



## Generation of a low temperature NO linkage isomer in a transition metal complex of group 9: $\text{K}[\text{IrCl}_5\text{NO}]$



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### ABSTRACT

The  $[\text{IrCl}_5\text{NO}]^{-1}$  ion in the potassium salt can be partially transformed into a metastable state by light irradiation in the violet-near UV region at low temperature (77 K). The excitation process was followed by infrared spectroscopy, comparing the spectra before and after irradiation.

A new band grew at  $1812\text{ cm}^{-1}$  after irradiation with light in the 308–420 nm spectral region. The metastable state behavior is verified as this band decays upon heating the samples above 90 K or by subsequent irradiation using 450–680 nm light. The band at  $1812\text{ cm}^{-1}$  was assigned to  $\nu(\text{NO})$  of metastable state 1 (or an IrON linkage isomer) for comparison with the band position reported for other transition metal nitrosyls. To our knowledge, this is the first generation of a M-ON linkage isomer reported for a nitrosyl of transition metal of group 9. Its behavior is similar to that observed in other nitrosyl complexes of group 8.

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The biological role of NO [1] discovered in the last decades renewed the interest for research in transition metal nitrosyls as sources of that diatomic molecule, which in some cases, may be obtained by hydrolysis of the complexes under controlled conditions.

Moreover, the bonding property of a nitrosyl group gives valuable information on potential applications to biology and medicine, since releasing NO depends on the nature of nitric oxide bonds, which can be explored by vibrational spectroscopy.

The interest on  $[\text{IrCl}_5\text{NO}]^{1-}$  anions, among the transition metal nitrosyls, lies on that the nitrosyl group exhibits the highest vibrational  $\nu(\text{NO})$  wavenumber at  $2008\text{ cm}^{-1}$  at 77 K. The reported studies reveal the iridium metal in that complex as a strong electrophilic center [2].

Transition metal nitrosyls are also attractive due to the possibility of generating light induced metastable states at low temperatures.

The first member of the series studied was the well known sodium nitroprusside dihydrate ( $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$ , SNP), a compound used in medicine as hypotensive agent. The two metastable states generated in this compound were extensively studied by means of Mössbauer [3], infrared [4], Raman and UV–visible spectroscopies [5]. X-ray [6] and neutron diffraction [7] were carried out more recently.

It is known that metastable states may be understood in terms of linkage isomers generated by light at low temperatures [6] triggering the possibility of NO release in complexes like  $[\text{IrCl}_5\text{NO}]^{1-}$ . These are very stable at low temperatures but revert to the ground state by heating

or by appropriate wavelength irradiation (usually by red light). Compounds with these optical properties are thought to be useful for high density optical storage materials, switches for computers, and other applications [8].

The spectroscopic studies were extended to ruthenium and osmium nitrosyls containing different ligands [9–14].

All these compounds share a common  $\{\text{MNO}\}^6$  electronic configuration, according with the Enemark and Feltham notation [15]. In addition, two metastable states were also generated in  $\text{Ni}(\text{NO})\text{Cp}$  [16] and  $\text{Ni}(\text{NO})\text{Cp}^*$  (cp: cyclopentadienyl;  $\text{Cp}^*$  pentamethyl cp) [17], in  $[\text{Pt}(\text{NH}_3)_4\text{Cl}(\text{NO})]^{2+}$  cation [18] and other nitrosyl complexes [19]. Similar linkage isomers were reported for  $\text{N}_2$  and  $\text{SO}_2$  ligands in Ru complexes [20].

The generation of linkage isomers was widely discussed for the case of a metastable state 2 (MS2) found in the  $\text{K}_3[\text{Mn}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$  complex when the sample was irradiated at low temperature with ultraviolet light [21].

Thus, so far metastable states for the nitrosyl complex are known in a reduced number of metal centers of Fe, Ru, Os (group 8,  $\{\text{MNO}\}^6$ ), Ni(0) (group 10,  $\{\text{NiNO}\}^{10}$ ), Mn (group 7,  $\{\text{MnNO}\}^6$ ) and Pt (group 10,  $\{\text{PtNO}\}^8$ ).

