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Letter

Tuning of intramolecular electron transfer between Ru(II) and the disulfide bond

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Reaction of 2,2′-dithiodipyridine (DTDP) with *cis*-Ru(bpy)$_2$Cl$_2$ (bpy = 2,2′-bipyridine) and *cis*-Ru(phen)$_2$Cl$_2$ (phen = 1,10-phenanthroline) respectively yields the dicationic species [Ru(bpy)$_2$(DTDP)]$^{2+}$ and [Ru(phen)$_2$(DTDP)]$^{2+}$ in which the S–S bond of DTDP remains intact. The S–S bond undergoes a reductive cleavage when DTDP is reacted with *cis*-Ru(bisox)$_2$Cl$_2$ (bisox = 4,4,4′,4′-tetramethyl-2,2′-bisoxazoline) under identical conditions to generate the monocationic species [Ru(bisox)$_2$(2-thiolatopyridine)]$^+$. The intramolecular electron transfer between the metal and the S–S bond is found to be subtly controlled by the crystal field strength of the ancillary bidentate *N*-donor ligands.

The properties of a metal ion are governed by the ligands around it. But fine tuning a given property of a metal ion by appropriate choice of the ligand(s) seems to have been achieved only by nature. Demonstrations of such tuning in the laboratory have been rare.[1,2] Herein we show that the nature of the interaction of a disulfide (S–S) bond to ruthenium(II) can be controlled in a very delicate manner by the ancillary ligands.

Reaction of 2,2′-dithiodipyridine (DTDP) with *cis*-Ru(bpy)$_2$Cl$_2$ (bpy = 2,2′-bipyridine) and *cis*-Ru(phen)$_2$Cl$_2$ (phen = 1,10-phenanthroline) in equimolar proportions in a 1:1 methanol–water mixture under refluxing and anaerobic conditions, and subsequent addition of excess of NaClO$_4$ followed by recrystallisation of the products from a 3:1 dichloromethane–*n*-hexane mixture generates [Ru(bpy)$_2$(DTDP)](ClO$_4$)$_2$·H$_2$O (**1**) and [Ru(phen)$_2$(DTDP)](ClO$_4$)$_2$·2CH$_2$Cl$_2$ (**2**), respectively, in 75% yield. The solid state structures of the cations in **1** and **2** as determined by X-ray crystallography are shown in Figs. 1 and 2, respectively. In both the cations, Ru(II) has a distorted octahedral N$_5$S coordination sphere with the DTDP bonded to the metal *via* a pyridine N at 2.092(8)–2.103(7) Åand an S atom at 2.315(3)–2.316(3) Å. DTDP usually binds a metal ion *via* the two pyridine nitrogen atoms.[3–6] The present binding mode of DTDP has earlier been found only in bis(DTDP) copper(I) perchlorate.[7] Even in Cu(DTDP)$_2$$^+$, one of the two DTDP units binds copper(I) in

