ISSN 1070-3632, Russian Journal of General Chemistry, 2009, Vol. 79, No. 5, pp. 980–984. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © V.V. Pakal'nis, A.Yu. Sokolov, A.A. Slisenko, M.E. Borovitov, S.P. Tunik, O.V. Sizova, 2009, published in Zhurnal Obshchei Khimii, 2009, Vol. 79, No. 5, pp. 808–812.

Synthesis and Spectral Characteristics of a Novel Heterometallic Binuclear Complex on the Basis of 3,6-Bis(2-pyridyl)-1,2,4,5-tetrazine

V. V. Pakal'nis, A. Yu. Sokolov, A. A. Slisenko, M. E. Borovitov, S. P. Tunik, and O. V. Sizova

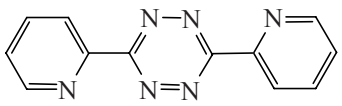
St. Petersburg State University, Universitetskii pr. 26, St. Petersburg, 198504 Russia
e-mail: pvchik@mail.ru

Received October 30, 2008

Abstract—Binuclear bridged complexes $[(bpy)_2Ru(\mu\text{-bptz})Re(CO)_3\cdot(Hlg)](X)_2$ [bptz = 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine; Hlg = Cl, X = BF_4 or Hlg = Br, X = NO_3]. Were synthesized and studied by mass spectrometry and infrared and electronic spectroscopy. The complexes give a strong long-wave band in the electronic absorption spectrum. The spectra were interpreted on the basis of TD DFT quantum-chemical calculations.

DOI: 10.1134/S1070363209050193

Over the past two decades much interest has been attached to the synthesis and properties of binuclear structures on the basis of 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine (bptz, **I**) [1].



I

Compound **I** has a peculiar electronic structure: Due to the presence of four nitrogen atoms in the tetrazine ring, the lowest unoccupied molecular orbital (LUMO) in **I** has a very low energy. Furthermore, the two pyridyl substituents allow bidentate coordination of one or more metal centers of a widely varied nature. However, the overwhelming majority of second- and third-raw transition metal complexes, synthesized by now, are homonuclear [1]. The only reported precedent is a heterometallic comples comprising rhodium and rhenium ions [2].

The polypirydine ruthenium center incorporated in mononuclear complexes is widely used as photosensitizer [3, 4], and a mononuclear pentacarbonyl halide complex of rhenium can catalyze a number of organic reactions [5, 6]. To combine these two structures in a binuclear complex with a bptz bridge is of great interest in terms of modification of chemical properties and appearance of new properties due to interaction of the components of this system.

The aim of the present work was to synthesize a novel heterobinuclear complex based on bptz and containing the $\{Ru(bpy)_2\}^{2+}$ and $\{Re(CO)_3(Hlg)\}$ fragments and to describe its spectral characteristics.

The synthesis involved two stages: (1) coordination of the first metal center to the free bridging ligand and (2) coordination of the second metal center to the resulting metal ligand. Theoretically, the starting complexes, both ruthenium and rhenium, can act both as the first and the second metal center. Both reactions are accompanied by a side reaction forming homobinuclear molecules, as well as incomplete binding of the free ligand. The intermediate mononuclear product was isolated by liquid chromatography. The rhenium complex was found to be a more efficient first reagent than the ruthenium complex. The reason lies in that the double- charged ruthenium cation is usually chromatographed in a mixture of saturated aqueous potassium nitrate with acetone, whereas the uncharged complex $(bptz)Re(CO)_3(Hlg)$, in a dichloromethane–acetone mixture. The use in the first case of an aqueous solvent can lead to hydrolysis of the coordination product, accompanied by cleavage of the tetrazine ring in the bridge, by analogy with what was described in [7], thereby radically changing the structure and composition of the intermediate compound.

Based on the above reasons, of the two possible synthetic approaches we chose the rhenium pentacarbonyl chloride complex as the first reagent.

$$Re(CO)_5(Hlg) + bptz \xrightarrow[\text{toluene–dichloromethane}]{\text{boiling in mixture}} (bptz)Re(CO)_3(Hlg) + 2CO.$$

The reaction between the rhenium metal ligand and the ruthenium complex at the second stage provides a hetebinuclear bridged compound.

$$(bptz)Re(CO)_3(Hlg) + [Ru(bpy)_2(solv)](X)_2 \xrightarrow[\text{dichloromethane}]{\text{stirring in}} [(bpy)_2Ru(bptz)Re(CO)_3(Hlg)](X)_2.$$

bpy = 2,2'-bipyridyl, solv = molecules of solvent used at the first stage (nonabsolutized EtOH).

