

[Re(CO)₃(bipy)(ClO₄): Synthesis in a Proton-Donor Solvent, Crystal, and Molecular Structure

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Abstract—The complex [Re(CO)₃(bipy)(ClO₄)] (bipy = 2,2'-bipyridine) was prepared by the reaction of [Re(CO)₃(H₂O,EtOH)₃](ClO₄) with bipy in aqueous ethanol, followed by crystallization from dichloromethane. The composition and structure of the complex were determined by single crystal X-ray diffraction analysis. The complex has a molecular octahedral structure with bidentate coordination of bipy and inner-sphere monodentate coordination of perchlorate ion in the *fac*-position to bipy. The complex was also characterized by IR and UV-visible absorption spectroscopy.

Keywords: rhenium tricarbonyl complexes, bipyridine complexes, perchlorate complexes, single crystal X-ray diffraction analysis

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The search for new coordination compounds for cancer chemotherapy is an important and urgent task. This is due to the need to select new drugs free from the disadvantages of platinum complexes. Recently, tricarbonyl rhenium complexes have been considered as promising compounds for this purpose. These compounds, on the one hand, have antitumor activity, and on the other hand, they exhibit luminescent properties and allow imaging of neoplasms [1, 2]. In addition, they can be used in combination with ^{99m}Tc-based analogs as tracers for diagnostics by single-photon emission computed tomography [3]. Of particular interest are the so-called 2+1 complexes with the metal coordination sphere filled with three carbonyl groups, one monodentate ligand, and one bidentate ligand. Variation of organic ligands makes it possible to change properties of 2+1 complexes, for example, their lipophilicity smoothly and in a wide range.

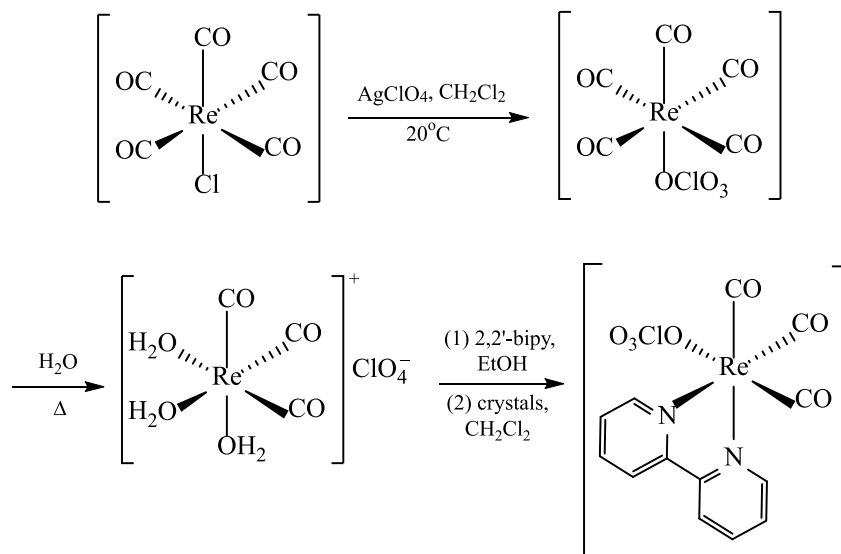
The first stage of synthesis of 2+1 complexes usually consists in obtaining complexes with a bidentate ligand and the sixth position occupied by a labile ligand, which can be a solvent molecule (water, alcohol, etc.) or a weakly coordinating anion. The question of their competition [1] not only is interesting from a scientific point of view, but may also be important for optimizing synthesis methods. In this work, we obtained the

2,2'-bipyridine complex [Re(CO)₃(bipy)(ClO₄)] in ethanol solution and characterized it (including X-ray diffraction analysis). The complex of this composition was previously synthesized in an inert medium [4] by treating [Re(CO)₃(bipy)(Br)] with silver perchlorate, but its structure has not been strictly proven. Later, it was reported that this complex was obtained from an aqueous-ethanol solution with subsequent recrystallization from a CH₂Cl₂–hexane mixture, but also without strict proof of the product structure [5].