Here, a metastable state, generated in a transition metal nitrosyl of group 9, is reported by irradiating the complex  $\text{K}[\text{IrCl}_5\text{NO}]$  at low temperature with ultraviolet light. This new state was detected using infrared spectroscopy.  $[\text{IrCl}_5\text{NO}]^{1-}$  ion shows the same  $\{\text{MNO}\}^6$  electronic configuration than those transition metal nitrosyls of group 8  $\text{M}(\text{II}) = \text{Fe, Ru, Os}$  [5,9,11,14] but with iridium in a higher oxidation state (Ir(III)).

Commercially available  $\text{K}[\text{IrCl}_5\text{NO}]$  (Sigma-Aldrich) was recrystallized from hydrochloric acid and dehydrated under a vacuum line below  $60\text{ }^\circ\text{C}$ .

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Infrared and Raman spectra of the anhydrous salt compare favorably with those reported in the literature [22].

The infrared spectra were recorded either on a Bruker 113v ( $2\text{ cm}^{-1}$  resolution,  $4000\text{--}250\text{ cm}^{-1}$ ) and in a Nicolet Impact 410 ( $4\text{ cm}^{-1}$  resolution,  $4000\text{--}400\text{ cm}^{-1}$ ).

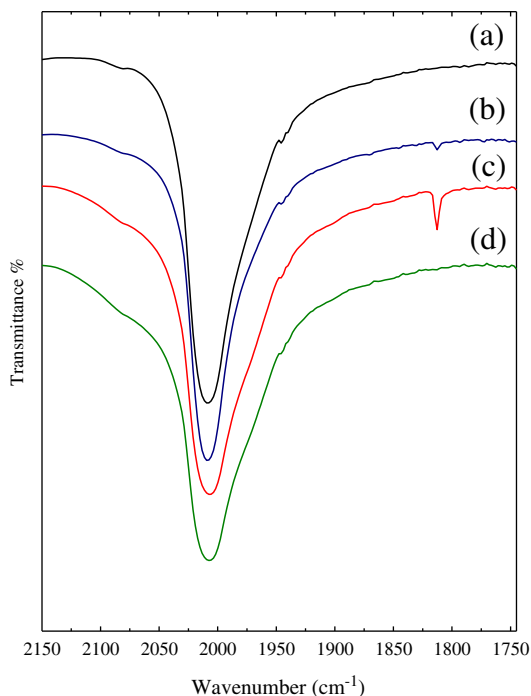
The samples for the low temperature infrared spectra were prepared as Nujol mulls of the powdered solid diluted between CsI or KBr disks. The windows were positioned in the cryostat (RIIC or an Oxford OX8ITL) cold finger at 77 K. The Oxford cryostat was the one used in getting the excited state decay temperature.

After cooling the samples at 77 K, the laser lines of  $\text{Ar}^+$ : 457.9, 488.0, 514.5 nm (Spectra Physics 2025-05);  $\text{Kr}^+$ : 350.6, 356.4, 406.7, 413.1, 530.9, 476.2, 568.1, 647.1, 676 nm (Coherent Innova 90); He–Ne (638.2 nm), excimers: 308 nm (Lambda Physics EMG 50), 347 nm (Lambda Physics EMG 101 MSC), Nd-YAG: 266, 1064 nm (Spectra Physics PDL-3) were used to populate or deactivate the metastable state.

The electronic spectra of  $\text{K}[\text{IrCl}_5\text{NO}]$  in acetonitrile show absorption bands below 600 nm, increasing molar absorptivity ( $\epsilon$ ) with wavenumber reduction. The low energy absorption ( $\lambda = 601\text{ nm}$ ) is assigned to  $M \rightarrow \pi^*(\text{NO})$  electronic transition as in other transition metal nitrosyls  $[\text{MX}_5\text{NO}]^{2-}$  ( $M = \text{Fe}, \text{Ru}, \text{Os}$ ;  $L = \text{CN}, \text{halogens}$ ) [5,9,11,14].

