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Excited state properties of silver(I) nitrite complexes: Nitrogen conproportionation in $Ag(NH_3)NO_2$ induced by LLCT excitation

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Abstract

The complex $Ag(NH_3)NO_2$, which can be viewed as a ligand-based mixed-valence compound, undergoes a photoconproportionation of nitrogen from −III and +III to 0. It is suggested that this photolysis originates from a NH_3 to NO_2^- LLCT state which is populated from a NO_2^- IL state. In this context, the excited state properties of $AgNO_2$ and $Ag(H_2O)NO_2$ are also discussed.

Keywords: Electronic spectra; LLCT; Nitrite complexes; Silver complexes; Photochemistry

While the photochemistry and photophysics of copper and gold complexes have been studied extensively, much less is known about the excited state properties of silver complexes [1]. Nevertheless, recent studies have revealed a considerable diversity of photoprocesses of silver complexes [2]. Our present work is a rather interesting contribution to this subject. Here, we present our observations on the photoproperties of $Ag(NH_3)NO_2$. This complex can be viewed as ligand-based mixed-valence compound which contains nitrogen in the oxidation states −III and +III. While the simultaneous presence of NH_3 and NO_2^- ligands applies also to many other complexes, the electronic interaction between both ligands is generally not apparent. For $Ag(NH_3)NO_2$ we expected to see an analogy to the salt NH_4NO_2 which undergoes the well-known thermal and photochemical conproportionation of N(−III) and N(+III) [3]. This reaction simply yields nitrogen and water. Our present study of $Ag(NH_3)NO_2$ is supplemented by some observations on the photoproperties of $AgNO_2$. In this context, the diversity of photoreactions of coordinated nitrite should be emphasized [4].

The preparation of $Ag(NH_3)NO_2$ from $AgNO_2$ and ammonia yields large yellow crystals [5]. While solutions of $Ag(NH_3)NO_2$ in aqueous ammonia are rather stable, the addition of water to $Ag(NH_3)NO_2$ leads to the precipitation of $AgNO_2$.

The absorption spectra of $Ag(NH_3)NO_2$ in aqueous ammonia with $\lambda_{max} = 354$ ($\varepsilon = 25\ M^{-1}\ cm^{-1}$), 288 (shoulder, 8) and 215 (6200) nm (Fig. 1), aqueous $NaNO_2$ and $AgNO_2$ are quite similar. The weak longest-wavelength absorption maximum of NO_2^- near 350 nm has been assigned to a spin-allowed $n\pi^*$ transition [6]. An additional, even weaker $n\pi^*$ singlet–triplet transition occurs near 450 nm. Its intensity is enhanced by Ag^+ and some other heavy metals. It is responsible for the suspicious yellow or orange color of these nitrites [6,7]. While solid $Ag(NH_3)NO_2$ is not luminescent under ambient conditions, solid $AgNO_2$ shows a relatively intense green emission (Fig. 2) at $\lambda_{max} = 550$ nm. This emission has been previously observed and suggested to originate from the nitrite $n\pi^*$ IL triplet [7–10]. In the excitation spectrum, the 450 nm band appears as a distinct inflection (Fig. 2). It overlaps with the emission spectrum.

The photolysis of aqueous $AgNO_2$, which probably exists as $Ag(H_2O)NO_2$, has been reported long ago [11]. It proceeds according to the equation

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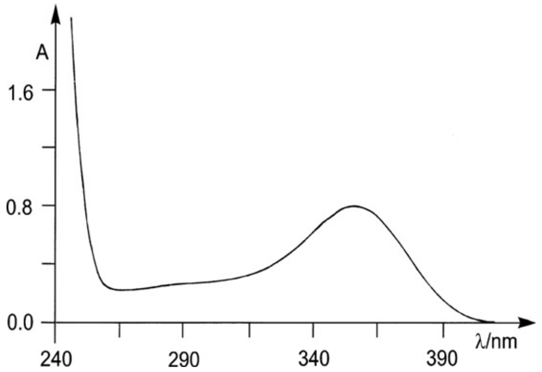

Fig. 1. Electronic absorption spectrum of 3.17×10^{-2} M $Ag(NH_3)NO_2$ in aqueous 1 M ammonia at room temperature, 1 cm cell.

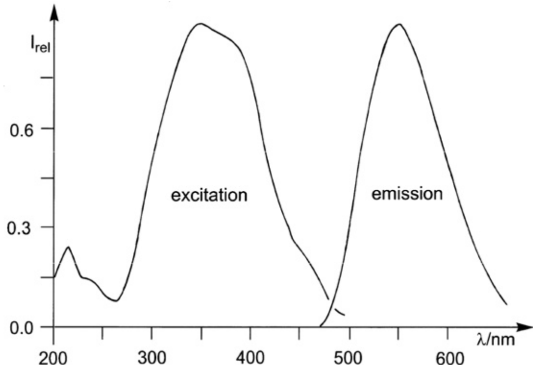

Fig. 2. Electronic excitation ($\lambda_{em} = 550$ nm) and emission ($\lambda_{exc} = 350$ nm) spectrum of solid $AgNO_2$ at room temperature, intensity in arbitrary units.

