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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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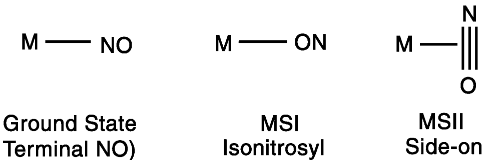
Abstract

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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[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

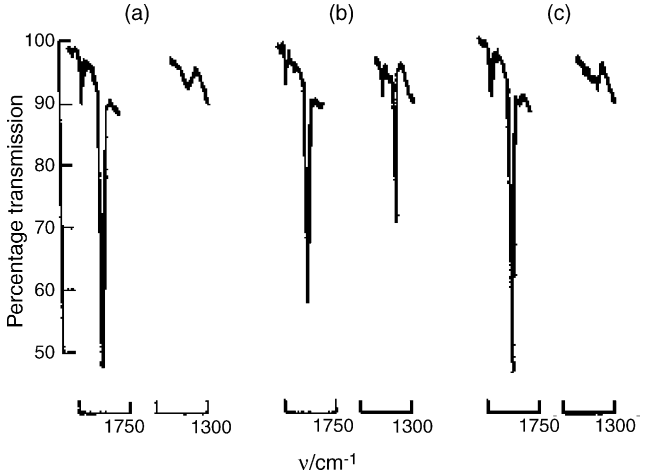

Fig. 1. Photolysis of CpNi(NO): (a) before photolysis; (b) after photolysis, 230 nm < λ_{irr} < 280 nm; (c) after backphotolysis, 290 < λ_{irr} < 350 nm [17].

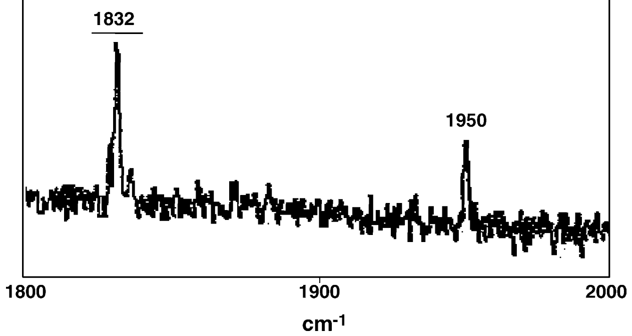

Fig. 2. Raman spectrum of SNP after photolysis at 70 K. Underlined band arises from the MSI [24].

Table 1
Linkage isomer/metastable states of transition metal nitrosyl derivatives

Compound	Td (MSI)	Td (MSII)	IR(GS)	IR (MSI)	GS-MSI	IR (MSII)	GS-MSII	Ref.
Trans-$[RuCl(en)_2NO]Cl_2$	246		1878	1744	134			[55]
Cis-$[RuCl(en)_2NO]Cl_2$	206		1901	1775	126			[55]
			1879	1759	120			
Trans-$[RuBr(en)_2NO]Br_2$	229		1877	1738	139			[55]
Cis-$[RuBr(en)_2NO]Br_2$	211		1902	1777	125			[55]
			1881	1759	122			
Trans-$[Ru(H_2O)(en)_2NO]Cl_3$	267		1904	1786	118			[55]
			1914	1773	141			[56]
$[RuCl_3(en)NO]$ fac and mer	205		1865	1744	121			[55]
				1728				
$K_2[RuCl_5NO]$ (1)	205	140	1893	1768	125			[28]
$K_2[RuCl_5NO]$			1921	1765	156	1554	367	[49]
			1909			1550	359	
	185							[55]
$[Ru(bipy)(NO)(NO_2)(OH)(H_2O)]$								
NO_2	193		1865					[32a]
Trans-$[Ru(NO)(OH)Py_4]PF_6$	223		1870					[32a]
Trans-$[RuBr(NO)Py_4]PF_6$	208		1902					[32a]
Trans-$[RuCl(NO)Py_4]PF_6$	256	171	1911					[32a]
$[Ru(NH_3)_5NO](NO_3)_3$	265		1917					[32a]
$[(RuIbipy)_2(NO)(H_2O)](ClO_4)_3$	231	188	1924					[32a]
$K_2[Ru(NO_2)_4(NO)(OH)]$	199	166	1886	1772	114	1623	263	[29]
$K_2[Ru(NO_2)_4(NO)(OH)]$	208	173	1886					[35]
Trans-$[Ru(NH_3)_4(NO)(nic)](SiF_6)(NO_3)$	250–260		1939	1810	129			[32b]
Trans-$[Ru(NH_3)_4(NO)(nic)](SiF_6)(BF_4)$	250–260		1974	1826	148			[32b]
			1918 (sh)					
$[Ru(NH_3)_5NO]Cl_3$			1955	1823	132			[32c]
$[Ru(NH_3)_4(NO)(OH)]Cl_2$			1847	1716	131			[32c]
Trans-$[Ru(Hox)(en)_2NO]Cl_2$	277		1900	1763	137			[32d]
Cis-$[Ru(Hox)(en)_2NO]Cl_2$	226		1917	1796	121			[32d]
Trans-$[Ru(Hox)(Ox)(en)NO]$	267		1904	1786	118			[32d]
Cis-$K[Ru(Ox)_2(en)NO]$	506		1881	1779	102			[32d]
$Cs_2[Ru(Ox)(NO)Cl_3]$	198	161						[32e]
$[Ni(cyclaim)][Ru(Ox)(NO)Cl_3]$	201	182						[32e]
$[Ru(terpy)(NO)(OH)]PF_6$	180	147						[32e]
$Na_2[Fe(CN)_5NO]$ (SNP)	195–200	151	1960	1835	125	1664	296	[48]
$Na_2[Ru(CN)_5NO]$	230	240	1932	1847	85	1648	284	[50]
				1839				
				1835				
$Na_2[Os(CN)_5NO]$	190	220	1897	1799	98	1546	351	[50]
				1790				
				1788 (sh)				
$Fe(por)(NO)(NO_2)$			1783	1699	84			[54]
$Fe(TTP)NO$			1672	1532	140			[52]
$Fe(OEP)NO$			1672	1554	118			[52]
$Ru(OEP)NO(O{-}i{-}C_5H_{11})$			1791	1645	146	1497	294	[53]
$Ru(OEP)NO(SCH_2CF_3)$			1788	1660	128	1546	242	[53]
$CpNi(NO)$			1828	1576	252	1385	443	[17]
$Mn(CO)(NO)_3$			2092 (2)	2105				[18]
			1829	1772				
			1742	1728				
				1502				
$CpV(CO)(NO)_2$			2055 (2)	2042				[20]
			1728	1653				
			1649	1394				

(1) Raman spectrum. (2) Carbonyl band.

and dsc studies carried out on the compounds [27]. As part of an effort to identify additional species with metastable states, the cyano coordination compounds, $K_3[Fe(CN)_6]$, $K_4[Fe(CN)_6]$, $K_2[Co(CN)_6]$ and $K_2[Ni(CN)_4]$ were examined but found not to exhibit metastable behavior. In contrast, $K_2[RuCl_5NO]$ was found by dsc to have two metastable states, Fig. 4, one of which was further examined by Raman spectroscopy. The nitrosyl stretching frequency in the metastable state was found to be

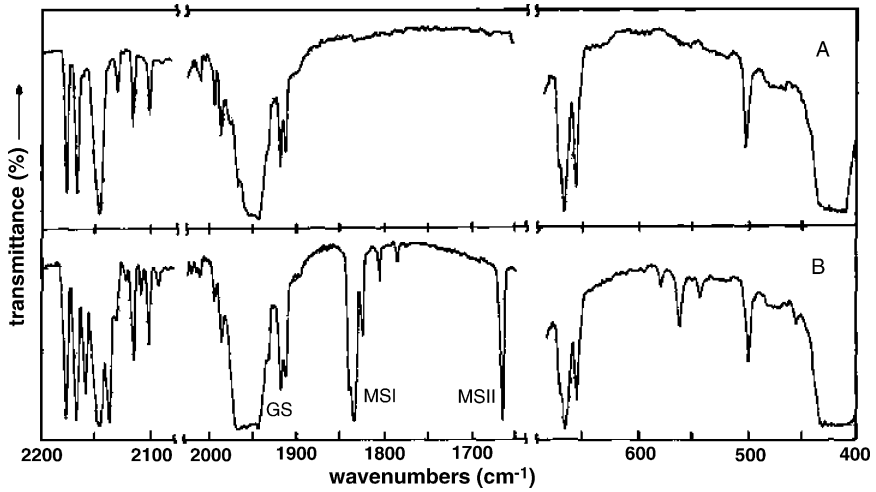

Fig. 3. IR spectra of SNP at boiling air temperature: (a) before irradiation, (b) after irradiation ($\lambda_{irr} = 514.5$ nm). Spectral lines of $E \| c$-axis removed for clarity. GS, MSI and MSII nitrosyl bands are labeled [25].

