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An unexpected cleavage of the boron–nitrogen bond in the coordinated dihydrobis(1-pyrazolyl)borate: synthesis and crystal structure of $[Ru^{II}(pz)_2(pzH)_3(DMSO)]$ and synthesis of $[Ru^{II}Cl_2(pzH)_2(DMSO)_2]$

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Abstract

The reaction of *cis*-$RuCl_2(DMSO)_4$ with $K[H_2B(pz)_2]$ in acetonitrile leads to a cleavage of the B–N bond followed by the formation of $[Ru(pz)_2(pzH)_3(DMSO)]$ (1). The crystal structure analysis of 1 (triclinic, space group $P\bar{1}$, $a=8.559(1)$, $b=15.431(2)$, $c=9.155(1)$ Å, $\alpha=90.1(1)$, $\beta=115.3(1)$, $\gamma=92.95(2)°$, $Z=2$, final conventional $R=0.059$) has revealed that two out of the five coordinated pyrazole groups are deprotonated (pyrazolyl anion) to satisfy the charge requirement of the central Ru^{2+} ion. There is a considerable difference in the two Ru–N(pz) distances which may be attributed to the *trans* effect of the coordinated DMSO molecule. The individual pyrazole rings are planar within 0.01 Å. The disposition of the rings are interpreted in terms of the torsion angles between these planes. The molecular structure is held in three dimensional space by an extensive network of intramolecular hydrogen bonding. Under similar reaction conditions, *cis*-$RuCl_2(DMSO)_4$ reacts with free pyrazole (pzH) to give $[Ru^{II}Cl_2(pzH)_2(DMSO)_2]$ (2).

Introduction

Over the past decade, research in inorganic photochemistry has expanded enormously with special reference to the storage and conversion of solar energy [1]. The coordination compounds of Ru with heterocyclic nitrogen donor ligands are among the most studied metal complexes [2] in this area.

Polypyrazolyl borates [3] are special class of ligands with heterocyclic N-donor sites and possess a versatile and varied chemistry because of their interesting steric and electronic properties [4]. A variety of complexes of 3d metal ions with the ligand $[H_nB(pz)_{4-n}]^-$ ($n=0$, 1, 2) have been reported [3, 4]. The bidentate ligand, bis(1-pyrazolyl)borate, coordinates to bipositive and terpositive 3d metal ions [3] usually with a metal to ligand ratio of 1:2 with the exception of V(II) [4] and In(III) [5] which coordinate with the ligand in a 1:3 mole ratio. Sporadic attempts were made for the synthesis of pyrazolyl borate compounds with second row and third row transition metal ions [6]. Surprisingly, examples of Ru complexes with this class of ligands are rather scanty and less documented [6].

In this paper, we report the synthesis and structure of $[Ru(pz)_2(pzH)_3(DMSO)]$ (1) obtained by the reaction of *cis*-$RuCl_2(DMSO)_4$ [7] with potassium dihydrobis(1-pyrazolyl)borate. The complex, $[RuCl_2(pzH)_2(DMSO)_2]$ (2), was synthesized by the direct reaction of pyrazole with *cis*-$RuCl_2(DMSO)_4$.

Results and discussion

During the course of developing Ru–polypyrazolyl borate chemistry, we found that the reaction between *cis*-$RuCl_2(DMSO)_4$ [7] and the bidentate ligand, potassium dihydrobis(1-pyrazolyl)borate, in acetonitrile, leads to the cleavage of the boron–nitrogen bond of the ligand followed by the formation of compound 1 as a red crystalline solid. Interestingly, however, under similar conditions, *cis*-$RuCl_2(DMSO)_4$ reacts with pzH to give $[RuCl_2(pzH)_2(DMSO)_2]$ as an orange-yellow crystalline solid (compound 2). Compound 1 is soluble in polar organic solvents (e.g. Me_2CO, MeCN, MeOH). The infrared spectrum of 1 (as KBr disc) gives an absorption at 1160 cm^{-1} which is assigned to the νSO stretch of the S-bonded DMSO molecule [7]. No BH_2 stretch multiplet [3] at 2230–2460 cm^{-1}

