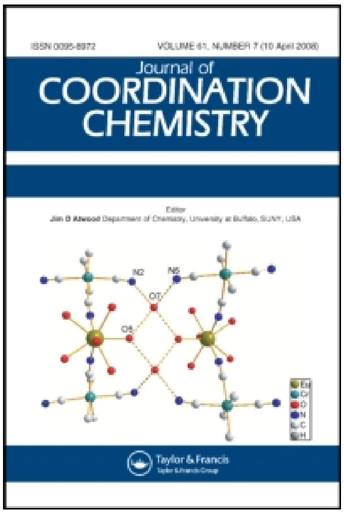

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^{1}H, ^{13}C, ^{15}N NMR and IR Spectroscopic Studies of a Rh(II) Complex of Thiourea

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^1H, ^{13}C, ^{15}N NMR AND IR SPECTROSCOPIC STUDIES OF A Rh(II) COMPLEX OF THIOUREA

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A rhodium(II) complex of thiourea (Tu), $Rh_2(OAc)_4Tu_2$, has been prepared from $Rh_2(OAc)_4(H_2O)_2$ and characterized. A shift of the ν(N–H) vibration towards higher frequencies in the IR spectrum is consistent with sulfur coordination to rhodium(II). ^{13}C NMR spectra recorded in DMSO-d_6 reveal that thiourea is replaced by DMSO-d_6 solvent, followed by replacement of acetate ions by free thiourea. ^{15}N NMR indicates some nitrogen involvement in coordination to form an S–N chelate.

Keywords: Rhodium acetate; Thiourea; NMR; IR; Exchange phenomena

INTRODUCTION

The ability of thiourea (Tu) to form stable adducts with a variety of transition metals (Cu, Ag, Au and Pt) is well established and the structures of several such complexes have been determined [1–6]. Fatima *et al.* [7] studied the reactions of mono-, di- and tri-substituted thiourea with chloride salts of Pd(II), Pt(IV), Rh(III) and Ir(III) and on the basis of IR data suggested S coordination in all Tu derivatives. Daniele and co-workers [8] investigated the behaviour of substituted thioureas with rhodium(I) and reported the crystal structure of a dinuclear, sulfur-bridged rhodium(I) complex. In 1993 Carlos and co-workers [9] studied the reaction of thiocyanate and thiourea with rhodium(III) aqua ions. However, it was Mal'kova and Shafranskii [10] who first reported infrared spectroscopic and thermogravimetric studies of thiourea compounds of dirhodium(II) tetraacetate. Structural studies [2–5] using spectroscopic techniques (IR and NMR) of thiourea complexes of silver(I), $[Ag(Tu)_2Cl$, $Ag(Tu)_2SCN$ and $Ag(Tu)_3ClO_4]$ have shown that Tu can act both as a bridging and terminal ligand (Scheme 1).

In order to observe the coordination behaviour of Tu with rhodium(II) acetate, we have prepared the Rh(II)–Tu complex. Additionally, we have also investigated exchange phenomenon of the Tu ligand with acetate ion in dimethylsulfoxide using ^1H, ^{13}C and ^{15}N NMR spectroscopy. The complexes were characterized by elemental

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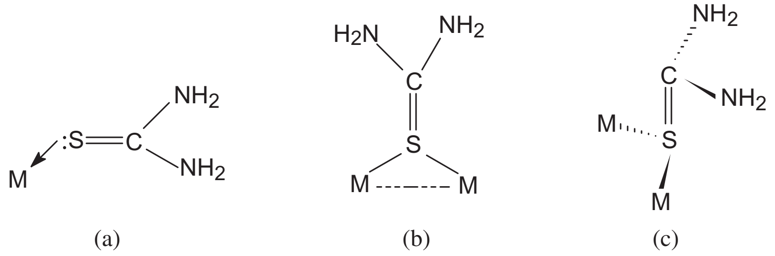


SCHEME 1 Different modes of linkage of thiourea with metal.

analysis, and electronic, FTIR and NMR (^{1}H, ^{13}C, ^{15}N) spectroscopic techniques. Characterization of rhodium(II) complexes with Tu would provide a basis for understanding and predicting the interactions with more complex sulfur-containing ligands.

