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Binary, Ternary, and Quarternary Complexes of Ruthenium(II) Involving the Flexidentate ONNS Donor Mono(4-(4-tolyl)thiosemicarbazone) of 2,6-Diacetylpyridine (L_2H). First Report on Ruthenium Complexes of a Mono(thiosemicarbazone) of a Diketone: Crystal Structure of $[Ru(L_2)(PPh_3)_2]ClO_4$

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A series of Ru(II) complexes of the ONNS donor ligand mono(4-(4-tolyl)thiosemicarbazone) of 2,6-diacetylpyridine (L_2H) synthesized by using three different ruthenium-containing starting materials $RuCl_3 \cdot xH_2O$, $Ru(PPh_3)_3Cl_2$, and $[Ru(NH_3)_5Cl]Cl_2$ are reported. Chemical and electrochemical studies of the complexes $[Ru(L_2)(PPh_3)_2]ClO_4$ (**1**), $[Ru(L_2)(PPh_3)_2]Cl$ (**2**), $[Ru(L_2)(PPh_3)]ClO_4 \cdot EtOH$ (**3**), $[Ru(L_2)(PPh_3)(bpy)]ClO_4$ (**4**), $[Ru(L_2)(PPh_3)(ophen)]ClO_4$ (**5**), $[Ru(L_2)_2]$ (**6**), and $[Ru(L_2)(L_2H)]Cl$ (**7**) have been carried out. The structure of the compound $[Ru(L_2)(PPh_3)_2]ClO_4$ (**1**) has been determined by single-crystal X-ray diffraction techniques. The crystals are triclinic, space group $P\bar{1}$ with $a = 12.716(1)$ Å, $b = 13.213(1)$ Å, $c = 15.951(1)$ Å, $\alpha = 87.66(1)°$, $\beta = 73.81(1)°$, $\gamma = 70.93(1)°$, and $Z = 2$, where the deprotonated ligand mono(4-(4-tolyl)thiosemicarbazone) of 2,6-diacetylpyridine (L_2) is chelated to the Ru(II) center through the oxygen of the carbonyl group, pyridine ring nitrogen, imine nitrogen, and the thiolate sulfur atoms. Strong coordination of the carbonyl group suggested from its IR spectral characteristics has been confirmed from the appreciable shortening of the Ru−O bond and lengthening of the C═O bond in the structure of **1**.

Introduction

Apart from the biological relevance in terms of their presence in the prosthetic groups of several important metalloenzymes,[1,2] the N−S and NSO donor ligands are known to generate unusual stereochemical, electrochemical, and electronic properties in many of their metal complexes.[3−16] For the past few years we have been working with complexes of ruthenium wtih a variety of nitrogen−sulfur donor ligands which include a number of thiosemicarbazides[8] and thiosemicarbazones.[9] We have already explored the ligational behaviour of a host of N−S,[8] N−N−S,[17,18] and S−N−N−S[18,19] donor ligands toward Ru(II) and Ru(III) along with Fe(II), Fe(III), Co(III),[20] Ni(II),[21] and Cu(II).[22] The major objective of those studies was to probe into the stereochemistry and electronic structure of the complexes and to study their influence on the electron-transfer behavior of these complexes, as well as the stability of the products of such electron-transfer reactions. Results of such studies are expected to be useful to formulate electrochemical synthesis of a series of complexes in which identical ligand framework will hold the metal center in different oxidation states. Such complexes

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are difficult to prepare by conventional chemical methods. Thus, through such a study one can explore how the stereochemistry and the relative energy of the redox orbitals can modulate each other. In addition to these chemical and electrochemical interests, a number of such complexes are found to possess interesting biological properties like antibacterial and even antitumor activities.[8,9,23] In this paper we report the results of our investigation on some ruthenium complexes of a mono(thiosemicarbazone) of 2,6-diacetylpyridine, which is, to our knowledge, the first report on the ruthenium complexes of a mono(thiosemicarbazone) of a diketone.

Experimental Section

Elemental analysis were performed with a Perkin-Elmer 240 CNH analyzer. IR and electronic spectra were recorded on a Perkin-Elmer 783 spectrophotometer (as KBr disks) and on a Shimadzu UV−vis recording spectrophotometer, respectively. Solution conductance was measured on a Systronics direct reading conductivity meter (Model 304) and magnetic susceptibility (at room temperature) was measured with a PAR vibrating sample magnetometer using $Hg[Co(SCN)_4]$ as the calibrant. NMR spectra were recorded on a Jeol FX 100 NMR spectrometer using TMS as an internal standard. Electrochemical data were collected with a BAS CV-27 and a BAS Model X-Y recorder at 298 K. Cyclic voltammetry experiments were carried out with platinum working and auxiliary electrodes and a SCE reference electrode.