The reaction product was isolated by recrystallization at –15°C. The binuclear complex is less soluble compared to the starting complexes under these conditions.

Mass spectral analysis of the resulting complexes by electrospray ionization (ESI) gave evidence for their suggested composition. The complexes $[(bpy)_2Ru(\mu\text{-bptz})Re(CO)_3(Cl)](BF_4)_2$ (**II**) and $[(bpy)_2Ru(\mu\text{-bptz})Re(CO)_3(Br)](NO_3)_2$ (**III**), having different halide ligands and counter ions, undergo various transformations in the course of mass spectral experiment. Chloride complex **II** gives a molecular ion at *m/z* 1043, corresponding to the composition $\{[(bpy)_2Ru(\mu\text{-bptz})Re(CO)_3(Cl)](BF_4)\}^+$, whereas the mass spectrum of complex **III**contains a signal at *m/z* 989 corresponding to the fragment $\{[(bpy)_2Ru(\mu\text{-bptz})Re(CO)](NO_3)_2\}^+$ formed by cleavage of two carbonyl groups and bromide ligand. The calculated isotope patterns [8] for signals of both complexes completely fit experimental ones.

Mass spectral analysis of complex **II** points to the presence of species containing Ru and Re surrounded by aromatic nitrogen-containing ligands but provides no direct evidence showing that compound **III** contains a bromide ligand. The fact that the synthesized complex contains a halide ion is confirmed by IR spectral data implying the presence of a characteristic $\{Re(CO)_3(Hlg)\}$ fragment. The table lists the vibration frequencies and relative intensities of carbonyl ligand signals of complexes **II** and **III**, and a series of previously described complexes [2, 5, 6] containing the $\{Re(CO)_3(Hlg)\}$ fragment. All the compounds feature similar signal distributions, which suggests that the bromide ligand is present in the inner coordination sphere of complex **III** and is eliminated in the course of the mass spectral experiment.

The IR spectrum of complex **II**, too, contains a series of three characteristic absorption bands in the carbonyl region, which, together with mass spectral data, is evidence in favor of the formation of a binuclear complex with a $\{Re(CO)_3(Hlg)\}$ fragment.

As shown in several works dealing with α-diimine halocarbonyl rhenium complexes [9, 10], the observed characteristic distribution of IR signals corresponds (see table) to an axial arrangement of the halide ligand with respect to the plane of the nitrogen atoms of the bridging ligand and two their opposite carbonyl groups. The IR spectra show that the synthesized complexes contain no isomers with an equatorial halide ligand at the rhenium coordination center. However, the synthesis of the binuclear complex can form diastereomers with different mutual arrangements of terminal ligands at the two metal centers, as shown in Fig. 1.

In the case of complexes **II** and **III**, infrared spectroscopy is not sensitive enough to detect such isomeric species. Ernst et al. [11] showed that in this case a sufficiently sensitive technique is ^{1}H NMR spectroscopy and demonstrated, using the example of $[(bpy)_2Ru(\mu\text{-bppz})Ru(bpy)_2]^{4+}$ [bpy = 2,2'-bipyridyl, bppz = 2,5-bis(2-pyridyl)pyrazine], the possibility to detect such diastereomers. As would be expected, the ^{1}H NMR spectra of complexes **II** and **III**contain a series of multiplets at 7–10 ppm corresponding to bptz and bpy pyridine proton signals and impossible to assign unambiguously. Therefore, we cannot detect the potentially existing forms in this case but, on the other hand, cannot rule out their presence.

Binuclear complexes $[(bpy)_2Ru(\mu\text{-bptz})Re(CO)_3(X)]^{2+}$ (X = Cl, Br) give a strong absorption band in the region of 650 nm and a short-wave absorption band. The latter band is fairly broad and unsymmetric (Fig. 2), which implies that it is formed by a number of closely lying transitions. According to TD–DFT calculations for preliminary optimized structures with inclusion of solvent (H_2O) effects, the electronic absorption spectra of both complexes has a resolved strong transition in the region of 650 nm and a weaker transition which explains the unsymmetric pattern of the experimentally observed band, with a suggested maximum at 515 nm.