EXPERIMENTAL

Chemicals

Rhodium(II) acetate, $Rh_2(OAc)_4(H_2O)_2$, thiourea and DMSO-d_6 were obtained from the Fluka Chemical CO., Germany and used as received. ^{13}C and ^{15}N labelled thiourea was obtained from the Isotec Co., USA; 5% ^{13}C and ^{15}N enriched Tu was made by mixing 5% labelled 95% unlabelled Tu by weight.

Preparation of the Complex

The complex was synthesized by adding Tu in MeOH to $Rh_2(OAc)_4(H_2O)_2$ [**Ia** in Fig. 1] in acetone in a mol ratio of 2 : 1, respectively. The solution was stirred for 30 min. After filtration the product was washed with methanol, acetone and ether, respectively. Mixing of Tu and **Ia** (Fig. 1) at a 4 : 1 ratio did not result in a change in the number of Tu ligands in the resulting complex; the same $Rh_2(OAc)_4Tu_2$ [**IIa** in Fig. 1] complex was obtained. Anal. Calcd. for $Rh_2(OAc)_4Tu_2$ (%): C, 22.79; H, 3.98; N, 9.84. Found: C, 24.20; H, 3.36; N, 9.42.

NMR Measurements

All NMR measurements were carried out on a Jeol JNM-LA 500 NMR spectrophotometer at 297 K using 0.05 M solutions of the complexes in DMSO-d_6. ^{13}C spectra were obtained at 125.65 MHz with ^{1}H broadband decoupling. Conditions were: 32 k data points, 0.967 s acquisition time, 1.00 s pulse delay and 45° pulse angle. The ^{15}N NMR spectrum was recorded at 50.55 MHz using $^{15}NH_4\ NO_3$ as external reference, which lies at −358.62 ppm relative to pure $MeNO_2$ [11]. Conditions for ^{15}N were: 32 K data points, 0.721 s acquisition time, 2.50 s delay time, 60° pulse angle and approx. 5000 scans.

FTIR

The solid state FTIR spectrum of the complex was recorded in the range 3500–450 cm^{-1} on a Perkin-Elmer 16 FPC FT-IR using KBr pellets, with 8 scans and a resolution of 4 cm^{-1}. Results are summarized in Table I.

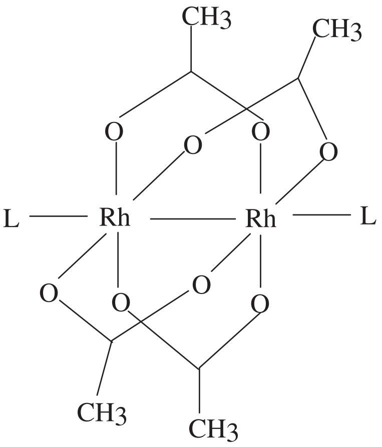


FIGURE 1 Structure of $Rh_2(OAc)_4 \cdot 2L$. L = H_2O (**Ia**), L = Tu (**IIa**), L = DMSO (**IIIa**).

TABLE I Comparison of IR absorption peaks for thiourea and its corresponding complexes

