Ligand-Induced Disproportionation of Silver(I)

Sir:

In the course of our investigations of metal complexes of 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (L or tet a[1]), it was observed that addition of silver(I) perchlorate or nitrate to an aqueous suspension or 50% methanolic solution of L resulted in the disproportionation of Ag(I) to the free metal and the Ag(II) complex at an observable and rather rapid rate depending on conditions of concentration and temperature. We believe that this is the first reported example of a ligand-induced disproportionation of silver(I) in solution.[2]

The univalent states of copper and gold have a well-known, pronounced tendency to disproportionate in solution according to the reactions[3]

$$2Cu^+ = Cu + Cu^{2+}$$

$$3Au^+ = 2Au + Au^{3+}$$

The equilibrium constant[4] for the disproportionation of the copper(I) ion in aqueous solution is 1.2×10^6. With the exception of the compounds described herein, no tendency of silver(I) compounds to disproportionate has been reported. In striking contrast to soluble copper(I) and gold(I) compounds, the equilibrium constant[4] at 25° for the formation of Ag and Ag^{2+} from Ag^+ in water is only 1×10^{-20}. Presumably, the relatively low heat of hydration of Ag^{2+} compared with that of Cu^{2+} and Au^{3+} disfavors the reaction.

The reaction of Ag^+ with L proceeds according to the following stoichiometry.

$$2Ag^+ + L \xrightarrow{H_2O} AgL^{2+} + Ag^0$$

In a typical experiment yields of the Ag(II) complex approach 80–90% of the theoretical value. The free metal is usually deposited as a mirror on the walls of the reaction vessel. The silver(II) complex, isolated as the perchlorate or nitrate, is a yellow solid which is conveniently recrystallized from water, alcohol, or acetonitrile. The infrared spectrum is typical of divalent metal complexes of L. The compound is paramagnetic having an effective moment of 2.14 BM and the esr spectrum, Figure 1, is characteristic of a silver(II) d^9 system ($g_\parallel = 2.090$, $g_\perp = 2.041$). Elemental analysis confirms the formulation $Ag(C_{16}H_{36}N_4)(ClO_4)_2$ (Calcd: C, 32.50; H, 6.14; N, 9.50. Found: C, 32.11; H, 6.67; N, 9.33).

If the same reaction is carried out in dry acetonitrile no disproportionation occurs. Instead a white compound analyzing for $Ag(C_{16}H_{36}N_4)ClO_4$ precipitates immediately (Calcd: C, 39.07; H, 7.40; N, 11.39. Found: C, 38.80; H, 7.57; N, 11.20). This silver(I) compound is insoluble in all common solvents but in water or methanol disproportionates according to the reaction

$$2AgL^+ \longrightarrow AgL^{2+} + L + Ag^0$$

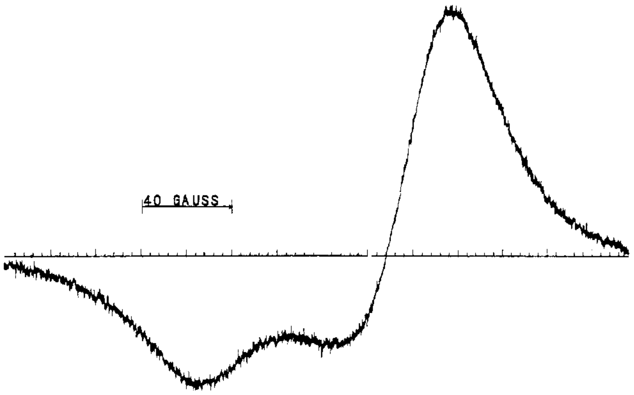

Figure 1. Electron spin resonance spectrum of $AgL(ClO_4)_2$.

When placed in water, the silver(I) compound slowly dissolves to yield a murky green solution. The water-insoluble L and the free metal are filtered off leaving a clear yellow solution of AgL^{2+}. The ligand may be extracted from the metal with alcohol and characterized by its ir spectrum. This disproportionation reaction is not catalyzed by glass or mercury surfaces as reported[5] for the disproportionation reaction of CuL^+ in acetonitrile.

The compound $AgLClO_4$ does not yield an esr spectrum. The infrared spectrum resembles that of the Ag(II) complex except in the N–H stretching region. The strong band due to N–H stretching observed for the Ag(II) complex at 3220 cm^{-1} is split into two equally intense bands in the spectrum of the Ag(I) complex. This observation may indicate that the Ag^+ ion, which favors linear coordination, is bonded relatively strongly by the two nitrogens at the 1 and 8 positions in the macrocyclic ring. The Ag(II) ion is more likely to be coordinated by the tetranitrogen macrocyclic ligand in an approximately square-planar geometry than is the larger Ag(I) ion. The driving force of the reaction and the stability of the high oxidation state of silver are most likely consequences of the four donor nitrogens being tightly bound to Ag(II) in an approximately square-planar geometry. Also, the ligand field stabilization energy should be large.[6] Nmr studies of L and the related 1,4,8,11-tetraazacyclotetradecane (cyclam) system,[7,8] as well as an examination of space-filling Corey–Pauling–Koltun models, indicate that a planar geometry of the ligand in AgL^{2+} should be possible. Unfortunately, nmr spectra of the Ag(I) and Ag(II) complexes could not be obtained because of the insolubility of the former and the paramagnetism of the latter.

Ligand oxidation did not occur in the above reaction mixtures as shown by infrared and ultraviolet spectroscopy, and the compounds appear to be stable in the solid state. The silver(II) complex does undergo a slow internal oxidation, however, to yield as yet undefined products when refluxed in aqueous solution.

These results lead to the conclusion that soluble silver(I) salts react rapidly with L at room temperature to form AgL^+ which then disproportionates at a some-

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(1) N. F. Curtis, *J. Chem. Soc.*, 2644 (1964).

(2) It has been suggested that Ag^+ ions on the surfaces of halides may react photochemically to form Ag and Ag^{n+} ions which oxidize halide ions: J. A. S. Manzanares, *An. Univ. Murcia, Cienc.*, **26**, 57 (1968); *Chem. Abstr.*, **56**, 51836s (1970).

(3) N. V. Sidgwick, "The Chemical Elements and Their Compounds," Vol. 1, Clarendon Press, Oxford, 1950, pp 106–108.

(4) Calculated from data in "Selected Values of Chemical Thermodynamic Properties," Technical Note 270-4, National Bureau of Standards, Washington, D. C., 1969, pp 13, 29.

(5) D. C. Olson and J. Vasilevskis, *Inorg. Chem.*, **10**, 463 (1971).

(6) D. H. Busch, *Helv. Chim. Acta, Fasciculus Extraordinarius, Alfred Werner*, 174 (1967).

(7) B. Bosnich, C. K. Poon, and M. L. Tobe, *Inorg. Chem.*, **4**, 1102 (1965).

(8) L. G. Warner and D. H. Busch, *J. Amer. Chem. Soc.*, **91**, 4092 (1969).