IR spectra of complexes **II** and **III**, and previously described complexes

Complex	Solvent	Carbonyl absorption frequencies, cm^{-1}		
II	CH_2Cl_2	2024 s	1938 m	1930 m
III	CH_2Cl_2	2025 s	1942 m	1927 m
$(bptz)Re(CO)_3Cl$ [2]	CH_2Cl_2	2032 s	1946 m	1919 m
$(bptz)Re(CO)_3Br$[a]	CH_2Cl_2	2032 s	1946 m	1920 m
$[(\eta^5\text{-Cp*})ClRh(bptz)Re(CO)_3Cl]PF_6$ [2]	CH_2Cl_2	2015 s	1912 m	1884 m

[a] The data were obtained in the present work.

The calculation shows that both bands are formed by metal-to-ligand charge transition. The long-wave band corresponds to the electron transition from the d_π orbitals of two metal centers to the π^* orbital of the tetrazine ring of bptz. The second, a shorter wave and weaker (three times in the case of the chloride and two times in the case of the bromide) compared to the first band, corresponds to the transition between the d_π orbitals of ruthenium and π^* orbitals of the bipyridyl ligands.

EXPERIMENTAL

The starting compounds **II** and **III**and complexes were synthesized using the following reagents and solvents: methanol, acetone, diethyl ether, carbon tetrachloride, DMF, toluene, methylene chloride (Vekton), 2,2'-bypiridyl (bpy), silver tetrafluoroborate (Aldrich), potassium nitrate, silver chloride, potassium chloride (Vekton). All the materials were used as received. 3,6-Bis(2-pyridyl)-1,2,4,5-tetrazine (bptz, **I**)

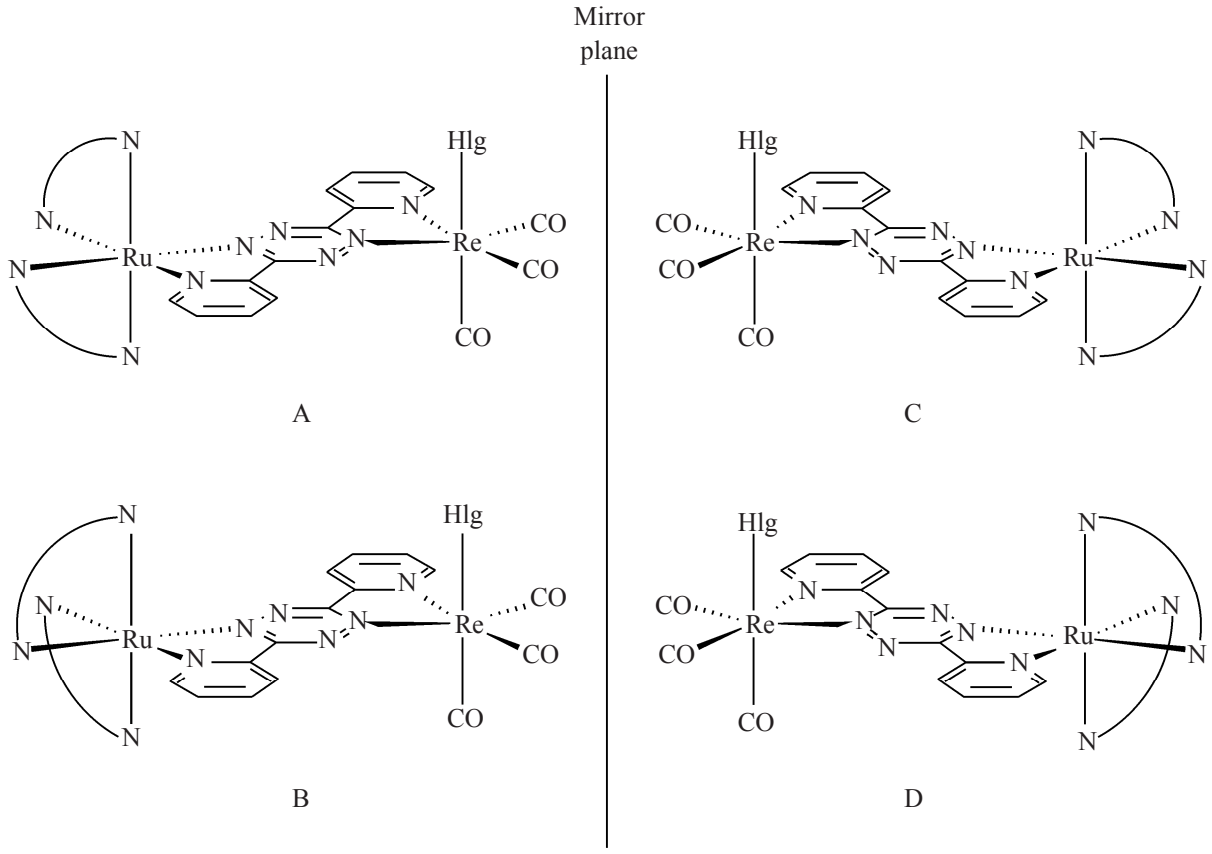


Fig. 1. Structures of possible diastereomers (AB and CD pairs) and their corresponding enantiomers (AC and BD pairs).