In contrast to previously published works in which [Re(CO)₃(bipy)(ClO₄)] [4] and [Re(CO)₅(ClO₄)] [6] were obtained by treating [Re(CO)₃(bipy)Br] and [ReCl(CO)₅], respectively, with silver perchlorate in a non-coordinating solvent (CH₂Cl₂), in this work, the complex [Re(CO)₃(bipy)(ClO₄)] was obtained from an ethanol solution (Scheme 1).

When bidentate diimine ligands interact with the Re(CO)₃⁺ core in a donor solvent, the sixth coordination position can be occupied by both the solvent molecule and the counterion. In the system with an aqueous solution of trifluoromethanesulfonate [1], this position is occupied by a water molecule, but during crystallization, depending on the nature of a diimine ligand, both external and internal

Scheme 1.



coordination of the CF_3SO_3^- ion can be realized. In this paper, we have shown that, despite the use of ethanol (not absolute) in the synthesis and the presence of moisture in all stages of the synthesis (operations were performed without protection from atmospheric moisture), a product with a coordinated perchlorate ion is obtained.

It follows from the published data on technetium analogues that bidentate L^2 ligands, which have some π -acceptor properties [7–11], shift the equilibrium of competitive coordination of water and chloride ion in system (1) toward coordination of the chloride ion compared to system (2) [12].

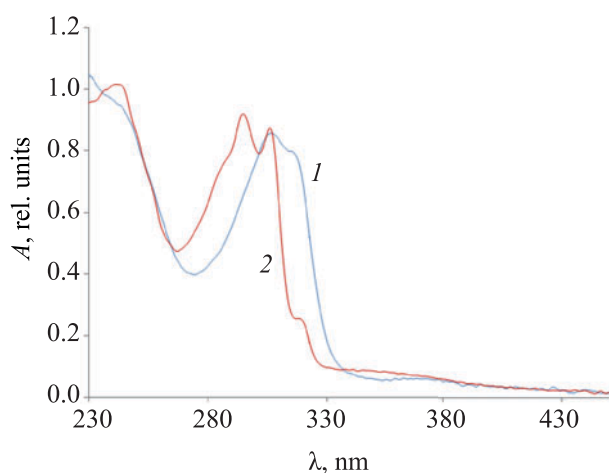
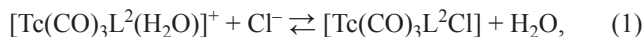


Fig. 1. Absorption spectra of complex **1** in (1) dichloromethane and (2) ethanol.

In our case, the inner-sphere coordination of the perchlorate ion also seems to be additionally stabilized due to the π -acceptor properties of the bidentate ligand. For comparison, we note that in [1] the inner-sphere coordination of the CF_3SO_3^- ion was observed in the complex with bipyridine, which contains acceptor methoxycarbonyl substitutes, and the outer-sphere coordination, in the complex with the methyl-substituted phenanthroline, i.e. with a weaker π -acceptor.

The IR spectrum of complex **1** in dichloromethane is typical for *fac*-tricarbonyl complexes. In the electronic absorption spectrum of complex **1** in dichloromethane (Fig. 1), by analogy with the data of [13], bands with maxima below 250 nm should be attributed to intra-ligand π - π^* transitions, and in the region of 300 nm – to the charge transfer from metal to ligand (MLCT). A significant change in the spectrum on transition from inert CH_2Cl_2 to donor and highly polar ethanol suggests that in this latter, the perchlorate ion is displaced from the inner sphere of the complex by a solvent molecule. On the other hand, removal of excess ethanol and extraction of the residue with methylene chloride create conditions for the entry of the perchlorate ion into the coordination sphere.

The crystal structure of complex **1** contains six crystallographically independent molecules (Table 1). The structure of one of them is shown in Fig. 2. The rhenium atoms in molecule **1** are in a distorted octahedral environment. The bond angles within the octahedron range from $74.9(3)^\circ$ to $100.8(3)^\circ$. The perchlorate anion is coordinated monodentately to the central metal. The

