

## Preparation and X-ray crystal structure study of a polypyridyl ruthenium(II) complex containing a dehydrodithizone ligand

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### Abstract:

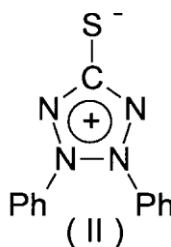
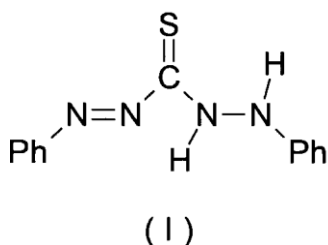
Coordination of 2,3-diphenyltetrazolium-5-thiolate (tet) to an Ru(trpy)(bpy)(OH<sub>2</sub>)<sup>2+</sup> (trpy=2,2':6',2''-terpyridine; bpy=2,2'-bipyridine) centre resulted in the formation of [Ru(trpy)(bpy)(tet)](ClO<sub>4</sub>)<sub>2</sub>. Single-crystal X-ray analysis revealed that the tet ligand is bound through the sulfur atom to a somewhat distorted-octahedral ruthenium centre. The Ru–S bond distance is 2.393(2) Å, and the Ru–S–C bond angle is 115.1(2)°; the tet N–N bonded distances [1.306(10)Å 1.316(9)Å] are essentially equal. These data, as well as spectroscopic and electrochemical evidence, suggest that the tetrazolium ring exhibits delocalized, mesoionic character with some thiolate character on the sulfur atom.

**Keywords:** ruthenium; tetrazolium-5-thiolate; terpyridine; bipyridine; synthesis; structure.

### Article:

In spite of uncertainty about its composition and stability [1], dithizone has been used for years as a ligand in colourimetric determination of metals such as lead, mercury, copper, and silver [2]. Our interest in potential sulfur-nitrogen bidentate ligands for polypyridyl ruthenium complexes has led to the preparation of polypyridyl ruthenium complexes containing dithizone [3], dtz (I), and to the consideration of redox products of dithizone as ligands. In particular, 2,3- diphenyltetrazolium-5-thiolate, tet (II), is readily prepared by oxidation of dithizone and can be reduced back to dithizone [4].

In considering that there may be interesting relationships between the coordination of dithizone and tet to metal centres, we have prepared complexes of each using polypyridyl ruthenium moieties as the coordination centres. Dithizone often acts as a bidentate ligand, binding through the sulfur and a nitrogen atom to form a five-membered ring. NMR studies [3] indicate that this is the case also with Ru(bpy)2(dtz)<sup>+</sup>(bpy-2,2'-bipyridine). Tet has not, however, been extensively studied as a ligand, and thus its coordination characteristics are poorly defined. In general, tetrazoles can coordinate to metal centres through either the 1 or 4 nitrogen [5–12], through the 2 or 3 nitrogen [13–17], or through two nitrogens as a bridging ligand [19, 20]. The tin complex, Sn(CH<sub>3</sub>)<sub>2</sub>(phen)L<sub>2</sub> (phen=1,10-phenanthroline; L=1-phenyl-5-thione1,2,3,4-tetrazolate), contains one tetrazolate unit bound through nitrogen and another bound through sulfur [21]. In [HgCl<sub>2</sub>(tet)], the tet sulfur atom acts as a bridging ligand in a polymeric structure [22]. Because of the limited reports of characterization of tet complexes, especially structural characterization of classical transition metal complexes involving this ligand, we have performed a single crystal X-ray analysis of the tet complex reported here.



## EXPERIMENTAL

The complex [Ru(trpy)(bpy)Cl]Cl [23] and tet [1] were prepared according to literature procedures. Other substances were of reagent grade quality and were used as received. Spectrophotometric measurements were made with a Varian DMS-100 spectrophotometer. Electrochemical measurements were made with a Bioanalytical Systems Model CS-1087 Electrochemical Analyzer.

