent molecule.<sup>15</sup>

(22) Koknat, F. W.; McCarley, R. E. *Inorg. Chem.* **1974**, *13*, 295.