125 cm^{-1} down from the ground state value [28]. Further work established that *trans*-$K_2[Ru(NO_2)_4(NO)(OH)]$ [29] and ruthenium [30] and osmium [31] analogues of nitroprusside, as well as a number of other ruthenium derivatives [32] also formed metastable states upon irradiation.

Early neutron [33] and X-ray [34] crystallographic studies hinted at small changes in the NO, Fe–NO and Fe–CN bond lengths for the metastable states which were still being regarded as uniquely stable electronic states. It was not until Fomitchev and Coppens [35] carried out a 50 K X-ray analysis of *trans*-$K_2[Ru(NO_2)_4(NO)(OH)]$ that an alternative interpretation presented itself during the refinement of the data set. It was found that there were discrepancies in the isotropic temperature parameters of the nitrogen and oxygen atoms of the metastable state that resulted in the scattering power of the proximal atom being understated and/or that of the distal atom being overstated. Reversing the order of the nitrogen and oxygen atoms in the refinement model led to a solution with reasonable mean square displacements, Fig. 5. A reanalysis of the earlier neutron and X-ray structural data for MSI of SNP suggested that the NO might also be reversed yielding a better fit with the data. Shortly thereafter Carducci, Pressprich and Coppens reported a new X-ray structure of SNP with data collected at 50 K [36]. This data provided strong evidence for assigning the MSI metastable state to an isonitrosyl linkage isomer and yielded the first experimental evidence for side-on bonding of the nitrosyl group in the MSII state, Fig. 6.

Up until 1998 all of the studies on photochemically induced nitrosyl metastable species had focused on coordination compounds of the Group VIII metals. This changed dramatically with a report by Formitchev et al. [37] of the X-ray structure of the ground state and MSII of Cp*Ni(NO), Fig. 7. As noted above, Crichton and Rest had observed new nitrosyl bands upon photolysis of this compound in frozen gas matrices but were unable to assign the bands to a specific structure. The side-on nitrosyl structure revealed by the X-ray structure solved the assignment

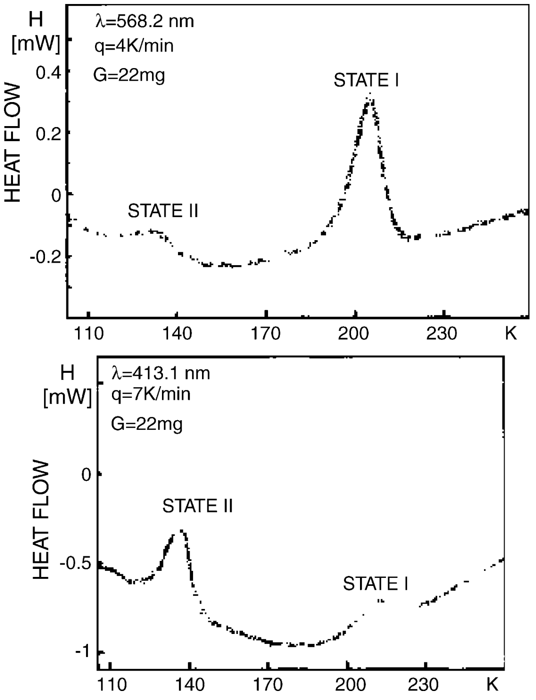

Fig. 4. Thermal decay of metastable states of $K_2[RuCl_5(NO)]$ [28].

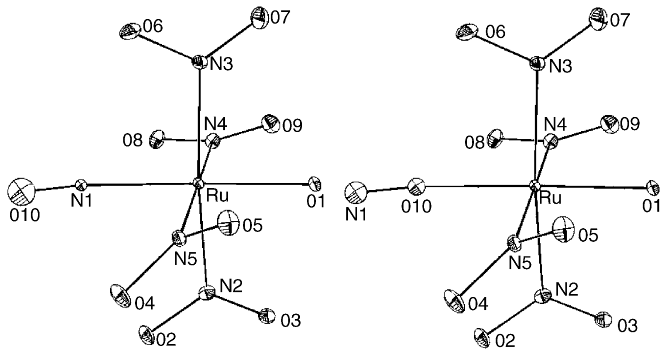

Fig. 5. ORTEP drawings of the Ru–NO (left) and Ru–ON (right) models for the MSI excited state of $K_2[Ru(NO_2)_4(OH)(NO)]$ showing the differences in the nitrosyl thermal parameters [35].

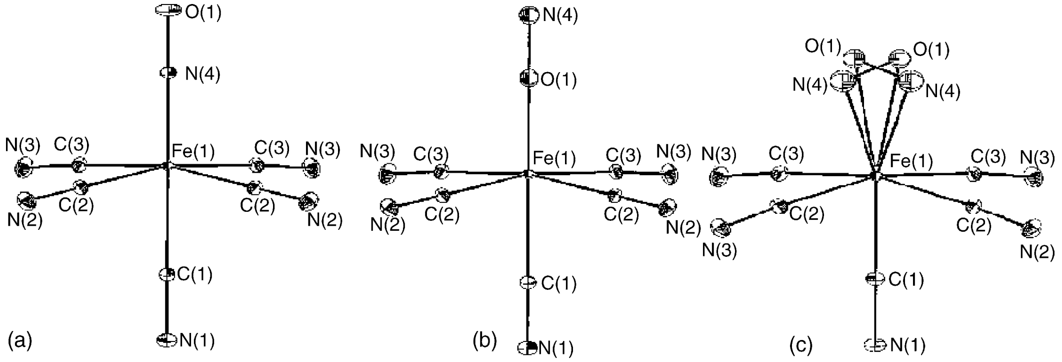

Fig. 6. Molecular structures of the nitroprusside anion (a) and its MSI (b) and MSII (c) states [36].

problem for the matrix results and, more importantly, brought the Rest frozen matrix studies and organometallic nitrosyl compounds into the broader picture of metastable species.

The association of the metastable species with nitrosyl linkage isomers also offered an explanation of the unusual stability of these species. As early as 1990, Güdel had demonstrated that the observed stabilities had to be associated with substantial geometric or electronic distortions of the metastable states with respect to the ground states [38]. Güdel proposed a MS species modeled after known spin crossover compounds in which two electrons were transferred to the NO* orbital. Linkage isomers offered a geometric solution to the question of metastable state stability. Several theoretical studies have demonstrated that there are energetic minima corresponding to the isonitrosyl and side-on nitrosyl isomers. For example, Boulet et al. have applied dft methods to the examination of the ground and metastable states of CpNi(NO) [39], and several groups have carried out theoretical studies of SNP [40] and its ruthenium analogue [41].

Several of the theoretical studies have traced the initial bending of the nitrosyl ligand in the excited states of SNP and CpNi(NO) to a Jahn–Teller, or Renner–Teller, distortion arising from a degenerate excited state. A particularly clear description of this effect appears in work by Boulet et al. [39a] Detailed Walsh diagrams of the effect of Fe–N–O bond angle on the energy of the ground state and metastable species as well as on the various transition states in the series of transformations between the ground state and MSII and MSI species have been reported [40a,40e].

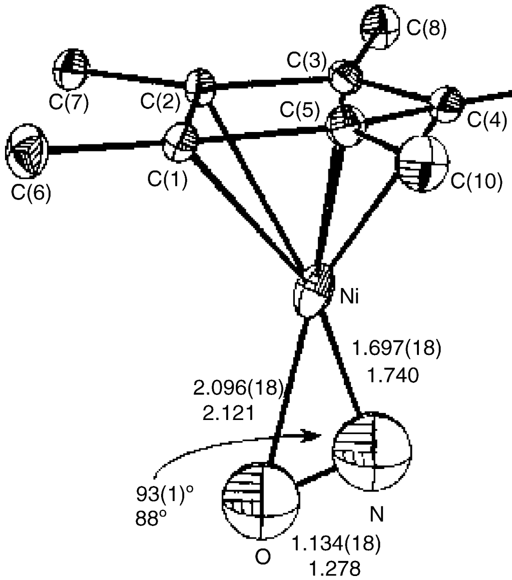

Fig. 7. Molecular structure of the MSII of CpNi(NO) showing the side-on nature of the nitrosyl ligand [37].

Angle dependent Mössbauer spectral studies of SNP in the ground state and both metastable states have been carried out by Rusanov et al. [42]. The calculated values for the isomer shift and quadrupole splitting for all three states accurately model the experimental values. Additionally the sign of the electric field gradient for the GS and MSI states are correctly predicted. In contrast, the calculated sign of the electric field gradient for the MSII state is opposite to that found experimentally, and both the predicted asymmetry parameter and orientation angle for the MSII state are inconsistent with experiment. The authors suggest that the discrepancy may lie in the assumption of a static side-on nitrosyl in the models. A rotation and possible bending of the side-on nitrosyl may account for the differences. Earlier work [43] had also suggested the possibility of rotation of the NO group and our work on several cyclopentadienyl metal nitrosyl compounds supports the possibility of two orientations for the side-on nitrosyl (vide infra).