### Synthesis

Preparation of [Ru(trpy)(bpy)(tet)](ClO<sub>4</sub>)<sub>2</sub>. A mixture of 0.300g (0.535 mmol) of [Ru(trpy)(bpy)Cl]Cl and 0.241 g (1.07mmol) of AgClO<sub>4</sub>·H<sub>2</sub>O was placed in a 100 cm<sup>3</sup> flask and 40 cm<sup>3</sup> of 75/25 acetone/water was added. The solution was flushed with nitrogen and refluxed for 1.5 h and then cooled. After filtration, 0.200g (0.79 mmol) of tet was added to the filtrate. The solution was flushed with nitrogen and refluxed for 6h. After cooling, the solution volume was reduced to 10 cm<sup>3</sup> by rotary evaporation. After cooling overnight, the solution was filtered to collect a brown precipitate. The precipitate was chromatographed on an alumina column using dichloromethane/acetone as eluent. Reprecipitation of the red-brown band gave 0.164 g (0.174 mmol) of product (33) yield). Anal. Calcd for RuC<sub>38</sub>H<sub>29</sub>Cl<sub>2</sub>N<sub>9</sub>O<sub>8</sub>S: C, 48.36; H, 3.10; N, 13.36. Found: C, 46.77; H, 3.08; N, 12.88.

### Crystal structure determination

Crystals of [Ru(trpy)(bpy)(tet)](ClO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O were grown by slow evaporation of solvent from a 2:1:1 acetone: ethanol: water solution of [Ru(trpy)(bpy)(tet)](ClO<sub>4</sub>)<sub>2</sub>.

A crystal of dimensions ca. 0.06 × 0.06 × 0.60 mm was mounted on the end of a thin glass fibre. Oscillation and Weissenberg photographs yielded preliminary unit-cell parameters and space group information. An Enraf—Nonius CAD-4 diffractometer (Cu-Kα radiation, graphite monochromator) was used for all other measurements. Refined unit-cell parameters were derived from the diffractometer setting angles for 25 reflections (36° < θ < 40°) widely separated in reciprocal space. Intensity data were corrected for the usual Lorentz and polarization effects; an empirical absorption correction [T<sub>max</sub>:T<sub>min</sub>(rel.) = 1.00:0.93], based on the φ-dependency of the intensities of several reflections with χ ca. 90°, was also applied. Laue symmetry indicated that the crystals belonged to the trigonal system. The systematic absences (00l when l ≠ 3n) were consistent with the space group P3<sub>1</sub> and its enantiomorph P3<sub>2</sub>.

The crystal structure was solved by direct methods (MULTAN11/82) [24] assuming at the outset that the space group was P3<sub>1</sub>. Approximate non-hydrogen atom coordinates were derived in part from an E-map and from a series of weighted F<sub>o</sub> and difference Fourier syntheses phased successively by an increasing number of atoms. One of the perchlorate ions and the water molecule are disordered over two sites, with the alternative location of the latter being masked by a perchlorate ion; moreover, the perchlorate ion at one of these sites is further disordered over two orientations. Non-hydrogen atom positional and temperature factor parameters (first isotropic and then anisotropic), with hydrogen atoms incorporated at their calculated positions in the later cycles, were adjusted by means of several rounds of full-matrix least-squares calculations. An extinction correction was included as a variable during the later iterations. The parameter refinement converged at R = 0.0495 (R<sub>w</sub> = 0.0637). The chirality of the crystal used for data collection was established at this stage by introducing the imaginary contributions to the anomalous dispersion corrections into the structure-factor calculations. For parameters in space group P3<sub>1</sub>, R was 0.0522 while R<sub>w</sub> was 0.0692, whereas when those for the enantiomer were used in space group P3<sub>2</sub>, the values were R' = 0.0578 and R<sub>w</sub> = 0.0782. These differences are significant at the 0.005 level [25] when R'<sub>w</sub> / R<sub>w</sub> (0.0782/0.0692 = 1.130) equals to or exceeds 1.0012 and indicated that P3<sub>1</sub> was the correct choice. Continuation of the least-squares parameter refinement led to convergence at R = 0.048 (R<sub>w</sub> = 0.062). A final difference Fourier synthesis contained no unusual features.