$RuCl_3 \cdot xH_2O$ was obtained from Arora Matthey (Calcutta, India), and 2,6-diacetylpyridine, from Aldrich. 4-(4-Tolyl)thiosemicarbazide, $Ru(PPh_3)_3Cl_2$,[24] and $[Ru(NH_3)_5Cl]Cl_2$[25] were prepared according to published procedures. The ligand 2,6-diacetylpyridine mono[4-(4-tolyl)thiosemicarbazone] (L_2H) was prepared as described below. Acetonitrile (pure) obtained from E Merck (India) was freshly distilled over calcium hydride for electrochemical experiments. Dichloromethane used was of G.R. E. Merck (Darmstadt, Germany) quality.

Synthesis of the Ligand (L_2H). A 3.62 g (0.02 mmol) amount of 4-(4-tolyl)thiosemicarbazide was dissolved in 70 mL of methanol by refluxing, and 2 mL of acetic acid was then added to it followed by 1.63 g (0.01 mol) of 2,6-diacetylpyridine in 40 mL of methanol. The mixture was refluxed, and a yellow colored solid separated out within 15 min. After 3 h of refluxing, the mixture was allowed to cool to room temperature and filtered. The yellow residue analyzed for the bis(thiosemicarbazone). The desired mono(thiosemicarbazone) ligand (L_2H; mp 156 °C) was isolated by evaporation of the filtrate. The ligand was thoroughly washed with water to remove acetic acid and then recrystallized from dichloromethane. The yield was low (about 40%), which can be increased to 50−55% by slow addition of thiosemicarbazide to the 2,6-diacetylpyridine solution in methanol with stirring at room temperature.

Syntheses of Complexes. A series of Ru(II) complexes were prepared using (i) $Ru(PPh_3)_3Cl_2$, (ii) $RuCl_3 \cdot xH_2O$, and (iii) $[Ru(NH_3)_5Cl]Cl_2$. All reactions were carried out under a nitrogen atmosphere.

Synthesis of $[Ru(L_2)(PPh_3)_2]ClO_4$ (1) and $[Ru(L_2)(PPh_3)_2]Cl$ (2). *Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only a small amount of compound should be prepared, and it should be handled with caution.*

An 81.5 mg (0.25 mmol) amount of the ligand L_2H was dissolved in 30 mL of ethanol by refluxing, and 239.7 mg (0.25 mmol) of solid $Ru(PPh_3)Cl_2$ was added to it. The mixture was refluxed for 4 h. The clear solution was then concentrated in a rotary evaporator to about 10 mL. The perchlorate compound was isolated by adding saturated aqueous lithium perchlorate to the concentrated solution. The precipitated compound was filtered out, washed thoroughly with distilled water, and dried over fused calcium chloride. It was finally recrystallized from dichloromethane. The chloride compound (**2**) was obtained by concentrating the reaction mixture to about 5 mL, adding ether, and then cooling the solution to 0 to −4 °C. A brown solid separated and was filtered out washed thoroughly with ether, and then recrystallized from dichloromethane. Anal. Calcd for $RuC_{53}H_{47}N_4O_5P_2SCl$: C, 60.54; H, 4.47; N, 5.33. Found: C, 60.4; H, 4.68; N, 5.08. Conductance in CH_3CN (Λ_M): 190.26 Ω^{-1} cm^2 mol^{-1}. Electronic spectrum (CH_2Cl_2) [λ_{max}, nm ($10^3\epsilon_{max}$, M^{-1} cm^{-1})]: 460 (sh) (11.19), 395 (18.36), 255 (43.98), 233 (64.07). Anal. Calcd for $RuC_{53}H_{47}N_4OP_2SCl$: C, 66.47; H, 4.76; N, 5.67. Found: C, 64.29; H, 5.03; N, 5.38. Conductance in CH_3CN (Λ_M): 121.86 Ω^{-1} cm^2 mol^{-1}. Electronic spectrum (CH_2Cl_2) [λ_{max}, nm ($10^3\epsilon_{max}$, M^{-1} cm^{-1})]: 460 (sh) (8.2), 395 (17.70), 258 (36.32), 232 (60.75).

Synthesis of $[Ru(L_2)(PPh_3)]ClO_4 \cdot EtOH$ (3). An 81.5 mg (0.25 mmol) amount of the ligand L_2H was dissolved in 25 mL of dichloromethane, and 239.7 mg (0.25 mmol) of $Ru(PPh_3)_3Cl_2$ dissolved in 25 mL of dichloromethane was added. The mixture was refluxed for 4 h and then concentrated to about 15 mL in a rotary evaporator. Petrolium ether (60−80 °C fraction) was then added to the solution to precipitate the crude product, which was filtered out, washed with ether, and dried over fused calcium chloride. The dried compound was dissolved in ethanol and precipitated with lithium perchlorate. It was finally recrystallized from dichloromethane. Anal. Calcd for $RuC_{37}H_{38}N_4O_5PSCl$: C, 53.28; H, 4.55; N, 6.71. Found: C, 53.43; H, 4.34; N, 6.27. Conductance in CH_3CN (Λ_M): 120.16 Ω^{-1} cm^2 mol^{-1}. Electronic spectrum (CH_2Cl_2) [λ_{max}, nm ($10^3\epsilon_{max}$, M^{-1} cm^{-1}): 460 (sh) (7.4), 395 (11.68), 258 (28.38), 234 (36.87).

