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**mer-Trichlorotrakis(1,3-thiazole-N)-
ruthenium(III)**

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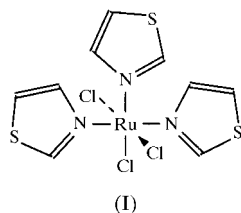
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The potentially cytostatic title compound, *mer*-[RuCl₃(C₃H₃NS)₃], is the first Ru^{III}-thz (thz is 1,3-thiazole) complex characterized *via* X-ray diffraction and consists of discrete complex molecules with an octahedral coordination sphere in which the metal centre is linked to three chloride ions and to three thz ligands through the N atoms. The Ru—Cl and Ru—N bond distances average 2.3462 (6) and 2.0851 (19) Å, respectively.

Comment

On continuing our research efforts to prepare and structurally characterize complexes of platinum group metals of potential cytostatic and antitumoral activity (Cini *et al.*, 1998; Pifferi & Cini, 1998; Cavaglioni & Cini, 1997; Cini, 1996), we have carried out the synthesis and the X-ray structural characterization of the title compound, (I), from the reaction of K₃RuCl₆ with thz (thz is 1,3-thiazole) in methanol. It is interesting to note that the thz group is frequently encountered in several biomolecules and active drugs (Hansch *et al.*, 1990), and that other workers found that thz-metal complexes possess cytostatic activity (Van Beusichem & Farrell, 1992).



Furthermore, several Ru^{II} and Ru^{III} complexes have shown cytostatic and antitumoral activity (Clarke & Stubbs, 1996).

The crystals of the title compound contain octahedral molecules in which the metal atom is linked to three chloride anions (meridional positions) and to three thz molecules through their N atoms. The S atoms do not have any significant contact distance to the metal. The Ru—Cl bond distances have the same values within three times the estimated standard uncertainty and are in the range 2.3446 (6)–2.3491 (6) Å, in

agreement with previously published Ru^{III}—Cl bond lengths (Ziegler *et al.*, 1999). The Ru—N bond distances also are equal within three times the e.s.d. and are in the range 2.0826 (19)–2.0889 (18) Å; they are very close to the Ru^{II}—N(thz *trans* to thz) bond distances [average 2.094 (5) Å] previously found for *trans*-[RuCl₂(PPh₃)(thz)₃] (Pifferi & Cini, 1998). The bond angles at the metal centre have almost idealized values; the largest deviations from 90 and 180° were found for Cl1—Ru—Cl2 [92.93 (3)°] and Cl1—Ru—Cl3 [175.47 (2)°]. All three thz ligands are affected by a statistical disorder (see *Experimental*) and have a planar arrangement of the atoms. The type of disorder found in the present work has been reported previously for several metal—N(thz) complexes (Pifferi & Cini, 1998; Cavaglioni & Cini, 1997; Cornia *et al.*, 1997; James *et al.*, 1997); by contrast, a similar disorder for N1-coordinated imidazole (imz, a frequently encountered and biologically significant ligand) is rarely reported in the literature (see, for instance, Hu *et al.*, 1997).

The molecule of the title compound is stabilized by eight intramolecular C—H···Cl interactions. Two C—H groups from *trans* thz(1) and thz(3) ligands interact with two Cl atoms each and have the shortest C···Cl distances (range 3.217–3.296 Å). The smallest C—N—Ru—Cl torsion angles for thz(1) and thz(3) are 27.6 (2) and 38.2 (2)° (absolute values), respectively, in agreement with the strongest interactions. The smallest C—N—Ru—Cl torsion angle for thz(2) is 51.3 (2)°. This means that the thz(2) system, which is closer to the Ru—N1/N3 vectors than to the Ru—Cl1/Cl3 ones, must experience a repulsive net effect from thz(1) and thz(3). The orientation of thz(2) can have a rationale through the intermolecular interactions to Cl2(−*x* + $\frac{1}{2}$, *y* + $\frac{1}{2}$, −*z* + $\frac{1}{2}$) and Cl2(*x* + $\frac{1}{2}$, −*y* + $\frac{1}{2}$, *z* + $\frac{1}{2}$), as well as through the stacking interactions to thz(3)(−*x* + $\frac{1}{2}$, *y* + $\frac{1}{2}$, −*z* + $\frac{1}{2}$). It has to be noted that the unconventional *M*—Cl···H—C bonding mode may play a structural role for *M*—C bond-formation reactions (Huang *et al.*, 1998; Cavaglioni & Cini, 1997), and for stabilizing electronically and coordinatively unsaturated organometallic and coordination compounds (Cini & Cavaglioni, 1999).