Crystallographic calculations were performed on PDP11/44 and MicroVAX computers by use of the Enraf—Nonius Structure Determination Package (SDP 3.0) [26]. For all structure-factor calculations, neutral atom scattering factors and their anomalous dispersion corrections were taken from ref. [27]. Further information concerning data collection and refinement are provided in Table 1. Atomic coordinates, thermal parameters,

least-squares planes, and a listing of observed and calculated structure amplitudes have been deposited with the Editor as supplementary material.

Table 1. Crystallographic data and data collection parameters for [Ru(trpy)(bpy)(tet)](ClO<sub>4</sub>)<sub>2</sub> · H<sub>2</sub>O

Molecular formula	[C <sub>38</sub> H <sub>29</sub> N <sub>9</sub> RuS][ClO <sub>4</sub> ] <sub>2</sub> · H <sub>2</sub> O
Formula weight	961.77
Crystal system	trigonal
Space group	<i>P</i> 3 <sub>1</sub> ( <i>C</i> <sub>3</sub> <sup>2</sup> )-No.144
<i>a</i> (Å)	13.185(1)
<i>b</i> (Å)	13.185(1)
<i>c</i> (Å)	21.288(2)
$\alpha$ (°)	90.0(—)
$\beta$ (°)	90.0(—)
$\gamma$ (°)	120.0(—)
<i>V</i> (Å <sup>3</sup> )	3205.0(8)
<i>Z</i>	3
<i>D</i> <sub>calcd.</sub> (g cm <sup>-3</sup> )	1.495
Radiation ( $\lambda$ , Å)	Cu-K $\alpha$ (1.5418)
Absorption coefficient, $\mu$ (cm <sup>-1</sup> )	51.9
Temp.(°C)	25
Scan type	$\omega$ -2 $\theta$
Scanwidth (°)	0.90 + 0.14tan $\theta$
$\theta$ <sub>max.</sub> (°)	75
Intensity control reffs.;	2 1 4, 2 1 3, 4 - 5 2, 4 - 2 1;
Variation; repeat time (hr)	< 1.0%; 2
Total no. of reffs. (+ <i>h</i> , ± <i>k</i> , + <i>l</i> ) recorded	7050
No. of non-equiv. reffs. recorded	4958
<i>R</i> <sub>merge</sub> (on <i>I</i> )	0.025
No. of reffs. retained [ <i>I</i> > 3.0 $\sigma$ ( <i>I</i> )]	4050
No. of parameters refined	557
Extinction correction	6.2(5) × 10 <sup>-7</sup>
<i>R</i> ( <i>R</i> <sub>w</sub> ) <sup>a</sup>	0.048 (0.062)
Goodness-of-fit <sup>b</sup>	1.37
Max. shift/esd in final least-squares cycle	0.03
Final $\Delta\rho$ (e/Å <sup>3</sup> )max.; min.	0.80; -1.19

<sup>a</sup>  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ ;  $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ ;  $\sum w\Delta^2 [w = 1/\sigma^2(|F_o|)$ ,  $\Delta = (|F_o| - |F_c|)$  was minimized.

<sup>b</sup> Goodness-of-fit =  $[\sum w\Delta^2 / (N_{\text{observations}} - N_{\text{parameters}})]^{1/2}$ .

## RESULTS AND DISCUSSION

The complex [Ru(trpy)(bpy)(tet)](ClO<sub>4</sub>)<sub>2</sub> was prepared by direct reaction of tet with Ru(trpy)(bpy)Cl<sup>+</sup> in aqueous ethanol solution. The intensely red-coloured complex exhibits properties consistent with the tet binding as a monodentate ligand through the sulfur atom. An MLCT absorption band at 489 nm ( $\epsilon = 7299 \text{ M}^{-1} \text{ cm}^{-1}$ ) is similar to those of Ru(trpy)(bpy)X<sup>+</sup> (X = anion) complexes [28]. The cyclic voltammogram of Ru(trpy)(bpy)(tet)<sup>2+</sup> in acetonitrile exhibits a pseudoreversible wave at 9.86V vs. SSCE ( $\Delta E_p = 89 \text{ mV}$ ), consistent with Ru<sup>III/II</sup> potentials for Ru(trpy)(bpy)X<sup>+</sup> complexes. However, bulk oxidation at a potential just above 9.86 V leads to complete loss of the wave. The foregoing evidence suggests that tet binds through the sulfur atom which possesses significant thiolate character, consistent with the mesoionic character of the free ligand. Thioether or thione ligands [29, 39] exhibit higher energy MLCT bands and higher Ru<sup>III/II</sup> redox couples.