Synthesis of $[Ru(L_2)(PPh_3)(bpy)]ClO_4$ (4) and $Ru[(L_2)(PPh_3)(ophen)]ClO_4$ (5). A 131.2 mg (0.1 mmol) amount of $[Ru(L_2)(PPh_3)_2]ClO_4$ was dissolved in 10 mL of ethanol, and 0.1 mmol of 2,2′-bipyridine (15.61 mg) or *o*-phenthroline (19.82 mg) was added to it. The mixture was refluxed for 4 h. It was cooled to room temperature, and the compound was precipitated by adding aqueous lithium perchlorate. The compound was filtered out, thoroughly washed with water and ether, and finally dried over fused calcium chloride. Anal. Calcd for $RuC_{45}H_{40}N_6O_5PSCl$: C, 57.21; H, 4.23; N, 8.90; Found: C, 57.19; H, 4.36; N, 8.82. Conductance in CH_3CN (Λ_M): 208.76 Ω^{-1} cm^2 mol^{-1}. Electronic spectrum (CH_2Cl_2) [λ_{max}, nm ($10^3\epsilon_{max}$, M^{-1} cm^{-1})]: 465 (sh) (12.2), 408 (25.43), 258 (40.46), 230 (58.5). Anal. Calcd for $RuC_{47}H_{40}N_4O_5PSCl$: C, 58.27; H, 4.13; N, 8.67. Found: C, 58.27, H, 4.33; N, 8.61. Conductance in CH_3CN (Λ_M): 155.62 Ω^{-1} cm^2 mol^{-1}. Electronic spectrum (CH_2Cl_2) [λ_{max}, nm ($10^3\epsilon$, M^{-1} cm^{-1})]: 460 (sh) (14.32), 402 (25.68), 268 (57.41), 232 (75.60).

Synthesis of $[Ru(L_2)_2]$ (6). A 65.24 mg (0.1 mmol) amount of $[Ru(NH_3)_5Cl]Cl_2$ was suspended in 4 mL of water, and 0.2 mL of triethylamine was added to it. When the solution became clear and pinkish red in color, it was added to a solution of 65.2 mg (0.2 mmol) of L_2H dissolved in ethanol. The mixture was refluxed for 8 h and then filtered hot. The mother liquor was concentrated to one-third of its volume. The desired compound was precipitated on addition of water. It was filtered out, washed thoroughly with water, dried over fused calcium chloride, and recrystallized from dichloromethane. Anal. Calcd for $RuC_{34}H_{34}N_8O_2S_2$: C, 54.32; H, 4.52; N, 14.91. Found: C, 54.46; H, 4.66; N, 14.82. Conductance in DMF (Λ_M): 17.89 Ω^{-} cm^2 mol^{-1}. Electronic spectrum (DMF) [λ_{max}, nm ($10^3\epsilon_{max}$, M^{-1} cm^{-1})]: 530 (sh) (4.5), 376 (sh) (19.0), 327 (27.6), 268 (24.4).

Synthesis of $[Ru(L_2)(L_2H)]Cl \cdot CH_2Cl_2$ (7). A 261.5 mg (1 mmol) amount of $RuCl_3 \cdot xH_2O$ was dissolved in 20 mL of methanol and added to about 130.4 mg (0.4 mmol) of the ligand (L_2H) solution in methanol (30 mL). The mixture was refluxed for 10 h. It was cooled to room temperature and filtered. The filtrate was concentrated to half of its original volume, and the desired compound was precipitated with ether. The compound was filtered out, washed with water and ether, and dried over fused calcium chloride. It was recrystallized from dichloromethane. Anal. Calcd for $RuC_{35}H_{37}N_8O_2S_2Cl_3$: C, 48.13; H, 4.22; N, 12.83. Found: C, 48.27; H, 4.06; N, 13.02. Conductance in DMF (Λ_M): 47.29 Ω^{-1} cm^2 mol^{-1}. Electronic spectrum (DMF) [λ_{max}, nm ($10^3\epsilon_{max}$, M^{-1} cm$^{-)}$]: 500 (sh) (8.4), 389 (24.9), 265 (32.4).

Yields of the pure products ranged from 45 to 60% based on the ruthenium starting material used. The important IR bands of the compounds are tabulated in Table 4.

