Crystal Structure of Bis(2,2′-bipyridine)(purine-6-thione)ruthenium(II) Complex

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Two bis(2,2′-bipyridine)ruthenium(II) complexes containing purine-6-thione were prepared. The crystal structure of $[Ru(H_2put)(bpy)_2](ClO_4)_2 \cdot 2.5H_2O$ (bpy = 2,2′-bipyridine; H_2put = 7*H*-purine-6(1*H*)-thione) revealed that the H_2put ligand coordinates through the S^6/N(7) donors and can form the double N–H···N intermolecular hydrogen bonds in the crystal.

Purine-6-thione is an established clinical agent for the therapy of human leukaemia[1] and some metal complexes of put, especially platinum and palladium, show antitumor activity.[2] Since this compound has multiple binding sites, such as N1, N3, S^6, N7, and N9, it is interesting to investigate its coordination modes.[3] Our recent studies showed that Hput acts not only in a bidentate manner[4] but also in a terdentate manner.[5] Here we describe the synthesis and characterization of bis(2,2′-bipyridine)ruthenium(II) complexes (2,2′-bipyridine = bpy) containing 7*H*-purine-6(1*H*)-thione (H_2put) and 3,6-dihydro-6-thioxo-7*H*-purine-2(1*H*)-one (H_3tpuo) (Chart 1).

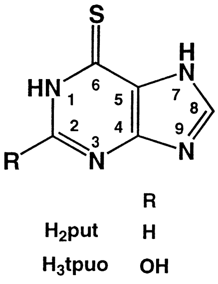

Chart 1.

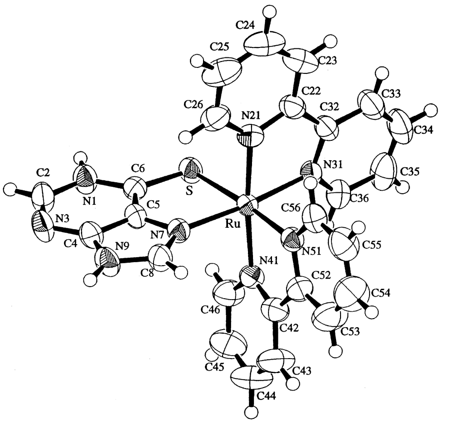

Fig. 1. An ORTEP drawing of the cation in $[Ru(H_2put)(bpy)_2](ClO_4)_2 \cdot 2.5H_2O$ with thermal ellipsoids drawn at the 50% probability level.

Table 1. Selected Bond Distances (Å) and Bond Angles (°) for $[Ru(H_2put)(bpy)_2](ClO_4)_2 \cdot 2.5H_2O$

Bond distances			
Ru–S	2.434(1)	Ru–N(7)	2.097(4)
Ru–N(21)	2.049(4)	Ru–N(31)	2.040(4)
Ru–N(41)	2.069(4)	Ru–N(51)	2.055(4)
S–C(6)	1.674(5)	N(1)–C(2)	1.358(6)
N(1)–C(6)	1.374(6)	N(3)–C(2)	1.303(7)
N(3)–C(4)	1.358(6)	N(7)–C(5)	1.374(6)
N(7)–C(8)	1.319(6)	N(9)–C(4)	1.347(6)
N(9)–C(8)	1.364(6)	C(4)–C(5)	1.379(6)
C(5)–C(6)	1.381(6)		
Bond angles			
S–Ru–N(7)	84.5(1)	S–Ru–N(51)	175.7(1)
N(7)–Ru–N(31)	174.6(1)	N(21)–Ru–N(31)	78.5(2)
N(21)–Ru–N(41)	172.9(2)	N(41)–Ru–N(51)	78.7(2)
Ru–S–C(6)	96.6(2)	C(2)–N(1)–C(6)	122.5(4)
C(2)–N(3)–C(4)	113.1(4)	Ru–N(7)–C(5)	112.1(3)
Ru–N(7)–C(8)	142.9(3)	C(5)–N(7)–C(8)	104.9(4)
C(4)–N(9)–C(8)	107.7(4)	N(1)–C(2)–N(3)	126.3(5)
N(3)–C(4)–C(5)	123.1(5)	N(9)–C(4)–C(5)	105.7(4)
N(7)–C(5)–C(4)	110.2(4)	N(7)–C(5)–C(6)	126.9(4)
C(4)–C(5)–C(6)	122.8(4)	S–C(6)–C(5)	119.7(4)
N(1)–C(6)–C(5)	111.9(4)	N(7)–C(8)–N(9)	111.4(4)