Single-crystal X-ray analysis of [Ru(trpy)(bpy)(tet)](ClO<sub>4</sub>)<sub>2</sub> · H<sub>2</sub>O, Fig. 0 [30], confirms that the six-coordinate ruthenium centre binds to the sulfur atom of the tetrazolium ligand. Important bond distances and angles are listed in Table 2. Distortions from an octahedral arrangement around the ruthenium centre may be ascribed to constraints imposed by the bite angles of the bpy and trpy ligands, and are probably little influenced by the tet ligand. Distances and angles within the trpy ligands are close to the average values in related species [32-37] such as Ru(bpy)<sub>3</sub><sup>2+</sup> and Ru(trpy)L<sub>3</sub><sup>2+</sup> complexes. The Ru $\Delta$ N distances and angles are also in accord with expected values. The short Ru-N(7) distance [0.957(6)Å] and the N(1)-Ru-N(13) angle of only 058.5(2)° are the result of the restricted bite angle of the trpy. Likewise, the bpy bite angle is only 78.4(2)°.

Comparison of the structure of the bound tet to that of the free ligand [38, 39] reveals very little difference. In particular, the C(40)-S(46) and N(43)-N(44) bond lengths in the coordinated tet [1.686(8) Å and 1.316(9) Å,

respectively] do not differ significantly from those in the free ligand {1.692(4) Å and 1.328(4) Å [38], and 1.687(5) Å and 1.313(4) Å [39], respectively, from two independent determinations}. The tetrazolium ring is essentially planar and its directly bonded substituents lie close to the ring plane [ $\Delta(\text{Å})$ : S(46) 0.008, C(47) 0.110, C(53) 0.035] as does the Ru atom [ $\Delta$  0.062 Å N(45)-C(41)-S(46)-Ru torsion angle = 2(1)°]. Dihedral angles between the tetrazolium and phenyl ring planes are 63.1° and 70.8°, while that between the latter is 85.7° [torsion angles: N(44)-N(43)-C(47)-C(48) = 70(1)°, N(43)-N(44)-C(53)-C(58) = -72(2)°]. The bent geometry at the sulfur atom [C(41)-S(46)-Ru = 115.1(2)°] and the Ru-S distance [2.393(2) Å] are comparable to those observed in species like Ru(CO)<sub>2</sub>(pyridine)<sub>2</sub>(mercaptobenzothiazole)<sub>2</sub> [40] where the corresponding values are 109.0(1)° and 2.406(4) Å.

