coordinating more than one carbonyl group even in a carbon monoxide atmosphere,[18] whereas Ni(0) complexes with two, three, and four carbonyl groups are well-known.[6] These properties of Cu(I)–ethylene and –carbonyl complexes are a manifestation of the poor π-back-bonding ability of cuprous ion relative to that of Ni(0) species. These experimental results are in accord with recent theoretical studies of the bonding of small, unsaturated molecules to cuprous ion.[19]

Registry No. **1**, 93757-51-8; **2**, 93757-53-0; **3**, 93757-55-2; **4**, 93757-56-3; **5**, 93757-58-5; **6**, 93757-60-9; **7**, 93781-70-5; **8**, 93757-62-1; **9**, 93757-64-3; **10**, 93757-66-5; **11**, 93757-67-6; **12**, 93757-69-8; **13**, 93757-71-2; **14**, 93757-73-4; **15**, 93757-74-5; **16**, 93757-76-7; $Cu(ClO_4)_2$, 13770-18-8; Cu, 7440-50-8; C_2H_4, 74-85-1; C_3H_6, 115-07-1; C_6H_{10}, 110-83-8.

---

(18) (a) Kitagawa et al.[18b] have reported the preparation of $[Cu(bpy)(CO)_2]ClO_4$, solely on the basis of ^1H NMR data. We have been unable to isolate this material with our procedure, although our NMR data agree with published values. (b) Kitagawa, S.; Munakata, M.; Miyaji, N. *Inorg. Chem.* **1982**, *21*, 3842–3843.

(19) Sakaki, S.; Kitaura, K.; Morokuma, K. *Inorg. Chem.* **1982**, *21*, 760–765.

Contribution from the Department of Chemistry,
The University of Texas at Austin,
Austin, Texas 78712

Evidence for the Gold Anion in Ethylenediamine

R. Jagannathan, D. B. Wallace, and J. J. Lagowski*

Received May 9, 1984

The dissolution of alkali metals in several types of nonaqueous solvents (amines, ethers, and amides) has been conclusively shown to produce a new species, metal anions, M^- (M = alkali metal).[1] Recent work has led to the isolation of substances incorporating some of these species.[2] Similarly, several post transition elements have been shown to form homonuclear polyatomic cluster anions in ammonia and in ethylenediamine.[3] Among the transition metals, however, gold alone is known to form a metal monoanion (Au^-) in liquid ammonia.[4] We report here spectroscopic and electrochemical evidence for the existence of Au^- in ethylenediamine. Thus, Au^- is the only metal monoanion that exists in liquid ammonia, a solvent in which alkali-metal anions have not been detected to date, and in other solvents such as ethylenediamine in which alkalide anions are known to exist.

Experimental Section

A standard three-electrode configuration was used for electrochemical studies. A platinum button and a wire served as the working and auxiliary electrodes, respectively. A silver wire separated by a double frit was used as the pseudoreference electrode. The Ag-wire pseudoreference electrode was found to be stable during the period of the experiment. It was not possible to obtain standard potentials with ferrocene or cobaltocene because of the instability of the compounds and/or the products of the redox process. Naphthalene however exhibited a quasi-reversible process with $E_{1/2}$ of −2.15 V with reference to the Ag-wire electrode. The standard reduction potential for naphthalene is invariant with solvents and appears at −2.55 ± 0.1 V with reference to the SCE. Electrochemical experiments at 30 °C were performed on a Princeton Applied Research Model 173 potentiostat and Model 175 universal programmer and a Houston Instrument X-Y recorder.

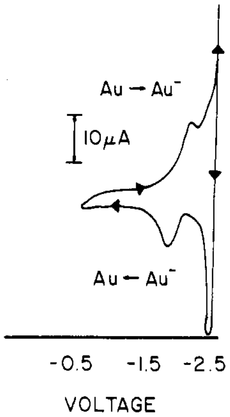

Figure 1. Typical current–voltage plot in ethylenediamine (supporting electrolyte 0.1 M K(crypt) triflate; reference Ag wire; scan rate 200 mV/s).

The supporting electrolyte (0.1 M) was potassium trifluoromethanesulfonate (triflate), which is superior to potassium iodide because it is not susceptible to oxidation. In liquid ammonia, bulk coulometric generation of solvated electrons in a three-compartment cell was performed with potassium iodide and with potassium trifluoromethanesulfonate. With KI, the anode compartment became colored with the formation of iodine and its reaction products with ammonia. In the case of potassium trifluoromethanesulfonate, copious gas evolution was observed at the anode during electrolysis, indicating ammonia oxidation to nitrogen as the predominant process at the anode. Up to 1 mmol of Au^- could be routinely generated electrochemically with 0.1 M potassium trifluoromethanesulfonate electrolyte in liquid ammonia at −50 °C.

Anhydrous ethylenediamine (Fisher Scientific) was refluxed over calcium hydride for 24 h and distilled onto Na–K alloy. After 24 h, this solution was distilled directly into the electrochemical or spectroscopic cell under high vacuum (10^{-4} torr). Experiments in methylamine were performed in a high-pressure cell with an O-ring seal and a pressure stopcock. Methylamine was purified by storing over Na–K alloy (1:1) for 24 h and distilled into the reaction cell.