Re–C≡O bond in the *trans*-position to the perchlorate ligand is shorter [average Re–C1 distance 1.898 (10) Å] than the Re–C≡O bonds in the *trans*-position to bipy [average distance 1.921(10) Å]. The weakening of the Re–C≡O bond is probably due to the weak π -acceptor properties of the bipyridine ligand, which competes with *trans*-carbonyl groups for the d-electrons of the metal. A similar trend was observed in the structure of [Re(4,4'-(MeOCO)₂-2,2'-bipy)(OTf)(CO)₃], where the Re–C≡O bond in the *trans*-position to triflate ligand ion is shorter [1.896(3) Å] than the Re–C≡O bond in the *trans*-position to the bipyridine derivative [1.921(4) and 1.924(4) Å] [1], and also in the structure of [Re(CO)₃(bipy)(PO₂F₂)], where the Re–C≡O bond in the *trans*-position to PO₂F₂ is shorter [1.89(21) Å] than the Re–C≡O bond *trans* to bipy [1.910(20) and 1.941(17) Å] [4]. The Re–N bond lengths range from 2.136 (8) to 2.182(7) Å [average 2.163(7) Å] and are very close to those for similar rhenium tricarbonyl complexes containing bipyridine ligands: 2.178 (4) Å for [Re(CO)₃(4,4'-Me₂-2,2'-bipy)(NO₃)]; 2.180(3) and 2.175(3) Å for {Re(CO)₃[4,4'-(MeOCO)₂-2,2'-bipy]·(OTf)} [1]. The Re–O distance in complex **1** varies from 2.162(6) to 2.200(7) Å [average 2.181(7) Å], and the Re–O distances fall in the same range in [Re(ClO₄)(CO)₅] [2.190(3) Å] [6], in {Re[4,4'-(MeOCO)₂-2,2'-bipy](OTf)·(CO)₃} [1], and [Re(CO)₃(bipy)(PO₂F₂)] (2.188 Å) [4]. At the same time, the Re–O distance in the case of coordinated nitrate in [Re(CO)₃(4,4'-Me₂-2,2'-bipy)·(NO₃)] is slightly shorter [2.154 (4) Å] [1].

Thus, the possibility of formation of a rhenium carbonyl–bipyridine complex with inner-sphere coordination of perchlorate ion by synthesis in a donor medium is shown by X-ray diffraction analysis. This points to a relatively strong coordination of the perchlorate ion in the system with π -acceptor ligands.

EXPERIMENTAL

Chemically pure reagents were used for the synthesis. Methylene chloride was distilled from P₂O₅. Silver perchlorate was prepared from a silver nitrate aqueous solution by precipitation of silver carbonate with sodium carbonate, followed by dissolution of the precipitate in concentrated perchloric acid. Before use, silver perchlorate was dehydrated by heating in a vacuum at 50–60°C.

IR spectra were recorded on a Shimadzu FT-IR 8700 spectrometer in the range of 1800–2200 cm⁻¹ using cells with CaF₂ windows. Electronic absorption spectra were

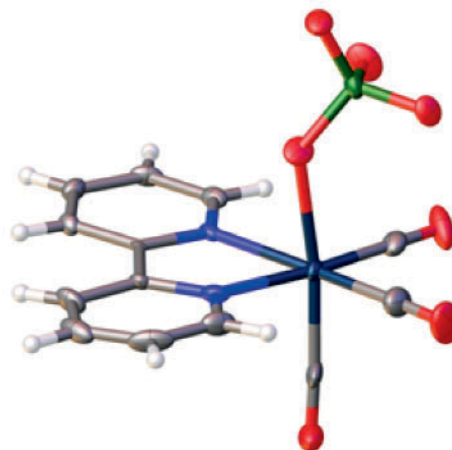


Fig. 2. General view of the [Re(CO)₃(bipy)(ClO₄)] molecule in the crystal.

recorded on a Mettler Toledo UV5 spectrometer using 10 mm long cells made of high-purity quartz from Hellma Analytics (type QS).

Table 1. Crystallographic parameters of [Re(CO)₃(bipy)(ClO₄)]