Recent neutron diffraction studies have confirmed the assignment of the MSII state of SNP to a side-on nitrosyl [44], but the structural evidence for the isonitrosyl linkage isomer is less consistent. A new, single crystal neutron diffraction study of SNP with two different relative amounts of the MSI species failed to provide support for the isonitrosyl structure. A synchrotron X-ray single crystal study of the ground state and MSI state of $Na_2Ru(NO_2)_4(NO)(OH)$ found changes in the RuNO group roughly similar to those observed for SNP and $K_2[Ru(NO_2)_4(NO)(OH)]$ [45]. The observed increase in the Ru–NO bond length for the MSI species was found to be intermediate in value between those of the SNP and $K_2[Ru(NO_2)_4(NO)(OH)]$, while the bending of the Ru–N–O angle in the three samples was comparable. Unfortunately, attempted refinement of the NO group in the metastable state independent of the ground state was unsuccessful.

In the absence of unambiguous crystallographic support for the isonitrosyl nature of MSI, low temperature IR and Raman studies, and nuclear inelastic scattering studies have become central in making the case for assignment of MSI to the isonitrosyl linkage isomer. Morioka et al. have carried out Raman spectral studies on SNP and its ^{15}NO derivative [46]. It is found that the δ(Fe–N–O) bending mode of the ground state shifts from 669 to 655 cm^{-1} upon isotopic substitution, but that the comparable mode of MSI shifts only from 582 to 581 cm^{-1}. Employing normal coordinate analysis for MSI assuming Fe–N–O and Fe–O–N isomers it was found that the bending mode is very insensitive to isotopic substitution in the Fe–O–N isomer, but much more sensitive in the Fe–N–O orientation. The results were judged to only be consistent with the isonitrosyl linkage isomer.

Güida and co-workers have carried out low temperature IR studies on ^{15}NO and N^{18}O labeled SNP and compared observed shifts in ν(XY), δ(FeXY) and ν(FeX) with those calculated by DFT methods for both the MSI [47] and MSII [48] states. In both cases the observed isotopic shifts of the bands were consistent with the linkage isomeric model. The ν(NO) values for the ground and MSI states of $K_2RuCl_5(NO)$ [49] and $Na_2Ru(CN)_5NO{\cdot}2H_2O$ [50] have been measured for natural abundance NO, ^{15}NO, and N^{18}O. The observed isotopic shift of the ground state vibrational bands, $\Delta\nu = \nu(^{15}\mathrm{NO})-\nu(\mathrm{N}^{18}\mathrm{O})$, are small (3 and 5 cm^{-1}, respectively), while the isotopic shifts for MSI are large (20 and 18 cm^{-1}, respectively). The corresponding isotopic shifts of SNP are 5 and 20 cm^{-1}. The similarity of the isotopic shifts for the ruthenium and SNP compounds is taken as evidence for the Ru–O–N configuration in MSI.

Paulsen et al. have applied nuclear inelastic scattering of synchrotron radiation (NIS) to the question of the identity of the MSI state [51]. In this case a guanidium nitroprusside crystal was examined after photolysis and following warming to erase the metastable state. Comparison of the experimentally derived NIS spectra with those calculated by DFT methods provided strong support for the isonitrosyl structure.

A series of important studies of nitrosyl linkage isomerism in iron and ruthenium porphyrin have been carried out by Coppens, Richter-Addo and Bagley and their coworkers. Irradiation of KBr pellets of Fe(por)(NO), where por = tetratolyporphyrinato (TTP) and octaethylporphyrinato (OEP) dianions, at 25 K resulted in the bleaching of vibrational bands of the ground state species and growth of a set of new, isotope sensitive NO bands assigned to the isonitrosyl and side-on (OEP only) linkage isomers, Fig. 8 [52]. The observed NO frequency shifts from the ground state to the linkage isomers are consistent with those observed for SNP and related ruthenium compounds. Warming the samples to 40 K resulted in decay of the signals of the linkage isomers and restoration of those of the ground state.

Photolysis of KBr pellets of Ru(OEP)(NO)L, where L = SCH_2CF_3 or O–*i*-C_5H_{11}, at 20 K also resulted in the appearance of new bands consistent with the formation of isonitrosyl and side-on linkage isomers [53]. Interestingly, photolysis of a KBr pellet of Fe(TTP)(NO)(NO_2) gives rise to both nitrosyl and nitro ligand isomerism [54]. A nitrite species is produced that is stable up to 200 K, while the isonitrosyl linkage isomer formed at 11 K was found to be stable up to 50 K but decays below 200 K.

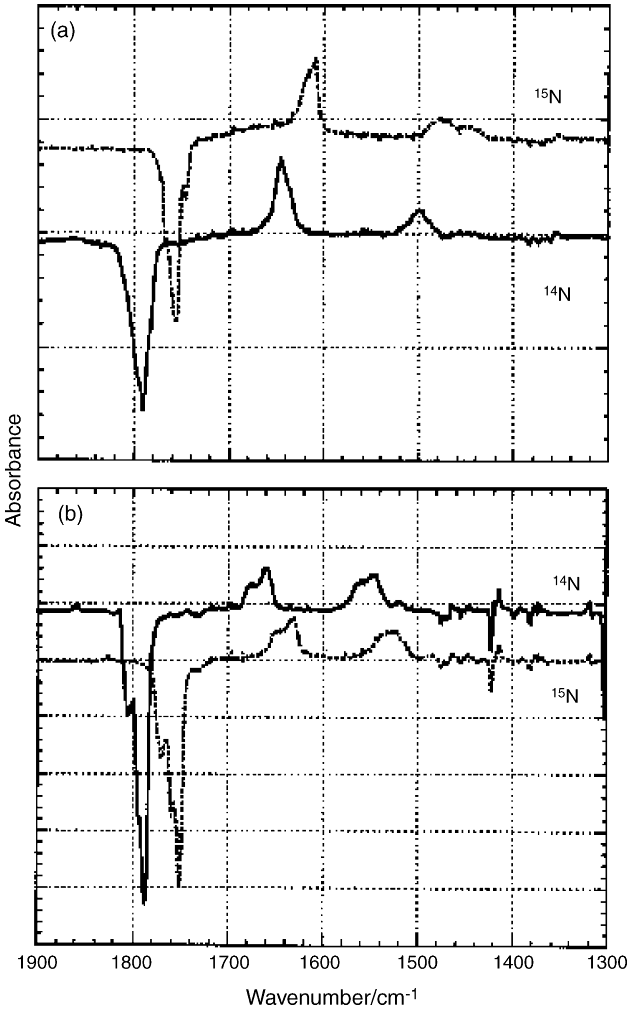

Fig. 8. Difference IR spectra of (a) Fe(TTP)(NO) and (b) Fe(OEP)(NO) following irradiation of samples at 25 K. Negative bands correspond to GS nitrosyl bands while positive bands correspond to isonitrosyl and side-on nitrosyl bands that grow in upon photolysis [52].

A series of Ru(en)$_2$(NO)L derivatives have been examined by Ookubo et al. and shown by IR spectroscopy to form MSI species [55]. *Trans*-Ru(en)$_2$(NO)(H_2O) has been examined by Kawano et al. [56]. Upon low temperature photolysis of a single crystal sample, IR spectra establish the appearance of a new nitrosyl band shifted 118 cm^{-1} from that of the ground state. Shifts of this magnitude are characteristic of the MSI or isonitrosyl linkage isomer species. Raman spectra detected new bands that were assigned to ν(Ru–O) and δ(Ru–O–N) modes. Finally, crystallographic analysis of the MSI species refined well for an isonitrosyl linkage isomer and was inconsistent with a distorted Ru–NO, Fig. 9.

In addition to the linkage isomers observed for the compounds described above, similar species have been observed by Andrews and co-workers in frozen matrices arising from the reaction of metal atoms and NO. For example side-on nitrosyl ligands have been observed for V [57], Cr [58], Mn and Re [59], Fe [60], Co [60], and Ni [60] nitrosyl species and for mixed Fe(CO)(NO) species [61]. This work has recently been reviewed [62]. Vibrational bands of the simple triatomic species,

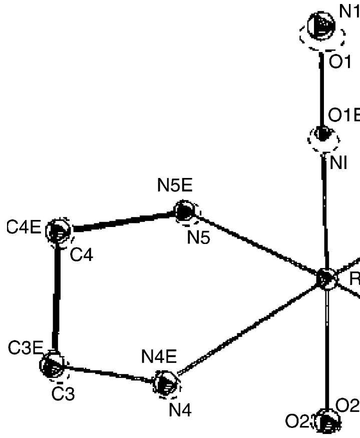

Fig. 9. Superimposition of GS (dotted lines) and MSI (solid lines) of [*trans*-Ru(en)$_2$(H$_2$O)(NO)]Cl$_3$. Sample was irradiated at $\lambda_{irr} = 427.7$ nm yielding 8.0 (4)% MSI [56].

