*Russian Journal of General Chemistry, Vol. 74, No. 5, 2004, pp. 651–654. Translated from Zhurnal Obshchei Khimii, Vol. 74, No. 5, 2004, pp. 713–716.*

# Chemistry of Ruthenium Polypyridine Complexes: IX.[1] Nitro–Nitrosyl Equilibrium in *cis*-$[Ru(2,2'\text{-}bpy)_2(L)NO_2]^+$ Complexes

**A. Yu. Ershov, P. V. Kucheryavyi, and A. B. Nikol'skii**

*St. Petersburg State University, St. Petersburg, Russia*

Received October 2, 2003

**Abstract**—Ruthenium(II) bisbipyridyl complexes *cis*-$[Ru(bpy)_2(L)NO_2](BF_4)$ (bpy is 2,2'-bipyridyl) with 4-substituted pyridine ligands L = 4-(Y)py (Y = $NH_2$, Me, Ph, and CN) were obtained. The equilibrium constants of the reversible nitro–nitrosyl transition $[Ru(bpy)_2(L)NO_2]^+ + 2H^+ \rightleftarrows [Ru(bpy)_2(L)NO]^{3+} + H_2O$ were measured in solutions with pH 1.5–8.5 (ionic strength 0.4). The constants correlate with the protonation constants of free ligands 4-(Y)py.

Reactions of reversible inner-sphere conversion of coordinated nitrite ion to nitrosyl group and of decomposition of nitrosyl group with azide ion are widely used in preparative chemistry of ruthenium(II) polypyridine complexes for purposeful synthesis of mononuclear and polynuclear compounds [2–4]. The interest in reactions involving coordinated nitrite ions and nitrosyl groups is associated by the discovery of the key role NO plays in functioning vascular, immune, and nervous systems of mammals [5–7] and by the ecological impact of nitrogen(II) and nitrogen(IV) oxides [7–9]. One of approaches to solving practical problems of the chemistry of nitrogen(II) and nitrogen(IV) oxides is connected with the possibility of electrophilic activation of NO by its coordination into transition metal complexes [8, 9]. Nitrosyl group exhibits electrophilic properties in ruthenium(II) complexes if other π-acceptor ligands, such as $CN^-$, pyridine (py), and 2,2'-bipyridyl (bpy), are present in the inner sphere. The electrophilic properties of the nitrosyl group in ruthenium(II) polypyridine complexes were revealed and investigated in [2, 3, 10–12]. We showed in [13, 14] that in *cis*-$[Ru(bpy)_2(NO)(X)]^{2+}$ (X = Cl, Br, $NO_2$) complexes the rate constant of NO reaction with $OH^-$ ions [scheme (1)] increases in the series X = $Cl^- < Br^- < NO_2^-$, which is attributable to the enhancing π-acceptor power of the acido ligands. However, quantitative data describing the electrophilic properties of transition metal nitrosyl complexes as a function of the properties of inner-sphere ligands are absent.

$$[Ru(bpy)_2(NO)(X)]^{2+} + 2OH^- \rightleftarrows [Ru(bpy)_2(NO_2)(X)] + H_2O. \qquad (1)$$

The aim of the present work was to trace the relationship between the electronic characteristics of ligand L and the electrophilic properties of the coordinated nitrosyl group in bisbipyridyl complexes *cis*-$[Ru(bpy)_2(L)(NO)]^{3+}$. For the measure of electrophilicity we took the constant of reverse equilibrium (1) between nitrosyl and nitro complexes in aqueous solutions [scheme (2)].

$$[Ru(bpy)_2(L)(NO_2)]^+ + 2H^+ \rightleftarrows [Ru(bpy)_2(L)(NO)]^{3+} + H_2O. \qquad (2)$$

The objects of the study were nitro complexes *cis*-$[Ru(bpy)_2(L)NO_2]^+$ (**I**) with 4-substituted pyridine ligands L = 4-(Y)py (Y = CN, H, Ph, Me, and $NH_2$), the electronic parameters of substituents in which are characterized by the Hammett constants or protonation constants of the pyridine nitrogen atom [15].