Vibrational band	*Thiourea*[a]	$Rh_2(OAc)_4(Tu)_2$[a]	$Rh_2(OAc)_4(Tu)_2$[b]
δ (NCN)	488 m,b	484 w	485
$\gamma(CH_3)$		588 m,b, 626 w	602, 625
$\nu_s(CS)$	730 s	650 w	645
$\nu_s(CC)$		702 s, 726 m, 742 w	705, 730
$\delta_s(HCC)$		1046 w	1049
$\delta_s(CH_3)$		1346 w	1350
$\nu(CN) + \nu(CS) + \delta(HNC)$	1084 s	1102 w	1090
$\delta_{as}(CH_3)$		1410 s	1415
$\nu(CN) + \nu(CS) + \delta(NH_2) + \delta(HNC)$	1414 s, 1470 s	1490 m	1400 i, 1492
$\nu_s(COO)$		1440 sh	1145
$\nu_{as}(COO)$		1584 s	1587
$\delta(NH_2)$	1616 s	1616 m, 1648 m	1618
$\nu(NH)$	3174 m, 3274 m, 3380 m	3216 m, 3326 m, 3398 m	3325, 3407

[a]This study; [b]Values taken from Ref. [10].

Electronic Spectra

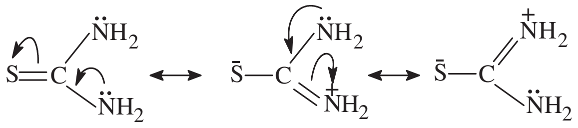
Electronic spectra of 1.862×10^{-4} M solutions of the complex in DMSO were recorded at different time intervals in the range 500–200 nm on a Perkin-Elmer Lambda 5 spectrophotometer. The following instrumental conditions were used: slit = 2 nm, scan speed = 60 nm/min, response = 0.2 s. Results are summarized in Table II.

RESULTS AND DISCUSSION

Ambidentate thiourea, $SC(NH_2)_2$, is capable of bonding to transition metals via sulfur or nitrogen. Thiourea can exist in more than one form due to resonance as shown in Scheme 2. Upon complexation through sulfur to metal ions such as Ag(I), Au(I) and

TABLE II Time dependent study of electronic absorption for peaks around 262 nm and 304 nm of 1.76×10^{-4} M $Rh_2(OAc)_4(Tu)_2$ complex

Time (h)	*Absorption 1* (nm)	A_1	ε_1 ($cm^{-1}M^{-1}$)	*Absorption 2* (nm)	A_2	ε_2 ($cm^{-1}M^{-1}$)
1	262.0	1.731	9830	304.4	2.255	12800
2	262.0	1.720	9760	305.7	2.243	12730
5	262.1	1.701	9660	305.7	2.203	12510
15	261.6	1.811	10280	305.7	2.305	13090
17	261.9	1.793	10180	305.8	2.257	12810
22	261.9	1.783	10120	305.7	2.225	12630
24	261.9	1.788	10150	305.6	2.216	12580
36	261.1	1.844	10470	305.4	2.264	12850



I II III

SCHEME 2 Resonance structures of thiourea.

Rh(II), resonance structures II and III also become significant. When Tu is complexed with **Ia** (Fig. 1) to produce **IIa** (Fig. 1), three diagnostic vibrational IR bands, ν(C=S), ν(C–N), and $\nu(NH_2)$, produce significant changes in frequency. Upon coordination via the sulfur atom, the (C=S) double bond character is expected to be reduced [11]. Therefore, a decrease in frequency for the ν(C=S) mode with concomitant increases in ν(C–N) and $\nu(NH_2)$ modes should be observed. On the other hand, if thiourea is coordinated through nitrogen [12], an opposite effect should be expected.

