

NITRILE HYDROLYSIS INDUCED BY OXIDATION OF A DINUCLEAR DIRUTHENIUM COMPLEX

NOEMÍ D. LIS DE KATZ, FLORENCIA FAGALDE and
 NÉSTOR E. KATZ*

Instituto de Química Física, Facultad de Bioquímica, Química y Farmacia,
 Universidad Nacional de Tucumán, Ayacucho 491, 4000 San Miguel de
 Tucumán, Argentina

(Received 4 January 1995; accepted 27 January 1995)

Abstract—On oxidation of the dinuclear complex $[(\text{terpy})(\text{bipy})\text{Ru}^{\text{II}}(4\text{-pyCN})\text{Ru}^{\text{II}}(\text{NH}_3)_5]^{4+}$ (terpy = 2,2':6',2''-terpyridine, bipy = 2,2'-bipyridine, 4-pyCN = 4-cyanopyridine) by excess $\text{S}_2\text{O}_8^{2-}$ in an aqueous solution a mixed-valent species is formed, which undergoes nitrile hydrolysis according to the reaction: $[(\text{terpy})(\text{bipy})\text{Ru}^{\text{II}}(4\text{-pyCN})\text{Ru}^{\text{III}}(\text{NH}_3)_5]^{5+} + \text{H}_2\text{O} \rightarrow [(\text{terpy})(\text{bipy})\text{Ru}^{\text{II}}(4\text{-pyC(O)NH})\text{Ru}^{\text{III}}(\text{NH}_3)_5]^{4+} + \text{H}^+$ [with 4-pyC(O)NH = isonicotinamido]. The observed rate constant $k_{\text{h}} = 5.8 \times 10^{-3} \text{ s}^{-1}$ at 25.0°C, pH = 3.3 (CF_3COOH), $\mu = 0.1 \text{ M}$ (KCl), is *ca* twice as high as that of the mononuclear complex $[(4\text{-pyCN})\text{Ru}^{\text{III}}(\text{NH}_3)_5]^{3+}$, but *ca* half that of the dinuclear species $(\text{CN})_5\text{Fe}^{\text{II}}(4\text{-pyCN})\text{Ru}^{\text{III}}(\text{NH}_3)_5$ and *ca* four times lower than that of the dinuclear complex $[(\text{NH}_3)_5\text{Ru}^{\text{III}}(4\text{-pyCN})\text{Ru}^{\text{III}}(\text{NH}_3)_5]^{6+}$, indicating that the catalytic effect of a $\text{Ru}^{\text{III}}(\text{NH}_3)_5$ group on the rate of nitrile hydrolysis is somewhat enhanced by a $\text{Ru}^{\text{II}}(\text{terpy})(\text{bipy})$ moiety, due to an inductive effect, although to a less extent than by a $\text{Fe}^{\text{II}}(\text{CN})_5$ or a $\text{Ru}^{\text{III}}(\text{NH}_3)_5$ group, probably because of the π -back-bonding ability of Ru^{II} , which makes the nitrile carbon atom of 4-pyCN less susceptible to the nucleophilic attack of a water molecule.

The metal-catalysed conversion of nitriles to amides is a subject of interest in relation to amide syntheses of industrial and biological relevance.^{1–3} In particular, nitriles undergo hydrolysis when bonded to a $\text{Ru}^{\text{III}}(\text{NH}_3)_5$ group at least 10^6 times faster than when coordinated to a $\text{Ru}^{\text{II}}(\text{NH}_3)_5$ group.⁴ Several related studies on dinuclear ruthenium complexes with 4-pyCN as a bridging ligand (4-pyCN = 4-cyanopyridine)^{5,6} and mononuclear ruthenium complexes with 4-pyCN derivatives⁷ have shown that the rate of hydrolysis of the nitrile group of 4-pyCN is increased on protonation, derivatization or metallation of the pyridine N site of 4-pyCN.