Results and Discussion

A cyclic voltammogram of the supporting electrolyte in ethylenediamine under prepurified argon at this stage revealed a single electrode process at −2.65 V in the cathodic scan and a return wave on the reverse scan. Holding the potential at −2.7 V resulted in a rapidly disappearing blue coloration around the electrode. Na–K alloy (1:1; 0.1 mL) was then syringed into the cell; the cyclic voltammogram of the resulting deep blue solution was similar to the one obtained earlier, with no additional electrode processes being observed. Gold powder (0.02 g) was then added and the solution vigorously stirred for about 15 min. A positive cyclic voltammetric scan initiated at −2.6 V resulted in an anodic peak at −1.80 V and a cathodic peak at −2.10 V on reversing the scan. A representative cyclic voltammogram is presented in Figure 1. This observation immediately points to the presence of a gold-related species, and comparison with experiments in liquid ammonia[4] suggests that the gold powder was reduced to auride ion ($Au + e^- \rightarrow Au^-$). The anodic peak corresponds to the oxidation of Au^- at the electrode, and the cathodic peak represents the formation of Au^- from freshly deposited gold. The peak separation is about 300 mV, which is larger than in ammonia and suggests a greater kinetic barrier to the electrode process occurring in ethylenediamine. A surface effect was also apparent. Use of a gold plate instead of the powder under similar reaction conditions resulted in similar results, except that longer reaction times were required to produce Au^-; in these cases, competitive solvent decomposition was also observed, which resulted in smaller peak

---

(1) (a) Matalon, S.; Golden, S.; Ottolenghi, M. *J. Phys. Chem.* **1969**, *73*, 3098. (b) Fletcher, J. W.; Seddon, W. A. *J. Phys. Chem.* **1975**, *79*, 3055. (c) Dye, J. L. In "Progress in Macrocyclic Chemistry"; Izatt, R. M., Christensen, J. J., Eds.; Wiley-Interscience: New York, 1979; Vol. I, pp 63–113.

(2) Van Eck, Bradley; Le, Lon Dinh; Issa, Dheek; Dye, James L. *Inorg. Chem.* **1982**, *21*, 1966.

(3) Burns, R. C.; Corbett, J. D. *J. Am. Chem. Soc.* **1981**, *103*, 2627.

(4) (a) Peer, W. J.; Lagowski, J. J. *J. Am. Chem. Soc.* **1978**, *100*, 6260. (b) Teherani, T.; Peer, W. J.; Lagowski, J. J.; Bard, A. J. *J. Am. Chem. Soc.* **1978**, *100*, 7768.

0020-1669/85/1324-0113$01.50/0

currents. The gold plate was extensively corroded and gold particles were recovered at the end of the experiment. A study of the scan rate dependence of the electrode process revealed a positive shift of the anodic peak with increasing scan rate similar to that observed in ammonia.[4] The E° value for the Au^-/Au^0 redox couple is −1.95 V (vs. Ag wire).

Use of (18-crown-6)potassium triflate as a supporting electrolyte and Na–K alloy + cryptand [2.2.2][5] produced a rapid dissolution of gold, and identical voltammograms were obtained as before except that larger peak currents due to higher concentrations of Au^- in solution were observed. However, solvent decomposition was equally rapid and extensive under these conditions. Disappearance of the blue solution was followed by Au^- decomposition to gold as seen by the slow disappearance of the cyclic voltammetric peaks and a return to the initial current–voltage curve obtained in the presence of supporting electrolyte alone.

Attempts to generate large concentrations of solvated electrons coulometrically to react with metallic gold were unsuccessful in our hands. The solvent decomposition was rapid, and a sufficient steady-state concentration of electrons could not be established to dissolve the gold samples.

The ΔG° for the reaction of solid gold with solvated electrons to produce Au^- in ethylenediamine can be estimated from the E° for the reaction $Au + e^- \rightarrow Au^-$ (vs. the electron electrode): ΔG° is −14.9 kcal/mol at 30 °C. Conclusive evidence confirming the presence of Au^- was obtained by observing the characteristic charge-transfer-to-solvent (CTTS) band of metal anions. In a typical spectroscopic experiment ethylenediamine (3 mL) was distilled into a reservoir and reacted with a potassium mirror; a medium to deep blue solution was produced. Reaction of this solution with gold foil (0.0015 g) was followed by filtering the solution into an attached quartz optical cell (0.1 mm); a new broad band at 278 nm was present in the spectrum. The blue color faded rapidly. A spectrum obtained after considerable reaction time had elapsed (1 h) showed an Au^- band off-scale and an additional peak at about 340 nm. Blank experiments allow us to assign the 340-nm band to a product from solvent decomposition (amide band?). In the presence of 18-crown-6 and cryptand [2.2.2], the reaction of gold was rapid and the decomposition of the solutions was equally rapid.