In the FTIR spectrum of the complex, the ν(C=S) mode of thiourea was observed at a lower frequency (726 cm^{-1}) compared to that for free thiourea (730 cm^{-1}). We have observed this signal at 724 cm^{-1} for thiourea terminally coordinated to Ag(I) through the S atom. This decrease is indicative of reduction in the C=S bond order on sulfur coordination to rhodium(II). Free thiourea has a band of medium intensity at 1084 cm^{-1}, primarily assigned to the ν_s(NCN) stretch [12] and which is markedly reduced in intensity in FTIR spectra of transition metal complexes containing S-bonded thiourea. However, Mal'kova and Shafranskii [10] assigned the band at 1086 cm^{-1} to a combination band, $\nu(CN) + \nu(CS) + \delta(HNC)$. This band shifted to higher frequency (1090 cm^{-1}) in their reported complex **IIa** (Fig. 1). In our study, this peak at 1084 cm^{-1} was shifted to 1102 cm^{-1} with reduced intensity and is in accord with an increase in (C–N) double bond character upon Rh–S bond formation. The $\nu(NH_2)$ modes of Tu occur at 3174, 3274 and 3380 cm^{-1}, and after complexation with Rh(II) were observed at 3216, 3326 and 3398 cm^{-1}, respectively. A low frequency shift in ν(C=S) and a high frequency shift in $\nu(NH_2)$ shows that Tu is coordinated to Rh(II) through S. Furthermore, the strong band at 1414 cm^{-1} for Tu is assigned to a combination mode involving ν(NCN), $\delta(NH_2)$ and ν(C=S). This mode is clearly split in the FTIR spectrum of the complex (1382, 1410 and 1437 cm^{-1}), in further support for Tu being coordinated to Rhodium(II) via the sulfur atom. The increase of ν_a(NCN) from 1470 cm^{-1} in free Tu to 1490 cm^{-1} in the complex further substantiates

(Rh–S) bond formation. Furthermore, the strong IR band at $1616\,cm^{-1}$ for free Tu due to the $\delta(NH_2)\,cm^{-1}$ mode is split upon complexation into three bands of higher frequency at 1627, 1648 and $1684\,cm^{-1}$.

For free Tu the $n \rightarrow \pi^*$ transition occurs at 291 nm [13] with a molar extension coefficient (ε) value of $77\,cm^{-1}\,M^{-1}$. The value of λ_{max} for the complex in DMSO at 267.6 nm with molar extension coefficient $432\,cm^{-1}\,M^{-1}$ has been observed, probably due to a $\pi \rightarrow \pi^*$ transition. For complex **Ia** (Fig. 1), three prominent absorptions at 240.6, 290.7 and 332.9 nm with molar extension coefficients of 2817, 9327 and $998\,cm^{-1}\,M^{-1}$, respectively, have been recorded. For complex **IIa**, as Table II shows, after 1 h two dominant peaks appear around 262.0 and 304.5 nm with average molar extension coefficients of 9830 and $12\,800\,cm^{-1}\,M^{-1}$, respectively. Absorption at 304.5 nm with an ε value of $12\,800\,cm^{-1}\,M^{-1}$ for **IIa** indicates ligand to metal charge transfer (LMCT). Since sulfur is a soft ligand and C=S has a low lying empty π^* orbital and at the same time Rh(II) is a $4d^7$ system, the $d \rightarrow \pi^*$ back bonding (MLCT) transition with an ε value of $9830\,cm^{-1}\,M^{-1}$ is also significant. While for both the peaks there is a very slight change both in λ and ε value with time, no new distinguishable signal was observed over 36 h.

NMR spectra in DMSO-d_6 solvent reveal some interesting features. Both ^1H and ^{13}C NMR indicate time dependent exchange of OAc with the Tu ligand. In ^1H NMR a broad signal (after 15 min) between 6.5 and 8.0 ppm indicates that both free Tu and a complex containing Rh–Tu are present (Figure not shown). Al-Etri and co-workers [12] have reported the ^1H signal of $-NH_2$ in free Tu in DMSO-d_6 at 7.18 ppm. However, in the present study this was observed at 7.10 ppm, as reported earlier [11]. It is noted that with time two peaks for bonded and free Tu separate and appear at 7.19 and 7.66 ppm. The signal at 7.66 ppm indicates substantial reduction in electron density on the nitrogen atom and thus indicates possible Rh–S bond formation.