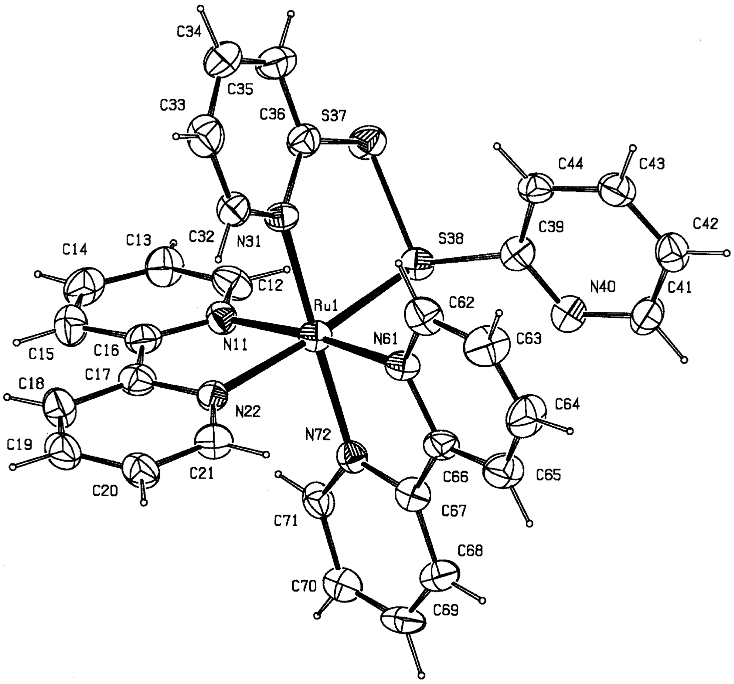


Fig. 1 The structure of the cation in **1** with ellipsoids at 15% probability. Selected bond distances (Å) and angles (°): Ru1–N11 2.069(8), Ru1–N22 2.086(8), Ru1–N61 2.073(8), Ru1–N72 2.072(8), Ru1–N31 2.092(8), Ru1–S38 2.315(3), S37–S38 2.068(4), N11–Ru1–N22 79.3(3), N61–Ru1–N72 79.6(3), N31–Ru1–S38 86.3(2).

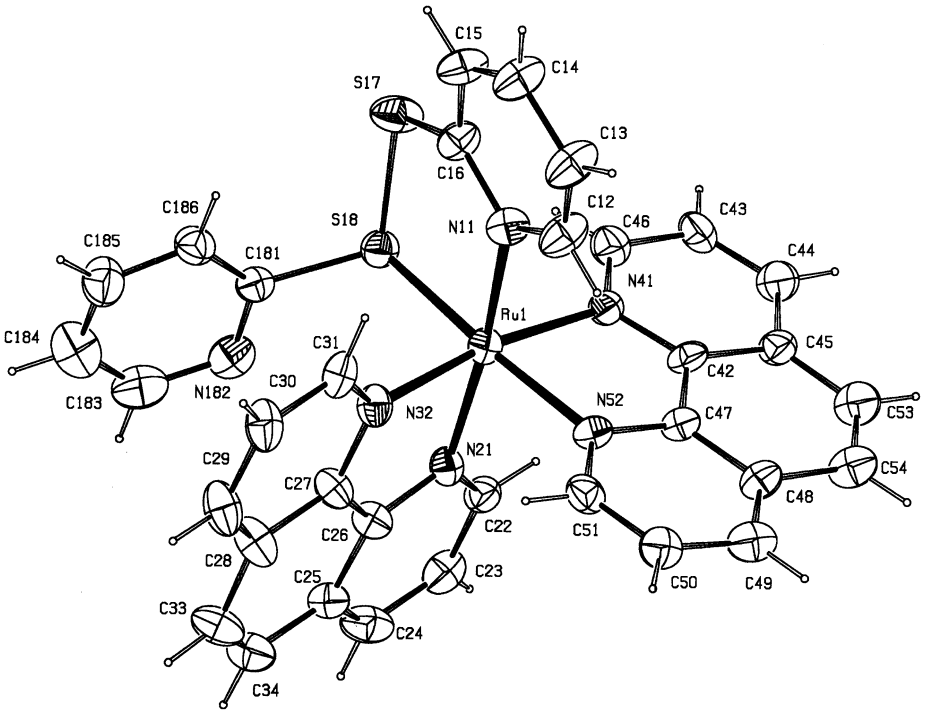


Fig. 2 The structure of the cation in **2** with ellipsoids at 15% probability. Selected bond distances (Å) and angles (°): Ru1–N11 2.103(7), Ru1–N21 2.087(6), Ru1–N32 2.086(6), Ru1–N41 2.108(6), Ru1–N52 2.101(6), Ru1–S18 2.316(3), S17–S18 2.065(4), N11–Ru1–S18 87.9(2), N21–Ru1–N32 79.7(2), N41–Ru1–N52 79.7(2).

the *N*,*N* mode; the S–S distance in the DTDP moiety that binds copper(I) in the present *N*,*S* mode, is 2.032(4) Å. In free DTDP, the S–S bond length is 2.016 Å.[7] This S–S bond is found to be somewhat lengthened in **1** and **2** to 2.068(4) and 2.065(4) Å, respectively. Thus, the S–S bond in **1** and **2** seems to be under some kind of "electronic strain". The Ru–N(bpy) bond lengths in **1** lie in the range 2.069(8)–2.086(8) Å and the Ru–N(phen) ones in **2** at 2.086–2.108 Å.