X-ray Crystallography. Suitable crystals of compound **1** were grown by slow diffusion of *n*-hexane into a dichloromethane solution

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Table 1. Crystal Data for $[Ru(L_2)(PPh_3)_2]ClO_4$ (1)

formula	$RuC_{53}H_{47}O_5N_4SP_2Cl$
fw	1049.50
space group	$P\bar{1}$
a, Å	12.716(1)
b, Å	13.213(1)
c, Å	15.950(1)
α, deg	87.66(1)
β, deg	73.81(1)
γ, deg	70.93(1)
V, Å^3	2429(1)
Z	2
$F(000)$	1054
μ(Mo Kα), mm^{-1}	0.539
ρ_{calcd}, g cm^{-3}	1.426
R_F[a]	0.072
wR[b]	0.092

[a] $R_F = \Sigma||F_o| - |F||/\Sigma|F_o|$. [b] $wR = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $[Ru(L_2)(PPh_3)_2]ClO_4$ (1)

Ru(1)−S(1)	2.398(3)	N(1)−C(1)	1.338(11)
Ru(1)−N(2)	1.981(5)	N(1)−N(2)	1.367(10)
Ru(1)−N(3)	1.961(6)	O(1)−C(9)	1.270(11)
Ru(1)−O(1)	2.232(5)	C(2)−C(3)	1.500(9)
Ru(1)−P(1)	2.370(2)	C(2)−C(4)	1.430(11)
Ru(1)−P(2)	2.372(2)	C(8)−C(9)	1.472(9)
C(9)−C(10)	1.473(12)		

S(1)−Ru(1)−N(2)	81.5(2)	S(1)−Ru(1)−N(3)	161.6(1)
N(2)−Ru(1)−N(3)	80.1(2)	S(1)−Ru(1)−O(1)	123.5(1)
N(2)−Ru(1)−O(1)	154.9(2)	N(3)−Ru(1)−O(1)	74.9(2)
S(1)−Ru(1)−P(1)	85.8(1)	N(2)−Ru(1)−P(1)	93.9(2)
N(3)−Ru(1)−P(1)	95.2(2)	O(1)−Ru(1)−P(1)	86.5(1)
S(1)−Ru(1)−P(2)	87.8(1)	N(2)−Ru(1)−P(2)	97.7(2)
N(3)−Ru(1)−P(2)	94.9(2)	O(1)−Ru(1)−P(2)	86.5(1)
P(1)−Ru(1)−P(2)	165.8(1)		

Table 3. Atomic Coordinates (×10^5 for Ru; ×10^4 for Others) and Equivalent Isotropic Temperature Factors[a] (Å^2 × 10^4 for Ru; Å^2 × 10^3 for Others)

atom[b]	x	y	z	U_{eq}
Ru(1)	17841(5)	26573(4)	25695(4)	408(2)
S(1)	609(2)	2664(2)	1625(2)	65(1)
N(1)	2663(5)	988(5)	1087(4)	58(3)
N(2)	2871(4)	1422(4)	1767(3)	45(2)
N(3)	3083(4)	2257(4)	3088(3)	40(2)
O(1)	1192(4)	3788(3)	3738(3)	54(2)
N(4)	1329(6)	1188(4)	355(4)	122(5)
C(1)	1609(8)	1552(6)	1010(6)	74(4)
C(2)	3882(6)	944(5)	1922(4)	45(3)
C(3)	4797(7)	−3(6)	1376(5)	65(4)
C(4)	4027(6)	1403(5)	2661(4)	45(3)
C(5)	4989(7)	1060(6)	2999(5)	61(3)
C(6)	4961(8)	1589(7)	3733(6)	80(5)
C(7)	3975(8)	2435(6)	4184(5)	67(4)
C(8)	3050(6)	2758(5)	3819(4)	48(3)
C(9)	1944(7)	3630(5)	4156(5)	52(3)
C(10)	1727(9)	4320(7)	4930(5)	76(4)
C(11)	1678(4)	209(4)	−132(4)	115(6)
C(12)	920(5)	−17(6)	−524(7)	87(6)
C(13)	1263(6)	−985(6)	−1006(8)	100(7)
C(14)	2363(5)	−1729(4)	−1093(5)	153(8)
C(15)	3103(6)	−1522(5)	−672(8)	88(6)
C(16)	2758(6)	−555(5)	−189(7)	82(6)
C(17)	2737(7)	−2789(6)	−1618(7)	185(10)
C(12′)	1391(13)	187(5)	−914(7)	346(36)
C(13′)	1707(12)	−786(6)	−1381(7)	291(29)
C(15′)	2703(10)	−1698(4)	−338(6)	69(4)
C(16′)	2390(9)	−724(4)	128(6)	58(4)
P(1)	775(2)	1610(2)	3478(1)	53(1)
C(18)	2063(9)	−507(7)	2853(8)	99(5)
C(19)	2290(11)	−1457(8)	2401(8)	110(6)
C(20)	1451(15)	−1581(9)	2076(8)	127(9)
C(21)	410(13)	−799(8)	2212(8)	122(8)
C(22)	200(10)	170(7)	2647(6)	88(5)
C(23)	1009(7)	310(6)	3002(5)	62(4)
C(24)	450(8)	2048(8)	5243(6)	88(5)
C(25)	811(10)	2022(9)	5995(7)	102(6)
C(26)	1855(10)	1358(9)	6040(7)	88(6)
C(27)	2572(9)	734(8)	5332(7)	86(5)
C(28)	2242(8)	730(7)	4557(6)	81(4)
C(29)	1159(6)	1405(6)	4515(5)	57(3)
C(30)	−1496(7)	1709(9)	4374(6)	80(4)
C(31)	−2667(9)	2180(12)	4677(7)	105(6)
C(32)	−3199(9)	3185(11)	4447(7)	99(6)
C(33)	−2550(8)	3750(8)	3938(7)	92(5)
C(34)	−1330(7)	3267(7)	3637(6)	78(4)
C(35)	−794(6)	2239(9)	3848(5)	60(3)
P(2)	2330(2)	4031(1)	1745(1)	47(1)
C(36)	3047(12)	3150(10)	44(6)	137(9)
C(37)	3697(14)	2991(12)	−832(6)	150(10)
C(38)	4685(12)	3298(13)	−1088(9)	150(9)
C(39)	4868(19)	3952(30)	−517(8)	303(25)
C(40)	4272(15)	3999(23)	366(8)	322(25)
C(41)	3271(8)	3716(6)	655(5)	68(4)
C(42)	1134(14)	5643(12)	857(9)	199(10)
C(43)	130(18)	6470(16)	793(12)	308(16)
C(44)	−861(13)	6731(12)	1460(11)	173(10)
C(45)	−915(10)	6213(8)	2181(8)	108(6)
C(46)	52(8)	5399(6)	2262(7)	77(4)
C(47)	1084(8)	5126(6)	1604(5)	66(4)
C(48)	4126(7)	4138(6)	2389(5)	61(4)
C(49)	4613(7)	4593(7)	2900(5)	69(4)
C(50)	3989(9)	5573(7)	3343(6)	78(5)
C(51)	2909(10)	6109(7)	3283(6)	87(5)
C(52)	2392(8)	5666(7)	2790(6)	76(4)
C(53)	2996(6)	4685(5)	2339(4)	50(3)
Cl(1)	5526(2)	−2039(2)	3447(1)	64(1)
O(11)	4568(7)	−2012(7)	3133(5)	125(5)
O(12)	5987(8)	−3048(5)	3756(5)	130(5)
O(13)	6365(5)	−1781(5)	2772(4)	93(3)
O(14)	5122(7)	−1258(6)	4149(4)	106(4)