^{13}C NMR spectra of 0.05 M **IIa** in DMSO-d_6 solvent recorded at different time interval (Figs. 2a and 2b) indicate exchange phenomena among various species in solution including DMSO, Tu and OAc. The spectrum recorded after 1 h shows only three signals at 23.63, 183.76 (triplet) and 191.16 ppm, corresponding to δ-^{13}C (OAc bonded to Rh(II) in **Ia** of Fig. 1), $^{13}C{=}S$ (free Tu) and β-$^{13}C{=}O$ of OAc (bonded to Rh), respectively. The signal at 183.76 is a triplet because of ^{13}C–^{15}N coupling in **IIa**. The coupling constant $J_{C\text{–}N}$ is 15.0 Hz compared to a value of 14 Hz reported earlier [11]. These signals were confirmed from individual ^{13}C spectra of Tu and **Ia** recorded in DMSO-d_6. Complex **Ia** produces only two ^{13}C signals at 23.7 and 191.3 ppm corresponding to δ–^{13}C and β–$^{13}C{=}O$ (Fig. 1) of OAc (bonded to Rh(II)), respectively. Based on these assignments for the ^{13}C spectrum of complex **IIa** after 1 h, it is apparent that DMSO has replaced only Tu. However, signals at 23.63 and 191.12 ppm indicate that the Rh–O bond persists. This observation is in accord with the earlier work [10] of Mal'kova and Shafranskii, who reported that the Rh–O bond is more stable than Rh–S. Therefore, DMSO initially replaces Tu rather than OAc. The ^{13}C spectrum recorded after 5 h (Figs. 2a and 2b) shows six prominent signals, and incorporates three new signals at 21.44, 172.30 and 181.59 (triplet) ppm with $J_{C\text{–}N}$ 12.0 Hz. Two new singlets at 21.44 and 172.30 ppm are from $-CH_3$ and C=O of free OAc, being replaced by Tu ligand. The signal at 191.06 ppm indicates that C=O carbon in bonded OAc is deshielded due to an increase in C=O character by loss of resonance in bonded bidentate acetate ion. Moreover, the carbon atom of the methyl group in bonded OAc is also deshielded due to possible hyperconjugation of $-CH_3$ with C=O