The excited metastable state 1 (MS1) (M–ON linkage isomer) was typically generated in  $[\text{MX}_5\text{NO}]^{2-}$  ions by irradiation with light matching the lower energy electronic transition at low temperatures [5,9,11,14] and, in some cases, it was required UV irradiation to generate the metastable state MS2 in  $[\text{M}(\text{CN})_5\text{NO}]^{n-}$  ( $M = \text{Os}, \text{Mn}$ ) [14,20]. New states in  $\text{K}[\text{IrCl}_5\text{NO}]$  were then explored by sample irradiation at 77 K using a wide range of wavelengths (266–638 nm).

Fig. 1(a) shows the infrared spectra of  $\text{K}[\text{IrCl}_5\text{NO}]$  at 77 K in the ground state (GS). The resulting spectra after simultaneous irradiation with laser lines 413 and 406 nm are shown in Fig. 1(b), and that using 350 and 356 nm lines are in Fig. 1(c). A relatively weak new band at  $1812\text{ cm}^{-1}$  (Fig. 1) was observed when irradiated with light in the range from 308 to 413 nm and it was found to reach a



**Fig. 1.** Infrared spectrum of  $\text{K}[\text{IrCl}_5\text{NO}]$  at 77 K: (a) in the ground state, (b) after simultaneous irradiation with 413 and 406 nm laser lines, (c) after irradiation with  $\text{Kr}^+$  350 and 356 nm laser lines, and (d) de-exciting of the metastable state by additional irradiation with  $\text{Ar}^+$  488.0 nm laser line.

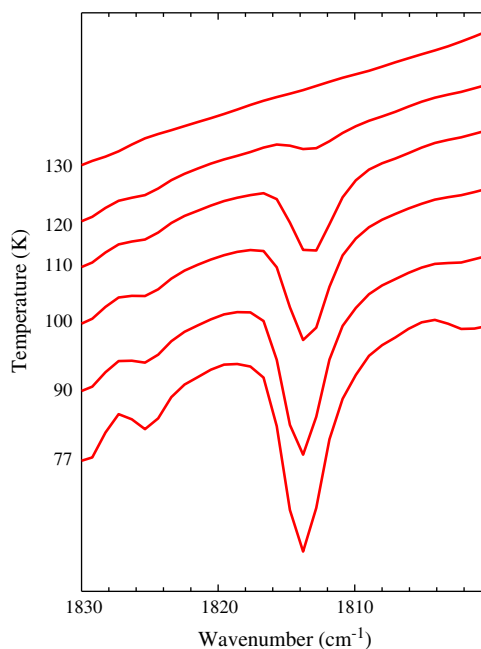
maximum intensity when the GS sample was alternatively excited with 350 and 356 nm lines of a  $\text{Kr}^+$  laser.

Fig. 1(d) shows the decay of the  $1812\text{ cm}^{-1}$  band as an example of deactivation by an additional irradiation by using the 488.0 nm line on a sample which was previously excited with the 350 and 356 nm lines. In our specific case it was found that the excited sample decays after subsequent irradiation with light in the 450–680 nm spectral region.

Fig. 2 shows the deactivation of the  $1812\text{ cm}^{-1}$  band by thermal heating, analogous to what was found in irradiation using the lines in the 450–680 nm range. It starts to decay at 90 K and was completely vanished at 130 K.

The band at  $1812\text{ cm}^{-1}$  was assigned to the MS1 by comparison with the wavenumber position observed in other similar transition metal nitrosyls [5,9,11,14]. It was attributed to the M–ON linkage isomer. Due to the relatively poor conversion to MS1, no other new band was detected in the spectra.