In conclusion, we have prepared and structurally characterized a new Ru^{II} complex that can exert some cytostatic activity *via* metal–nucleic acid interactions once the labile chloride ligands have been removed inside the cell. Furthermore, the analysis confirms that *M*—Cl···H—C-type interactions have a significant structural role in coordination compounds. Finally, the work says that twofold-type disorders around the *M*—N(thz) vectors [and possibly around the *M*—N(imz) vectors] are highly probable. This indicates that very accurate structural determinations have to be performed in order to treat such a type of disorder for *M*—imz complexes, because the small geometrical and electronic differences between the CH and NH functions, when compared to those between the CH and S ones.

Experimental

A suspension of K₃RuCl₆ (150 mg, 0.35 mmol) in MeOH (10 ml) was added to excess thiazole (350 mg, 4.1 mmol) and refluxed for 2 h. The

mixture was cooled to 298 K and filtered. The filtrate (green) was concentrated by evaporating the solvent (298 K) and then stored at 278 K. Red crystals formed within 3–5 weeks. They were filtered off and stored in the air.

Crystal data

[Ru(C₃H₃NS)₃Cl₃]
M_r = 462.79
 Monoclinic, *P*2₁/*n*
a = 9.446 (1) Å
b = 11.486 (1) Å
c = 14.342 (1) Å
 β = 93.14 (1)°
V = 1553.7 (2) Å³
Z = 4
D_x = 1.978 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 33 reflections
 θ = 7.5–20.0°
 μ = 1.915 mm⁻¹
T = 293 (2) K
 Prism, dark red
 0.3 × 0.2 × 0.2 mm

Data collection

Siemens *P*4 diffractometer
 ω scans
 Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.647, *T_{max}* = 0.682
 4609 measured reflections
 3564 independent reflections
 3111 reflections with *I* > 2σ(*I*)
R_{int} = 0.013
 θ_{max} = 27.50°
h = -1 → 12
k = -1 → 14
l = -18 → 18
 3 standard reflections every 97 reflections
 intensity decay: none

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.0232
wR(*F*²) = 0.055
S = 1.01
 3564 reflections
 235 parameters
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0274P)^2 + 0.8664P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.34 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.46 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

| | | | |
|------------|-------------|------------|-------------|
| Ru—N3 | 2.0826 (19) | N1—C21 | 1.333 (3) |
| Ru—N1 | 2.0837 (19) | N1—C51 | 1.341 (3) |
| Ru—N2 | 2.0890 (18) | N2—C22 | 1.339 (3) |
| Ru—Cl2 | 2.3446 (6) | N2—C52 | 1.346 (3) |
| Ru—Cl1 | 2.3458 (6) | N3—C53 | 1.334 (3) |
| Ru—Cl3 | 2.3491 (6) | N3—C23 | 1.341 (3) |
| N3—Ru—N1 | 179.69 (8) | N2—Ru—Cl3 | 87.37 (5) |
| N3—Ru—N2 | 89.86 (7) | Cl2—Ru—Cl3 | 91.47 (2) |
| N1—Ru—N2 | 90.28 (7) | Cl1—Ru—Cl3 | 175.47 (2) |
| N3—Ru—Cl2 | 91.08 (6) | C21—N1—C51 | 111.4 (2) |
| N1—Ru—Cl2 | 88.77 (6) | C21—N1—Ru | 123.25 (17) |
| N2—Ru—Cl2 | 178.50 (5) | C51—N1—Ru | 125.38 (18) |
| N3—Ru—Cl1 | 89.89 (6) | C22—N2—C52 | 110.8 (2) |
| N1—Ru—Cl1 | 90.40 (6) | C22—N2—Ru | 124.00 (16) |
| N2—Ru—Cl1 | 88.24 (5) | C52—N2—Ru | 125.16 (15) |
| Cl2—Ru—Cl1 | 92.93 (3) | C53—N3—C23 | 111.1 (2) |
| N3—Ru—Cl3 | 88.96 (6) | C53—N3—Ru | 125.84 (16) |
| N1—Ru—Cl3 | 90.77 (6) | C23—N3—Ru | 123.01 (18) |

The three thz ligands are affected by statistical disorder around the Ru—N vectors with two distinct orientations each (pseudo-twofold type). The occupancies of the sets of atoms for the two orientations were refined to 0.609 (4)/0.391 (4), 0.581 (4)/0.419 (4) and 0.522 (4)/0.478 (4) for thz(1), thz(2), and thz(3), respectively. The C—S and C—C bond distances were restrained to be 1.70±0.02 and 1.36±0.01 Å, respectively. All the H atoms were set in calculated positions and allowed to ride on the respective C atoms during refinement. They were considered isotropic and their displacement parameters were restrained to 1.2*U_{eq}* of the atoms to which they are bound.

Data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); software used to prepare material for publication: *CIFTAB* (Sheldrick, 1997).

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