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could be observed in the IR spectrum indicating that the bis(pyrazolyl)borate ligand had broken up. Its electronic spectrum shows two characteristic bands—one with moderate intensity at λ_{max} 435 nm and the other, a high intensity charge transfer band, at 247 nm. The ^1H NMR spectrum of **1** (298 K, CD_3CN) is shown in Fig. 1. The actual spectrum is complicated because of intensive overlap. However, it is evident from the spectrum that two well separated main resonances at δ 7.41 and δ 6.12 ppm in the ratio 2:1, in the aromatic region, are due to the three non-equivalent C-protons (3-H, 5-H and 4-H). The high field resonance at δ 3.12, δ 2.99, δ 2.79 and δ 2.42 ppm in the ratio 1:1:1:6 is due to three pyrazole nitrogen protons and six methyl protons of DMSO, respectively. The pyrazole nitrogen protons resonances in the present case are rather unusually high (δ 13.97) as compared to that in some $[Ru^{II}(bipy)_2(pzH)_{1-2}]^{2+}$ complexes reported by Meyer and coworkers [8]. The $^{13}C\{^1H\}$ NMR spectrum of **1** (298 K, CH_3CN) shows seven resonances at δ 133.04, δ 130.70, δ 113.06, δ 104.92, δ 103.94, δ 102.58 and δ 39.20 ppm. The first six low field signals may be assigned to the carbon atom of the two types of pyrazole rings in the molecule (i.e. pyrazole and pyrazolyl anion). Meyer and coworkers [8] have argued that coordinated pzH acts as a π-acceptor ligand whereas the pyrazolyl anion has the capacity to act as a π-donor ligand. The remaining high field resonance at δ 39.20 ppm is due to the methyl carbon of the bound dimethyl sulfoxide molecule. At this point, it is worth mentioning that the present work, for the first time, provides X-ray structural evidence in support of the rupture of the boron–nitrogen bond in the dihydrobis(1-pyrazolyl)borate ligand under near neutral and mild reaction conditions. Jones *et al.* [9] claimed cleavage of the B–N bond in the ligand $K[HB(Me_2pz)_3]$, by treatment with $[\{Ru(\eta\text{-}C_6H_6)Cl_2\}_2]$ on the basis of spectroscopic data. Subsequently, Alobaidi *et al.* [10] reported the partial degradation of the coordinated ligand (L), $K[HB(3,5\text{-}Me_2pz)_3]$, in $[Mo(NO)LX_2]$ (X = OEt, I) in the presence of strong base (NEt_3) and under drastic reaction conditions (reflux for 72 h). However, both the reports warrant X-ray crystal and molecular structure determination of the alleged decomposition products.

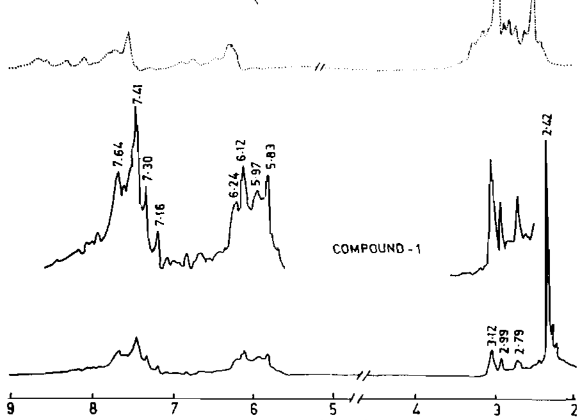


Fig. 1. ^1H NMR spectra of **1** (——) and **2** (– – –) in acetonitrile-d_3 (Me_4Si used as internal standard).

In order to ensure the absence of free pyrazole impurity in the ligand, $K[H_2B(pz)_2]$, we checked the elemental analyses and also, the melting point of the latter which tallies with the literature value [3].