Table 2
Laser ablated metal deposition with NO

	GS	η^2-NO	$\Delta\nu$
V	1606.0	1075.7	530.3
Cr	1614.3	1108.8	505.5
Mn	1748.6	1236.8	511.8
Fe	1766.0	1342.2	423.8
Co	1794.2	1317.4	476.8
Ni	1680.1	1292.6	385.5

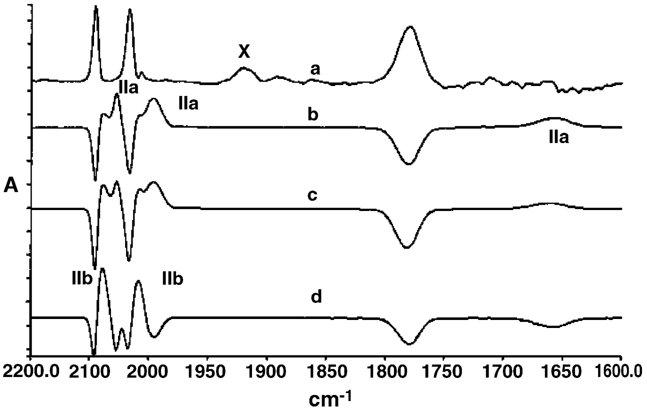

Fig. 10. Difference spectra of the photolysis of 1,2-Me$_2$-3,3-(CO)$_2$-3-NO-closo-3,1,2-ReC$_2$B$_9$H$_{11}$ in 2-MeTHF: (a) before photolysis, (b) photolysis ($\lambda_{irr} = 450 \pm 35$ nm) − (a), (c) photolysis ($\lambda_{irr} = 400 \pm 35$ nm) − photolysis ($\lambda_{irr} = 450 \pm 35$ nm), (d) photolysis (350 nm < λ_{irr} < 400 nm) − photolysis ($\lambda_{irr} = 400 \pm 35$ nm) [63].

M–NO and M–η^2-NO have been assigned, Table 2, and the observed $\Delta\nu$ arising from the transformation from nitrosyl to side-on nitrosyl is consistent with the corresponding changes in molecular species although they are at the high end of the observed range. Similarly, the vibrational bands of Fe(CO)(NO) and Fe(CO)(NO)$_2$ and their side-on nitrosyl isomers have been assigned, Table 3, and the decrease in nitrosyl stretching frequencies upon isomerization is consistent with related molecules. We shall return to these values below, but we note in passing that the carbonyl stretching frequencies of the Fe(CO)(η^2-NO)$_x$ increase in frequency relative to those of the terminal nitrosyl isomers. Another significant finding arising from these studies of the deposition of iron atoms with CO and NO is the observation of isocyanate species resulting from the disproportionation of NO. The resulting OFe(NCO) species clearly relate to the observation of CpW(CO)(NCO) and CpW(NCO) species in the photolysis of CpW(CO)$_2$(NO). It is a reasonable hypothesis that the actual species observed by Rest were the corresponding oxo derivatives, CpW(O)(CO)(NCO) and CpW(O)(NCO). We have attempted unsuccessfully to isolate the putative oxo species from solution photolyses.

Table 3
Laser ablated Fe deposition with NO and CO

	CO	NO	η^2-NO
Fe(CO)(NO)	1956.3	1727.7	
Fe(CO)(η^2-NO)	1971.2		1282.1
Fe(CO)(NO)$_2$	1940.9	1797.6, 1750.0	
Fe(CO)(NO)(η^2-NO)	2079.8	1791.2	1392.3

In collaboration with Jellis and co-workers [63] we examined the frozen Nujol matrix photochemistry of a series of (dicarborane)Re(CO)$_2$(NO) compounds and found that two new species were formed upon photolysis. For one species carbonyl and nitrosyl stretching bands were found to shift to lower frequency, while for the second species there was a new set of carbonyl bands, but no observable NO band, Fig. 10. A set of representative IR spectral data from our studies of nitrosyl photochemistry in frozen matrices is presented in Table 4. The observed change in frequency for the nitrosyl band in the first species was consistent with those observed for nitrosyl to MSI (or isonitrosyl) transformations of the various compounds described above. Reasoning that the unseen nitrosyl of the second isomer might be a side-on nitrosyl we attempted without success to unearth this band from the large C–H bending bands of the Nujol matrix.

Greater success was achieved in an examination of [CpM(CO)$_2$(NO)]BF$_4$, where M = Mn and Re [64]. Using OctEt$_3$NPF$_6$ as an ionic matrix material we directly observed two new species. This is illustrated in Fig. 11 for [CpRe(CO)$_2$(NO)]BF$_4$. The $\Delta\nu$ values for the new nitrosyl bands of CpMn(CO)$_2$(NO) were −134 and −320 cm^{-1}, respectively, while those of the rhenium derivative were −117 and −364 cm^{-1}, respectively. The assignment of these bands to a nitrosyl ligand was confirmed by isotopic substitution. These bands are consistent with the changes observed for the transition to isonitrosyl and side-on nitrosyl linkage isomers, respectively. The photolysis of [MeCpMn(CO)$_2$(NO)]BF$_4$ was similar to that of the Cp derivative except that two bands were resolved for the side-on nitrosyl. These bands are believed to be evidence for two rotational isomers of the side-on nitrosyl ligand. In contrast to the shift of the carbonyl bands of Fe(CO)(NO) and Fe(CO)(NO)$_2$ to higher frequencies in the side-on nitrosyl isomers reported by Andrews, the carbonyl bands of the manganese and rhenium compounds were shifted to lower frequency in both the isonitrosyl and side-on nitrosyl isomers.

Table 4
IR spectral data for representative metal nitrosyl compounds and their linkage isomeric photoproducts in frozen matrix spectra

Compound	νCO (cm^{-1})	νNO (cm^{-1})	Matrix	Ref.
1,2-Me_2-3,3-$(CO)_2$-3-NO-closo-3,1,2-$ReC_2B_9H_{11}$	2089, 2034	1762	Nujol	[3]
	2056, 2001	1612 (Ru–ON)		
	2079, 2014	Unobserved		
$[CpMn(CO)_2(NO)]BF_4$	2121, 2083	1860	$OctEt_3NPF_6$	[64]
	2069, (1)	1726 (Mn–ON)		
	2101, 2053	1549 (Mn–η^2-NO)		
$[CpRe(CO)_2(NO)]BF_4$	2112, 2058	1824	$OctEt_3NPF_6$	[64]
	2079, 2023	1707 (Re–ON)		
	2099, 2038	1460 (Re–η^2-NO)		
$(2\text{-}MeC_3H_4)Fe(CO)_2(NO)$	2032, 1974	1749	Nujol	[65]
	2009, 1949	1586 (Fe–ON)		
$(2\text{-}PhC_3H_4)Fe(CO)_2(NO)$	2034, 1981	1652	Nujol	[66]
	2013, 1956	1588 (Fe–ON)		
$Co(CO)_2[P(OMe)_3](NO)$	2050, 1997	1770	Nujol	[69]
	2032, 1981	1362 (Co–η^2-NO)		
$Co(CO)_2(PBu_3)(NO)$	2027, 1970	1755	Nujol	[69]
	2013, 1961	1350 (Co–η^2-NO)		
$Cp^*Mo(CO)_2(NO)$	2004, 1926	1662	Nujol	[70]
	1992, 1907	1267, 1212 (Mo–η^2-NO)		
$[Mo(CO)_3(dppe)(NO)]PF_6$	2105, 2027	1741	PVC	[73]
	2091, 1993	1636, 1407 (Mo–η^2-NO)		
$Mo(CO)(dppe)(S_2CNEt_2)(NO)$	1902	1577	$BMIMPF_6$	[73]
	1864	1218 (Mo–η^2-NO)		
$Fe[P(OMe)_3]_2(NO)_2$		1746, 1737, 1697, 1675	Nujol	[69]
		1713 (Fe–NO), 1331, 1262 (Fe–η^2-NO)		
$Fe(PBu_3)_2(NO)_2$		1704, 1653	Thin film	[69]
		1670 (Fe–NO), 1316, 1239 (Fe–η^2-NO)		
$Fe_2(NO)_4(S\text{-}t\text{-}Bu)_2$		1810, 1775, 1749	Nujol	[75]
		1794, 1756 (Fe–NO) (2), 1540 (Fe–η^2-NO)		

(1) Second carbonyl band overlaps with that of the η^2-NO species. (2) Third nitrosyl band overlaps with GS bands.

