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A ruthenium complex with 1,5-diphenyl-3-thiocarbazonate (dithizone) as monodentate ligands: bis(2,2'-bipyridyl- κ^2N,N')bis(dithizonato- κS)-ruthenium(II)

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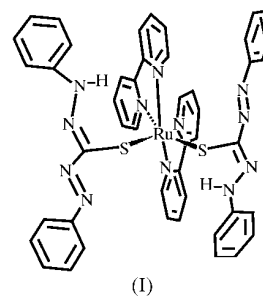
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The title compound, $[\text{Ru}(\text{C}_{13}\text{H}_{11}\text{N}_4\text{S})_2(\text{C}_{15}\text{H}_8\text{N}_2)_2]$, has C_2 symmetry, with bidentate 2,2'-bipyridyl ligands dictating a *cis* geometry around the Ru^{II} center. The monodentate *S*-bonded dithizone ligands are almost planar, except for one of the phenyl rings, which is twisted by $34.2(4)^\circ$ from the $\text{N}/\text{N}/\text{C}(\text{S})/\text{N}/\text{N}$ plane. The $\text{Ru}-\text{S}$ bond length is $2.4140(13)$ Å, and the $\text{Ru}-\text{N}$ bond lengths are $2.048(4)$ and $2.074(4)$ Å.

Comment

Very few X-ray structural reports have described either dithizone (H_2dtz ; Harrowfield *et al.*, 1983*a,b*; Kong & Wong, 1999; Ortner & Abram, 1999; Mawby & Irving, 1972; Niven *et al.*, 1982; Harding, 1958; Math & Freiser, 1970, 1971; Irving & Irving, 1986) or its oxidation product, 2,3-diphenyl-tetrazolium-5-thiolate (*tet*; Walsh *et al.*, 1998; Liu & Zubieta, 1989; Kozarek & Fernando, 1972) as ligands in transition metal complexes. The structure of $[\text{Ru}(\text{tpy})(\text{bpy})(\text{tet})](\text{ClO}_4)_2$ (*tpy* is 2,2':6',2'-terpyridyl and *bpy* is 2,2'-bipyridyl) involves monodentate coordination of the *tet* ligand through the *S* atom (Walsh *et al.*, 1998). Bond distances and angles are consistent with the *tet* ligand having delocalized mesoionic character (Liu & Zubieta, 1989; Kushi & Fernando, 1970). Because of the nature of the redox chemistry of the *tet* ligand while coordinated to the ruthenium center (Seamans & Walsh, 2003), the synthesis of ruthenium-dithizone complexes with monodentate ligands and the preparation of crystals suitable for structural characterization were attempted. A direct analog of the *tet* complex, *viz.* $[\text{Ru}(\text{tpy})(\text{bpy})(\text{Hdtz})]\text{ClO}_4$, was prepared, but suitable crystals could not be obtained. Subsequently, $[\text{Ru}(\text{bpy})_2(\text{Hdtz})_2]$, (I), was prepared and its structure, the first of a monomeric transition metal complex with a monodentate dithizonate ligand, is reported here (Fig. 1 and

Table 1). Other examples of monodentate binding of dithizone have involved a main group metal (Harrowfield *et al.*, 1983*b*) and bridging ligands (Kong & Wong, 1999).



The ruthenium center exhibits the typical characteristics of *cis*- $\text{Ru}(\text{bpy})_2$ complexes, with an $\text{N}-\text{Ru}-\text{N}$ bite angle close to 80° (Table 1). The $\text{N}6-\text{Ru}1-\text{N}6^i$ angle is $173.7(2)^\circ$ and the $\text{N}5-\text{Ru}1-\text{N}5^i$ angle is $86.2(2)^\circ$ [symmetry code: (i) $1-x, y, \frac{1}{2}-z$]. The atoms of the planar *bpy* ligands show an r.m.s. out-of-plane deviation of 0.0288 Å.