Recently,⁸ we have described the preparation and characterization of a dinuclear complex, of formula $[(\text{terpy})(\text{bipy})\text{Ru}^{\text{II}}(4\text{-pyCN})\text{Ru}^{\text{II}}(\text{NH}_3)_5]^{4+}$, (**1**) (with terpy = 2,2':6',2''-terpyridine, bipy = 2,2'-bipyridine), where 4-pyCN acts as a good electronic con-

ductor between two metal sites of very different redox properties. The corresponding asymmetric mixed-valent species, $[(\text{terpy})(\text{bipy})\text{Ru}^{\text{II}}(4\text{-pyCN})\text{Ru}^{\text{III}}(\text{NH}_3)_5]^{5+}$ (**2**) has been obtained by oxidation of **1** with Br_2 vapour in MeCN solutions.⁹ In this work, the kinetics of nitrile hydrolysis of **2**, prepared now by $\text{S}_2\text{O}_8^{2-}$ oxidation of **1** in aqueous acidic solutions, has been investigated in order to elucidate the influence of a $\text{Ru}^{\text{II}}(\text{terpy})(\text{bipy})$ moiety on the catalytic effect of the $\text{Ru}^{\text{III}}(\text{NH}_3)_5$ group and to make comparisons with related systems.

EXPERIMENTAL

The PF_6^- salt of **1** was prepared as described previously⁸ and purified by column chromatography using SP-Sephadex C-25. The hydrolysis product, $[(\text{terpy})(\text{bipy})\text{Ru}^{\text{II}}(4\text{-pyC(O)NH})\text{Ru}^{\text{III}}(\text{NH}_3)_5]^{4+}$ (**3**) was obtained as a PF_6^- salt by

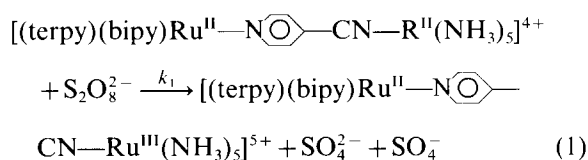
* Author to whom correspondence should be addressed.

$S_2O_8^{2-}$ oxidation of **1** in CF_3SO_3H (10^{-3} M). All chemicals were reagent grade and used as received. Tri-distilled water was used for all kinetic determinations.

A Luftman-reliance II pH meter was used for pH measurements, with a precision of ± 0.05 pH units. IR spectra were recorded as KBr pellets on a Perkin-Elmer model 983G spectrophotometer. UV-vis spectra and kinetic measurements were carried out with a Shimadzu UV-160A spectrophotometer. The hydrolysis reaction was studied at pseudo-first-order conditions ($[complex] = 2.0 \times 10^{-4}$ M, $[S_2O_8^{2-}] = 2.0 \times 10^{-3}$ M), $T = 25.0^\circ C$, pH between 1 and 7 (with adequate buffers) and $\mu = 0.1$ M (KCl). Triplicate runs were made at each value of pH, and the rate constants were obtained from least-squares fits of $\ln(A_t - A_\infty)$ vs. t , which were linear up to three half-lives.

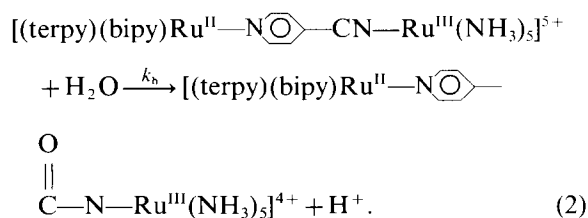
RESULTS AND DISCUSSION

In previous work,⁸ we demonstrated that 4-pyCN can act as a bridging ligand in the dinuclear species **1**, where the pyridine nitrogen of 4-pyCN is coordinated to a $Ru^{II}(terpy)(bipy)$ group and the nitrile N to a $Ru^{II}(NH_3)_5$ group. In aqueous solution, peroxydisulphate ($S_2O_8^{2-}$) can oxidize the ruthenium bonded to ammine ligands, but not that bonded to polypyridine ligands. The rate of the oxidative process in which **1** is converted into **2**:



has been determined by stopped-flow techniques.¹⁰ The measured value of $k_1 = 3.3 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ (at $25.0^\circ C$, 0.1 M KCl and $pH = 4.84$) and the products obtained are consistent with previous studies of oxidation of ruthenium(II) amines with peroxydisulphate.¹¹

In this work, we have investigated the subsequent hydrolysis reaction in which **2** is converted into **3**:



The identity of the product is confirmed by comparing the IR spectra of the PF_6^- salts of **1** and **3**,

as shown in Fig. 1. In effect, the nitrile stretching band, which appears at 2174 cm^{-1} in **1**,⁸ disappears completely in **3**. Besides, a new and intense band appears in **3** at 1398 cm^{-1} , which can be ascribed to amide vibrations, while the ammonia symmetric deformation frequency, $\delta_{sym}(NH_3)$, shifts from 1287 cm^{-1} in **1**—indicative of a $Ru^{II}(NH_3)_5$ group—to 1307 cm^{-1} in **3**—indicative of a $Ru^{III}(NH_3)_5$ group.⁵