was synthesized as described in [12]. The ruthenium and rhenium complexes were synthesized by published procedures: $Na_2[Ru(H_2O)Cl_5]$ and $Ru(bpy)_2Cl_2{\cdot}2H_2O$ [13, 14], $Re(CO)_5(Hlg)$, (Hlg = Cl, Br) [15], and (bptz) $Re(CO)_3(Hlg)$ (Hlg = Cl, Br) [2].

The ^1H NMR spectra were obtained on a Bruker DPX 300 instrument. The IR spectra were measured on a PerkinElmer FT–IR System Spectrum BX spectrometer. The mass spectra were taken on a Micromass LCT instrument with an ESI source. The electronic absorption spectra were run on a Specord M40 spectrophotometer.

Complexes $[(bpy)_2Ru(\kappa^4,\mu\text{-bptz})Re(CO)_3(Hlg)](X)_2$ (II, III) [(II), Hlg = Cl, X = BF_4; (III), Hlg = Br, X = NO_3]. A solution of 19.5 mg of $AgBF_4$ or 17 mg of $AgNO_3$ in 1 ml of ethanol was added to a stirred solution of 26 mg of $Ru(bpy)_2Cl_2{\cdot}2H_2O$ in 10 ml of ethanol. The mixture was left to stand for 10 min at room temperature and was then filtered to remove AgCl precipitate, and the solvent was evaporated. The residue was dissolved in 20 ml of methylene chloride, 27.1 mg of (bptz)$Re(CO)_3Cl$ or 29.3 mg of (bptz)$Re{\cdot}(CO)_3Br$ was added, and the solution was left to stand for 12 h. A change in color from violet to blue was observed. Hexane, 30 ml, was then added, and the solution was left to stand for 24 h at –15°C. The resulting precipitate was filtered off and dried in air.

κ^4,μ-3,6-Bis(2-pyridyl)-1,2,4,5-tetrazine-bis(2,2'-bipyridyl)ruthenium(II)chlorotricarbonylrhenium(I) ditetrafluoroborate (II). Yield 36%. Mass spectrum: *m/z* 1043.0. IR spectrum (CH_2Cl_2), ν, cm^{-1}: 2024 s, 1938 m, 1930 m.

κ^4,μ-3,6-Bis(2-pyridyl)-1,2,4,5-tetrazine-bis(2,2'-bipyridyl)ruthenium(II)bromotricarbonylrhenium(I) dinitrate (III). Yield 30%. Mass spectrum: *m/z* 989.0. IR spectrum (CH_2Cl_2), ν, cm^{-1}: 2025 s, 1942 m, 1927 m.

Calculational procedure. Quantum-chemical calculations of the geometry of the ground state of the electronic absorption spectra of the synthesized complexes were performed using Gaussian03 [16] in the framework of the DFT theory with the B3LYP hybrid functional [17], LanL2DZ basis set [18, 19], and effective core potential for ruthenium. The electronic absorption spectra were calculated by the TD DFT method, solvation effects were included in the framework of the polarized continuum model (PCM) [20].

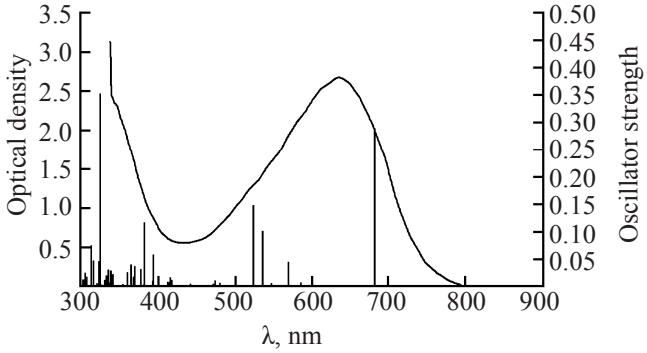


Fig. 2. (Solid line) Experimental and (vertical lines) calculated visible absorption spectrum of complex **III**. Experimental spectrum: aqueous solution, c_{II} 1.45×10^{-3} M, ε_{max} 17200 l cm^{-1} mol^{-1}.