The X-ray single crystal analysis revealed that the central Ru^{2+} ion has a distorted octahedral geometry (Fig. 2), the coordinating positions on the metal ion being occupied by nitrogen of each of the five pyrazole rings and the sulfur of the ligated DMSO molecule. Two out of the five pyrazole ligands are deprotonated (i.e. pyrazolyl anion) and are at distances of 2.064(5) and 2.100(6) Å from the central Ru^{2+} ion. The other three Ru–N(pzH) distances vary from 2.089(5) to 2.093(5) Å (Table 1). The considerable difference in the two Ru–N (pz) distances may be attributed to the *trans* effect of the coordinated DMSO molecule. As expected, the individual pyrazole rings are planar

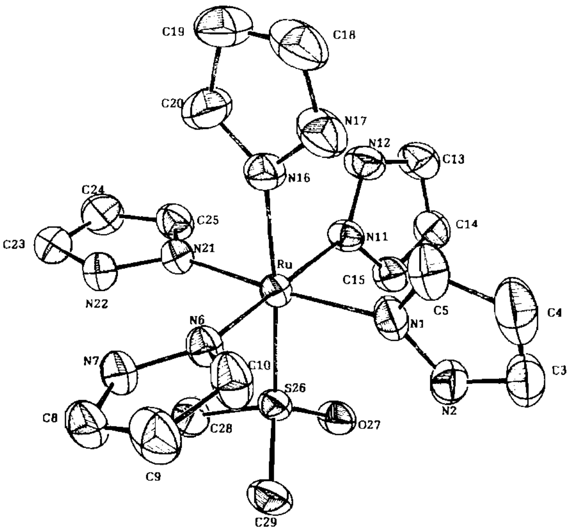


Fig. 2. ORTEP representation of $[Ru(pz)_2(pzH)_3(DMSO)]$ (**1**) with H atoms omitted for clarity. Ellipsoide are drawn with 50% probability.

TABLE 1. Selected bond distances (Å) and angles (°) for 1

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Ru	S26	2.212(1)	N6	N7	1.355(7)	C3	C4	1.33(1)
Ru	N1	2.090(5)	N6	C10	1.34(2)	C4	C5	1.40(1)
Ru	N6	2.093(5)	N7	C8	1.36(2)	C8	C9	1.39(2)
Ru	N11	2.089(5)	N11	N12	1.33(1)	C9	C10	1.39(2)
Ru	N16	2.100(6)	N11	C15	1.383(9)	C13	C14	1.31(2)
Ru	N21	2.064(5)	N12	C13	1.40(1)	C14	C15	1.38(1)
S26	O27	1.497(5)	N16	N17	1.35(1)	C18	C19	1.35(2)
S26	C28	1.800(8)	N16	C20	1.36(2)	C19	C20	1.42(2)
S26	C29	1.798(7)	N17	C18	1.33(1)	C23	C24	1.36(1)
N1	N2	1.361(7)	N21	N22	1.379(6)	C24	C25	1.41(1)
N1	C5	1.344(7)	N21	C25	1.35(2)			
N2	C3	1.355(9)	N22	C23	1.33(1)			