[a] U_{eq} defined as one-third of the trace of the orthogonalized **U** tensor. [b] Atoms C(12), C(13), C(15), C(16), C(12′), C(13′), C(15′), and C(16′) represent two orientations of a phenyl ring about the C(11)−C(14) axis, and each has a site occupancy factor of $^1/_2$.

of the complex at room temperature. A dark red prismatic crystal of 0.12 × 0.16 × 0.22 mm^3 was chosen for diffraction study. The compound crystallized in the triclinic space group $P\bar{1}$. The unit cell dimensions and cell volume are given in the Table 1. Intensity data were collected on a MSC/Rigaku Raxis-IIC imaging plate diffractometer using graphite-monochromatized Mo Kα radiation (λ = 0.710 73 Å) from a rotating anode generator powered at 60 kV and 90 mA. A total of 10 122 reflections were collected, with 8562 independent reflections (R_{int} = 6.56%), covering indices $-16 \le h \le 14$, $-16 \le k \le 0$, and $-20 \le l \le 20$, by oscillation photographs (36 frames in total), with $\phi = -30$ to 150° and $\Delta\phi = 5°$ at a scan rate of 10 min/frame.[26] The intensities were corrected for Lorentz and polarization effects and for absorption using the ABSCOR program. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically by full matrix least squares, with a riding model for the hydrogen atoms, using the SHELXTL-PC package.[27] For 6392 observed reflections ($|F_o| \ge 6\sigma|F_o|$), refinement converged ($\Delta/\sigma = 0.004$) with $R_F = 0.072$ and $R_w = 0.092$. The weighting scheme was $w = [\sigma^2|F_o| + 0.0005|F_o|^2]^{-1}$. Goodness of fit $S = 2.17$. Selected bond lengths and bond angles are given in Table 2, and atomic parameters of the non-hydrogen atoms are listed in Table 3.

Description of the Structure. The deprotonated ligand acts as a quadridentate donor in complex **1**, coordinating to the ruthenium(II) center through the thiolate sulfur (S(1)), imino nitrogen (N(2)), pyridine nitrogen (N(3)), and acetyl oxygen (O(1)) atoms, all of which occupy a square plane (Figure 1). The two triphenylphosphine moieties are trans to each other. The trans Ru−P bond distance (∼2.370 Å) is well within the range of values reported for Ru(II) complexes of triph-

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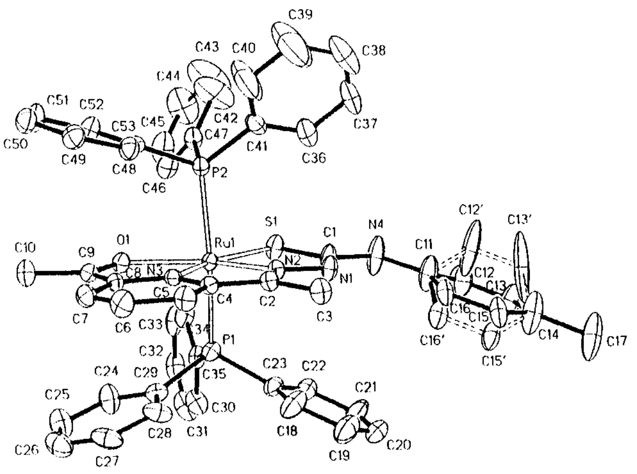

Figure 1. Perspective view of the $[Ru(L_2)(PPh_3)_2]^+$ cation in compound **1** with atom labeling. The thermal ellipsoids are drawn at the 25% probability level, and the alternative orientation of the phenyl ring is indicated by broken double lines.