Since reaction (2) is slower than (1) by almost three orders of magnitude, k_h can be measured by conventional spectrophotometric techniques. Fig. 2 shows the consecutive spectra obtained upon mixing **1** ($C = 2.5 \times 10^{-4}$ M) and $S_2O_8^{2-}$ ($C = 2.5 \times 10^{-3}$ M) at $25.0^\circ C$, 0.1 M KCl, $pH = 3.0$ (CF_3COOH). During a time-scale of several minutes, **2** is converted into **3**, as evidenced by the shifting of $\lambda_{max} = 440$ (absorption maximum of **2**) to 427 nm (absorption maximum of **3**); an isosbestic point at $\lambda = 410$ nm being obtained. The spectrum of the final product is coincident with that obtained when dissolving the solid PF_6^- salt of **3** in CF_3COOH (10^{-3} M). Moreover, the metal-to-metal charge transfer (MMCT) or intervalence band of **2**, which appears at $\lambda_{max} \cong 680$ nm under the same conditions stated above (and detected at a similar wavelength in MeCN solutions),⁹ is shifted to a value of $\lambda_{max} \leq 650$ nm in **3**, being masked by the long tail of the metal-to-ligand charge transfer (MLCT) band corresponding to $d_\pi(Ru^{II}) \rightarrow \pi^*$ ($terpy, bipy$) transitions. These changes can be accounted for by the difference in redox potentials of both metal sites in **2** and **3**. Since isonicotinamido-bridged complexes exhibit higher redox asymmetry than 4-cyanopyridine-bridged complexes,⁶ a higher value of energy is expected for the absorption maximum of its MMCT band.¹²

By fixing the measuring wavelength at 440 nm (absorption maximum of **2**), we could measure k_h under pseudo-first-order conditions: $[complex] = 2.0 \times 10^{-4}$ M and $[S_2O_8^{2-}] = 2.0 \times 10^{-3}$ M. A value of $k_h = 5.8 \times 10^{-3} \text{ s}^{-1}$ was obtained at $25.0^\circ C$, $pH = 3.3$ (CF_3COOH) and $\mu = 0.1$ M (KCl). This nitrile hydrolysis rate constant is reproducible to $\pm 5\%$, and is almost pH-independent between values of $pH = 2.0$ (CF_3COOH) and $pH = 6.5$ (buffer of $NaOH/KH_2PO_4$). At $pH = 1.0$ (CF_3COOH), $k_h = 7.4 \times 10^{-3} \text{ s}^{-1}$, an increase which can be due to the onset of protonation of the isonicotinamide group, for which an upper limit of $pK_a = 0.6$ has been estimated.⁶

The value of k_h for reaction (2) is *ca* double that of the mononuclear complex $[(4\text{-pyCN})Ru^{III}(NH_3)_5]^{3+}$ ($k_h = 2.85 \times 10^{-3} \text{ s}^{-1}$),⁵ indicating that the catalytic effect of a $Ru^{III}(NH_3)_5$ moiety on the rate of nitrile hydrolysis is enhanced by coordination of the pyridine N of 4-pyCN to a Ru^{II}