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
S26	Ru	N1	95.2(1)	Ru	N1	N2	123.5(4)	C3	C4	C5	106.5(6)
S26	Ru	N6	90.1(2)	Ru	N1	C5	131.6(5)	N1	C5	C4	110.8(7)
S26	Ru	N11	92.4(2)	N2	N1	C5	103.9(5)	N7	C8	C9	106.5(6)
S26	Ru	N16	174.5(1)	N1	N2	C3	111.6(6)	C8	C9	C10	105.4(9)
S26	Ru	N21	89.1(2)	Ru	N6	N7	123.1(4)	N6	C10	C9	111.1(8)
N1	Ru	N6	90.6(2)	Ru	N6	C10	131.3(5)	N12	C13	C14	111(2)
N1	Ru	N11	84.8(3)	N7	N6	C10	105.8(5)	C13	C14	C15	105.9(9)
N1	Ru	N16	88.0(3)	N6	N7	C8	111.4(6)	N11	C15	C14	109.4(9)
N1	Ru	N21	173.8(3)	Ru	N11	N12	122.9(5)	N17	C18	C19	110(2)
N6	Ru	N11	175.0(2)	Ru	N11	C15	130.2(6)	C18	C19	C20	103.5(9)
N6	Ru	N16	85.4(3)	N12	N11	C15	106.8(6)	N16	C20	C19	110.8(9)
N6	Ru	N21	93.8(2)	N11	N12	C13	106.9(9)	N22	C23	C24	111.6(6)
N11	Ru	N16	92.3(2)	Ru	N16	N17	125.3(4)	C23	C24	C25	103.8(9)
N11	Ru	N21	90.6(3)	Ru	N16	C20	130.2(6)	N21	C25	C24	109.5(6)
N16	Ru	N21	88.0(2)	N17	N16	C20	104.4(7)				
Ru	S26	O27	118.8(2)	N16	N17	C18	111.5(7)				
Ru	S26	C28	114.2(3)	Ru	N21	N22	124.4(5)				
Ru	S26	C29	113.4(3)	Ru	N21	C25	128.3(3)				
O27	S26	C28	104.8(4)	N22	N21	C25	106.8(5)				
O27	S26	C29	105.1(4)	N21	N22	C23	108.2(6)				
C28	S26	C29	98.3(4)	N2	C3	C4	107.2(7)				

Numbers in parentheses are e.s.d.s in the least significant digits.

within 0.01 Å. Ring 2 (N(6)–N(7)–C(8)–C(9)–C(10)) is inclined to ring 5 (N(21)–N(22)–C(23)–C(24)–C(25)) by 16.8 ± 0.8°, while ring 3 (N(11)–N(12)–C(13)–C(14)–C(15)) is inclined to ring 4 (N(16)–N(17)–C(18)–C(19)–C(20)) by 13.3 ± 0.3°, showing that the two pairs of rings are parallely disposed. All the other interplanar angles involving the pyrazole and pyrazolyl ring vary from 78.6 ± 0.3° to 106.2 ± 0.4°, showing the relative perpendicular alignments of the rings.

The Ru–S(26) distance of 2.212(1) Å is shorter than those found for *cis*-$RuCl_2(DMSO)_4$ (average 2.267(2) Å) and *trans*-$RuCl_2(DMSO)_4$ (average 2.352(4) Å) [11]. The *cis* angles in the coordination octahedron vary considerably from 90° and the *trans* angles from 180° showing that the coordination polyhedron is distorted (Table 1). This distortion arises partly from atoms of unequal size in the coordination sphere (S and N) and partly due to the steric overcrowding arising from the necessity to accommodate five pyrazole rings.

Figure 3 shows the packing of 1 in the unit cell (projected along *b* axis). The structure is held in three dimensional space by an extensive network of intramolecular hydrogen bonding. The intramolecular hydrogen bonding distance between N(2) and O(27) (the oxygen of the DMSO molecule) is 2.75 Å. The N(2)–H(21) and H(21)–O(27) distances are 1.06 and 1.92 Å, respectively and the N(2)–H(21)–O(27) angle is 132.8°. There are two