Table 4. Important IR Bands (cm^{-1}) of the Compounds

compd	ν(C=O)	ν(C=N) + ν(C=C)	ν(C=S)
ligand (L_2H)	1690	1590, 1570	810
$[Ru(L_2)(PPh_3)_2]ClO_4$ (**1**)		1585, 1570	755
$[Ru(L_2)(PPh_3)_2]Cl$ (**2**)		1585, 1570	755
$[Ru(L_2)(PPh_3)]ClO_4 \cdot EtOH$ (**3**)		1590, 1565	750
$[Ru(L_2)(PPh_3)(bpy)]ClO_4$ (**4**)	1710	1590, 1570	755
$[Ru(L_2)(PPh_3)$(*o*-phen)$]ClO_4$ (**5**)	1705	1590, 1570	750
$[Ru(L_2)_2]$ (**6**)	1690	1590	750
$[Ru(L_2)(L_2H)]Cl \cdot CH_2C_2l$ (**7**)	1710	1595	750

enylphosphine.[28,29] The ligand framework (excepting the N4 phenyl group) is grossly planar permitting extensive delocalization. The observed C(1)−S(1) bond distance (1.713 Å) is close to C−S single bond lengths (1.69 Å) reported for free thiosemicarbazides and thiosemicarbazones.[30,31] An appreciable shortening of C(2)−C(4) (1.430 Å) and the C(8)−C(9) (1.472 Å) bonds compared to the standard C−C bond length (1.54 Å) is noticed. Again, the C(9)−O(1) bond (1.270 Å) is longer than the normal C=O bond (1.22−1.24 Å), whereas the Ru(1)−O(1) bond (2.232 Å) is appreciably shorter and is comprable to Ru−O bond distances reported for Ru(II) phenolato complexes.[32] All these data point to the highly conjugated nature of the ligand/framework of the complex. The appreciable shortening of the Ru−O and lengthening of the C=O bond explain the absence of the ν(C=O) mode in the expected position in the IR spectrum of the complex (vide infra). The tolyl group of the ligand L_2 exhibits 2-fold orientational disorder about its long axis, and accordingly the atoms C(12), C(13), C(15), C(16), C(12′), C(13′), C(15′), and C(16′) were assigned half site-occupancy.