$(\eta^3\text{-}C_3H_4R)Fe(CO)_2(NO)$ and its related derivatives are well known and extensively studied compounds. Matrix photolysis of $(\eta^3\text{-}C_3H_5)Fe(CO)_2(NO)$ found only small shifts in the positions of the carbonyl and nitrosyl vibrational bands characteristic of changes in the rotational orientation of the allyl ligand [65]. In contrast, the 2-methyl derivative shows weak bands for a second nitrosyl species in addition to bands that may be assigned to rotameric shifts. The downward shift of the nitrosyl stretching frequency is in the range expected for isonitrosyl ligands. Substitution of a phenyl group onto the allyl ligand completely suppresses allyl rotation so that only formation of an isonitrosyl band is observed. The difference spectra of $(2\text{-}MeC_3H_4)Fe(CO)_2(NO)$ and $(2\text{-}PhC_3H_4)Fe(CO)_2(NO)$ [66] are presented in Fig. 12. To the best of our knowledge this is the first example of a choice of photochemical pathways being determined by steric influences alone.

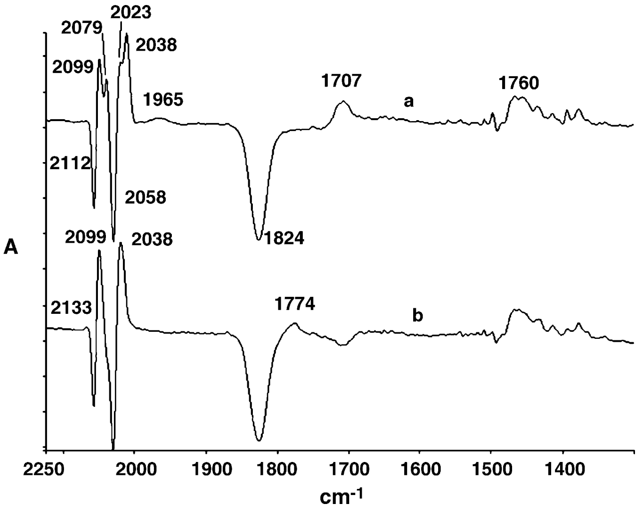

Fig. 11. Photolysis of $[CpRe(CO)_2(NO)]BF_4$ in $OctEt_3N\ PF_6$: (a) photolysis ($\lambda_{irr} = 400 \pm 35$ nm) − spectrum before photolysis, (b) photolysis (330 nm < λ_{irr} < 400 nm) − ($\lambda_{irr} = 400 \pm 35$ nm). The noise in the side-on nitrosyl band at 1460 cm^{-1} arises from subtraction of the overlapping solvent bands [64].

Rest examined the matrix photochemistry of $Co(CO)_3(NO)$ [67] and $Fe(CO)_2(NO)_2$ [68] and found that CO-loss was the only observed photoprocess. We have repeated these studies in frozen Nujol at lower energies than employed by Rest and confirm that CO-loss is the only photoprocess even at low incident radiation energies. Noting that the symmetric A band carbonyl stretching frequencies of $Co(CO)_3(NO)$ and $Fe(CO)_2(NO)_2$ are very high (>2100 cm^{-1}), we reasoned that introduction of a phosphine ligand might strengthen the back bonding to the carbonyl and nitrosyl ligands and perhaps suppress CO-loss. Indeed, photolysis of $Co(CO)_2[P(OEt)_3](NO)$ and $Co(CO)_2(NO)(PBu_3)$ give rise to bands of new species with side-on nitrosyl stretching bands at 1362 and 1350 cm^{-1}, respectively, Fig. 13 [69].

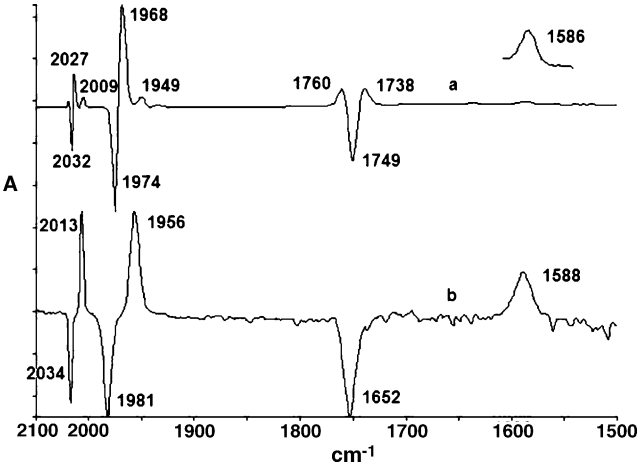

Fig. 12. Difference photolysis of (a) (2-MeC_3H_4)$Fe(CO)_2(NO)$ (λ_{irr} = 450 ± 35 nm), and (b) (2-PhC_3H_4)$Fe(CO)_2(NO)$ (λ_{irr} = 450 ± 35 nm) in Nujol. The features at 1760 and 1738 in spectrum (a) are subtraction artifacts [65,66].

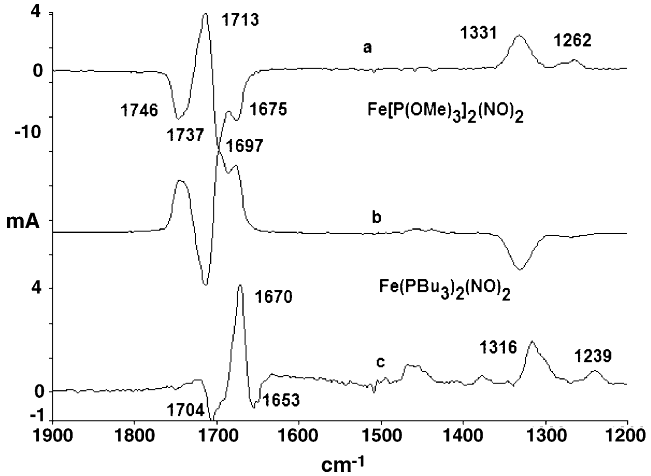

Fig. 14. Difference spectra of $Fe[P(OMe)_3]_2(NO)_2$ in Nujol: (a) photolysis λ_{irr} = 450 ± 35 nm – starting spectrum, (b) photolysis λ_{irr} = 550 ± 35 nm – λ_{irr} = 450 ± 35 nm. Difference spectrum of $Fe(PBu_3)_2(NO)_2$ thin film: photolysis λ_{irr} = 450 ± 35 nm – starting spectrum. Bands between 1400 and 1500 cm^{-1} in (c) are subtraction artifacts.

Substitution of a single carbonyl of $Fe(CO)_2(NO)_2$ by PBu_3 resulted in complete suppression of all photochemistry including CO-loss even upon irradiation in the UV. Upon substitution of the second carbonyl ligand by PBu_3 it was found that the compound undergoes photolysis to give a new species having one nitrosyl vibrational band at 1672 cm^{-1} between the two bands of the ground state species, 1697 and 1653 cm^{-1}, and a second pair of bands at 1362 and 1316 cm^{-1}. The two bands in the side-on nitrosyl region are believed to arise from rotational isomers of the side-on nitrosyl ligand. The analogous PPh_3 and $P(OMe)_3$ derivatives undergo similar photochemical processes. In the case of the $P(OMe)_3$ compound the ground state exhibits splitting of the nitrosyl bands at low temperature that probably arise from rotational conformers of the methoxy groups in the $P(OMe)_3$ ligand. The difference spectra of $Fe[P(OMe)_3]_2(NO)_2$ and $Fe(PBu_3)_2(NO)_2$ are presented in Fig. 14 [69].

A further example of rotational isomers of a side-on nitrosyl ligand can be seen in the difference spectra of the photolysis of $Cp^*Mo(CO)_2NO$. When a Nujol solution of this compound is photolyzed (λ_{irr} = 450 ± 35 nm) as illustrated in Fig. 15, bands of the ground state complex are bleached and new bands of a side-on nitrosyl species arise. Back photolysis at long wavelength (λ_{irr} > 500 nm) reverses this process [70]. Nitrosyl linkage isomers have been observed for all of the Group VI Cp and $Cp^*M(CO)_2(NO)$ compounds. The earlier Rest photochemical studies of the Group VI $CpM(CO)_2(NO)$ compounds were carried out in the UV. Observation of the linkage isomers requires photolysis in the blue portion of the spectrum. The higher energies employed in the earlier work bleach these linkage isomeric intermediates and gives rise to isocyanate ligand formation and CO-loss.