In conclusion in this manuscript an excited metastable state is reported for  $[\text{IrCl}_5\text{NO}]^{-1}$  ion. The new state, first reported here for transition metal nitrosyl of group 9, was generated by irradiation of sample at 77 K with light of 308 to 413 nm. The new band was detected by infrared spectroscopy by comparing the spectra before and after irradiation. It grows at  $1812\text{ cm}^{-1}$  after irradiation of  $\text{K}[\text{IrCl}_5\text{NO}]$ . The metastable nature of the excited state was characterized by thermal heating decay at 90 K or by subsequent irradiation with light in the 308–420 nm range. The band at  $1812\text{ cm}^{-1}$  was assigned to a metastable state 1 (or an IrON linkage isomer) for comparison with the band position reported for other transition metal nitrosyls. It is important to note that the metastable population, which is observed much stronger in other transition metal nitrosyls of group 8 ( $[\text{MX}_5\text{NO}]^{-n}$ ,  $M = \text{Fe}, \text{Ru}, \text{Os}$ ;  $X = \text{Cl}, \text{CN}$ ) [5,9,11,14], is in  $\text{K}[\text{IrCl}_5\text{NO}]$  weaker in spite of the similar  $\{\text{IrNO}\}^6$  electronic configuration. It is concluded that a small population prevents the detection of other weaker vibrational modes than the  $\nu(\text{NO})_{\text{MS1}}$ . Moreover, the metastable state generated in  $[\text{IrCl}_5\text{NO}]^{-1}$  ion opens the possibility to find similar behavior in other nitrosyl of transition metal of group 9.



**Fig. 2.** Thermal deactivation of  $1812\text{ cm}^{-1}$  band (MS1). Excitation achieved by excimer laser 347 nm line.