Of nitro complexes **I**, *cis*-$[Ru(bpy)_2(py)(NO_2)]^+$ (Y = H) is the only reported previously [2]. Complexes **I** with Y = CN, Ph, Me, and $NH_2$ we obtained for the first time. Their elemental analyses are given in Table 1. As with chloride complexes *cis*-$[Ru(bpy)_2 \cdot (L)(Cl)]^+$ [1], the synthesis of compounds **I** is based on irreversible destruction of the coordinated nitrosyl group by azide ion [3] in methanol or other weakly coordinated solvents (Solv) [scheme (3)] and on replacement of the labile solvent molecule by a ligand with a stronger donor power [scheme (4)].

$$[Ru(bpy)_2(NO)(NO_2))]^{2+} + N_3^- + Solv \longrightarrow [Ru(bpy)_2(Solv)(NO_2)]^+ + N_2 + N_2O, \qquad (3)$$

$$[Ru(bpy)_2(Solv)(NO_2))]^+ + L \longrightarrow [Ru(bpy)_2(L)(NO_2)]^+ + Solv. \qquad (4)$$

---

[1] For communication VIII, see [1].

**Table 1.** Elemental analyses of complexes *cis*-$[Ru(bpy)_2(L)NO_2]^+$

| Complex | Yield, % | Found, % | | | Formula | Calculated | | |
|---|---|---|---|---|---|---|---|---|
| | | C | H | N | | C | H | N |
| $[Ru(bpy)_2(4\text{-NH2py})(NO2)](BF4)\cdot 2H_2O$ | 65 | 44.50 | 3.45 | 14.55 | $C_{25}H_{22}N_7BF_4O_2Ru\cdot 2H_2O$ | 44.39 | 3.88 | 14.50 |
| $[Ru(bpy)_2(4\text{-Mepy})(NO2)](BF4)\cdot H_2O$ | 60 | 47.02 | 3.79 | 12.70 | $C_{26}H_{23}N_6BF_4O_2Ru\cdot H_2O$ | 47.50 | 3.83 | 12.78 |
| $[Ru(bpy)_2(4\text{-Phpy})(NO2)](BF4)\cdot H_2O$ | 66 | 52.01 | 3.75 | 11.73 | $C_{31}H_{25}N_6BF_4O_2Ru\cdot H_2O$ | 51.75 | 3.78 | 11.68 |
| $[Ru(bpy)_2(4\text{-CNpy})(NO2)](BF4)\cdot H_2O$ | 55 | 46.22 | 3.31 | 14.45 | $C_{26}H_{20}N_7BF_4O_2Ru\cdot H_2O$ | 46.72 | 3.32 | 14.67 |

**Table 2.** Band maxima and extinction coefficients in the electronic absorption spectra of complexes $[Ru(bpy)_2(NO_2)]^+$ [L = 4-(Y)py], constants of equilibrium (2), p$K_a$ of free ligands 4-(Y)py at 298 K, and ν(NO) frequencies in complexes $[Ru(bpy)_2(L)(NO)](BF_4)_3$

| Y | $\lambda_{max}$, nm ($\varepsilon_{NO_2}$, l mol$^{-1}$ cm$^{-1}$)$^a$ | $K\times 10^{-6}$, l$^2$ mol$^{-2}$ | pH$_c^b$ | p$K_a$[4-(Y)py] [15] | ν(NO), cm$^{-1c}$ |
|---|---|---|---|---|---|
| CN | 406 [10 400] | 0.34 ± 0.05 | 2.78 | 1.35 | 1937 |
| H | 415 [7200] | 8.6 ± 0.08 | 3.48 | 5.23 | 1945 |
| Ph | 403 [9500] | 9.4 ± 1.3 | 3.52 | 5.35 | 1934 |
| Me | 420 [7800] | 20 ± 3 | 3.74 | 6.26 | 1935 |
| $NH_2$ | 426 [7900] | 1900 ± 300 | 4.64 | 9.31 | 1941 |

[a] In sodium citrate buffer. [b] The pH value at which the concentrations of nitro and nitrosyl complexes [scheme (2)] are equal to each other. [c] In KBr.

However, the synthesis of compounds **I** is complicated by the fact that, unlike chloride ligand, nitrite ion can coordinate in the ambidentate fashion and thus gives a mixture of nitro [reaction (4)] and nitrite complexes [reaction (5)].

$$[Ru(bpy)_2(Solv)(NO_2))]^+ + L$$
$$\longrightarrow [Ru(bpy)_2(L)(ONO)]^+ + Solv. \qquad (5)$$