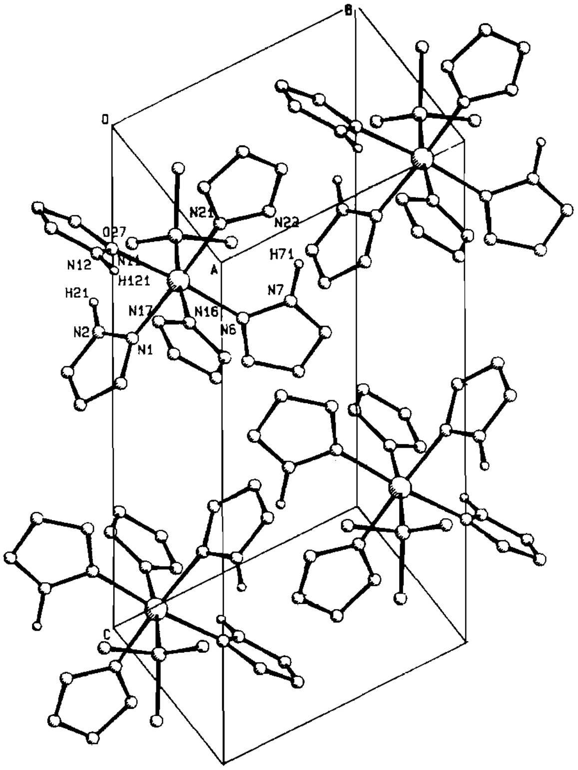


Fig. 3. A view (projected along *b* axis) of the structure of showing the crystal packing.

other intramolecular hydrogen bondings in the structure, between N(7) and N(22) and N(12) and N(17). H(71) gets bonded to N(22) of the pyrazolyl ring 5 at a distance of 2.67 Å, the N(7)-H(71) and H(71)-N(22) distances are 1.07 and 1.76 Å, respectively, while the angle subtended at H(71) is 140.6°. H(121) of the pyrazole ring (ring 3) connects N(12) and N(17) at a distance of 2.59 Å, the N(12)-H(121) and H(121)-N(17) bond distances being 0.95 and 1.81 Å, respectively; the hydrogen bonding angle in this case is 137.7 Å. In the bis(1-pyrazolyl)borate ligand, the N–B–N angles vary from 109.8(2.5) to 115(2.0)°, but the deviation of these values [12] from the expected tetrahedral value is barely significant. However, when the boron–nitrogen bond breaks down to yield pyrazole fragments, the stable conformation which would result would be the one involving hydrogen bonding as these interactions would lead to energy minimization. We do find only three intramolecular hydrogen bonds in this structure. The N–H–N bond angles have values more than that of the tetrahedral angle, This result is a compromise between the two factors of a linearly directed hydrogen bond and otherwise occurring N–H–N angle near to the tetrahedral value.

In order to reconcile the present situation with an authentic preparation from pyrazole (pzH), we have investigated the reaction between *cis*-$RuCl_2(DMSO)_4$ and pzH under similar reaction conditions and have obtained **2** as a hygroscopic orange–yellow solid. Interestingly, even in presence of a large excess of pzH (6:1 mole ratio with respect to Ru), only two DMSO molecules were replaced by pzH. That **2** is distinctly different from **1** is evident from their elemental analysis and spectroscopic data. The appearance of an IR absorption band at 1100 cm^{-1} and the absence of any strong band in the 900–950 (νSO (O-bonded DMSO)) cm^{-1} region are indicative of the presence of only S-bonded DMSO molecules [7]. The *trans* disposition of the two ligated chloride ions is revealed from the appearance of one Ru–Cl stretch at 340 cm^{-1} [7]. The UV–Vis spectrum of **2** is distinctly different from that of **1**. Moderate intensity bands at 420 and 300 nm and a high intensity charge transfer band at 245 nm are observed for **2**. Its ^1H NMR spectrum is shown in Fig. 1. Unfortunately, here also, the spectrum (in CD_3CN) gave no useful structural information because of the complexity of the spectrum. However, the low field resonances at δ 8.65, δ 8.52, δ 8.27, δ 8.04, δ 7.76, δ 7.66, δ 7.51, δ 6.87, δ 6.73 and δ 6.29 ppm and high field resonances at δ 3.04, δ 2.89, δ 2.54 ppm in the ratio 3:7 accounted for 20 protons as expected and are assigned to three pyrazole protons in each pyrazole ring (3-H, 5-H and 4-H), two pyrazole nitrogen protons and twelve methyl protons of the two coordinated DMSO molecules. Its $^{13}C\{^1H\}$ NMR spectrum reveals three low field resonances at δ 140.36, δ 130.47 (3-C, 5-C) and δ 105.9 (4-C) which is consistent with an N-bonded pyrazole ring. The resonance at δ 43.42 is assigned to two S-bonded DMSO molecules. Isolation of *trans*-dichloro compound **2** from *cis*-$RuCl_2(DMSO)_4$ points out that *cis*-$RuCl_2(DMSO)_4$ undergoes isomerization during the course of the reaction with pzH.