When the reaction of DTDP with *cis*-Ru(bisox)$_2$Cl$_2$ (bisox = 4,4,4′,4′-tetramethyl-2,2′-bisoxazoline) in a 1:1 molar proportion is carried out under conditions exactly similar to those used for reacting DTDP with *cis*-Ru(bpy)$_2$Cl$_2$ and *cis*-Ru(phen)$_2$Cl$_2$, we obtain [Ru(bisox)$_2$(2-thiolatopyridine)]ClO$_4$ (**3**) in 70% yield. The structure of the cation in **3** as found by X-ray crystallography is shown in Fig. 3. Here also the cation has a distorted N$_5$S coordination sphere. The Ru–N(bisox) bonds

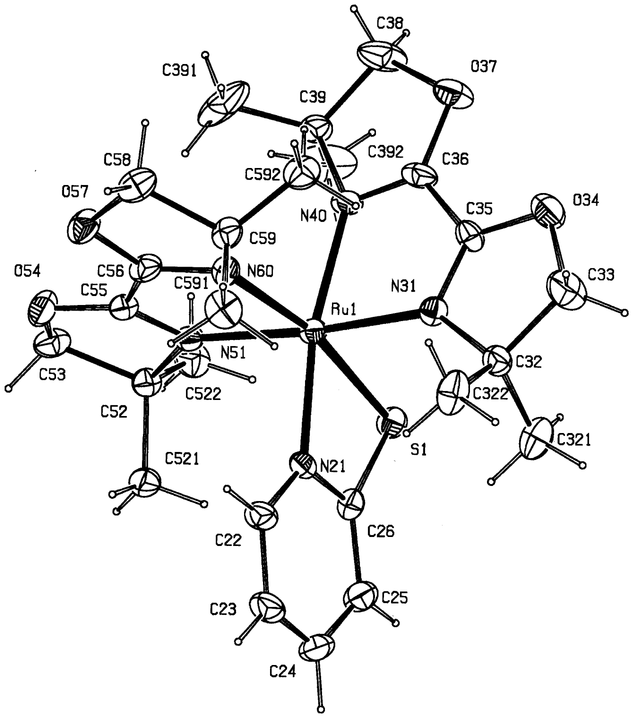
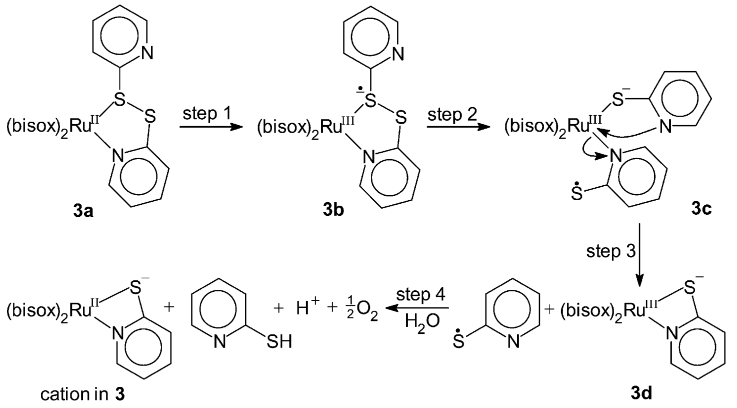


Fig. 3 The structure of the cation in **3** with ellipsoids at 15% probability. Selected bond distances (Å) and angles (°): Ru1–N21 2.068(6), Ru1–N31 2.109(8), Ru1–N40 2.101(7), Ru1–N51 2.112(7), Ru1–N60 2.159(7), Ru1–S1 2.428(4), N21–Ru1–S1 67.9(2), N31–Ru1–N40 77.9(3), N51–Ru1–N60 77.2(3).