According to [16], the nitro–nitrite isomerism in the complex $[Ru(bpy)_2(NO)(NO_2)]^{2+}$ occurs even at room temperature, and its rate increases with temperature. The IR spectra of nitro complexes **I** contain bands at 1320, 1290, and 830 cm$^{-1}$, which are characteristic of the nitrite ion coordinated through the nitrogen atom [$\nu_{as}(NO_2)$, $\nu_s(NO_2)$, and δ(ONO), respectively]. The ν(N=O) and ν(N–O) bands in the region of 1480 and 990 cm$^{-1}$ are characteristic of nitrite complexes [10]. To increase the yield of nitro complexes **I**, we used a 3–4-fold excess of ligand L = 4-(Y)py and reduced as much as possible the time of reactions (3) and (4), controlling the yield of their products by electronic absorption spectra. In the course of the synthesis, the dark red color ($\lambda_{max}$ 445 nm) of the solvation complex $[Ru(bpy)_2(Solv)\cdot(NO_2)]^+$ formed by reaction (3) changed to the lighter orange-red color of compound **I** ($\lambda_{max}$ 400–425 nm, depending on L). Compared to related chloride complexes, nitro complexes **I** are stronger retained by $Al_2O_3$, which results in additional losses in the course of their chromatographic purification. Therefore, the final yield of complexes **I** after synthesis and purification was 60 ± 5%.

The equilibrium constants of reaction (2) were measured in freshly prepared aqueous solutions, the state of complexes **I** being controlled by electronic absorption spectra. The resulting constants are given in Table 2 alongside with the characteristics of the electronic absorption spectra of complexes **I** in the visible region. Unlike the position of the long-wave absorption band in the spectrum, the constants of equilibrium (2) for the series of complexes **I** strongly depend on the nature of substituent Y in the pyridine ligand 4-(Y)py. As the donor power of Y increases, the stability of the *cis*-nitro group in 4-(Y)py decreases. In other words, the nitrosyl group become more stable and less electrophilic in the series Y = CN < H ~ Ph < Me < $NH_2$, as evidently illustrated by the pH values of the solutions (pH$_s$, Table 2), at which the concentrations of nitro and nitrosyl complexes in equilibrium (2) are equal to each other.

Bottomley *et al.* [18, 19] have summarized data on reactions of transition metal nitrosyl complexes with nucleophilic reagents and proposed an empirical criterion according to which electrophylic properties are characteristic of complexes whose ν(NO) is higher than 1886 $cm^{-1}$. The higher is ν(NO), the higher is the electrophilic reactivity of the coordinated nitrosyl group. In the present work we did not set ourselves the aim to isolate nitrosyl complexes $[Ru(bpy)_2(L)\cdot(NO)](BF_4)_3$ with pyridine ligands L = 4-(Y)py on a preparative scale. We obtained small amounts of complexes **II** by adding diethyl ether to methanol solutions of compounds **I** acidified with $HBF_4$ to determine ν(NO) values (Table 2). The results of the measurements showed that these values are only slightly affected by the nature of substituent Y in the series of complexes **II**, implying that ν(NO) cannot serve as a quantitative criterion of the electrophilic power of coordinated nitrosyl groups. It follows from our data that the constants of equilibrium (2) are more sensitive to the nature of inner-sphere ligands in complexes **I** or **II**. In whole, the logarithms of equilibrium (2) constants linearly correlate with the p$K_a$ values (protonation constants of the pyridine nitrogen atom) of the pyridine ligands [15] in compounds **I.**

## EXPERIMENTAL

The electronic absorption spectra of aqueous solutions of the complexes were taken on an SF-121 spectrophotometer. The IR spectra of the compounds in KBr were obtained on a Nicolet FT-IR Model-400 spectrophotometer. The $^1H$ NMR spectra were measured on a Bruker DPX-300 (300 MHz) spectrometer; the chemical shifts were measured against residual proton signals of the solvent (acetonitrile-$d_3$).

The pH values of aqueous solutions were measured using an I-131 pH-meter with an ESL-43-07 glass electrode and an EVL-1M3,1 silver chloride reference electrode. The electrode system was calibrated by standard buffer solutions at 298 K [17].

The pyridine ligands (Aldrich) and solvents: acetonitrile, methanol, and toluene (Vekton), were used as received, and diethyl ether was distilled over sodium. The complexes *cis*-$[Ru(bpy)_2(NO)(NO_2)](BF_4)_2$ and *cis*-$[Ru(bpy)_2(py)(NO_2)](BF_4)$ were synthesized by the procedures in [2, 3] in a light-proof apparatus. All ruthenium(II) bisbipyridyl complexes obtained in this work were *cis* isomers.