Jones *et al.* [9] have argued that steric constraints play an important role in this class of ligands. Recently, Trofimenko *et al.* [13] have shown that by selective substitution at the 3-C of pyrazole rings in the polypyrazolylborate ligand using bulky iso-propyl group, it is possible to achieve 1,2-boratropic shifts involving B–N bond cleavage. In the present case, it seems quite reasonable to assume that **1** may be the decomposition product of an intermediate polypyrazolylborate complex of ruthenium where the coordinated pyrazolyl borate ligands, in a crowded coordination sphere, are under steric strain to provide a suitable 'bite'. The rupture of B–N bonds is possibly the consequence of such strain. Alternatively, the intermediate may have undergone solvolytic cleavage of the B–N bonds. One strong evidence in support of this supposed 'intermediate' is the isolation of **2** even in presence of a large excess of free pzH. Had the cleavage taken place before complexation of the ligand, we should have obtained a compound identical to **2** instead of **1**. However, we failed to obtain any meaningful elemental analysis data of the solid samples obtained by intercepting the course of the above reaction at different time intervals.

Experimental

$RuCl_3 \cdot xH_2O$ was purchased from Johnson Mathey, $K[H_2B(C_3H_3N_2)_2]$ was obtained from Strem Chemicals and $C_3H_4N_2$ from Aldrich Chemicals. *cis*-$RuCl_2(DMSO)_4$ was prepared according to the literature method [7]. The solvents were dried by standard procedures and distilled prior to use. Infrared spectra were recorded by using KBr pellets on a Perkin-Elmer PE597 IR instrument. UV–Vis spectra were recorded on a Shimadzu UV-240 spectrophotometer. ^1H and $^{13}C\{^1H\}$ NMR spectra were obtained on a Jeol FX-100 FT-NMR in acetonitrile-d_3 using $Si(CH_3)_4$ as an internal standard, operating at 40.27 and 24.99 MHz, respectively. Elemental analysis were performed by using a Carlo Erba strumentazional Analyzer model 1106.

Synthesis of $[Ru^{II}(pz)_2(pzH)_3(SO(CH_3)_2)]$ *(1)*

cis-$RuCl_2(SO(CH_3)_2]_4$ [7] (0.2 g, 0.4 mmol) and $K[H_2B(pz)_2]$ (0.23 g, 1.2 mmol) were added to 20 ml of CH_3CN. After heating the reaction mixtures at 60 °C for 45 min, the resulting deep red solution was evaporated to dryness under reduced pressure. The solid mass was extracted with dry acetone. Red crystals of **1** were obtained upon slow evaporation of the solvent (0.07 g, 33% yield). *Anal.* Calc. for $C_{17}H_{24}N_{10}SORu$: C, 39.44; H, 4.68; N, 27.10. Found: C, 39.5; H, 4.8; N, 26.9%. Infrared spectral data (KBr, cm^{-1}): 3400(w), 3160(w), 1650(w), 1400(s), 1360(w), 1300(w), 1200(m), 1160(s), 760(s), 710(w), 690(w), 660(w), 605(w), 445(w), 435(w), 395(w). UV–Vis (CH_3CN): λ_{max} ($\epsilon = 1\ mol^{-1}, cm^{-1}$): 435(380), 247(4217), 240(sh) nm. $^{13}C\{^1H\}$ NMR (ppm) (24.99 Hz, CH_3CN, $Si(CH_3)_4$ reference): 133.04, 130.70, 117.2 (CH_3CN), 113.06, 104.92 (broad), 103.94, 102.58, 39.20, 0.3 (CH_3CN).