Scheme 1

are all equivalent at 2.101(7), 2.109(8), 2.112(7) Å in length, apart from N(60), which is *trans* to the sulfur and has a significantly longer bond length at 2.159(7) Å. In the 2-thiolatopyridine fragment the Ru–N distance is 2.068(6) Å and the Ru–S one is 2.428(4) Å. In each of the bisoxazolines the two five-membered rings are approximately coplanar with angles of intersection being 0.9(6) and 5.6(6)°. It is interesting to note that the Ru–S bond in **3** is much longer than that in **1** and **2**.[8,9]

We can now summarise our results as follows. When DTDP interacts with the RuN_4^{2+} moiety in $Ru(bpy)_2^{2+}$ or in $Ru(phen)_2^{2+}$, the S–S bond of DTDP remains intact but when DTDP interacts with the RuN_4^{2+} moiety in $Ru(bisox)_2^{2+}$, the S–S bond is cleaved. A tentative mechanism for the cleavage of the disulfide bond in the reaction of DTDP with $Ru(bisox)_2Cl_2$ is proposed in Scheme 1. It seems reasonable to presume that in this case also a species of the type **3a** (like the cations in **1** and **2**) is formed initially, which subsequently undergoes an intramolecular one-electron transfer giving rise to a Ru(III) species in which the metal is bound to a disulfide radical anion (**3b**). The formation of the disulfide radical anion leads to cleavage of the S–S bond yielding **3c** (nondissociative electron capture by disulfide bonds in the gas phase is known[10]). Chelation of the anionic species seems to be the driving force for step 3. The Ru(III) species **3d** then oxidises water present in the reaction medium, releasing 2 H^+ and 2 e^- (eqn. 1):

$$\tfrac{1}{2}O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O \qquad (1)$$

$[Ru^{III}(bisox)_2(2\text{-thiolatopyridine})]^{2+}$ (**3d**) has a $Ru^{III/II}$ couple of 0.43 V *vs.* SCE (saturated calomel electrode), as found from the cyclic voltammetry of **3** in acetonitrile at a Pt electrode under N_2 atmosphere (Fig. 4). The redox potential of couple (1) at pH 7 is 0.57 V *vs.* SCE.[11] However, in a methanol–water mixture it is lowered. Earlier we have shown that a copper(II) complex having a $Cu^{II/I}$ couple of 0.39 V *vs.* SCE is capable of oxidising water in a methanol–water mixture.[12] Thus, the species **3d** also can oxidise water in methanolic medium.[13,14] Incidentally, **1** and **2** are not redox active in the region 0.0–1.3 V *vs.* SCE.That pyridine-2-thiol is liberated in the reaction of $Ru(bisox)_2Cl_2$ and DTDP is evidenced by the fact that the same yield of **3** is obtained when DTDP and $Ru(bisox)_2Cl_2$ are reacted in a 0.5:1 molar ratio instead of 1:1.

We now try to explain why the intramolecular electron transfer occurs only when the ancillary ligand is bisox and not when it is bpy or phen. The situation can be described by considering a double-well potential with one of the wells localised on the S–S fragment of the bound DTDP and the other one localised on the RuN_4 moieties in **1**, **2** and **3a** (Fig. 5). When we take into account the known 10 Dq values of bpy (12 650 cm^{-1}),[15] phen (12 745 cm^{-1})[16] and unsubstituted 2,2′-bisoxazoline (10 100 cm^{-1})[17] with respect to Ni(II), we realise that in the equilibrium geometries, the energies of the potential well in the RuN_4^{2+} moieties in **1**, **2** and **3a** follow the order **2** < **1** < **3a** (Fig. 5). If we now assume that the energy of the potential well localised on the S–S fragment of the bound DTDP in the equilibrium geometry lies in-between the energies of **1** and **3a**, as shown in Fig. 5, then it is evident that Ru(II) → S–S electron transfer is thermodynamically feasible only in the case of **3a** and not in the cases of **1** and **2**. It should be noted that in constructing the potential wells in Fig. 5 we have not considered the perturbation exerted by the ancillary ligands on the potential well centred on the S–S fragment.