In the title complex, the negatively charged dithizonate ligand exhibits monodentate coordination through the *S* atom, with an $\text{Ru}1-\text{S}1-\text{C}1$ bond angle of $106.74(18)^\circ$. Unlike the *trans-cis* structure of *S*-methyldithizone (Preuss & Gieren, 1975), which contains a five-membered hydrogen-bonded ring, the structure of (I) is *trans-trans* about the *N* atoms, with no hydrogen bonding to the *H* atom attached to atom *N2*. This structure is similar to that of a monodentate Hdtz^- ligand in an indium complex (Harrowfield *et al.*, 1983*b*), a bridging monodentate Hdtz^- ligand in an osmium cluster (Kong & Wong, 1999) and the iodine adduct of dithizone (Herbstein &

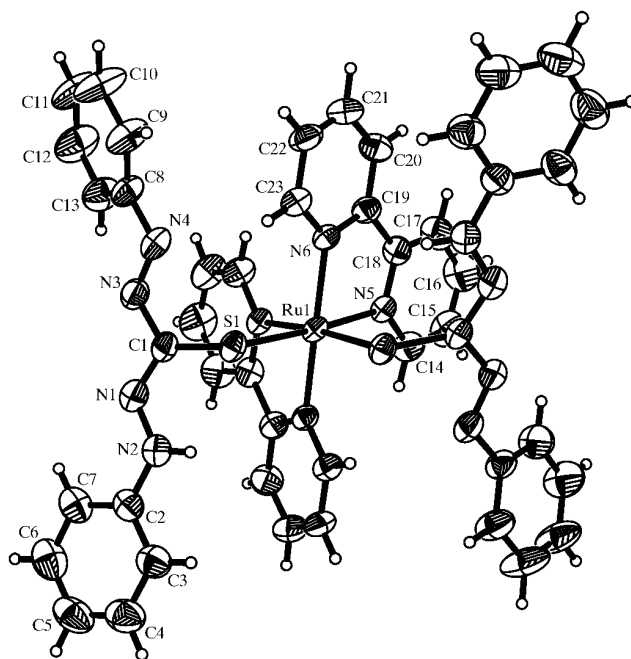
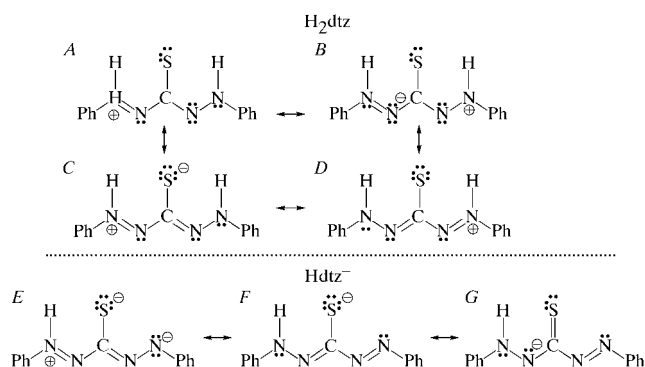


Figure 1

A view of the title ruthenium complex, with displacement ellipsoids drawn at the 30% probability level.

Schwotzer, 1982, 1984). Bidentate coordination of Hdtz^- ligands usually occurs in a similar *trans-trans* fashion. The dithizonate unit is nearly planar (Table 2), except for the twist of the C8–C13 phenyl ring out of the plane of the C/N/N/C(S)/N/N/C moiety by $34.2(4)^\circ$; the C2–C7 phenyl ring is twisted only $3.9(4)^\circ$ out of the C/N/N/C(S)/N/N/C plane. The phenyl rings of coordinated dithizone ligands have been observed to be coplanar with the N/N/C(S)/N/N plane (Harding, 1958; Mawby & Irving, 1972; Math & Freiser, 1971; Laing, 1977) or twisted at some angle (Laing *et al.*, 1971; Math & Freiser, 1970). The latter cases are often the result of steric effects, but steric effects do not appear to be a major factor leading to non-planarity in the present case. Packing effects may be involved.