Synthesis of $[Ru^{II}Cl_2(C_3H_4N_2)_2(SO(CH_3)_2)_2]$ *(2)*

cis-$RuCl_2(DMSO)_4$ (0.2 g, 0.4 mmol) was reacted with $C_3H_4N_2$ (0.06 g, 0.8 mmol) in CH_3CN under reaction conditions similar to those stated for **1**. After removing the solvent under reduced pressure, the resulting orange–yellow mass was extracted with dry acetone. Removal of the solvent acetone furnished a bright orange–yellow hygroscopic solid which was recrystallized from dry acetone–n-hexane solvent mixture and dried *in vacuo* over P_2O_5. (0.06 g, 31%

TABLE 2. Summary of crystallographic data for $[Ru(pz)_2(pzH)_3(DMSO)]$ (1)

Formula	$C_{17}H_{24}N_{10}SORu$
Formula weight	517.35
Crystal system	triclinic
Space group	$P1$ or $P\bar{1}$ ($P\bar{1}$ chosen after consideration of intensity stabilities and confirmed by structural analysis and refinement)
a (Å)	8.559(1)
b (Å)	15.431(2)
c (Å)	9.155(1)
α (°)	90.10(1)
β (°)	115.30(1)
γ (°)	92.95(2)
V (Å^3)	1091.6(9)
μ(Cu Kα) (cm^{-1})	71.2
Z	2
D_{calc} (g/cm^3)	1.69
Equipment	Enraf-Nonius CAD-4
Data collection	zigzag method
No. unique reflections	3607
No. observed reflections ($I \geq 3\sigma(I)$)	3245
2θ (°)	4–130
Radiation (monochromated in incident beam)	Cu Kα ($\lambda\bar{\alpha} = 1.54018$ Å)
$F(000)$	524
Temperature (°C)	20 ± 1

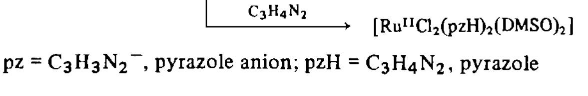
TABLE 3. Positional parameters and their e.s.d.s for **1**

Atom	x	y	z	B (Å^2)
Ru	0.32258(5)	0.12782(4)	0.25189(2)	3.724(6)
S26	0.4090(2)	0.0774(1)	0.12717(8)	4.28(2)
O27	0.3874(8)	−0.0907(4)	0.1076(3)	5.44(9)
N1	0.3350(6)	−0.0690(5)	0.3156(3)	4.18(8)
N2	0.3258(8)	−0.2034(5)	0.2734(4)	5.0(1)
N6	0.5797(7)	0.2744(6)	0.2928(3)	4.43(9)
N7	0.6601(7)	0.4337(6)	0.2753(4)	4.7(1)
N11	0.0651(7)	−0.0310(6)	0.2204(4)	5.0(1)
N12	−0.0665(9)	−0.0343(9)	0.2645(6)	6.5(2)
N16	0.2595(8)	0.1980(6)	0.3699(3)	4.9(1)
N17	0.098(1)	0.1446(9)	0.3987(5)	6.8(1)
N21	0.2844(6)	0.3148(5)	0.1946(3)	4.25(8)
N22	0.4157(8)	0.4563(5)	0.1689(4)	5.0(1)
C3	0.309(1)	−0.3228(7)	0.3294(5)	5.8(1)
C4	0.303(1)	−0.2678(9)	0.4087(5)	6.3(2)
C5	0.322(1)	−0.1101(8)	0.3994(4)	5.6(1)
C8	0.828(1)	0.5003(9)	0.3079(5)	5.9(2)
C9	0.854(1)	0.377(1)	0.3495(7)	6.8(2)
C10	0.698(1)	0.2405(9)	0.3377(5)	5.5(1)
C13	−0.218(1)	0.156(1)	0.226(1)	8.4(2)
C14	−0.182(1)	−0.224(1)	0.1598(7)	7.7(2)
C15	−0.005(1)	−0.1498(9)	0.1560(5)	6.3(2)
C18	0.100(1)	0.206(1)	0.4773(7)	8.2(2)
C19	0.265(2)	0.304(1)	0.5048(6)	8.4(2)
C20	0.364(1)	0.296(1)	0.4353(6)	7.4(2)
C23	0.345(1)	0.5381(7)	0.1239(5)	5.8(1)
C24	0.169(1)	0.4583(8)	0.1177(7)	6.9(2)
C25	0.134(1)	0.3163(7)	0.1646(6)	5.9(1)
C28	0.314(1)	0.1312(8)	0.0330(4)	6.1(2)
C29	0.6323(9)	0.205(1)	0.1101(5)	6.2(1)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2B(1,1)+b^2B(2,2)+c^2B(3,3)+ab(\cos\ \gamma)B(1,2)+ac(\cos\ \beta)B(1,3)+bc(\cos\ \alpha)B(2,3)]$.