Results and Discussion

2,6-Diacetylpyridine reacts with 4-(4-tolyl)thiosemicarbazide to yield both bis(thiosemicarbazone) and mono(thiosemicarbazone). Though a number of Fe(II) and Fe(III) complexes of the dihydrazone and the bis(thiosemicarbazone) of 2,6-diacetylpyridine[33,34] have been reported, none of them have addressed the mono(thiosemicarbazone) ligand. To our knowledge this is the first report of the synthesis and characterization of mono(thiosemicarbazone) complexes of 2,6-diacetylpyridine. The ligand (L_2H) reacts with $Ru(PPh_3)_3Cl_2$ to give different products depending on the nature of the reaction medium. In ethanol medium the product is $[Ru(L_2)(PPh_3)_2]X$ [X = ClO_4 (**1**), Cl (**2**)], while in dichloromethane $[Ru(L_2)(PPh_3)]ClO_4$ is isolated as the product. The compounds behave as uni-univalent electrolytes in accetonitrile, indicating nonparticipation of Cl^- or ClO_4^- in coordination. Careful analysis of the IR spectrum of the ligand L_2H and its complexes (Table 4) has helped in identifying the donor points of the ligand involved in coordination to the Ru(II) center. The ionic nature of the ClO_4^- and Cl^- is corroborated by the broad band around 1090 cm^{-1} characteristic of ionic perchlorate[9] and the absence of the ν(Ru−Cl) band, respectively. The ligand bands[9] ν(CS) and ν(CN) and pyridine ring vibrations at 750, 1590, 600, and 400 cm^{-1}, respectively, exhibit a shift of 5−10 cm^{-1} in the IR spectra of the complexes. These observations clearly indicate the coordination of the thiolate sulfur, the azomethine, and the pyridine nitrogen atoms to the Ru(II) center. Such small perturbation of the azomethine (ν(CN)) mode on coordination is not uncommon.[20] The ν(CO) vibration of the acetyl group, which is fairly sensitive toward coordination, is found to behave in an intriguing manner. The ν(CO) vibration of the ligand, observed at 1690 cm^{-1}, could not be located between 1650 and 1800 cm^{-1} in the complexes **1**−**3**.[35] This implies that the acetyl oxygen is very strongly bonded to the Ru(II) moiety and there must be appreciable π-backing-bonding from the Ru(II) center to the π^* orbital of the carbonyl group resulting in a considerable decrease in the carbon−oxygen bond order. Consequently the ν(CO) mode experiences a downward shift by more than 100 cm^{-1} and gets merged with the ν(CN) and ν(CC) bands present in the same region. This is confirmed from the structure of the compound $[Ru(L_2)(PPh_3)_2]ClO_4$ (**1**) (vide supra) determined by single-crystal X-ray diffraction techniques. Thus in the compounds **1**−**3** the ligand L_2 behaves as a monoanionic tetradentate ONNS donor, coordinating through the pyridine nitrogen, the imine nitrogen, the thiolato sulfur, and the carbonyl oxygen atoms. The conjugated framework of the ligand demands the positioning of the donor points of the ligand moiety on a square plane. Under this constraint reaction of the ligand with $Ru(PPh_3)_3Cl_2$ can lead to two possible products. Product a could be identified with the compounds **1** and **2** whereas product b could be identified with the compound **3**. Compounds **1** and **2** react with bidentate ligands like 2,2′-bipyridine or *o*-phenanthroline to produce the compounds $[Ru(L_2)(PPh_3)(N-N)]ClO_4$. [N−N = bpy (**4**)/*o*-phen (**5**)]. In the IR spectra of complexes **4** and **5**, the ν(CO) band appears at 1710 cm^{-1} indicating the nonparticipation of the carbonyl oxygen in coordination. Thus, in the compounds **4** and **5** the ligand behaves as a monoanionic tridentate NNS^- donor occupying a meridional plane and coordinating through the pyridine nitrogen, imine nitrogen, and thiolato sulfur, the other meridional plane being occupied by two nitrogens of the bipyridine or the *o*-phenanthroline and the phosphorus of triphenylphosphine. The strong affinity of Ru(II) for nitrogen donors is amply displayed in this case by the decoordination of the carbonyl oxygen by the nitrogen of bipyridine or *o*-phenanthroline. The mononegative tridentate NNS^- coordination of the ligand is also manifested in the bis-chelate compounds $[Ru(L_2)_2]$ (**6**) and $[Ru(L_2)(L_2H)]Cl \cdot CH_2Cl_2$ (**7**), which are the products of the reaction of L_2H with $[Ru(NH_3)_5Cl]Cl_2$ and $RuCl_3 \cdot xH_2O$, respectively. The nonparticipation of the carbonyl moiety in coordination is confirmed

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Table 5. Cyclic Voltammetric Data[a,b] at 298 K

compd	oxidn: $E_{1/2}$, V (ΔE_p, mV) in CH_3CN	 in CH_2Cl_2
$[Ru(L_2)(PPh_3)_2]ClO_4$ (**1**)	0.70 (90)	0.85 (230)
$[Ru(L_2)(PPh_3)_2]Cl$ (**2**)	0.68 (70)	0.82 (250)
$[Ru(L_2)(PPh_3)]ClO_4 \cdot EtOH$ (**3**)	0.74 (70)	0.85 (90)
$[Ru(L_2)(PPh_3)(bpy)]ClO_4$ (**4**)	0.58 (110)	0.73 (130)
$[Ru(L_2)(PPh_3)(o\text{-phen})]ClO_4$ (**5**)	0.58 (110)	0.75 (170)
$[Ru(L_2)_2]$ (**6**)	0.065 (50)	0.105 (190)
$[Ru(L_2)(L_2H)]Cl \cdot CH_2Cl_2$ (**7**)	0.065 (50)	0.065 (170)

[a] Conditions: solvent, as given; supporting electrolyte, TEAP (0.1 M); working electrode, platinum; reference electrode, SCE; solute concentration, 10−3 M. [b] $E_{1/2}$ is calculated as the average of anodic (E_{pa}) and cathodic (E_{pc}) peak potential. $\Delta E = E_{pa} - E_{pc}$, $I_{pc}/I_{pa} = 1$, and scan rate = 50 mV s^{-1}.

by the presence of a ν(CO) band at 1700−1710 cm^{-1} in the IR spectra of these complexes. Compound **6** is nonconducting whereas compound **7** behaves as 1:1 electrolyte in DMF solution. Thus in compounds **6** and **7** both of the ligands are involved in tridentate coordination through NNS^- donor sites occupying a meridional plane.