There is considerable interest in the development of nitrosyl compounds that might be used as NO delivery agents in pharmacology. Photochemical initiation of NO release has the potential of delivering NO to a specific organ or tissue. In this context we have been interested in establishing a relationship between

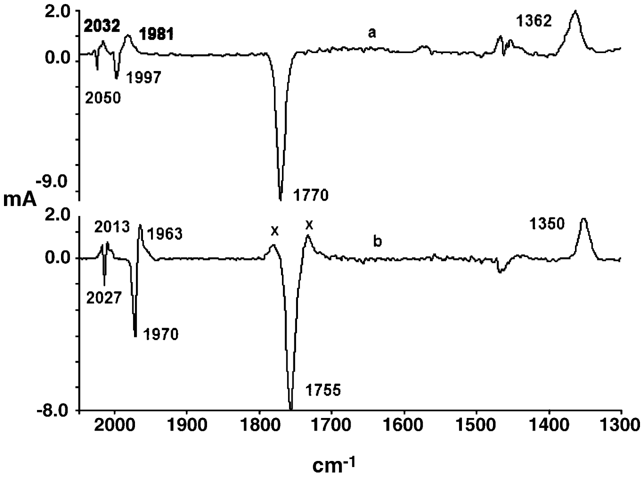

Fig. 13. Difference spectra of (a) $Co(CO)_2[P(OMe)_3](NO)$ and (b) $Co(CO)_2(PBu_3)(NO)$ in Nujol. λ_{irr} = 450 ± 35 nm – starting spectrum. Features marked with 'x' are subtraction artifacts. Bands between 1400 and 1500 cm^{-1} are due to solvent subtraction.

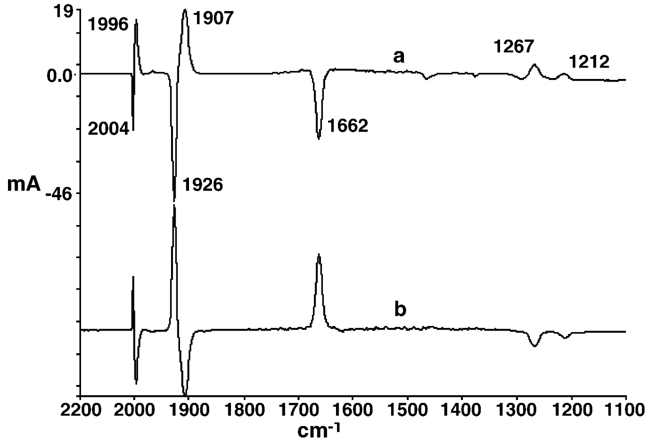

Fig. 15. Difference spectra of the photolysis of $Cp^*Mo(CO)_2(NO)$ in frozen Nujol: (a) λ_{irr} = 450 ± 35 nm photolysis – spectrum before photolysis, (b) back photolysis (λ_{irr} > 500 nm).

compounds that exhibit both linkage isomerism and NO release in solution. For example, Fe(TTP)NO discussed above is known to undergo linkage isomerism at low temperatures, but ultrafast photochemical studies of this compound and its cobalt analogue in benzene solution indicate that NO loss is virtually instantaneous (<10 ns) after excitation [71]. Since the excited states of the porphyrin compounds are centered on the ligand, and NO loss is believed to take place by charge transfer from an excited ligand state it is not clear whether these conclusions extrapolate to other metal nitrosyl compounds.

Kunkely and Vogler have demonstrated that Mo(CO)(NO)(dppe)(dtc), where dtc = S_2CNMe_2, has an absorption band at 520 nm that is assigned to a LLCT (dct → NO*) transition. Photolysis into this band ($\lambda_{irr} = 546$ nm) in benzene solutions results in loss of NO ($\Phi = 0.0018$ mol/einstein) [72]. We have examined the photolysis of the ethyl analogue of this compound in an ionic liquid matrix at ca. 90 K and found that upon irradiation ($\lambda_{irr} = 400 \pm 35$ nm) the bands of the ground state species are bleached and new bands corresponding to a red-shifted carbonyl band and a side-on nitrosyl band. Back photolysis of this sample ($\lambda_{irr} = 500 \pm 35$ nm) cleanly reverses the photolysis as shown in Fig. 16.

The precursor for the dithiocarbamate compound, $[Mo(CO)_3(NO)(dppe)]PF_6$, also undergoes photolysis, Fig. 17, to generate both isonitrosyl and side-on nitrosyl species [73].

An important class of compounds that have been investigated as NO delivery agents are the Roussin's red salt esters, $(NO)_2Fe(\mu\text{-SR})_2Fe(NO)_2$. An excellent dft study of Roussin's red salt and its esters by Jaworska and Stasicka has recently appeared [74]. Photolysis ($\lambda_{irr} = 365$ nm) of a deaerated water solution of $Na_2[(NO)_2Fe(\mu\text{-SCH}_2CH_2SO_3)_2Fe(NO)_2]$ was found to release NO with a quantum yield of 0.052 ± 0.005 mol/einstein [75]. Flash photolysis in the absence of air shows NO loss as the sole photochemical event after the flash. A trace of the flash photolysis of $Na_2[Fe_2(NO)_4(SCH_2CH_2SO_3)_2]$ in aqueous solution under an excess of NO is presented in Fig. 18. If linkage isomer formation competes with, or precedes, NO loss the lifetime of these species must be 100 ns or less to avoid detection.

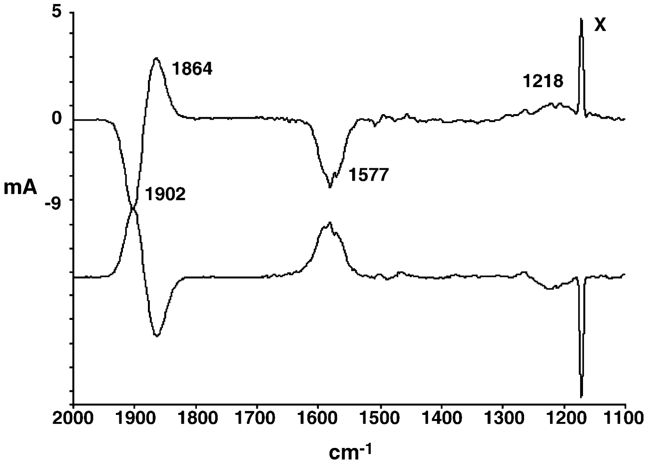

Fig. 16. Difference spectra of the photolysis of $Mo(CO)(NO)(dppe)(S_2CNEt_2)$ in butyl, methylimidazolium PF_6: (a) ($\lambda_{irr} = 400 \pm 35$ nm) − spectrum before photolysis, (b) ($\lambda_{irr} = 500 \pm 35$ nm) − ($\lambda_{irr} = 400 \pm 35$ nm). Band marked with 'x' is due to subtraction of an intense solvent band.

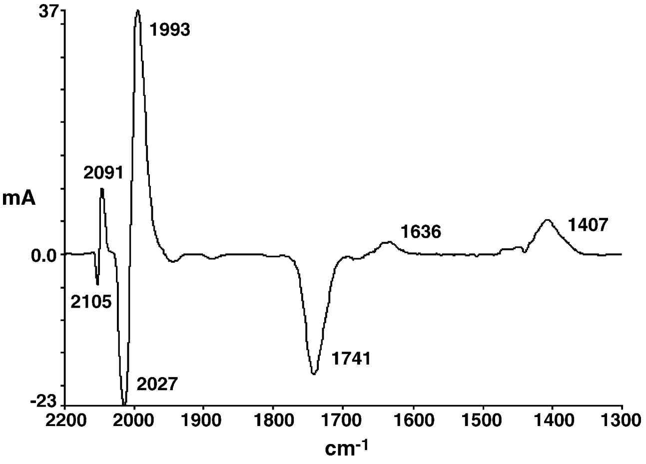

Fig. 17. Difference spectrum of the photolysis of $[Mo(CO)_3(NO)(dppe)]PF_6$ in PVC film: photolysis ($\lambda_{irr} = 450 \pm 35$ nm) − spectrum before photolysis.

We have examined the photolysis of several alkyl derivatives of the Roussin's red salt esters in frozen Nujol matrices and find that they undergo photolysis in which one of the four nitrosyl ligands transforms to a side-on linkage isomer leaving the other three as terminal nitrosyls. The difference spectra of the photolysis of $Fe_2(NO)_4(S\text{-}t\text{-}Bu)_2$ in frozen Nujol solution is presented in Fig. 19 [76]. Two of the terminal nitrosyl bands of the photoproduct can be clearly seen, and a third overlaps with the parent nitrosyl band at 1749 cm^{-1} as evidenced by the small negative band at that position in Fig. 19b.

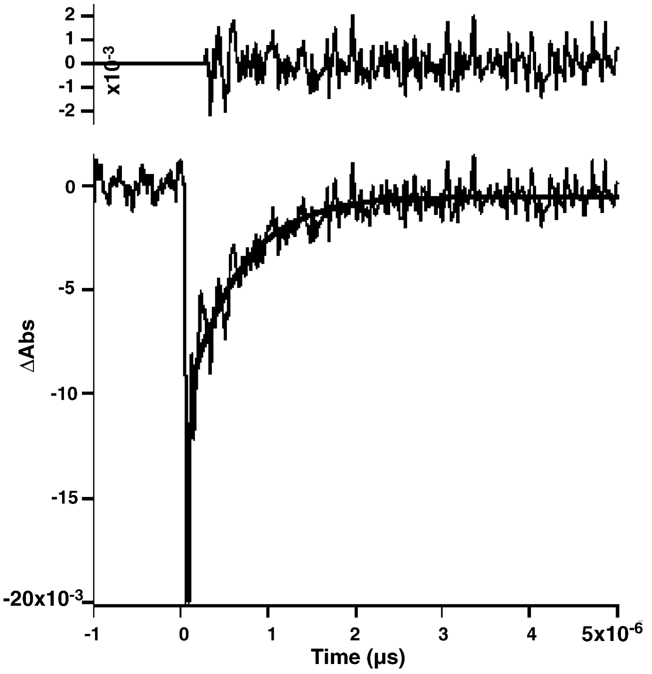

Fig. 18. Flash photolysis of $Na_2[Fe_2(NO)_4(SCH_2CH_2SO_3)_2]$ in aqueous solution with an excess of NO. The solid line is the exponential fit to the temporal absorbance change while the line at top is the residual of that fit [74].