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## References

- [1] NO is responsible of endothelium-dependent vascular relaxation. It is also involved in central and peripheral neurotransmission, i.e., the defense mechanisms of the body as utilized by macrophages and many other cells, in: M. Feelisch, J.S. Stamler (Eds.), *Methods in Nitric Oxide Research*, John Wiley and Sons, Chichester, England, 1996.
- [2] The higher oxidation state of iridium reduce the NO back bonding (mainly  $\pi^*(\text{NO})$  population), therefore the wavenumber of this vibration is the largest as consequence of high NO bond order.
- [3] U. Hauser, V. Oestreich, H.D. Rohrweck, On optical dispersion in transparent molecular systems. Part I *Z. Phys. A280* (1977) 17; *ibid* Part II *Z. Phys. A280* (1977) 125; *ibid* Part III *Z. Phys. A284* (1978) 9.
- [4] J.A. Güida, O.E. Piro, P.J. Aymonino, Polarized infrared absorption spectra of  $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]\cdot 2\text{H}_2\text{O}$  with part of the anions in the electronically excited metastable state, *Solid State Commun.* 57 (1986) 175–178.
- [5] Th. Woike, W. Krasser, P.S. Bechthold, S. Haussühl, Investigation of the metastable state of  $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]\cdot 2\text{H}_2\text{O}$  by optical spectroscopy. Part I *Solid State Commun.* 45 (1983) 499; *ibid* Part II *Solid State Commun.* 45 (1983) 503.
- [6] M.D. Carducci, M.R. Pressprich, P. Coppens, Diffraction studies of photoexcited crystals: metastable nitrosyl-linkage isomers of sodium nitroprusside, *J. Am. Chem. Soc.* 119 (1997) 2669.
- [7] H. Paulsen, V. Rusanov, R. Benda, C. Herta, V. Schünemann, C. Janiak, T. Dorn, A.I. Chumakov, H. Winkler, A.X. Trautwein, Metastable isonitrosyl structure of the nitroprusside anion confirmed by nuclear inelastic scattering, *J. Am. Chem. Soc.* 124 (2002) 3007–3011.
- [8] Th. Woike, W. Krasser, P.S. Bechthold, S. Haussühl, Extremely long-living metastable state of  $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]\cdot 2\text{H}_2\text{O}$  single crystals: optical properties, *Phys. Rev. Lett.* 53 (1984) 1767–1770.
- [9] Th. Woike, H. Zöllner, W. Krasser, S. Haussühl, Raman spectroscopic and differential scanning calorimetric studies of the light induced metastable states in  $\text{K}_2[\text{RuCl}_5\text{NO}]$ , *Solid State Commun.* 73 (1990) 149–152.
- [10] Th. Woike, S. Haussühl, Infrared-spectroscopic and differential scanning calorimetric studies of the two light-induced metastable states in  $\text{K}_2[\text{Ru}(\text{NO})_2(\text{OH})\text{NO}]$ , *Solid State Commun.* 86 (1993) 333–337.
- [11] J.A. Güida, O.E. Piro, P.S. Schaiquevich, P.J. Aymonino, Infrared absorption spectra of electronically excited long-lived metastable states in  $\text{Na}_2[\text{Ru}(\text{CN})_5\text{NO}]\cdot 2\text{H}_2\text{O}$ , *Solid State Commun.* 101 (1997) 471–475.
- [12] D.V. Fomitchev, P. Coppens, T. Li, K.A. Bagley, L. Chen, G.B. Richter-Addo, Photo-induced metastable linkage isomers of ruthenium nitrosyl porphyrins, *Chem. Commun.* (1999) 2013–2014.
- [13] Y. Morioka, A. Ishikawa, H. Tomizawa, E. Miki, Light-induced metastable states in nitrosyl-ruthenium complexes containing ethylenediamine and oxalate ion ligands, *J. Chem. Soc. Dalton Trans.* (2000) 781–786.
- [14] J.A. Güida, O.E. Piro, P.J. Aymonino, Infrared absorption spectra of sodium pentacyanonitrosylsulfate(II) dihydrate in two excited electronic metastable states, *Inorg. Chem.* 34 (1995) 4113–4116.
- [15] J.H. Enemark, R.D. Feltham, Principles of structure, bonding, and reactivity for metal nitrosyl complexes, *Coord. Chem. Rev.* 13 (1974) 339–406.
- [16] P.S. Schaiquevich, J.A. Güida, P.J. Aymonino, Low temperature infrared spectra of photoexcited ( $\eta^5$ -cyclopentadienyl)nitrosylnickel,  $[\text{Ni}(\text{C}_5\text{H}_5)\text{NO}]$ , *Inorg. Chim. Acta* 303 (2000) 277–281.
- [17] D.V. Fomitchev, T.R. Furlani, P. Coppens, Combined X-ray diffraction and density functional study of  $[\text{Ni}(\text{NO})(\eta^5\text{-Cp}^*)]$  in the ground and light-induced metastable state, *Inorg. Chem.* 37 (1998) 1519–1526.
- [18] D. Schaniel, T. Woike, B. Delley, D. Biner, K.W. Krämer, H.-U. Güdel, Generation of one light-induced metastable nitrosyl linkage isomer in  $[\text{Pt}(\text{NH}_3)_4\text{Cl}(\text{NO})]\text{Cl}_2$  in the red spectral range, *Phys. Chem. Chem. Phys.* 9 (2007) 5149–5157.
- [19] P. Coppens, I. Novozhilova, A. Kovalevsky, Photoinduced linkage isomers of transition-metal nitrosyl compounds and related complexes, *Chem. Rev.* 102 (2002) 861–883.
- [20] (a) D.V. Fomitchev, I. Novozhilova, P. Coppens, Photo-induced linkage isomerism of transition metal nitrosyl and dinitrogen complexes studied by photocrystallographic techniques, *Tetrahedron* 56 (2000) 6813–6820; (b) A.Y. Kovalevsky, K.A. Bagley, P. Coppens, The first photocrystallographic evidence for light-induced metastable linkage isomers of ruthenium sulfur dioxide complexes, *J. Am. Chem. Soc.* 124 (2002) 9241–9248.
- [21] D. Schaniel, T. Woike, Necessary conditions for the photogeneration of nitrosyl linkage isomers, *Phys. Chem. Chem. Phys.* 11 (2009) 4391–4395.
- [22] M.J. Cleare, H.P. Fritz, W.P. Griffith, Vibrational spectra of nitrosyl and carbonyl complexes – I. Nitrosylpentahalogeno complexes of osmium, ruthenium and iridium, *Spectrochim. Acta A Mol. Biomol. Spectrosc.* 28 (1972) 2013–2018.