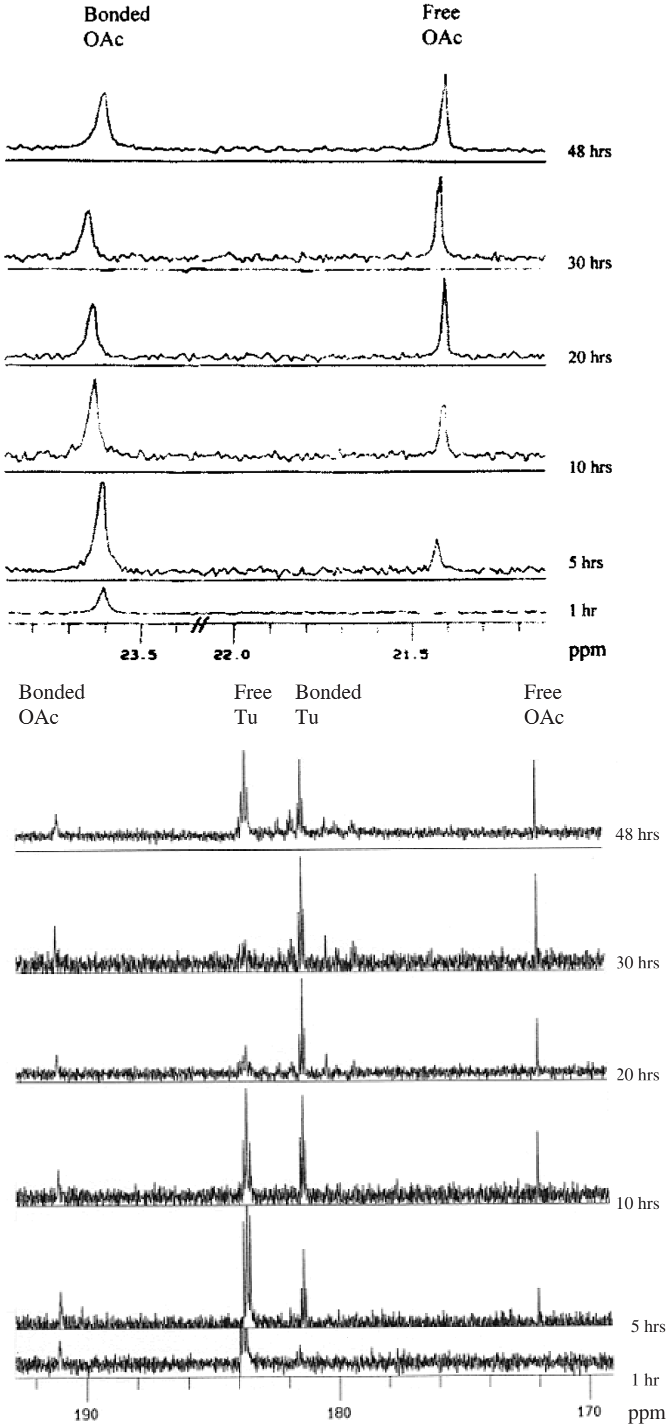


FIGURE 2 Top (a) ^{13}C spectrum of 0.05 M $Rh_2(OAc)_4(Tu)_2$ complex in DMSO-d_6 (^{13}C, ^{15}N labelled Tu was used) (Expanded version of Fig. 1b); Bottom (b) ^{13}C spectrum of 0.05 M $Rh_2(OAc)_4(Tu)_2$ complex in DMSO-d_6 (^{13}C, ^{15}N labelled Tu was used).

in **IIa**. Thus, both C-atoms in bonded OAc ligand are deshielded and appear downfield compared to the free acetate ion, for which both carbons appear upfield at 21.44 and 172.30 ppm respectively.

Further, the ^{13}C spectrum of **Ia** recorded in DMSO-*d*$_6$ shows only two peaks at 191.32 and 23.63 ppm even after one week, thus indicating no exchange between DMSO solvent and OAc bonded ligand. This validates our assumption that the OAc ligand of complex **IIa** in DMSO is replaced by Tu but not the solvent. It was also observed that as time passes, the intensity of the signal at 21.4 ppm increases with concomitant decrease in intensity at 23.61 ppm. After 10 h additional peaks around 180 ppm were observed, and these may represent the formation of a Rh–N bond by Tu already bonded with S atom or slow exchange between isomers. The ^{13}C spectrum recorded after 20 h indicates three new signals at 116.59, 116.45 and 116.29 ppm, which are more intense for the ^{13}C spectrum recorded after 2 weeks (Fig. 3). These signals may indicate linkage b of Rh(II) with Tu as shown in Scheme 1. These three peaks also indicate some possibility of isomers being slowly exchanged. Figure 3 also reveals that the intensity of the signal at 21.39 ppm (due to free OAc ligand) is three to four times higher than the intensity for the bonded OAc ligand at 23.63 ppm. Thus, based on the ^{13}C spectra (Figs. 2a, 2b and 3), the following exchange phenomena are proposed.

$$\mathrm{Rh_2(OAc)_4(Tu)_2{+}DMSO(solvent){=}\ Rh_2(OAc)_4(DMSO)_2{+}2Tu} \quad (1)$$

$$\mathrm{Rh_2(OAc)_4(DMSO)_2{+}xTu{=}\ Rh_2(OAc)_{4-x}(DMSO)_2(Tu)_y{+}xOAc} \quad (2)$$

Cotton *et al.* [14] reported an extraordinarily short Rh–Rh bond length of 2.3855 Å for complex **Ia** and assigned a triple bond between Rh–Rh. However, Dubicki and Martin [15] concluded that spectroscopic behaviour is more consistent with a Rh–Rh single bond. We believe that this abnormally short and strong Rh–Rh bond remains intact during the exchange process. It is reported in the literature [16,17] that substitution of H_2O ligand in axial positions in **Ia** with ligands having either a strong *trans* influence