**(4-Aminopyridine)bis(2,2'-bipyridyl)nitroruthenium(II) tetrafluoroborate.** A methanol solution of the stoichiometric amount of $NaN_3$ (14 mg) was added dropwise to a suspension of 195 mg of $[Ru(bpy)_2(NO)(NO_2)](BF_4)_2$ in 30 ml of methanol, after which excess 4-aminopyridine (86 mg) was added, and the mixture was refluxed in the dark. The solvent was distilled off, the residue was dissolved in a minimal volume (10 ml) of anhydrous acetonitrile, the solution was filtered off, and 70 ml of diethyl ether was added dropwise. A redish orange precipitate formed and was filtered off, washed with diethyl ether, dried in air, and subjected to chromatography on a column (150 × 20 mm) of neutral $Al_2O_3$ (Brockmann activity grade 3; eluents acetonitrile–toluene mixtures) to recover three bands. The first band was eluted with a 2 : 1 acetonitrile–toluene mixture, the solvent was distilled off, and the reaction product was recrystallized from acetonitrile with diethyl ether added. Yield 123 mg (65%). $^1H$ NMR spectrum, ppm (*J*, Hz): 9.92 d (1H, 5.6), 8.67 d (1H, 5.6), 8.47 d (1H, 7.7), 8.38–8.27 m (3H), 8.17–8.05 m (2H), 7.92? 7.64 m (8H), 7.27 t (1H, 6.6), 7.17 t (1H, 6.6), 6.41 d (2H, 7.0), 5.31 s (2H).

**Bis(2,2'-bipyridyl)nitro(4-picoline)ruthenium(II) tetrafluoroborate** was synthesized in a similar way with the corresponding 4-(Y)py ligand. Yield 60%. $^1H$ NMR spectrum, ppm (*J*, Hz): 9.89 d (1H, 5.4), 8.59 d (1H, 5.4), 8.49 d (1H, 7.7), 8.36 d (1H, 8.4), 8.35 d (1H, 8.4), 8.29 d (1H, 7.7), 8.22–8.07 m (4H), 7.95–7.80 m (3H), 7.76 d (1H, 5.4), 7.66 t (1H, 6.6), 7.31 t (1H, 6.6), 7.20 t (1H, 6.6), 7.11 d (2H, 6.2), 2.33 s (3H).

The other complexes **II** were obtained similarly.

**Bis(2,2'-bipyridyl)nitro(4-phenylpyridine)ruthenium(II) tetrafluoroborate.** Yield 66%. $^1H$ NMR spectrum, ppm (*J*, Hz): 9.93 d (1H, 5.9), 8.65 d (1H, 5.0), 8.51 d (1H, 7.6), 8.45–8.29 m (5H), 8.18 t (1H, 8.4), 8.12 t (1H, 7.0), 7.96–7.64 m (8H), 7.60–7.49 m (5H), 7.33 t (1H, 6.6), 7.22 t (1H, 6.6).

**Bis(2,2'-bipyridyl)(4-cyanopyridine)nitroruthenium(II) tetrafluoroborate.** Yield of 55%. $^1H$ NMR spectrum, ppm (*J*, Hz): 9.86 d (1H, 5.3), 8.70–8.50 m (2H), 8.51 d (2H, 7.9), 8.37 d (2H, 7.9), 8.30 d (1H, [37.9), 8.22–8.05 m (2H), 7.95–7.63 m (7H), 7.55 t (1H, 7.3), 7.32 t (1H, 6.6), 7.22 t (1H, 6.6) [4].

**Measurement of equilibrium (2) constants.** A weighed sample of $[Ru(bpy)_2(L)(NO_2)](BF_4)\cdot H_2O$ (3–5 mg) was dissolved in 1.7–1.8 ml of water or 0.05 M HCl. A sample of this solution (0.2 ml) was taken in a test tube with a stopper and diluted with 15.0 ml of a buffer solution prepared from 0.1 M aqueous sodium citrate and 6 M HCl. A series of 7–9 buffer solutions with an average difference in 0.2 pH units and an ionic strength *I* of 0.4 ± 0.1 was selected for each complex. The concentration of complexes ($c_0$) in buffer solutions was (6–9) × $10^{-5}$ M. The solutions of complexes were thermostated for ~48 h at

(25.0 ± 0.1)°C until equilibrium (2) established, and their pH and optical density $D$ at the absorption maximum of the initial nitro complex were measured. The spectral measurements carried out in cells 1.0 cm long. The constants $K$ of equilibrium (2) were calculated by Eq. (6).

$$K = c_{NO}/c_{NO_2}c^2_{H^+}$$
$$= (1 - D_{lim})/[D_{lim} - (\varepsilon_{NO}/\varepsilon_{NO_2})] \times 10^{-2pH}. \qquad (6)$$