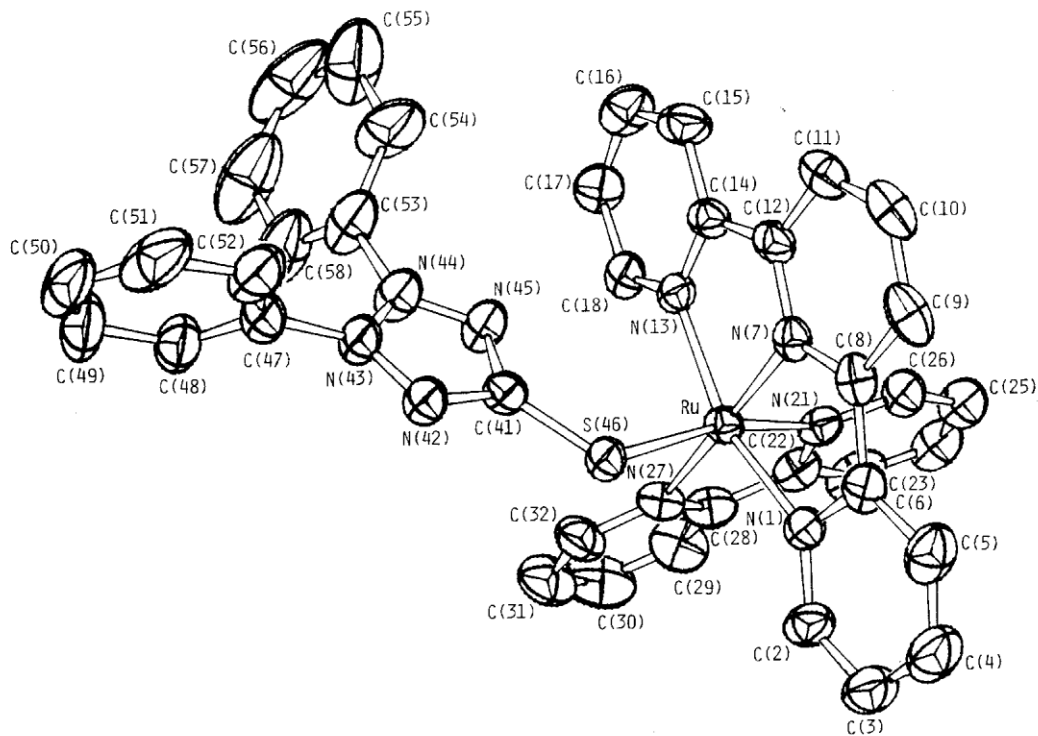


Fig. 1. ORTEP diagram (30% probability ellipsoids) showing the crystallographic atom numbering scheme and solid-state conformation of the  $[\text{C}_{38}\text{H}_{29}\text{N}_9\text{RuS}]^{2+}$  ion; hydrogen atoms have been omitted.

Table 2. Selected interatomic distances (Å) and angles (°) in  $[\text{Ru}(\text{trpy})(\text{bpy})(\text{tet})]^{2+}$ , with estimated standard deviations in parentheses

(a) Bond Lengths			
Ru–N(1)	2.087(6)	Ru–N(21)	2.075(6)
Ru–N(7)	1.957(6)	Ru–N(27)	2.088(6)
Ru–N(13)	2.077(6)	Ru–S(46)	2.393(2)
C(41)–N(42)	1.362(10)	N(43)–N(44)	1.316(9)
C(41)–C(45)	1.375(9)	N(43)–C(47)	1.443(11)
C(41)–S(46)	1.686(8)	N(44)–N(45)	1.306(10)
N(42)–N(43)	1.313(10)	N(44)–C(53)	1.473(13)
(b) Bond Angles			
N(1)–Ru–N(7)	79.2(3)	N(7)–Ru–S(46)	90.1(2)
N(1)–Ru–N(13)	158.5(2)	N(13)–Ru–N(21)	92.1(3)
N(1)–Ru–N(21)	88.5(2)	N(13)–Ru–N(27)	97.1(2)
N(1)–Ru–N(27)	104.0(3)	N(13)–Ru–S(46)	98.5(2)
N(1)–Ru–S(46)	83.6(2)	N(21)–Ru–N(27)	78.4(2)
N(7)–Ru–N(13)	79.4(2)	N(21)–Ru–S(46)	168.2(2)
N(7)–Ru–N(21)	97.0(2)	N(27)–Ru–S(46)	95.1(2)
N(7)–Ru–N(27)	174.2(2)	Ru–S(46)–C(41)–S(46)–C(41)	115.1(2)

Table 3 Bond Lengths (Å) in Tetrazoles\*, with estimated standard deviations in parentheses