The bonding in dithizone (H_2dtz) and the deprotonated dithizonate anion (Hdtz^-) is illustrated in the *Scheme* below. Structure *F* is expected to be the dominant form of the dithizonate ion in (I). In (I), the C1–S1 bond length of $1.737(5) \text{ \AA}$ is only slightly shorter than the C–S bond lengths in thiolate–ruthenium complexes (1.78 \AA ; Shiu *et al.*, 2002) and slightly longer than the C–S bond lengths in ruthenium–thione complexes (1.67 \AA ; Bellucci & Cini, 1999), indicating considerable single-bond character in the C–S bond. Delocalization in the N/N/C(S)/N/N framework, including a contribution from structure *G*, could provide some double-bond character, thus decreasing the C–S bond length.



The bond distances (Table 1) in the N/N/C/N/N moiety are consistent with the dithizone bonding shown in structure *F*. The long N1–N2 [$1.343(6) \text{ \AA}$], short N1–C1 [$1.310(7) \text{ \AA}$], long C1–N3 [$1.412(7) \text{ \AA}$] and short N3–N4 [$1.256(6) \text{ \AA}$] distances are as predicted (Ortner & Abram, 1999; Liu & Zubieta, 1989). In typical bidentate dithizonate coordination, the complementary C–N and N–N bonds on opposite sides of the C=S unit differ in length by $0.01\text{--}0.06 \text{ \AA}$. The title complex shows the greatest long–short distinction of any dithizonate–metal complex, with characteristics similar to *S*-methyl dithizone (Preuss & Gieren, 1975) and the monodentate dithizonate ligand in $\text{In}(\text{Hdtz})_3$ (Harrowfield *et al.*, 1983*b*).

In spite of the sp^3 -hybridized N2 atom in structure *F*, the C2–C7 phenyl ring is nearly coplanar with the C/N/N/C(S)/N/N/C moiety, with an angle of $3.9(4)^\circ$ between the planes, which suggests that structure *E* may provide some contribution to the electronic nature and structure of the molecule.

Experimental

Acetonitrile (16 ml) and ethanol (8 ml) were added to a round-bottomed flask (100 ml) and the flask was purged with N_2 . To the solution were added $[\text{Ru}(\text{bpy})_2(\text{tet})_2](\text{ClO}_4)_2$ (215 mg, 0.192 mmol) and hydrazine monohydrate (20 ml, 0.41 mol), and the resulting solution was stirred overnight. Ethanol (5 ml) was added and the solution was rotary evaporated until the desired compound precipitated. The product was collected by filtration and washed with ethanol and diethyl ether. The solid was chromatographed on an alumina column and reprecipitated to produce dark-red crystals (yield 160 mg, 0.173 mmol, 90%). Analysis calculated for $\text{C}_{46}\text{H}_{38}\text{N}_{12}\text{RuS}_2$: C 59.79, H 4.15, N 18.19%; found: C 59.53, H 4.13, N 18.01%. Crystals suitable for X-ray analysis were grown by vapor diffusion of diethyl ether into a solution of (I) in acetone and ethanol.

Crystal data

$[\text{Ru}(\text{C}_{13}\text{H}_{11}\text{N}_4\text{S})_2(\text{C}_{15}\text{H}_8\text{N}_2)_2]$
 $M_r = 924.07$
 Monoclinic, $C2/c$
 $a = 18.831(5) \text{ \AA}$
 $b = 16.423(4) \text{ \AA}$
 $c = 14.650(4) \text{ \AA}$
 $\beta = 98.107(6)^\circ$
 $V = 4485.3(19) \text{ \AA}^3$
 $Z = 4$

$D_x = 1.368 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 12 728 reflections
 $\theta = 2.4\text{--}26.4^\circ$
 $\mu = 0.49 \text{ mm}^{-1}$
 $T = 300(2) \text{ K}$
 Prism, dark red
 $0.50 \times 0.15 \times 0.15 \text{ mm}$

Data collection

Mercury CCD diffractometer
 ω scans
 Absorption correction: multi-scan (Jacobson, 1998)
 $T_{\min} = 0.766$, $T_{\max} = 0.929$
 21 449 measured reflections
 4596 independent reflections

3497 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.083$
 $\theta_{\max} = 26.4^\circ$
 $h = -23 \rightarrow 23$
 $k = -20 \rightarrow 20$
 $l = -16 \rightarrow 18$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.071$
 $wR(F^2) = 0.139$
 $S = 1.08$
 4596 reflections
 276 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0377P)^2 + 13.5485P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.42 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.26 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$).