$$Ag(H_2O)NO_2 \xrightarrow{h\nu} Ag^0 + NO_2 + H_2O \tag{1}$$

The irradiation of $Ag(NH_3)NO_2$ leads to different results

$$2Ag(NH_3)NO_2 \xrightarrow{h\nu} Ag_2O + 2N_2 + 3H_2O \tag{2}$$

In diluted aqueous ammonia (0.1 M) both reactions, (1) and (2), proceed simultaneously since $Ag(H_2O)NO_2$ and $Ag(NH_3)NO_2$ are apparently present in this case. The irradiations were performed in 1 cm spectrophotometer cells. The light source used was a Hanovia Xe/Hg 977 B-1 lamp. The excitation was limited to $\lambda_{irr} = 254$ nm by a Schoeffel monochromator GM-1. The photolysis yields a precipitate which consists of Ag_2O and elemental silver. While Ag_2O dissolves in concentrated ammonia, elemental silver is soluble only under oxidizing conditions as, e.g. in nitric acid. In more concentrated ammonia (~1 M), $AgNO_2$ dissolves only as $Ag(NH_3)NO_2$. The photolysis proceeds then according to Eq. (2). However, Ag_2O does not precipitate because Ag^+ stays as $[Ag(NH_3)_2]^+$ in solution. The occurrence of photolysis is indicated by the evolution of nitrogen.

The electronic structure [12] and spectra [6,7,9,10] of simple metal nitrites have been discussed in some detail. There is a general agreement on the nature of the lowest-energy excited states, including the $n\pi^*$ nitrite IL triplet which absorbs around 450 nm and emits near 550 nm. The enhancement of this spin-forbidden absorption by Ag^+ may be attributed to a non-specific heavy-atom effect. However, it was also emphasized that a $NO_2^- \rightarrow Ag^+$ LMCT transition may contribute to this intensity [6,7]. This assumption is also consistent with the photochemical observations. The $n\pi^*$ IL triplet of solid $AgNO_2$ is emissive while in solution the photoreactivity of the LMCT state determines the photobehavior. This situation can be described by a qualitative potential energy diagram (Fig. 3). In the solid state the dissociation of $AgNO_2$ to Ag^0 and NO_2 is prevented by the rigid lattice which favours the recombination. In distinction, in solution the LMCT state is dissociative. Although in absorption it may require rather high energies, it can now extend to much lower energies since the Ag–NO_2 distance is not restricted in solution. The photoactive LMCT state should be easily reached from the nitrite IL state which is originally populated by light absorption.

A modified version of Fig. 3 may now be applied to $Ag(NH_3)NO_2$. According to the spectral data, the IL $n\pi^*$ state of $Ag(NH_3)NO_2$ closely resembles that of $AgNO_2$ or $Ag(H_2O)NO_2$. However, the photochemical behavior of $Ag(NH_3)NO_2$ (Eq. (2)) is quite different from that of $Ag(H_2O)NO_2$ (Eq. (1)). This can be explained by two different types of reactive excited states. In the case of $Ag(H_2O)NO_2$ it seems quite clear that the photolysis originates from a $NO_2^- \rightarrow Ag^+$ LMCT state. In contrast, the photoreactivity of $Ag(NH_3)NO_2$ is now attributed to a $NH_3 \rightarrow NO_2^-$ LLCT state which can also be populated from a NO_2^- IL state. Amines including ammonia are reductants and CT donors. In distinction, nitrite is not only a reductant and CT donor as in $Ag(H_2O)NO_2$, but it is also an oxidant or CT acceptor since it provides an empty π^* orbital at relatively low energies [13]. The presence of a low-energy $NH_3 \rightarrow NO_2^-$ LLCT state in $Ag(NH_3)NO_2$ is supported by these considerations. Moreover, LLCT excitation of this type is also completely compatible with the occurrence of reaction (2). At this point it should be

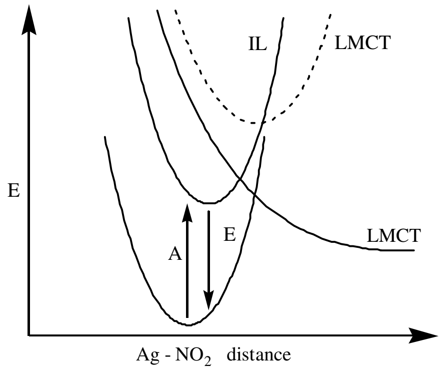

Fig. 3. Qualitative potential energy diagram of solid $AgNO_2$ and $Ag(H_2O)NO_2$ in aqueous solution involving NO_2^- IL and $NO_2^- \rightarrow Ag^+$ LMCT states (dotted line: $AgNO_2$, solid line: $Ag(H_2O)NO_2$); A = Absorption, E = Emission.

emphasized that this conproportionation of N(−III) and N(+III) is also well known to proceed thermally and photochemically in solutions of ammonium nitrite [3] although the mechanism is certainly quite different in both cases.

In summary, the complex $Ag(NH_3)NO_2$ can be viewed as a nitrogen-based mixed valence compound which upon $NH_3 \rightarrow NO_2^-$ LLCT excitation undergoes a conproportionation of nitrogen yielding molecular nitrogen. In this context, it is of interest that certain organic nitrogen-based mixed-valence compounds of a quite different type such as substituted *p*-phenylenediamine radical cations have attracted much attention in recent years [14].

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