

The Structure of *cis*-[Chloro(dimethylsulfoxide)bis(1,10-phenanthroline)ruthenium(II)]-tetraphenylborate, [RuCl(DMSO)(1,10-phen)₂][BPh₄]

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Abstract. The complex *cis*-[RuCl(DMSO)(phen)₂][BPh₄], where DMSO is dimethylsulfoxide and phen is 1,10-phenanthroline, crystallizes in the monoclinic space group P2₁/c with $a = 19.505(4)$, $b = 10.045(2)$, $c = 21.199(4)$ Å, $\beta = 90.137(4)^\circ$, $V = 4153(2)$ Å³, $Z = 4$, $D_{\text{calc}} = 1.430$ g cm⁻³. The ruthenium coordination geometry is that of a slightly distorted octahedron with a *cis*-RuN₄ClS arrangement of the ligand donor atoms. The Ru–Cl dis-

tance is 2.421(1) Å and the Ru–S distance 2.250(2) Å. The four Ru–N distances are 2.057(6), 2.066(4), 2.073(4), and 2.086(4) Å with the Ru–N bond *trans* to Cl the second shortest and the Ru–N bond *trans* to S the longest one.

Keywords: Ruthenium(II); 1,10-Phenanthroline; Dimethylsulfoxide (DMSO); Crystal Structure

Ruthenium complexes having sulfoxide, chloro and N-donor ligands are of recent interest for their antimetastatic (antitumor) properties [1], as precursors for the synthesis of heteroleptic polypyridyl complexes and for their DMSO- and chloro-ligand substitution with retention of the absolute configuration [2, 3], as catalysts for alkene epoxidation [4] or for the diastereoselective preparation of Ru-bis(diimine) sulfoxide complexes [5]. Of main interest in this regard, so far, has been the compound *cis*-[RuCl(2,2'-bipy)₂(DMSO)]⁺ [3, 4, 6–10]. The value of this complex arises from its ability to react with suitable bidentate ligands particularly those that could act as DNA intercalators in connection with the photophysical properties of ruthenium(II) polypyridyl complexes [11]. We report here on the structure of the related prototypical complex *cis*-[chloro(dimethylsulfoxide)bis(1,10-phenanthroline)ruthenium(II)]⁺ as the tetraphenylborate salt, [RuCl(DMSO)(1,10-phen)₂][BPh₄] (**1**).

The molecular structure of the ruthenium cation of compound **1** (Figure 1) shows a slightly distorted or near octahedral arrangement around the ruthenium atom. The metal atom is bonded to two bidentate 1,10-phenanthroline ligands, a chloro and a dimethylsulfoxide ligand through the sulfur atom. Each phenanthroline ligand is essentially planar with the largest deviations being 0.098 Å and 0.079 Å for the ligand based on N1, N2 and N3, N4, respectively. The dihedral angle between the phenanthroline planes is 80.2(1)°. The Ru–donor atom distances and their variation in **1** are very similar to those seen in other structures with a RuN₄ClS core. Besides the structure of *cis*-[RuCl(2,2'-bipy)₂(DMSO)]⁺ with the anions [PF₆·Et₂O]⁻ and [I·2H₂O]⁻ [6], [ClO₄·2H₂O]⁻ [7], and [PF₆]⁻ [9], data for comparison is available for *cis*-[RuCl(L)₂(S-methyl(p-tolyl)sulfoxide)]PF₆ with L = 2,2'-bipy, 1,10-phen and for *cis*-[RuCl(L)(DMSO)]⁺ (L = tris(2-pyridylmethyl)amine and derivative) with [ClO₄·MeOH]⁻ [12], PF₆⁻ [13], PF₆⁻·MeCN [14] and

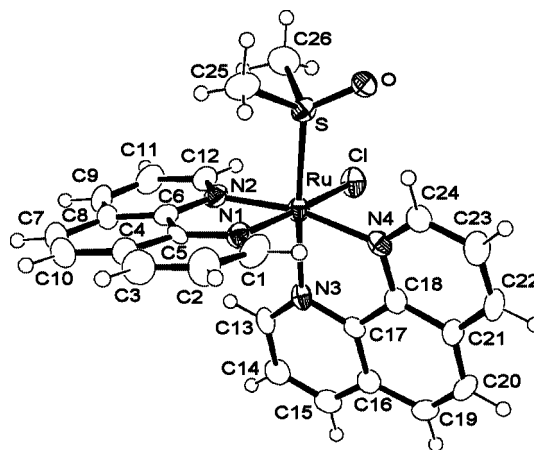


Fig. 1 The molecular structure of the [RuCl(DMSO)(phen)₂]-cation of **1**. Selected distances/Å and angles/°:

Ru–Cl 2.421(1), Ru–S 2.250(2), Ru–N1 2.066(4), Ru–N2 2.057(4), Ru–N3 2.086(4), Ru–N4 2.073(4), S–O 1.476(3), S–C25 1.783(5), S–C26 1.775(5), Cl–Ru–S 89.76(5), N1–Ru–Cl 174.5(1), N1–Ru–S 91.7(1), N1–Ru–N2 80.4(2), N1–Ru–N3 94.2(2), N1–Ru–N4 94.3(2), N2–Ru–Cl 94.3(1), N2–Ru–S 92.7(1), N2–Ru–N3 90.1(2), N2–Ru–N4 168.0(2), N3–Ru–Cl 84.6(1), N3–Ru–S 173.9(1), N3–Ru–N4 79.5(2), N4–Ru–Cl 90.7(1), N4–Ru–S 98.3(1).

