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Coordination Chemistry Reviews 250 (2006) 1196–1207

COORDINATION
CHEMISTRY REVIEWS

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Review

Photochemical nitrosyl linkage isomerism/metastable states

Thomas E. Bitterwolf*

Department of Chemistry, University of Idaho, Moscow, ID 83844-2343, United States

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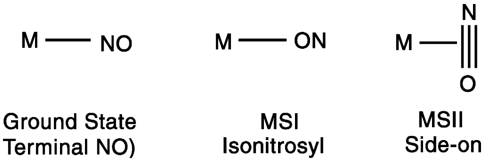
Abstract

Low temperature photolysis studies of metal nitrosyl compounds have revealed the existence of metastable states that have now been shown to be nitrosyl linkage isomers. This review explores the background of this field and highlights recent work in the author's laboratory.



Keywords: Photolysis; Nitrosyl compounds; Metastable

Nitrosyl photochemical linkage isomers, or metastable states as they are known in over half of the literature, were first observed in 1977, but their actual identities were not recognized until almost 20 years later. If it were not for interest within the solid-state community in using these metastable states for optical data storage it is likely that those early reports would have gone entirely unnoticed.

The study of these species faces particular challenges. The species themselves are generated photochemically at low temperature and even under ideal situations less than 50% conversion is achieved. Some conversions are as low as 1%. There is not one but two species that can be accessed photochemically and it is not unusual for one form to transform to another photochemically or thermally. With rare exceptions these complexes have very short lifetimes at room temperature, so our knowledge of them comes from low temperature infrared, Raman and Mössbauer spectroscopies, differential scanning calorimetery, and extraordinarily difficult photocrystallographic studies employing both X-ray and neutron diffraction methods. To the occasional consternation of referees it is not (yet) possible to obtain NMR spectra of these compounds or send them out for analysis.

It is my intent with this review to summarize the current knowledge of nitrosyl photochemical linkage isomers and to bring together the several different threads of the research. I also hope to place the research in my laboratory into the context of what is presently known.

There are, of course, several excellent reviews dealing with linkage isomerism in general and the metal nitrosyl compounds in particular. Burmeister has reviewed the literature on linkage isomers of coordination complexes several times with the most recent of these reviews appearing in this journal in 1990 [1]. Photoinduced linkage isomers of NO and related small molecules have been reviewed by Coppens and coworkers with an emphasis on photocrystallography [2]. Gütlich et al. have summarized the extensive literature on the light induced metastable states of the nitroprussides [3], and Ford and Wecksler have summarized the literature on photochemical generation of NO and NO_x [4]. Excellent reviews on metal nitrosyl chemistry have been published by Ford [5], Legzdins [6], van Eldik [7] and McCleverty

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* Tel.: +1 208 885 6361; fax: +1 208 885 6173.
E-mail address: bitterte@uidaho.edu.

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doi:10.1016/j.ccr.2005.12.016

[8] and their coworkers. A further review by Westcott and Enemark [9] may be found in the valuable two volume set *Inorganic Electronic Structure and Spectroscopy* edited by Solomon and Lever.

1. Photochemical linkage isomerism

The concept of linkage isomerism dates from the very earliest days of modern inorganic chemistry when Jørgensen noted that two distinct species could be isolated for $[Co(NH_3)_5(NO_2)]Cl_2$. Using organic analogies these were correctly identified as nitro and nitrite derivatives [10]. The correct formulation of these compounds was reported shortly thereafter by Werner [11]. Since that time extensive additional studies on linkage isomerism have been carried out and a host of ligands have been found to bind in two or more ways to metal centers.

The first example of photochemical linkage isomerism was reported by Adell in 1955 based on the observation of a color change of the red, room temperature stable $[Co(NH_3)_5(NO_2)]Cl_2$ derivative to the yellow, $[Co(NH_3)_5(ONO)]Cl_2$ nitrite derivative [12]. Subsequently photochemical linkage isomerization has been observed for a number of ligands including thiocyanate [13], dimethylsulfoxide [14] and sulfur dioxide [15]. In the latter case Johnson and Dew used IR analysis of isotopically substituted *trans*-$[Ru(NH_3)_4(SO_2)Cl]Cl$ to propose that the room temperature stable η^1-SO_2 was transformed to the η^2-SO_2 species upon photolysis. This assignment has recently been confirmed by Kovalevsky et al. who used photocrystallography to determine the structures of both the ground state and η^2-SO_2 complexes [16].