Here $D_{lim} = D/c_0\varepsilon_{NO_2}$, $\varepsilon_{NO_2}$ and $\varepsilon_{NO}$ are the extinction coefficients of nitro and nitrosyl complexes, measured at the absorption maximum of each nitro complex (Table 2). The $\varepsilon_{NO_2}$ (Table 2) and $\varepsilon_{NO}$ values were determined experimentally in solutions with pH 7.7 and 1.1, respectively, where equilibrium (2) is completely displaced to the left or to the right. The following $\varepsilon_{NO}$ values (l mol$^{-1}$ cm$^{-1}$) were obtained for the series of nitrosyl complexes $[Ru(bpy)_2(NO)(L)]^{3+}$ with L=4-(Y)py: 1200 (CN), 370 (H), 940 (Ph), 500 (Me), and 430 ($NH_2$).

## ACKNOWLEDGMENTAS

The work was financially supported by the Russian Foundation for Basic Research (project no. 02-03-32 715a) and *Universities of Russia* Program (project no. UR.05.01.025).

## REFERENCES

1. Sizova, O.V., Ivanova, N.V., Ershov, A.Yu., and Shashko, A.D., *Zh. Obshch. Khim.*, 2003, vol. 73, no. 12, p. 1950.
2. Goodwin, J.B. and Meyer, T.J., *Inorg. Chem.*, 1971, vol. 10, no. 3, p. 471.
3. Adeyemi, S.A., Miller, F.J., and Meyer T.J., *Inorg. Chem.*, 1972, vol. 11, no. 5, p. 994.
4. Ershov, A.Yu., Veletskii, N.I., Dement'ev, I.A., Popov, A.M., Sokolova N.I., and Nikol'skii, A.B., *Zh. Obshch. Khim.*, 1994, vol. 64, no. 8, p. 1233.
5. Butler, A.R. and Milliams, D.L.H., *Chem. Soc. Rev.*, 1993, vol. 22, no. 2, p. 233.
6. Granik, V.G., Ryabova, S.Yu., and Grigor'ev, N.B., *Usp. Khim.*, 1997, vol. 66, no. 8, p. 792.
7. Wolak, M. and van Eldik, R., *Coord. Chem. Rev.*, 2002, vol. 230, no. 1, p. 263.
8. Richter-Addo, G.B., *Metal Nitrosyls*, New York: Oxford Univ. Press., 1992, p. 335.
9. Nikol'skii, A.B., Ershov, A.Yu., and Veletskii, N.I., *Problemy sovremennoi khimii koordinatsionnykh soedinenii* (Problems of the Modern Chemistry of Coordination Compounds), Leningrad: Leningr. Gos. Universitet, 1992, issue 10, p. 3.
10. Keene, F.R., Salmon, D.J., Walsh, J.L., Abruna, H.D., and Meyer, T.J., *Inorg. Chem.*, 1980, vol. 19, no. 7, p. 1896.
11. Walsh, J.L., Bullock, R.M., and Meyer, T.J., *Inorg. Chem.*, 1980, vol. 19, no. 4, p. 866.
12. Bowden, W.L., Little, W.F., and Meyer, T.J., *J. Am. Chem. Soc.*, 1977, vol. 99, no. 13, p. 4340.
13. Nikolskii, A.B., Veletskii, N.I., Ershov, A.Yu., and Petrova, M.V., *Koord. Khim.*, 1990, vol. 16, no. 3, p. 411.
14. Nikolskii, A.B., Veletskii, N.I., Ershov, A.Yu., and Gavrilenko, E.A., *Koord. Khim.*, 1990, vol. 16, no. 5, p. 686.
15. *Tablitsy konstant skorosti i ravnovesiya geteroliticheskikh organicheskikh reaktsii* (Tables of Rate and Equilibrium Constants of Heterolytic Organic Reactions), Pal'ma, V.A., Ed., Available from VINITI, 1976, vol. II (1), p. 223.
16. Ooyama, D., Nagao, N., Nagao, H., Miura, Y., Hasegawa, A., Ando, K., Howell, F.S., Mukaida, M., and Tanaka, K., *Inorg. Chem.*, 1995, vol. 34, no. 24, p. 6024.
17. *Spravochnik Khimika* (Chemist's Handbook of a Chemist), Nikol'skii, B.P., Ed., Moscow: Khimiya, 1964, vol. 3, p. 168.
18. Bottomley, F., Brooks, W.V.F., Clarkson, S.G., and Tong, S.B., *J. Chem. Soc., Dalton Trans.*, 1974, no. 21, p. 3244.
19. Bottomley, F., Clarkson, S.G., and Tong, S.B., *Chem. Commun.*, 1973, no. 23, p. 919.