Parameter	Value
Formula	C ₁₃ H ₈ ClN ₂ O ₇ Re
Crystal system	Monoclinic
<i>a</i> , Å	14.9407(4)
<i>b</i> , Å	29.4483(5)
<i>c</i> , Å	21.2062(5)
β	106.967(3)
<i>V</i> , Å ³	8924.1(4)
Molecular weight	525.86
Space group	<i>P</i> 2 ₁ / <i>n</i>
μ , mm ⁻¹	8.391
Temperature, K	100(2)
<i>Z</i>	24
<i>D</i> _{calc} , g/cm ³	2.348
Crystal size, mm ³	0.41 × 0.34 × 0.25
Total	68531
Number of independent reflections	14832
Angle 2 θ range	5.10–49.00
Number of reflections with $ F_o \geq 4\sigma_F$	10690
<i>R</i> _{int}	0.0480
<i>R</i> _s	0.0417
<i>R</i> ₁ ($ F_o \geq 4\sigma_F$)	0.0433
<i>wR</i> ₂ ($ F_o \geq 4\sigma_F$)	0.0795
<i>R</i> ₁ (all data)	0.0685
<i>wR</i> ₂ (all data)	0.0925
<i>S</i>	1.060
<i>P</i> _{min} , <i>P</i> _{max} , e/Å ³	–2.655, 3.768

Synthesis of [Re(CO)₃(bipy)(ClO₄)] (1). As the initial compound, [ReCl(CO)₅] was used. This complex was obtained with a good yield by carbonylation of K₂[ReCl₆] with a mixture of formic and hydrochloric acids [14]. [Re(ClO₄)(CO)₅] was obtained by treating [ReCl(CO)₅] with silver perchlorate in dichloromethane according to the previously developed procedure [6]. The completeness of the transformation was controlled by the IR spectrum of the resulting complex (bands of [Re(ClO₄)(CO)₅] in CH₂Cl₂, ν , cm⁻¹: 2165.9 w, 2059.8 s, 2005.8 m). After removing the solvent, 8 mL of water was added to the solid product, and the reaction mixture was refluxed for 24 h. The IR spectrum of the resulting solution (H₂O, ν , cm⁻¹: 2034.8 s, 1915.2 s) points to the disappearance of the pentacarbonyl form and the formation of a tricarbonyl complex of the probable composition [Re(CO)₃(H₂O)₃]⁺ClO₄⁻ [15].

The aqueous solution of [Re(CO)₃(H₂O)₃]⁺ClO₄⁻ was evaporated to a wet salt, and the resulting residue was dissolved in 96% ethanol to form a 0.056 M solution. Next, 1 mL of a 2,2'-bipyridine ethanol solution (17.4 mg, 0.112 mmol) was added to its aliquot (2 mL, 0.112 mmol Re). The mixture was heated to boil and stirred for 2 h. The resulting yellow solution was slowly evaporated at room temperature. The dark brown oily residue was triturated with a glass rod under diethyl ether (0.5 mL) and then under hexane (0.5 mL). The amorphous brownish-green product was extracted with dichloromethane (3 × 3 mL). The extracts were combined and left to evaporate at room temperature. When the volume of 3 mL was reached, yellow-green needle-like crystals of complex **1**, suitable for X-ray diffraction analysis, began to form. The analysis showed that the product has the composition [Re(CO)₃(bipy)(ClO₄)]. IR spectrum (CH₂Cl₂), ν , cm⁻¹: 2036.7 v. s (C≡O), 1936.4 s, and 1917.1 s (C≡O) {IR spectrum (vaseline oil), ν , cm⁻¹: 2052 m, 1935 sh, 1915 m. [4]}. UV spectrum (CH₂Cl₂), λ_{max} , nm (ϵ , M⁻¹ cm⁻¹): 230.2 (1.2 × 10⁵), 243.6 sh (1.0 × 10⁵), 306.6 (9.8 × 10⁴), 316.2 sh (9.1 × 10⁴), 370 (7086).

X-ray diffraction analysis of complex 1 (CCCD 1898044) was performed on a SuperNova Atlas diffractometer using a monochromated microfocussed MoK_α radiation. Diffraction patterns were processed using the Bruker Apex II and CrysAlisPro programs [16]. The data were integrated and corrected for background, Lorentz effect, and polarization effect. Empirical absorption correction was performed using

the SADABS [17] and CrysAlisPro [18] programs. The unit cell parameters were refined using the least squares method. The structures were solved using the double space algorithm and refined using the SHELX programs [19, 20] included in the OLEX2 software package [21]. The final models included coordinates and anisotropic displacement parameters for all non-hydrogen atoms. Carbon-bound H atoms were placed in calculated positions and refined in the rider model with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ and C–H 0.93 Å for CH groups of cyclic fragments.

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CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

SUPPLEMENTARY INFORMATION

The online version contains supplementary material available at <https://doi.org/10.1134/S1070363220120178>.

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