The first hints that NO might undergo photochemical transformations appeared in a series of publications by Rest and his coworkers Crichton, Taylor and Hitam in the late 1970s. These papers explored the frozen gas matrix photolysis of CpNi(NO) [17], $Mn(CO)(NO)_3$ [18], $Mn(CO)_4(NO)$ [19], and $CpV(CO)(NO)_2$ [20]. In each case photolysis resulted in the transformation of the metal nitrosyl derivatives into a new species with an unusually low wavenumber nitrosyl band, Table 1. The IR spectra of CpNi(NO) and its photolysis products are presented in Fig. 1. These bands did not appear to correspond to the NO^{1-} anion and were far too low in wavenumber for either NO or the NO^{1+} cation. In these publications the new nitrosyl ligands were designated as NO^* reflecting their ambiguous character. At this time also Rest and Hitam, in collaboration with Herberhold and Kremnitz published a brief communication describing the photolysis of $CpM(CO)_2NO$, where M = Mo and W, in which they noted that broadband photolysis resulted in loss of the nitrosyl ligand and formation of an isonitrosyl ligand to give a species assigned as CpM(CO)(NCO). The fate of the nitrosyl oxygen atom in this transformation was unknown [21]. We shall return to this reaction below.

Almost exactly concurrent with the frozen matrix discoveries in the Rest laboratory, Mössbauer spectroscopic studies by Hauser et al. found an unexpectedly stable photolysis product of sodium nitroprusside, SNP, when the compound was photolyzed at low temperature [22]. Several years after the initial discovery of these metastable states their optical [23] and Raman spectra [24] were recorded. The Raman spectrum of SNP with nitrosyl bands of the GS and MSI species is presented in Fig. 2. The Raman spectra revealed shifts in both the cyano and nitrosyl stretching frequencies suggesting that the metastable states arose from optically induced changes of the anions and were not some feature of the crystal. In 1986, Güida and coworkers recorded IR spectra, Fig. 3, of photolyzed SNP and found spectral bands for a second metastable state [25]. The nitrosyl IR bands for the first metastable state, MSI, were shifted down in energy by about 110 cm^{-1} consistent with those observed in the Raman spectrum, and a new nitrosyl band was observed shifted down by 290 cm^{-1} and assigned to a second metastable state, MSII. The two bands assigned to the metastable states were found to decay at different temperatures upon warming, lending further support to their assignment to distinct species. Subsequent studies have made extensive use of differential scanning calorimetery to determine the stabilities of the metastable states and to calculate energies of activation for their relaxation to the ground states.

Interest in applying these metastable species as optical data storage devices [26] prompted a broad analysis of nitroprusside derivatives in which the cations were systematically substituted

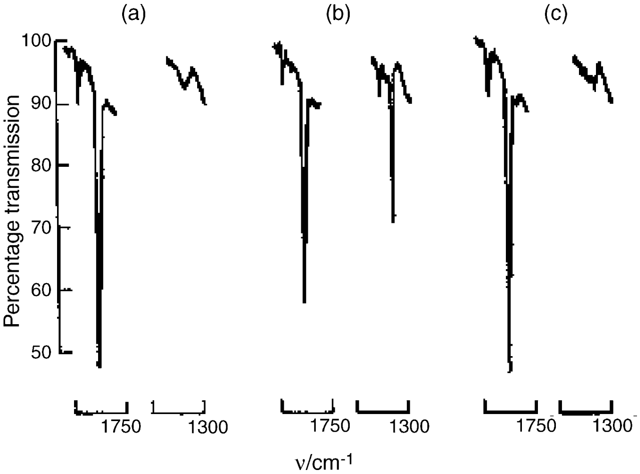

Fig. 1. Photolysis of CpNi(NO): (a) before photolysis; (b) after photolysis, 230 nm < λ_{irr} < 280 nm; (c) after backphotolysis, 290 < λ_{irr} < 350 nm [17].

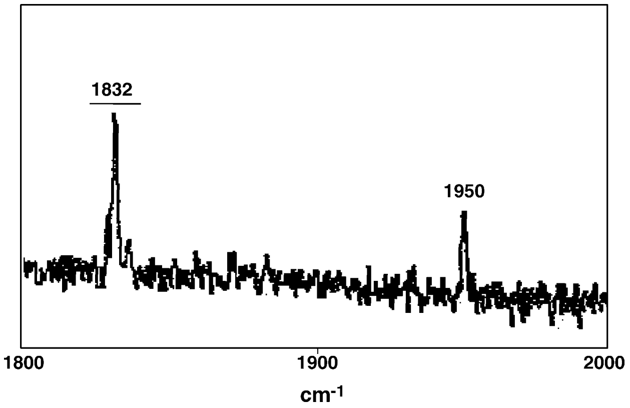

Fig. 2. Raman spectrum of SNP after photolysis at 70 K. Underlined band arises from the MSI [24].