[RuCl₃(DMSO)₃]⁻ [15]. In these structures the Ru–Cl distances typically vary between 2.403 and 2.438 Å (average 2.422 Å), the Ru–S bond lengths between 2.236 and 2.271 Å (average 2.256 Å), the range of Ru–N bonds is 2.030 to 2.105 Å. Unlike in most other of the above structures the Ru–N bond *trans* to Cl in **1** is not the shortest one. Usually the Ru–N bond *trans* to Cl (range 2.030 to 2.082, av. 2.054 Å) is found to be 0.02 to 0.03 Å shorter than the other Ru–N distances. The Ru–N bond *trans* to S in **1** is the longest one, in agreement with most of the other structures (range of Ru–N *trans* to S: 2.082 to 2.105, av. 2.093 Å). The typical Ru–N bond length variation *trans* to the Cl and S atoms can be explained by the *trans* influence with the competition for the metal- π -bonding orbitals [16]. The oxygen atom of the sulfoxide is oriented towards a C–H bond (H···O = 2.34 Å, C–H···O = 135°).

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The packing between the ruthenium cations and tetraphenylborate anions in **1** is dominated by C-H $\cdots\pi$ interactions [17] and exhibits only one π -stacking contact (between symmetry related arene moieties of N4, centroid-centroid contact 3.685, interplanar separation 3.205 Å) [18].

Experimental

Synthesis of *cis*-[chloro(dimethylsulfoxide)bis(1,10-phenanthroline)ruthenium(II)]-tetraphenylborate **1**:

[RuCl₂(phen)₂] (0.50 g, 0.94 mmol) [19] and excess DMSO (2.0 mL, 1.82 g, 23 mmol) were refluxed in EtOH (20 mL) for 12 h. The orange solution was filtered and the solvent of the filtrate evaporated *in vacuo*. The residue was extracted with H₂O and precipitated with a saturated NaBPh₄ solution. The orange product was recrystallized from DMSO/CH₃CN/Et₂O (crystal yield 0.55g, 44%).

C₅₀H₄₂BClN₄ORuS (894.27): calculated C 67.15, H 4.73, N 6.26, S 3.59; found C 67.30, H 4.08, N 6.02, S 2.91% (VarioEL from Elementaranalysensysteme GmbH).

Crystal structure determination of **1**:

Crystal data: Molecular formula C₅₀H₄₂BClN₄ORuS, formula weight 894.27 g mol⁻¹, $a = 19.505(4)$, $b = 10.045(2)$, $c = 21.199(4)$ Å, $\beta = 90.137(4)^\circ$, $V = 4153(2)$ Å³, $Z = 4$, $D_{\text{calc}} = 1.430$ g cm⁻³, monoclinic, space group P2₁/c. *Data collection*: Bruker Smart AXS CCD, Mo-K α radiation ($\lambda = 0.71073$ Å), graphite monochromator, crystal size 0.16x0.12x0.02 mm³, 233(2) K, ω -scan, $3.8^\circ \leq 2\theta \leq 50.1^\circ$, $-23 \leq h \leq 22$, $-11 \leq k \leq 11$, $-25 \leq l \leq 25$, 29820 reflections measured, 7344 independent, $\mu(\text{Mo-K}\alpha) 0.536$ mm⁻¹, experimental absorption correction with SADABS [20]. *Structural Analysis and Refinement*: The structure was solved by direct methods (SHELXS-97), refinement was done by full-matrix least squares on F^2 using the SHELXL-97 program suite [21]; all non-hydrogen positions were found and refined with anisotropic temperature factors; hydrogen atoms were calculated using appropriate riding models (AFIX 43, 33) and isotropic temperature factors of $U_{\text{eq}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$ for CH and $1.5 U_{\text{eq}}(\text{C})$ for CH₃. 532 refined parameters, final $RI = 0.0600$, $wR2 = 0.0699$ for 4199 reflections with $I > 2\sigma I$, final $RI = 0.0801$, $wR2 = 0.1284$ for all data, largest difference peak and hole 1.431/−1.458 e Å⁻³ in the vicinity of the Ru atom. The structural data has been deposited with the Cambridge Crystallographic Data Center (No. 254437).

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