Fig. 1 shows an ORTEP[6] drawing of the cation in $[Ru(H_2put)(bpy)_2](ClO_4)_2 \cdot 2.5H_2O$. The selected bond distances and angles are listed in Table 1. The H_2put ligand co-ordinates in a bidentate manner via the S and N(7) atoms and forms a five-membered chelate ring. Its bite angle S–Ru–N(7) is 84.5(1)°, which is considerably smaller than 88.6(1)° in [Co(put-*N*,*S*)(en)$_2$]Cl (en = 1,2-ethanediamine)[4] and 88.3(4)° in *cis*(*P*)*trans*(*S*)-$[Ru^{II}(H_2put)_2\{P(C_6H_5)_3\}_2]Cl_2$.[7] The Ru–S and Ru–N(7) lengths [2.434(1) and 2.097(4) Å] in the present complex are similar to av 2.432(4) and 2.16(1) Å in *cis*(*P*)*trans*(*S*)-$[Ru(H_2put)_2\{P(C_6H_5)_3\}_2]^{2+}$ which also has the neutral H_2put ligand. The C(6)–S bond length 1.674(5) Å is analogous to av 1.67(2) Å in $[Ru(H_2put)_2\{P(C_6H_5)_3\}_2]^{2+}$, which are very close to 1.679(1) Å of the free thione.[8] Hence there exists a considerable amount of double bond character for the C(6)–S bond in ruthenium(II) complexes. On the other hand, the C–S bond lengths 1.715(7) in [Ru(mpymt)(bpy)$_2$]ClO$_4$ (mpymt = 4-methylpyrimidine-2-thionate)[9] and 1.732(4) Å in [Co(put-*N*,*S*)(en)$_2$]$^+$ are considerably longer than that of the present complex. Since H_2put is neutral, protonation occurs at two sites among N(1), N(3) and N(9). Their hydrogen positions were determined and refined as the N(1) and N(9) sites by X-ray analysis. The bond angle C(2)–N(3)–

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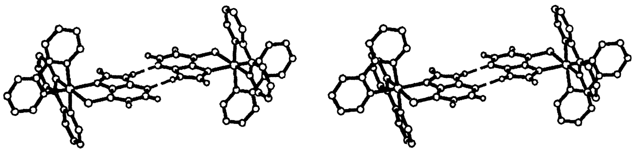

Fig. 2. Stereoview of double linear N–H···N intermolecular hydrogen bonds in $[Ru(H_2put)(bpy)_2]^{2+}$. The hydrogens of bpy were omitted for clarity.

C(4) 113.1(4)° is consistent with Singh's rule[10] that the valence angles for nitrogen without an extra-annular hydrogen atom are within 116 ± 3° for a six-membered ring, whereas the bond angle C(2)–N(1)–C(6) is 122.5(4)°.

An interesting structural feature of the present complex concerns the double linear N–H···N intermolecular hydrogen bonds, as shown in Fig. 2. The self-associated double hydrogen bonds are formed between N(9)–H and N(3) of one complex and N(3) and N(9)–H of an adjacent complex. They are in the same plane and related by an inversion center. The N(9)–H···N(3) distance is 2.862(6) Å, which is slightly longer than the double linear N–H···O intermolecular hydrogen bonds 2.750(5) Å in $[Co(Hatuc\text{-}atuc)(en)_2]^+$ {Hatuc-atuc = 6-amino-5-[6-amino-4-oxo-(1*H*)-pyrimidin-2-yl]thio-2-thioxo-pyrimidin-4-one}.[11]

The two ^1H NMR signals appear at δ 8.72 and 8.14 in $[Ru(H_2put)(bpy)_2]^{2+}$. The assignment was made by referring to that for Co(III) complex.[4] The upfield signal at δ 8.14 is assigned to the C(8)–H, though the shift is not so large irrespective of locating over one of bpy. A similar effect was successfully applied to the assignments of linkage isomers in $[Ru(\text{pyrimidine-2-thionato})(\text{bipy})_2]^+$.[9]

The C(8)–H signal of $[Ru(H_2tpuo)(bpy)_2]^+$ appears at considerably higher magnetic field of δ 6.71 than the corresponding value δ 8.08 in $[Co(H_2tpuo)(en)_2]^{2+}$.[4] This means that the C(8)–H is located over the bpy chelate ring; such a situation is not possible for the N(1)/S^6 coordination mode, but is possible for S^6/N(7) one. Thus we concluded that $[Ru(H_2tpuo)(bpy)_2]^+$ also adopts the S^6/N(7) mode.