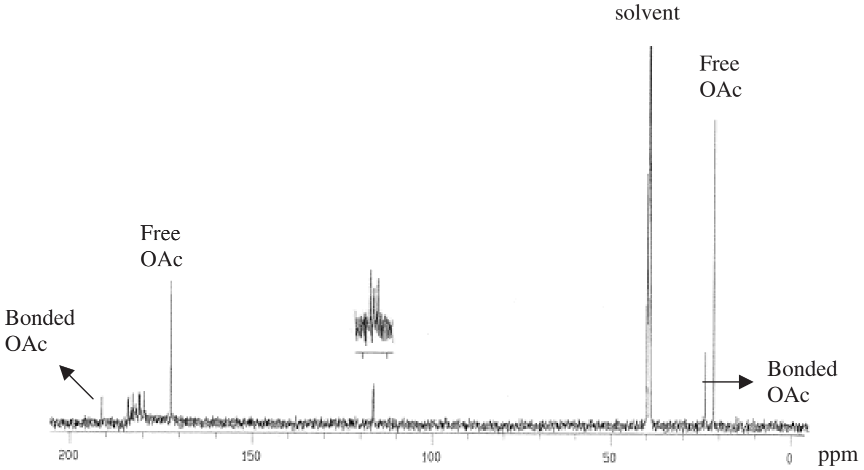


FIGURE 3 ^{13}C spectrum of 0.05 M $Rh_2(OAc)_4(Tu)_2$ complex in DMSO-*d*$_6$ recorded after 2 weeks (^{13}C, ^{15}N labelled Tu was used).

or π acceptor ability results in an increase of the Rh–Rh bond distance. Therefore, in **IIIa**, due to the π acceptor nature of DMSO, the Rh–Rh bond distance increases, resulting in a weakening of the Rh–O bond strength of the bidentate OAc ligand. Under such circumstances free Tu in solution starts to replace the bonded OAc ligand, as shown in reaction 2.

Further support for the probability of different linkage isomers of Tu during the exchange emerges from the ^{15}N spectrum (Fig. 4) of **IIa**. The resonance recorded at −271.35 ppm indicates free Tu and the signal around −262.57 ppm indicates deshielded ^{15}N in Tu bonded to Rh(II) via sulfur. However, an upfield shift of ^{15}N signals around −280.35 (dd), −281.75 (dd) and −282.95 ppm indicates involvement of N with Rh in the complex. The dd at −282.95 and −280.35 ppm have the same $J[^{103}\text{Rh}–^{15}\text{N}] = 25.0$ Hz, while $J[^{15}\text{N}–^{13}\text{C}] = 15.0$ Hz. Thus both these dd probably indicate isomers of **Ib** (Fig. 4) with similar Rh–Tu interactions. On the other hand, dd at −281.75 ppm has $J[^{103}\text{Rh}–^{15}\text{N}] = 18.0$ Hz and $J[^{15}\text{N}–^{13}\text{C}] = 10.0$ Hz. This lower value of $J[^{103}\text{Rh}–^{15}\text{N}]$ probably indicates a weak Rh(II)–N interaction and perhaps involvement of both N atoms with each Rh(II) as shown in **IIb** in Fig. 4. In Tu, bond angles calculated between NCN and NCS are 111.6 and 124.2 respectively, and for this purpose the Gaussian 98 program was used to carry out geometry optimization with Hartree Fock method (HF) using the Slater Type Orbital as a basis set. Since the Rh–Rh bond distance of any complex shown in Fig. 1 is around 2.4 Å, formation of both Rh–N bonds (owing to the smaller NCN bond angle) like OAc in complexes **Ia**, **IIa** and **IIIa** (Fig. 1) will result in strain, with a concomitant decrease