Ru1–N6	2.048 (4)	N1–N2	1.343 (6)
Ru1–N5	2.074 (4)	N2–C2	1.385 (7)
Ru1–S1	2.4140 (13)	N3–N4	1.256 (6)
S1–C1	1.737 (5)	N3–C1	1.412 (7)
N1–C1	1.310 (7)	N4–C8	1.436 (7)
N6–Ru1–N6 ⁱ	173.7 (2)	N4–N3–C1	113.9 (5)
N6–Ru1–N5	78.51 (16)	N3–N4–C8	113.8 (5)
N5 ⁱ –Ru1–N5	86.2 (2)	C14–N5–C18	119.7 (4)
N6–Ru1–S1	96.83 (11)	C14–N5–Ru1	125.6 (4)
N6 ⁱ –Ru1–S1	87.93 (11)	C18–N5–Ru1	114.5 (3)
N5 ⁱ –Ru1–S1	96.10 (10)	C23–N6–C19	118.2 (4)
N5–Ru1–S1	175.04 (12)	C23–N6–Ru1	125.4 (3)
S1 ⁱ –Ru1–S1	81.93 (6)	C19–N6–Ru1	116.5 (3)
C1–S1–Ru1	106.74 (18)	N1–C1–N3	108.9 (5)
C1–N1–N2	115.5 (5)	N1–C1–S1	126.2 (4)
N1–N2–C2	121.7 (5)	N3–C1–S1	125.0 (4)
C1–N1–N2–C2	178.9 (5)	Ru1–S1–C1–N1	102.0 (5)
C1–N3–N4–C8	177.6 (5)	Ru1–S1–C1–N3	–78.1 (5)
N2–N1–C1–N3	–179.4 (4)	N1–N2–C2–C7	–1.2 (8)
N2–N1–C1–S1	0.5 (7)	N1–N2–C2–C3	–178.9 (5)
N4–N3–C1–N1	171.3 (5)	N3–N4–C8–C9	154.5 (6)
N4–N3–C1–S1	–8.6 (7)	N3–N4–C8–C13	–25.1 (9)

Symmetry code: (i) $1 - x, y, \frac{1}{2} - z$.

Table 2

Angles between least-square planes.

Plane 1	Plane 2	Angle (°)
S1/N1/N2/N3/N4/C1/C2/C8 r.m.s. deviation = 0.0362 Å	C2/C3/C4/C5/C6/C7 r.m.s. deviation = 0.0071 Å	3.32
S1/N1/N2/N3/N4/C1/C2/C8 r.m.s. deviation = 0.0362 Å	C8/C9/C10/C11/C12/C13 r.m.s. deviation = 0.0119 Å	35.30

H atoms were placed in idealized positions and were allowed to ride on their parent atoms, with C—H distances of 0.93 Å for aromatic H atoms and an H2—N2 distance of 0.86 Å. The $U_{\text{iso}}(\text{H})$ parameters were taken to be $1.2U_{\text{eq}}$ of the parent C or N atom. There are four small voids of about 104 \AA^3 in each unit cell in the refined structure. These voids, which constitute approximately 9.2% of the total volume of the unit cell, probably contain disordered solvent molecules. However, no atoms could be located in the voids from the difference Fourier map. Instead, a disordered solvent correction based on the *SQUEEZE* algorithm (van der Sluis & Spek, 1990) in *PLATON* (Spek, 2003) was applied to account for the extra electron density in the voids. *SQUEEZE* located two additional electrons per void. After applying the disordered solvent correction, the minimum residual electron density changed from -0.60 to -0.26 e \AA^{-3} , and the maximum electron density was reduced from 1.26 to 0.42 e \AA^{-3} ; wR improved from 0.163 to 0.139.

Data collection: *CrystalClear* (Rigaku Corporation, 1998–2001); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXL97*; software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2003).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1686). Services for accessing these data are described at the back of the journal.

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