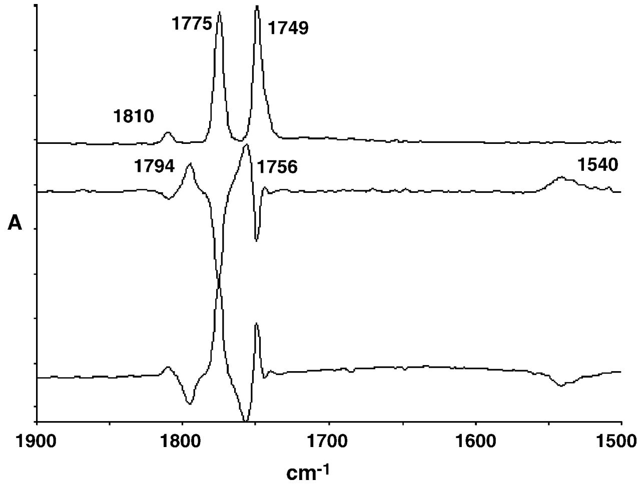

Fig. 19. Photolysis of $Fe_2(NO)_4(S\text{-}t\text{-}Bu)_2$ in Nujol at ca. 90 K: (a) before photolysis, (b) ($\lambda_{irr} = 450 \pm 35$ nm) − spectrum before photolysis, (c) ($\lambda_{irr} > 500$ nm) − ($\lambda_{irr} = 450 \pm 35$ nm) photolysis.

In a recent series of studies, da Silva and coworkers have examined the solution photochemistry of $[Ru(bipy)_2(NO)L]^{n+}$ complexes in aqueous solution [77]. The release of NO by these compounds was monitored by chronoamperometry. Upon photolysis of $[Ru(bipy)_2(NO)L]^{3+}$, where L = py, 4-pic, or 4-acpy, an intermediate was observed in the electronic spectrum that was assigned to an isonitrosyl linkage isomer. If correct, this constitutes the first observation of a linkage isomer in a room temperature solution and clearly has significant implications for the role of nitrosyl linkage isomers in chemistry.

Our studies of nitrosyl linkage isomerism have now screened over 100 compounds with evidence for linkage isomerism in about 80% of the compounds studied. As our photolyses are conducted at liquid nitrogen temperatures it is not known if some of the compounds for which we have not observed linkage isomerism may simply have low thermal or photochemical barriers to relaxation to the ground state.

Fundamental questions remain in our understanding of the photochemistry of the metal nitrosyl compounds. What is the solution lifetime of linkage isomers and is possible that these species might be sufficiently long lived to do unique chemistry. Is it possible to adjust the electronic and ligand environment so as to isolate and characterize a linkage isomer? The rich chemistry of metal nitrosyl compounds provides a broad pallet of compounds to explore in search of these questions.

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References

[1] (a) J.L. Burmeister, Coord. Chem. Rev. 105 (1990) 77;
(b) J.L. Burmeister, Coord. Chem. Rev. 3 (1968) 225;
(c) J.L. Burmeister, Coord. Chem. Rev. 1 (1966) 205.
[2] (a) P. Coppens, I. Novozhilova, A. Kovalevsky, Chem. Rev. 102 (2002) 861;
(b) D.V. Fomitchev, I. Novozhilova, P. Coppens, Tetrahedron 56 (2000) 6813;
(c) P. Coppens, D.V. Fomitchev, M.D. Carducci, K. Culp, J. Chem. Soc., Dalton Trans. (1998) 865.
[3] P. Gütlich, Y. Garcia, T. Woike, Coord. Chem. Rev. 219–221 (2001) 839.
[4] P.C. Ford, S. Wecksler, Coord. Chem. Rev. 249 (2005) 1382.
[5] P.C. Ford, I.M. Lorkovic, Chem. Rev. 102 (2002) 993.
[6] T.W. Hayton, P. Legzdins, W.B. Sharp, Chem. Rev. 102 (2002) 935.
[7] M. Wolak, R. van Eldik, Coord. Chem. Rev. 230 (2002) 263.
[8] J.A. McCleverty, Chem. Rev. 104 (2004) 403.
[9] B.L. Westcott, J.H. Enemark, Transition metal nitrosyls, in: E.I. Solomon, A.B.P. Lever (Eds.), Inorganic Chemistry and Spectroscopy, John Wiley, New York, 1999.
[10] (a) S.M. Jørgensen, Z. Anorg. Chem. 5 (1894) 147;
(b) S.M. Jørgensen, Z. Anorg. Chem. 19 (1899) 109.
[11] A. Werner, Ber. Deut. Chem. Ges. 40 (1907) 765.
[12] B. Adell, Zeit. Anorg. Allg. Chem. 279 (1955) 219.
[13] D.G. Always, K.W. Barnett, J. Organometall. Chem. 99 (1975) C52.
[14] (a) J.J. Rack, J.R. Winkler, H.B. Gray, J. Am. Chem. Soc. 123 (2001) 2432;
(b) M.K. Smith, J.A. Gibson, C.G. Young, J.A. Broomhead, P.C. Junk, F.R. Keene, Eur. J. Inorg. Chem. (2000) 1365.
[15] D.A. Johnson, V.C. Dew, Inorg. Chem. 18 (1979) 3273.
[16] (a) A.Yu. Kovalevsky, K.A. Bagley, J.M. Cole, P. Coppens, Inorg. Chem. 42 (2003) 140;
(b) A.Yu. Kovalevsky, K.A. Bagley, P. Coppens, J. Am. Chem. Soc. 124 (2002) 9241.
[17] O. Crichton, A.J. Rest, J. Chem. Soc., Dalton Trans. (1977) 986.
[18] O. Crichton, A.J. Rest, J. Chem. Soc., Dalton Trans. (1978) 202.
[19] M. Herberhold, W. Kremintz, H. Trampisch, R.B. Hitam, A.J. Rest, D.L. Taylor, J. Chem. Soc., Dalton Trans. (1978) 208.
[20] A.J. Rest, D.L. Taylor, J. Chem. Soc., Dalton Trans. (1982) 1261.
[21] R.B. Hitam, A.J. Rest, M. Herberhold, W. Kremnitz, J. Chem. Soc., Chem. Commun. (1984) 471.
[22] (a) U. Hauser, V. Osterreich, H.D. Rohrweck, Z. Physik. A 280 (1977) 17;
(b) U. Hauser, V. Osterreich, H.D. Rohrweck, Z. Physik. A 280 (1977) 125.
[23] T. Woike, W. Krasser, P.S. Bechthold, S. Haussühl, Solid State Commun. 45 (1983) 503.
[24] (a) T. Woike, W. Krasser, P.S. Bechthold, S. Haussühl, Solid State Commun. 45 (1983) 449;
(b) T. Woike, W. Krasser, P.S. Bechthold, S. Haussühl, J. Mol. Struct. 114 (1984) 57.
[25] J.A. Güida, O.E. Piro, P.J. Aymonino, Solid State Commun. 57 (1986) 175.
[26] (a) T. Woike, W. Kirchner, G. Schetter, T. Barthel, K. Hyung-sang, S. Haussühl, Opt. Commun. 106 (1994) 6;
(b) T. Woike, W. Krasser, P.S. Bechthold, Phys. Rev. Lett. 53 (1984) 1767.
[27] (a) H. Zöllner, W. Krasser, T. Woike, S. Haussühl, Chem. Phys. Lett. 161 (1989) 497;
(b) H. Zöllner, T. Woike, W. Krasser, S. Haussühl, Z. Krist. 188 (1989) 139.
[28] T. Woike, H. Zöllner, W. Krasser, S. Haussühl, Solid State Commun. 73 (1990) 149.
[29] T. Woike, S. Haussühl, Solid State Commun. 86 (1993) 333.
[30] J.A. Güida, O.E. Piro, P.S. Schaiquevich, P.J. Aymonio, Solid State Commun. 101 (1997) 471.

[31] J.A. Güdia, O.E. Piro, P.J. Aymonino, Inorg. Chem. 34 (1995) 4113.