Reactions of disulfide bonds are of much biological interest on many counts. A very recent and brief review of the situation is available.[10] Surface chemistry of disulfides in connection with the formation of self-assembled monolayers is also of no less importance.[18,19] Earlier we have demonstrated that insertion of an atom into an S–S bond is possible.[20] Our

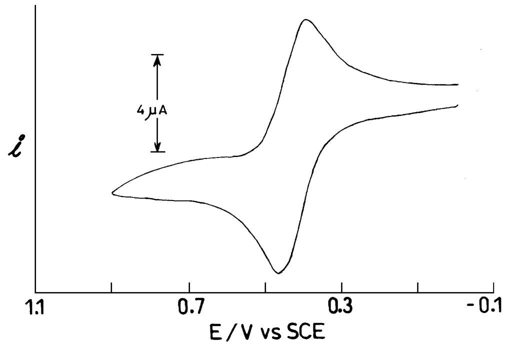


Fig. 4 Cyclic voltammogram of **3** (concentration = 1.12 mmol dm^{-3}) in acetonitrile (0.1 mol dm^{-3} in Et_4NClO_4) at a Pt electrode; scan rate = 50 mV s^{-1}. Under the same conditions, the ferrocene–ferrocenium couple appears at 0.34 V *vs.* SCE.

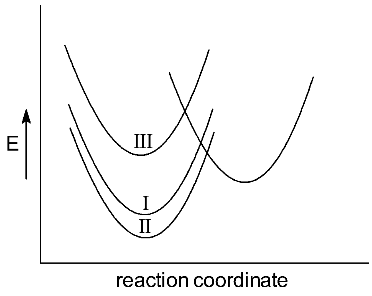


Fig. 5 A schematic representation of the potential wells for the intramolecular electron transfer in $[RuL_2(DTDP)]^{2+}$. The well on the right hand side is localised on the S–S bond in the bound DTDP. The well on the left hand side is localised on the metal: I, L = bpy; II, L = phen; III, L = bisox.

present study adds a further new dimension to the chemistry of the S–S bond.

Experimental

Syntheses

cis-Ru(bpy)$_2$Cl$_2$, *cis*-Ru(phen)$_2$Cl$_2$ and *cis*-Ru(bisox)$_2$Cl$_2$ were synthesised by reported procedures.[21–23]

[Ru(bpy)$_2$(DTDP)](ClO$_4$)$_2$ · H$_2$O (1). DTDP (0.055 g, 0.25 mmol) was dissolved in 20 ml of degassed MeOH–H$_2$O (1:1) mixture to which 0.13 g (0.25 mmol) of *cis*-Ru(bpy)$_2$Cl$_2$ was added. The reaction mixture was refluxed under N$_2$ atmosphere for 6 h. Then it was cooled to room temperature and filtered. To the filtrate, 1 g of NaClO$_4$ dissolved in 3 ml of water was added dropwise with constant stirring and left in air for 15 min. The reddish yellow compound precipitated was filtered, washed with 5 ml of water and dried *in vacuo* over fused CaCl$_2$. It was recrystallised from a 3:1 mixture of dichloromethane–*n*-hexane. Yield 0.16 g (75%). Single crystals were grown by direct diffusion of petroleum ether into a dilute dichloromethane solution of the complex. Anal. calcd for $C_{30}H_{26}Cl_2RuN_6O_9S_2$: C, 42.34; H, 3.08; N, 9.88; found: C, 42.71; H, 3.03; N, 9.90%. FTIR (KBr) ν/cm^{-1}: 1088 vs, 622 m (ClO$_4$). Λ_M (CH$_3$CN): 268 Ω^{-1} cm^2 mol^{-1} (1:2 electrolyte). UV/VIS (CH$_3$CN) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 198 (56 550), 245 (27 800), 284 (44 800), 388 (8 000), 441 (5 300), 515 (2 200).

[Ru(phen)$_2$(DTDP)](ClO$_4$)$_2$ · 2CH$_2$Cl$_2$ (2). **2** was synthesised by following exactly the same procedure described above for **1**, starting with 0.055 g (0.25 mmol) of DTDP and 0.14 g (0.25 mmol) of *cis*-Ru(phen)$_2$Cl$_2$ as red micro crystals. Yield 0.2 g (75%). Single crystals were grown by direct diffusion of *n*-hexane into a dilute dichloromethane solution of the complex. Anal. calcd for $C_{36}H_{28}RuCl_6N_6O_8S_2$: C, 41.13; H, 2.69; N, 8.00; found: C, 41.15; H, 2.67; N, 7.98%. FTIR (KBr) ν/cm^{-1}: 1086 vs, 622 m (ClO$_4$). Λ_M (CH$_3$CN): 252 Ω^{-1} cm^2 mol^{-1} (1:2 electrolyte). UV/VIS (CH$_3$CN) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 200 (82 700), 224 (71 300), 263 (78 600), 380 (13 300), 437 (7 100), 485 (1 300).