REFERENCES

1. Kaim, W., *Coord. Chem. Rev*., 2002, vol. 230, nos. 1–2, p. 127.
2. Scheiring, T., Fiedler, J., and Kaim, W., *Organometallics*, 2001, vol. 20, no. 7, p. 1437.
3. Balashev, K.P., *Soros. Obrazov. Zh*., 1998, no. 9, p. 52.
4. Nazeeruddin, M.K., Wang, Q., Cevey, L., Aranyos, V., Liska, P., Figgemeier, E., Klein, C., Hirata, N., Koops, S., Haque, S.A., Durrant, J.R., Hagfeld, A., Lever, A.B.P., and Gratzel, M., *Inorg. Chem*., 2006, vol. 45, no. 2, p. 787.
5. Hawecker, J., Lehn, J.-M., and Ziessel, R., *Chem. Commun*., 1983, no. 9, p. 536.
6. Sullivan, B.P., Bolinger, C.M., Conrad, D., Vining, W.J., and Meyer, J., *Chem. Commun*., 1985, no. 20, p. 1414.
7. Maji, S., Sarkar, B., Patra, S., Fiedler, J., Mobin, S.M., Puranik, V.G., Kaim, W., and Lahiri, G.K., *Inorg. Chem*., 2006, vol. 45, no. 3, p. 1613.
8. *Chemputer Program for Calculation of Isotope Patters, http://winter.group.shef.ac.uk/chemputer/*
9. Kaim,W. and Kohlmann, S., *Inorg. Chem*., 1990, vol. 29, no. 16, p. 2909.
10. Cotton, F.A. and Kraihanzel, C.S., *J. Am. Chem. Soc*., 1962, vol. 84, no. 23, p. 4432.
11. Ernst, S., Kasack, V., and Kaim, W., *Inorg. Chem*., 1988, vol. 27, no. 7, p. 1146.
12. Kohlmann, S., Ernst, S., and Kaim, W., *Angew. Chem. Int. Ed.*, 1985, vol. 24, no. 8, p. 684.
13. *Sintez kompleksnykh soedinenii metallov platinovoi gruppy* (Synthesis of Complexes of Platinum Group Metals), Chernyaev, I.I., Ed., Moscow: Nauka, 1964.
14. Sullivan, B.P., Salmon, D.J., and Meyer, T.J., *Inorg. Chem*., 1978, vol. 17,p. 3334.
15. *Handbuch der praparativen anorganischen Chemie*, Brauer, G., Stuttgart: Enke, 1978. Translated under the

title *Ruakovodstvo po neorganicheskomu sintezu*, Moscow: Mir, 1986, vol. 6.

16. Frisch, M.J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M.A., Cheeseman, J.R., Montgomery, J.A., Jr., Vreven, T., Kudin, K.N., Burant, J.C., Millam, J.M., Iyengar, S.S., Tomasi, J., Barone, V., Mennucci, B., Cossi, M., Scalmani, G., Rega, N., Petersson, G.A., Nakatsuji, H., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Klene, M., Li, X., Knox, J.E., Hratchian, H.P., Cross, J.B., Adamo, C., Jaramillo, J., Gomperts, R., Stratmann, R.E., Yazyev, O., Austin, A.J., Cammi, R., Pomelli, C., Ochterski, J.W., Ayala, P.Y., Morokuma, K., Voth, G.A., Salvador, P., Dannenberg, J.J., Zakrzewski, V.G., Dapprich, S., Daniels, A.D., Strain, M.C., Farkas, O., Malick, D.K., Rabuck, A.D., Raghavachari, K., Foresman, J.B., Ortiz, J.V., Cui, Q., Baboul, A.G., Clifford, S., Cioslowski, J., Stefanov, B.B., Liu, G., Liashenko, A., Piskorz, P., Komaromi, I., Martin, R.L., Fox, D.J., Keith, T., Al-Laham, M.A., Peng, C.Y., Nanayakkara, A., Challacombe, M., Gill, P.M.W., Johnson, B., Chen, W., Wong, M.W., Gonzalez, C., and Pople, J.A., *Gaussian 03, Revision B.05*, Pittsburgh, PA: Gaussian, 2003.
17. Becke, A.D., *J. Chem. Phys*., 1993, vol. 98, no. 7, p. 5648.
18. Wadt, W.R. and Hay, P.J., *J. Chem. Phys*., 1985, vol. 82, no. 1, p. 284.
19. Hay, P.J. and Wadt, W.R., *J. Chem. Phys*., 1985, vol. 82, no. 1, p. 299.
20. Tomasi, J. and Persiko, M., *Chem. Rev*., 1994, vol. 94, no. 7, p. 2027.