Experimental

Preparations. $[Ru(H_2put)(bpy)_2](ClO_4)_2\cdot 2.5H_2O$. The ligand H_2put (0.085 g, 0.5 mmol) was suspended in 50% aqueous methanol (50 cm^3) and the mixture was adjusted to pH 8–9 by adding aqueous NaOH. To the above solution was added *cis*-$[RuCl_2(bpy)_2]\cdot 0.5H_2O$[12] (0.25 g, 0.5 mmol) and the mixture was refluxed at 90 °C for 3 h. After cooling to room temperature, 0.12 g of $NaClO_4$ was added. The mixture was concentrated by a rotary evaporator to give the brownish crude product, which was recrystallized from water/methanol. The complex composition was $[Ru(H_2put)(bpy)_2](ClO_4)_2$ irrespective of the NaOH added. Yield; 60%. {Found: C, 36.77; H, 3.16; N, 13.70%. Calcd for $[Ru(H_2put)(bpy)_2](ClO_4)_2\cdot 2.5H_2O$ ($C_{25}H_{25}C_{12}N_8O_{10.5}RuS$): C, 37.09; H, 3.11, N, 13.84%}. UV/vis (water): λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 460 (14600) 430sh (14000) 344sh (8300) 288 (74400) 253sh (26300) 243 (31100). NMR(DMSO-d_6): δ_H 8.72 (H^2; s, 1H) 8.14 (H^8; s, 1H) 7.36–9.24(bpy).

$[Ru(H_2tpuo)(bpy)_2]ClO_4$. This complex was prepared in the same way as described above. Yield; 65%. {Found: C, 42.05; H, 3.22; N, 15.66%. Calcd for $[Ru(H_2tpuo)(bpy)_2]ClO_4\cdot 2H_2O$ ($C_{25}H_{23}ClN_8O_7RuS$): C, 41.93; H, 3.24, N, 15.65%}. UV/vis (water): λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) 487 (11600) 447 (11400) 363sh (10400) 325 (16300) 292 (65200) 243 (37600). NMR(DMSO-d_6): δ_H 6.71(H^8; s, 1H) 7.32–9.37(bpy). **Caution**: In general, perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handled with great care.

Crystallography. Crystal data for $[Ru(H_2put)(bpy)_2](ClO_4)_2\cdot 2.5H_2O$ were collected on a Rigaku AFC7R diffractometer with graphite-monochromated Mo-K_α radiation ($\lambda = 0.71069$ Å); $C_{25}H_{25}Cl_2N_8O_{10.5}RuS$, $M_W = 809.56$, crystal size 0.20 × 0.15 × 0.35 mm; $T = 23$ °C; monoclinic, space group $P2_1/c$ (No. 14), $a = 10.378(5)$, $b = 23.973(4)$, $c = 13.312(3)$ Å, $\beta = 93.52(3)°$, $Z = 4$, $U = 3305(1)$ Å^3, $D_c = 1.627$ g cm^{-3}, $\mu = 7.66$ cm^{-1}, $F(000) = 1636$. Of the 10369 reflections, 10046 were unique ($R_{int} = 0.020$). Reflection data were collected for both Lorentz and polarization effects and an empirical absorption correction was applied (transmission factors ranging from 0.82 to 0.89). Final $R1 = 0.059$ for 8348 reflections with $I > 2\sigma(I)$ (342 parameters) and $wR2 = 0.148$ for all reflections. All nonhydrogen atoms were refined anisotropically. H(1) and H(9) atoms were refined isotropically and the hydrogen atoms of $2.5H_2O$ were located but not refined. The remaining hydrogen atoms were located on the calculated positions. Refinements were carried out by a full-matrix least squares method based on F^2. All calculations were performed using the teXsan[13] crystallographic software package.

Measurements. UV/vis absorption spectra were measured with a Hitachi 330 spectrophotometer, ^1H spectra with a JEOL JNM-GSX-400 spectrometer in $(CD_3)_2SO$ at 30 °C. X-ray crystal analysis was made at the X-ray Diffraction Service of the Department of Chemistry.

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