[Ru(bisox)$_2$(2-thiolatopyridine)]ClO$_4$ (3). The same procedure described above for **1** was followed exactly, starting with 0.044 g (0.2 mmol) of DTDP and 0.113 g (0.2 mmol) of *cis*-Ru(bisox)$_2$Cl$_2$ to obtain red micro crystals of **3**. Yield 0.1 g (70%). The same yield was obtained when the procedure was carried out with 0.1 mmol of DTDP and 0.2 mmol of *cis*-Ru(bisox)$_2$Cl$_2$. Single crystals were grown by direct diffusion of *n*-hexane into a dilute dichloromethane solution of the complex. Anal. calcd for $C_{25}H_{36}ClRuN_5O_8S$: C, 42.68; H, 5.16; N, 9.95; found: C, 42.59; H, 5.25; N, 9.01%. FTIR (KBr) ν/cm^{-1}: 1094 vs, 624 m (ClO$_4$). Λ_M(CH$_3$CN): 139 Ω^{-1} cm^2 mol^{-1} (1:1 electrolyte). UV/VIS (CH$_3$CN) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 200 (26 650), 249 (16 500), 279 (5 800), 338 (6 800), 443 (6 000), 516 (6 900).

X-Ray crystallography

The data were collected at 293(2) K with MoKα radiation using the MARresearch image plate system. The crystals were positioned at 70 mm from the image plate. One hundred frames were measured at 2° intervals with a counting time of 2 min. Data analysis was carried out with the XDS program[24] and structure solution with the SHELXS-86 program.[25] The non-hydrogen atoms were refined anisotropically and remaining atoms isotropically. The hydrogen atoms bonded to carbon were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were bonded. The structures contained disordered perchlorate anions and solvent molecules. An empirical absorption correction was carried out using DIFABS.[26] The structures were refined on F^2 using SHELXL.[27]

CCDC reference numbers 183362–4. See http://www.rsc.org/suppdata/nj/b2/b206467f/ for crystallographic files in CIF or other electronic format.

Crystal data for 1. $C_{30}H_{26}Cl_2RuN_6O_9S_2$, $M_w = 850.66$, triclinic, space group P-1, $a = 10.046(14)$, $b = 12.988(17)$, $c = 15.224(17)$ Å, $\alpha = 68.99(1)°$, $\beta = 75.21(1)°$, $\gamma = 68.22(1)°$, $U = 1705(4)$ Å^3, $Z = 2$, $\mu = 0.801$ mm^{-1}, 7541 reflections collected, 5797 independent reflections, $R_{int} = 0.063$, $R_1 = 0.0887$ and $wR_2 = 0.2518$ for 3101 observed reflections.

Crystal data for 2. $C_{36}H_{28}RuCl_6N_6O_8S_2$, $M_w = 1050.29$, monoclinic, space group $P2_1/n$, $a = 12.759(17)$, $b = 17.05(2)$, $c = 19.59(2)$ Å, $\beta = 94.377(10)°$, $U = 4250(10)$ Å^3, $Z = 4$, $\mu = 0.902$ mm^{-1}, 11310 reflections collected, 6871 independent reflections, $R_{int} = 0.057$, $R_1 = 0.0784$ and $wR_2 = 0.2244$ for 3989 observed reflections.

Crystal data for 3. $C_{25}H_{36}ClRuN_5O_8S$, $M_w = 703.17$, monoclinic, space group $P2_1/c$, $a = 9.983(14)$, $b = 11.145(14)$, $c = 27.83(4)$ Å, $\beta = 94.836(10)°$, $U = 3085(7)$ Å^3, $Z = 4$, $\mu = 0.715$ mm^{-1}, 6325 reflections collected, 3730 independent, R(int) = 0.031, $R_1 = 0.0769$ and $wR_2 = 0.2148$ for 2599 observed reflections.

Acknowledgements

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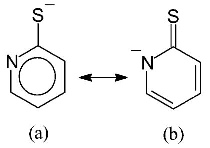

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