Species	C–N <sub>1</sub> , C–N <sub>4</sub>	N <sub>1</sub> –N <sub>2</sub> , N <sub>3</sub> –N <sub>4</sub>	N <sub>2</sub> –N <sub>3</sub>	Reference
<b>Tet and related species</b>				
tet <sup>a</sup>	1.360(4)	1.318(3)	1.313(4)	[38]
	1.368(3)	1.316(3)	1.328(4)	[30]
Ru(trpy)(bpy)(tet) <sup>2+</sup>	1.362(10), 1.375(9)	1.313(10), 1.306(10)	1.316(9)	This work
(tetHgCl <sub>2</sub> ) <sub>2</sub>	1.38(2), 1.31(3)	1.31(3), 1.33(3)	1.25(3)	[22]
2,3-diphenyltetrazolium-5-olate	1.377(4), 1.379(4)	1.312(4), 1.310(4)	1.326(4)	[41]
<b>Other tetrazoles</b>				
1,3-diphenyltetrazolium-5-thiolate	1.348(3), 1.390(4)	1.333(3), 1.331(3)	1.293(3)	[41]
Bis(1-phenyl-5-thiotetrazole)dibutyltin	1.34(2), 1.29(2)	1.35(2), 1.37(2)	1.28(2)	[42]
(5-methyltetrazolate)(OEP)indium(III) <sup>b</sup>	1.28(2), 1.33(2)	1.35(1), 1.34(1)	1.29(1)	[15]
(5-methyltetrazolate)(OEP)iron(III) <sup>b</sup>	1.31(2), 1.34(2)	1.39(3), 1.38(3)	1.32(2)	[15]
Co(PBu <sub>3</sub> )(DH) <sub>2</sub> (5-trifluoromethyl-tetrazole) <sup>c</sup>	1.320(9), 1.34(1)	1.321(9), 1.320(10)	1.321(9)	[18]

<sup>a</sup> Molecule lies on a crystallographic two-fold axis.

<sup>b</sup> OEP = 2,3,7,8,12,13,17,18-octaethylporphinate.

<sup>c</sup> DH = monoanion of dimethylglyoxime

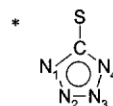


Table 3 lists bond distances in a number of tetrazoles. Distances in the coordinated and free tet are consistent with a mesoionic tetrazole structure. Thus, very similar N-N bond lengths are observed for tet [22, 38, 39] and related species [41]. Other tetrazoles [6-18, 41-43] typically exhibit longer N<sub>1</sub>-N<sub>2</sub>/N<sub>3</sub>-N<sub>4</sub> than N<sub>2</sub>-N<sub>3</sub> bond lengths indicative of greater double bond localization in the N<sub>2</sub>-N<sub>3</sub> bond. These observations are consistent with considerable electron delocalization within the tetrazole ring of tet [44].

Even though considerable anionic character is anticipated for the sulfur atom of tet (and spectral and electrochemical properties are consistent with that character), the C-S bond length at 1.686(8) Å in the coordinated tet is significantly shorter than that usually observed for thiolato C-S species. For example, thiolato ligands in ruthenium complexes have C-S bond lengths ranging from 1.769(3) Å in *cct*-RuH(SC<sub>6</sub>H<sub>4</sub>*p*-Me)(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> [45], 1.778(8), 1.788(7) Å in *cct*-Ru(SC<sub>6</sub>H<sub>4</sub>*p*-Me)<sub>2</sub>(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> [45], 1.77(2)- 1.83(2) Å in (η<sup>6</sup>-arene)Ru(SAr)<sub>2</sub> complexes [46], 1.77(1), 1.79(1) Å in *trans*-Ru-(2,6-C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>S)<sub>2</sub>(CN<sup>t</sup>Bu)<sub>4</sub> [46], to 1.848(5), 1.852(5) Å in Cp<sup>\*</sup>Ru(NO)(SCMe<sub>3</sub>)<sub>2</sub> [47]. The C-S bond length found here is also shorter than that at 1.711(8) Å in [Ru(4-methylpyrimidine-2-thionate)(bipy)<sub>2</sub>]<sup>2+</sup> [48], but it is slightly longer than that of 1.632(5) Å in the coordinated thione [Cp(dppe)RuSCHC<sub>6</sub>H<sub>4</sub>OMe]<sup>+</sup> [49].

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