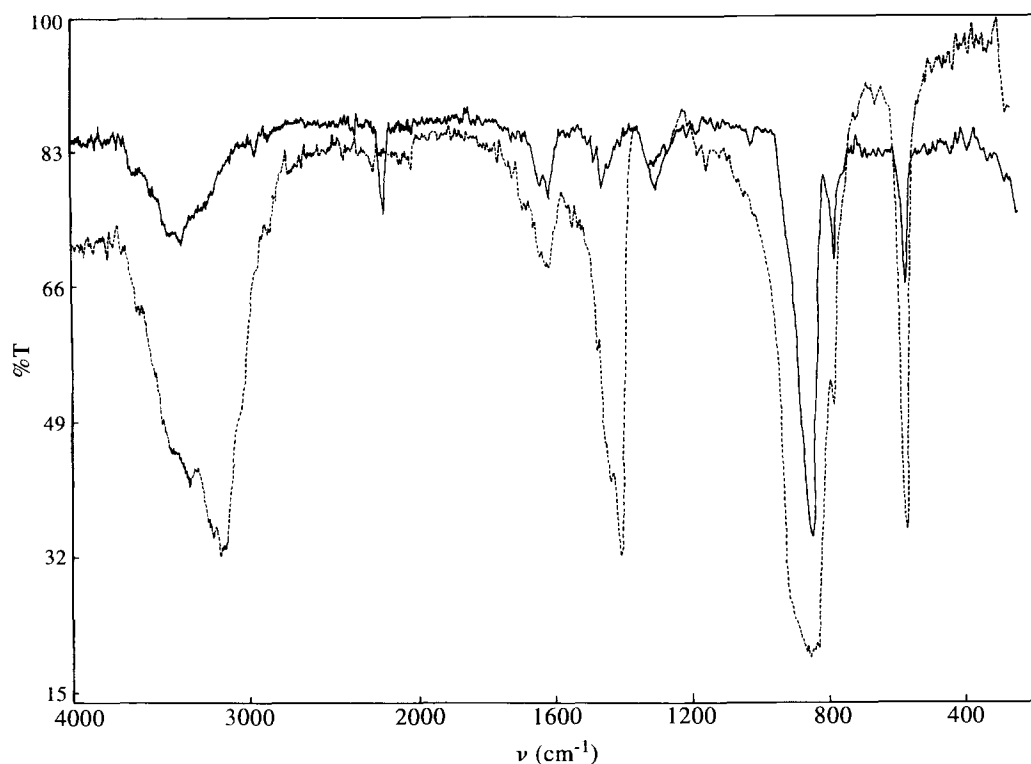


Fig. 1. IR spectra (as KBr pellets) of: (—) $[(\text{terpy})(\text{bipy})\text{Ru}^{\text{II}}(4\text{-pyCN})\text{Ru}^{\text{II}}(\text{NH}_3)_5](\text{PF}_6)_4$; (---) $[(\text{terpy})(\text{bipy})\text{Ru}^{\text{II}}(4\text{-pyC(O)NH})\text{Ru}^{\text{III}}(\text{NH}_3)_5](\text{PF}_6)_4$.