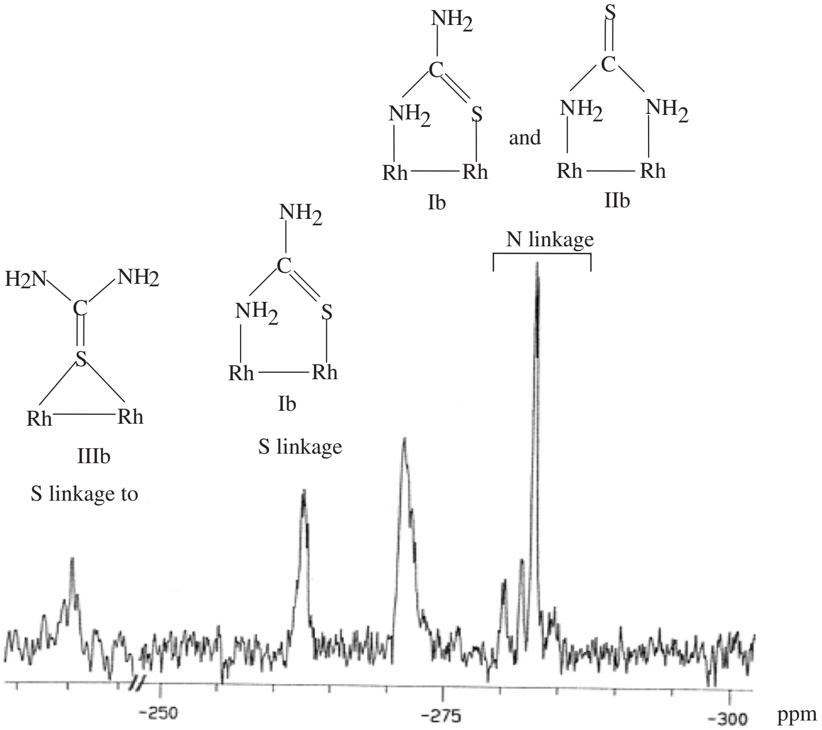


FIGURE 4 ^{15}N spectrum of 0.05 M $Rh_2(OAc)_4(Tu)_2$ complex in DMSO-d_6 (^{13}C, ^{15}N labelled Tu was used).

in coupling constant. Therefore, formation of the Rh(II) complexes in solution involving both N atoms of Tu (like the involvement of both O atoms of OAc in complexes shown in Fig. 1) is expected to give weak Rh–N interactions resulting in a lowering of $J[^{103}Rh–^{15}N]$ values. $J[^{103}Rh–^{15}N]$ values calculated in our study are somewhat higher than the previously noted $J[^{103}Rh–^{15}N] = 10.1$, 15.9 and 17.1 Hz for complexes $[Rh(H)_2(O_2CArN)(PPh_3)_2]$ (O_2CArN = isoquinoline-1-carboxylate) [18], $[RhCl(N_2Ph)(PMePh_2)_3][PF_6]$ [19] and [*trans*-$Rh(Py)_4Cl_2$]Cl [20], respectively.

Figure 4 also incorporates three weak ^{15}N signals around −186.21 ppm, which probably indicates binding of S to both Rh atoms simultaneously as shown (**IIIb**) in Fig. 4. This involves the transfer of electron density from the nitrogen atoms to the sulfur atom with partial transformation of the C=S double bond. This is matched by the ^{13}C signals around 116.0 ppm as discussed previously, and indicates flow of electrons from N→C, thus resulting in shielding of C in C=S with concomitant deshielding of N. Indeed such bonding of S to two metal centres has been reported in the literature [21–23] and coordination of a sulfur atom to three Cu(I) centres is also reported [24].

It is shown that H_2O can be replaced by Tu in $Rh_2(OAc)_4(H_2O)_2$ and it is bonded via the sulfur atom as shown by FTIR. Initially DMSO replaces Tu followed by exchange of OAc in the complex by Tu. However, these exchange reactions are slow and reversible as shown by ^{13}C and ^{15}N NMR spectra. ^{15}N NMR indicates a different linkage of Tu with Rh(II) in solution.

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