Preliminary electrochemical experiments in methylamine with the same supporting electrolyte revealed a different behavior. Coulometric generation of electrons and reaction with gold metal was feasible at about −20 °C in this solvent. At room temperature the decomposition of solvated electrons was rapid. A cyclic current–voltage curve obtained at −20 °C revealed cathodic and anodic peaks for Au^- at −2.40 and −1.95 V vs. a Ag wire. Warming the cell to room temperature results in rapid disappearance of solvated electrons, followed by a dark violet coloration throughout the cell. With time, we observe the agglomeration of the gold colloid and precipitation of black particles of gold metal. Cooling to −20 °C and regeneration of solvated electrons result in instantaneous dissolution of the freshly precipitated gold. Cooling this solution further (−40 °C) results in disappearance of Au^- peaks in the cyclic current–voltage curve, suggesting the precipitation of a Au^--containing salt at the lower temperatures. The absorption spectral data in methylamine at 25 °C indicate the presence of a Au^- peak at 274 nm that shifts to 280 nm in the presence of 18-crown-6. Effects due to ion pairing seem to be more pronounced in this low dielectric constant solvent compared to those in ammonia where the absorption band appears at 289 nm in the presence and absence of 18-crown-6 or the cryptand [2.2.2].

The foregoing results suggest that Au^- is the only metal anion that has been detected in both liquid ammonia and amines. Further research to observe and stabilize Au^- in other solvents is continuing in our laboratories. It appears that Au^- may be a useful probe, both electrochemically and spectroscopically, to study the nature of anion–solvent interactions.

Acknowledgment. We thank the National Science Foundation and the Robert A. Welch foundation for generous support.

Registry No. Au^-, 19498-55-6; Au, 7440-57-5; ethylenediamine, 107-15-3; Na–K alloy (1:1), 12675-23-9.

---

[5] The IUPAC name for 18-crown-6 is 1,4,7,10,13,16-hexaoxacyclooctadecane, and for cryptand [2.2.2] it is 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane.

Contribution from the Inorganic Chemistry Laboratory,
University of Oxford, Oxford OX1 3QR, U.K.

Interrelationships between the Topological Electron-Counting Theory and the Polyhedral Skeletal Electron Pair Theory

D. Michael P. Mingos

Received April 11, 1984

Teo et al.[1,2] have published papers in this journal describing the "new topological electron-counting theory" based on Euler's theorem for polyhedra and the effective atomic number (EAN) rule. It has been claimed that this approach represents a more widely applicable alternative to the *polyhedral skeletal electron pair theory* (PSEPT)[3] and provides new insights into the electronic requirements of various polyhedral cluster structures and their interrelationships.[1] This new approach is based on the fundamental formula

$$\mathrm{CVMO} = 8V - F + 2 + X \qquad (1)$$

which relates the number of cluster valence molecular orbitals (CVMO) to the number of vertices (V) and faces (F) of the polyhedron. Each polyhedron is characterized by a parameter X, which is defined as the number of "extra" electron pairs in excess of the EAN rule. The parameter X has been defined by Teo in terms of a set of rules. Some theoretical justification for these rules has been provided,[1] and Teo and his co-workers[2] have demonstrated its applicability in a well-documented and thorough review.[2]

The PSEPT is also based implicitly on the EAN rule and incorporates the topological features of the cluster by designating specific classes of polyhedra, e.g. deltahedra, electron-precise three-valent polyhedra, etc. Given that the two approaches are based on the same fundamental assumptions, they must share many of the same advantages and deficiencies.[4] It is the purpose of this paper to demonstrate that the rules described by Teo for deriving X in formula 1 are consistent with the basic assumptions of the PSEPT and indeed can be derived from them by using simple algebraic manipulations.

Table I summarizes in an economical fashion the CVMO characteristics for the important classes of polyhedra adopted by metal carbonyl clusters as set out in the PSEPT.[5] In order to make a connection with Teo's work, the number of faces for these polyhedra is also specified. The derivation of the rules is made by substituting these values into the PSEPT expressions for the CVMO's.

Rule 1: For All Three Connected Polyhedra $X = 0$. In the PSEPT, three connected polyhedra are described as either elec-

---

[1] Teo, B. K. *Inorg. Chem.* **1984**, *23*, 1251.
[2] Teo, B. K.; Longoni, G.; Chung, F. R. K. *Inorg. Chem.* **1984**, *23*, 1257.
[3] Williams, R. E. *Inorg. Chem.* **1971**, *10*, 210. Wade, K. *J. Chem. Soc. D* **1971**, 792. Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1. Mingos, D. M. P. *Nature (London), Phys. Sci.* **1972**, *236*, 99. Mingos, D. M. P. *Acc. Chem. Res.* **1984**, *17*, 311.
[4] Cox, D. N.; Mingos, D. M. P.; Hoffmann, R. *J. Chem. Soc., Dalton Trans.* **1981**, 1788.
[5] Evans, D. G.; Mingos, D. M. P. *Organometallics* **1983**, *2*, 435.

0020-1669/85/1324-0114$01.50/0