[32] (a) D.V. Fomitchev, P. Coppens, Comm. Inorg. Chem. 21 (1999) 134;
(b) C. Kim, I. Novozhilova, M.S. Goodman, K.A. Bagley, P. Coppens, Inorg. Chem. 39 (2000) 5791;
(c) S.C. Da Silva, D.W. Franco, Spectrochim. Acta A 55 (1999) 1515;
(d) Y. Morioka, A. Ishikawa, H. Tomizawa, E. Miki, J. Chem. Soc., Dalton Trans. (2000) 781;
(e) S. Ferlay, H.W. Schmalle, G. Francese, H. Stoeckli-Evans, M. Imlau, D. Schaniel, T. Woike, Inorg. Chem. 43 (2004) 3500.

[33] (a) M. Rüdlinger, J. Schefer, G. Chevrie, N. Furer, H.U. Güdel, S. Haussühl, G. Heger, P. Schweiss, T. Vogt, T. Woike, H. Zöllner, Z. Phys. B 83 (1991) 125;
(b) M. Rüdlinger, J. Schefer, T. Vogt, T. Woike, S. Haussühl, H. Zöllner, Physica B 180–181 (1992) 293;
(c) J. Schefer, T. Woike, S. Haussühl, M.T. Fernandez Díaz, Z. Kryst. 212 (1997) 29.

[34] (a) M.R. Pressprich, M.A. White, P. Coppens, J. Am. Chem. Soc. 115 (1993) 6444;
(b) M.R. Pressprich, M.A. White, Y. Vekhter, P. Coppens, J. Am. Chem. Soc. 116 (1994) 5233.

[35] D.V. Fomitchev, P. Coppens, Inorg. Chem. 35 (1996) 7021.

[36] M.D. Carducci, M.R. Pressprich, P. Coppens, J. Am. Chem. Soc. 119 (1997) 2669.

[37] D.V. Fomitchev, T.R. Furlani, P. Coppens, Inorg. Chem. 37 (1998) 1510.

[38] H.U. Güdel, Chem. Phys. Lett. 175 (1990) 262.

[39] (a) P. Boulet, H. Chermette, J. Weber, Inorg. Chem. 40 (2001) 7032;
(b) P. Boulet, M. Buchs, H. Chermette, C. Daul, F. Gilardoni, F. Rogemond, C.W. Schläpfer, J. Weber, J. Phys. Chem. A 105 (2001) 8991;
(c) P. Boulet, M. Buchs, H. Chermette, C. Daul, E. Furet, F. Gilardoni, F. Rogemond, C.W. Schläpfer, J. Weber, J. Phys. Chem. A 105 (2001) 8999.

[40] (a) T. Ishikawa, K. Tanaka, J. Chem. Phys. 122 (2005) 74314;
(b) D. Schaniel, T. Woike, B. Delley, J. Schefer, M. Imlau, J. Chem. Phys. 123 (2005) 47101;
(c) S.I. Gorelsky, A.B.P. Lever, Int. J. Quant. Chem. 80 (2000) 635;
(d) B. Delley, J. Schefer, T. Woike, J. Chem. Phys. 107 (1997) 10067;
(e) M. Atanasov, T. Schönherr, Theochem 592 (2002) 79.

[41] (a) O.V. Sizova, O.O. Luimova, Theochem 712 (2004) 33;
(b) J.A. Gómez, D. Guenzburger, Chem. Phys. 253 (2000) 73;
(c) O.V. Sizova, O.O. Lyubimova, V.V. Sizov, Russ. J. Gen. Chem. 74 (2004) 317.

[42] V. Rusanov, T. Woike, H.-S. Kim, V. Angelov, T. Bonchev, S. Haussühl, Solid State Commun. 126 (2003) 457.

[43] P. Blaha, K. Schwarz, W. Faber, S. Luitz, Hyp. Interact. 126 (2000) 389.

[44] D. Schaniel, T. Woike, J. Schefer, V. Petříček, Phys. Rev. B 71 (2005) 174112.

[45] A. Puig-Molina, H. Müller, A.-M. Le Quéré, G. Vaughn, H. Graafsma, Å. Kuick, Z. Anorg. Allg. Chem. 626 (2000) 2379.

[46] Y. Morioka, S. Takeda, H. Tomizawa, E. Miki, Chem. Phys. Lett. 292 (1998) 625.

[47] M.E. Chacón Villalba, J.A. Güida, E.L. Varetti, P.J. Aymonino, J. Spectrochim. Acta A57 (2001) 367.

[48] M.E. Chacón Villalba, J.A. Güida, E.L. Varetti, P.J. Aymonino, Inorg. Chem. 42 (2003) 2622.

[49] J.A. Güida, M.A. Ramos, O.E. Piro, P.J. Aymonino, J. Mol. Struct. 609 (2002) 39.

[50] J.A. Güida, O.E. Piro, P.S. Schaiquevich, P.J. Aymonio, Solid State Commun. 101 (1997) 471.

[51] H. Paulsen, V. Rusanov, R. Benda, C. Herta, V. Schünemann, C. Janiak, T. Dorn, A.I. Chumakov, H. Winkler, A.X. Trautwein, J. Am. Chem. Soc. 124 (2002) 3007.

[52] I. Chen, I. Novozhilova, C. Kim, A. Kovalevsky, K.A. Bagley, P. Coppens, G.B. Richter-Addo, J. Am. Chem. Soc. 122 (2000) 7142.

[53] D.V. Fomitchev, P. Coppens, T. Li, K.A. Bagley, L. Chen, G.B. Richter-Addo, Chem. Commun. (1999) 2013.

[54] J. Lee, A.Y. Kovalevsky, I.V. Novozhilova, K.A. Bagley, P. Coppens, G.B. Richter-Addo, J. Am. Chem. Soc. 126 (2004) 7180.

[55] K. Ookubo, Y. Morioka, H. Tomizawa, E. Miki, J. Mol. Struct. 379 (1996) 241.

[56] M. Kawano, A. Ishikawa, Y. Morioka, H. Tomizawa, E. Miki, Ohashi, J. Chem. Soc., Dalton Trans. (2000) 2425.

[57] M. Zhou, L. Andrews, J. Phys. Chem. A 103 (1999) 478.

[58] M. Zhou, L. Andrews, J. Phys. Chem. A 102 (1998) 7452.

[59] M. Andrews, M. Zhou, D.W. Ball, J. Phys. Chem. A 102 (1998) 10041.

[60] M. Zhou, L. Andrews, J. Phys. Chem. A 104 (2000) 3915.

[61] X. Wang, M. Zhou, L. Andrews, J. Phys. Chem. A 104 (2000) 10104.

[62] L. Andrews, A. Citra, Chem. Rev. 102 (2002) 885.

[63] T.E. Bitterwolf, W.B. Scallorn, C.A. Weiss, P.A. Jellis, Organometallics 21 (2002) 1856.

[64] T.E. Bitterwolf, J. Photochem. Photobiol. A 163 (2004) 209.

[65] T.E. Bitterwolf, Inorg. Chem. Commun. 7 (2004) 956.

[66] T.E. Bitterwolf, Unpublished observations, 2002.

[67] O. Crichton, A.J. Rest, J. Chem. Soc., Dalton Trans. (1977) 536.

[68] O. Crichton, A.J. Rest, J. Chem. Soc., Dalton Trans. (1977) 656.

[69] T.E. Bitterwolf, P. Pal, Unpublished observations, 2005.

[70] T.E. Bitterwolf, B. Frates, P. Pal, Unpublished observations, 2005.

[71] (a) E.A. Morlino, M.A.J. Rodgers, J. Am. Chem. Soc. 118 (1996) 11798;
(b) E.A. Morlino, L.A. Walker II, R.J. Sension, M.A.J. Rodgers, J. Am. Chem. Soc. 117 (1995) 4429.

[72] H. Kunkely, A. Vogler, Inorg. Chem. Commun. 7 (2004) 767.

[73] T.E. Bitterwolf, R.A. Penczek, P. Pal, Unpublished observations, 2005.

[74] M. Jaworska, Z. Stasicka, New J. Chem. 29 (2005) 604.

[75] C.C. Conrado, J.L. Bourassa, C. Egler, S. Wecksler, P.C. Ford, Inorg. Chem. 42 (2003) 2288.

[76] T.E. Bitterwolf, S.L. Kennedy, D. Chase, Unpublished observations, 2003.

[77] (a) M.G. Savaia, F.D. Oliveira, R.G. de Lima, A.D. Cacciari, E. Tfouni, R.S. Da Silva, Inorg. Chem. Commun. 8 (2005) 347;
(b) M.G. Savaia, F.D. Oliveira, T.C. Tedesco, R.S. da Silva, Inorg. Chim. Acta 355 (2003) 191;
(c) M.G. Savaia, R.G. de Lima, A.C. Tedesco, R.S. da Silva, J. Am. Chem. Soc. 125 (2003) 14718;
(d) V. Togniolo, R.S. da Silva, A.C. Tedesco, Inorg. Chim. Acta 316 (2001) 7.