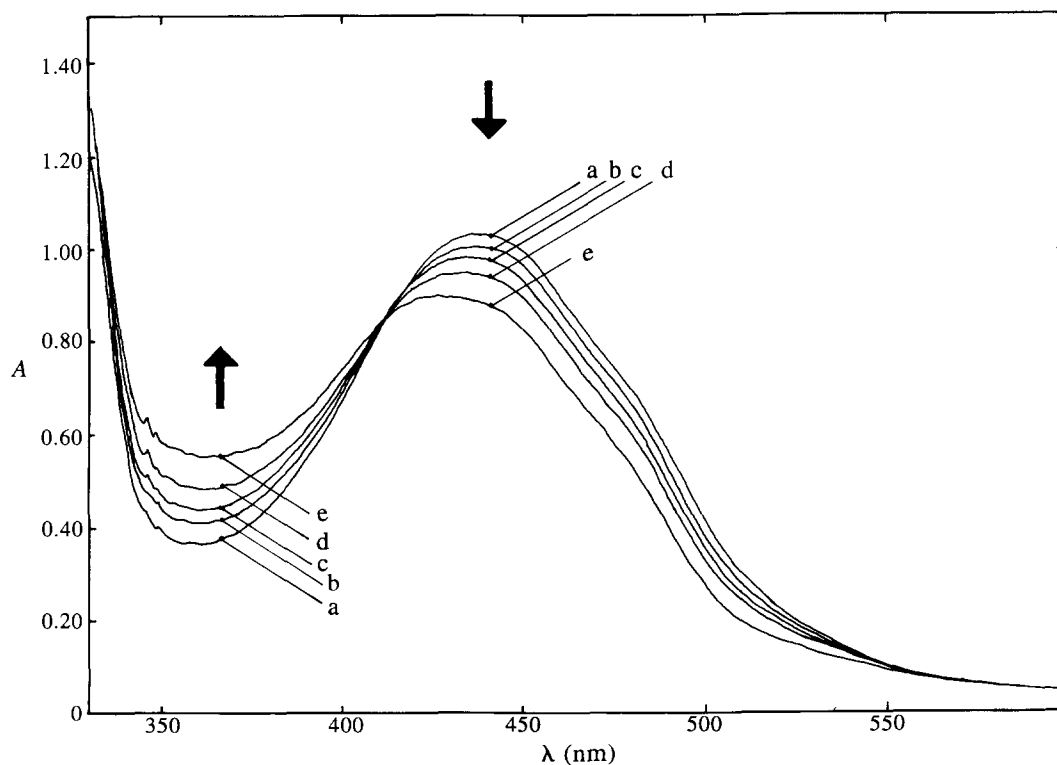


Fig. 2. Consecutive visible spectra obtained upon mixing of aqueous solutions of $[(\text{terpy})(\text{bipy})\text{Ru}^{\text{II}}(4\text{-pyCN})\text{Ru}^{\text{II}}(\text{NH}_3)_5]^{4+}$ ($C = 2.5 \times 10^{-4}$ M) and $\text{S}_2\text{O}_8^{2-}$ ($C = 2.5 \times 10^{-3}$ M) at 25.0°C , $\text{pH} = 3.0$ (CF_3COOH), 0.1 M KCl. Recording times were: (a) 30, (b) 75, (c) 115, (d) 190 and (e) 1830 s.

(terpy)(bipy) group, probably because of an inductive effect. However, k_h is *ca* half that of the dinuclear species $(\text{CN})_5\text{Fe}^{\text{II}}(4\text{-pyCN})\text{Ru}^{\text{III}}(\text{NH}_3)_5$ ($k_h = 13.1 \times 10^{-3} \text{ s}^{-1}$)⁵ and *ca* four times lower than that of $[(\text{NH}_3)_5\text{Ru}^{\text{III}}(4\text{-pyCN})\text{Ru}^{\text{III}}(\text{NH}_3)_5]^{6+}$ ($k_h = 25.0 \times 10^{-3} \text{ s}^{-1}$),⁶ indicating that the π -back-bonding ability of Ru^{II} bonded to terpy and bipy is greater than that of a $\text{Fe}^{\text{II}}(\text{CN})_5$ group and makes the nitrile carbon atom of 4-pyCN less susceptible to the nucleophilic attack of a water molecule. In basic solution, however, the catalytic effect of Ru^{II} bonded to polypyridines may be enhanced.¹³

To conclude, for the hydrolysis reaction (2) in acidic conditions, the electronic effect is dominant over the inductive effect, pointing to a good electronic communication between both ruthenium centres in the mixed-valent species **2**, with 4-pyCN as a bridging ligand.

Acknowledgements—We thank Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET, Argentina) and Consejo de Investigaciones de la Universidad Nacional de Tucumán (CIUNT, Argentina) for financial help. F. F. thanks CONICET for a graduate fellowship. N. E. K. is a Member of the Research Career (CONICET).

REFERENCES

1. C. M. Jensen and W. C. Troglor, *J. Am. Chem. Soc.* 1986, **108**, 723.
2. S.-I. Murahashi, T. Naota and E. Saito, *J. Am. Chem. Soc.* 1986, **108**, 7846.
3. R. Breslow, R. Fairweather and J. Keana, *J. Am. Chem. Soc.* 1967, **89**, 2135.
4. A. W. Zanella and P. C. Ford, *Inorg. Chem.* 1975, **14**, 42.
5. H.-Y. Huang, W.-J. Chen, C.-C. Yang and A. Yeh, *Inorg. Chem.* 1991, **30**, 1862.
6. M. H. Chou, C. Creutz and N. Sutin, *Inorg. Chem.* 1992, **31**, 2318.
7. Z. Naal, E. Tfouni and A. V. Benedetti, *Polyhedron* 1994, **13**, 133.
8. A. Ben Altabef, S. B. Ribotta de Gallo, M. E. Folquer and N. E. Katz, *Inorg. Chim. Acta* 1991, **188**, 67.
9. F. Fagalde and N. E. Katz, *Polyhedron* 1995, **14**, 1213.
10. F. Fagalde, V. Pouse and J. A. Olabe, unpublished data.
11. U. Fürholz and A. Haim, *Inorg. Chem.* 1987, **26**, 3243.
12. C. Creutz, *Prog. Inorg. Chem.* 1983, **30**, 1.
13. N. E. Katz, C. Creutz and N. Sutin, *Inorg. Chem.* 1988, **27**, 1687.