yield). *Anal.* Calc. for $C_{10}H_{20}N_4S_2O_2Cl_2Ru$: C, 25.85; H, 4.34; N, 12.10. Found: C, 26.0; H, 4.5; N, 11.9%. Infrared spectral data (KBr, cm^{-1}): 3400(s), 3120(s), 3040(w), 2940(w), 1640(m), 1520(m), 1480(s), 1400(s), 1360(s), 1340(w), 1260(m), 1100(b, s), 1040(s), 1020(s), 980(w), 765(s), 710(m), 690(m), 410(m), 340(m). UV–Vis (CH_3CN): λ_{max} (ϵ): 420 (16), 300 (364), 245 (3550). $^{13}C\{^1H\}$ NMR (ppm) (CH_3CN): 140.36, 130.47, 117.2 (CH_3CN), 105.90 and 43.42, 0.3 (CH_3CN).

The general method of synthesis of **1** and **2** is summarized below.



pz = $C_3H_3N_2^-$, pyrazole anion; pzH = $C_3H_4N_2$, pyrazole

Crystal data

A deep red crystal of **1** suitable for X-ray diffraction was obtained from its acetone solution at +4 °C. Relevant crystallographic data are shown in Table 2.

Data collection and processing

Data were collected with a small crystal of dimensions (0.21×0.21×0.31 mm) on a CAD4 diffractometer using the $\omega/2\theta$ scan method to a maximum 2θ of 130° with graphite monochromatized Cu Kα radiation. A total of 3607 unique reflections was measured and after correction for Lorentz, polarization and absorption effects, 3245 reflections with $I \geqslant 3\sigma(I)$ were considered observed and used in the structure solution and refinement.

Structure analysis and refinement

The structure was solved by the heavy-atom method. The three dimensional sharpened origin-removed Patterson map revealed the positions of both the Ru and S atoms (Table 3). Least-squares refinements, followed by a difference map gave the positions of all the non-hydrogen atoms. Hydrogen atoms were visible in the difference maps and were included in the final round of calculations, but, not refined. The structure was refined by full-matrix least-squares procedure. A mixed-mode refinement with all the non-hydrogen anisotropic and fixed hydrogen positions (with an isotropic temperature factor of 4.0 Å^2) was used for this purpose. The Dunitz–Seiler [14] weighting scheme was used. The structure converged to a final R value of 0.059 (R_w=0.063). A final difference map revealed small peaks of 0.5 e Å^{-3} (within 1 Å) from Ru, but, was otherwise featureless. All the calculations were performed on a PDP-11/73 computer system using the SDP set of programs [15].

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