Electrochemistry. The electron transfer reactions of the complexes were examined by cyclic voltammetry using a Pt working electrode and acetonitrile or dichloromethane as solvent. The results are given in Table 5. The cyclic voltammograms of all the complexes are dominated by the Ru(II)/Ru(III) redox couple. In acetonitrile the the mono ligand complexes **1**−**5** exhibit a reversible Ru(II)/Ru(III) couple around 0.6−0.7 V consistent with the strong π-withdrawing capability of these ligands. In the bis-ligand complexes, however, Ru(II)/Ru(III) couple is located at a much lower value (around 0.065 V). When cyclic voltammograms are recorded in dichloromethane, a similar trend is observed, but all the redox couples are anodically shifted by 0.10−0.15 V compared to those observed in acetonitrile; moreover, the differences between cathodic and anodic peaks, i.e. ΔE_p values, are much higher (70−230 mV) in dichloromethane than those in acetonitrile. It has been observed[36] that Ru(II)/Ru(III) couples do not generally depend on the solvent, unless the solvent participates in some reaction like solvolysis, etc. Under our experimental conditions, cyclic voltammograms of ferrocene in acetonitrile ($E_{1/2} = 0.43$ V; $\Delta E_p = 75$ mV) and in dichloromethane ($E_{1/2} = 0.53$ V; $\Delta E_p = 150$ mV) exhibit similar trends. We had much the same experience during our work[37] on a series of complexes containing other NNS donor ligands. On the basis of this observation, the significantly higher ΔE_p and $E°$ value in dichloromethane found in the present work may be ascribed to an appreciable change in the inner-sphere reorganization energy during the redox process in dichloromethane compared to that in acetonitrile. In compounds **1**−**3** the 6-acetyl group of the pyridine is coordinated to the metal, whereas in the remaining four compounds it does not participate in coordination and remains pendant. Ru(III) being a hard acceptor possesses a higher affinity toward the carbonyl oxygen than the borderline Ru(II). Moreover the binding between the carbonyl and the Ru(II) center will be dominated by M → O π-back-bonding, whereas that with Ru(III) will be dominated by O → M σ donation. Thus in compounds **1**−**3**, Ru(II)/Ru(III) oxidation will be accompanied by appreciable change in C−O and Ru−O bond lengths. A polar solvent like acetonitrile assists this process by better solvation of the doubly charged oxidized species, but in dichloromethane the energy barrier for electron transfer remains quite high due to poor solvation of these doubly charged species. In compounds **4**−**7** the pendant acetyl group is again very well solvated by acetonitrile and is not encouraged to participate in coordination to the metal center when Ru(II) to Ru(III) oxidation occurs. But in dichloromethane poor solvation of the acetyl group induces it to coordinate to the oxidized metal center leading to the formation of a seven-coordinate species. It is well-known that low-spin d^6 systems are reluctant to form seven-coordinate species, whereas a number of seven-coordinated complexes are known for low-spin d^5 systems.[38] Thus Fe(III) form a number of seven-coordinated species with bis(hydrazone) and bis(thiosemicarbazone) derivatives of 2,6-diacetylpyridine. Ru(III) having a larger size than Fe(III) is expected to form such seven-coordinate species even more readily. The considerable reorganization energy needed to effect a change of octahedral complex to pentagonal bipyramidal coordination geometry is responsible for the high ΔE_p values for the couples. No significant reductive electrochemistry is observed for any one of the complexes **1**−**7**. The possible reason for such an observation may be the reduction of the coordinated thiosemicarbazide moiety in the first step and subsequent decomposition of the resultant species before the bipyridine or the *o*-phenanthroline ligand can undergo reduction. Both **1** and **2** are found to be oxidized around a potential 0.7 V in acetonitrile. When any one of them is oxidized electrochemically at 0.9 V, the resultant solution is EPR silent even at 77 K indicating that the spin−lattice relaxation time for this complex is very short.[39] However, that the oxidation involves a Ru(II) to Ru(III) conversion is clearly established by recording the electronic spectrum of the oxidized solution which exhibited two absorption maxima at 1411 (ϵ_{max} 80) and 1910 (ϵ_{max} 92) nm characteristic of octahedral Ru(III) complexes with rhombic distortion.[40] Compounds **6** and **7** were oxidized by iodine in acetonitrile, and their electronic spectra exhibit the characteristic features of a Ru(III) complex.

Electronic Absorption Spectra. The electronic spectra of the complexes are dominated by several intense bands in the visible and UV regions, which, from the values of their molar extinction coefficients, can be ascribed to charge transfer transitions. The band at 460 nm present in the mono-ligand complexes can be ascribed to a Ru(4dπ) → π*(py) MLCT transition, whereas the band around 410 nm may be assigned to Ru(4dπ) → π*(imine) transition. In the bipyridine or *o*-phenanthroline complexes the second transition overlaps with a Ru(4dπ) → π*(bpy/ophen) transition enhancing the intensities of the band. In the bis-ligand complexes these two transitions are located at 500−530 and 370−380 nm, respectively. The band around 250−270 nm may be assigned to Ru(dπ) → π*(2) of the py, bpy, or *o*-phen moiety. The lowest energy band around 230 nm is due to an intraligand charge transfer transition.

NMR Spectroscopy. The NMR spectra of the ligand L_2H exhibit three CH_3 proton signals at δ 2.33 ppm (3H), δ 2.5 ppm (3H), and δ 2.73 ppm (3H). The free 2-acetylpyridine is known to exhibit its methyl signal at δ 2.72 ppm,[41] and in the NMR spectrum of the bis(thiosemicarbazone) of 2,6-diacetylpyridine only two CH_3 signals are present at δ 2.3 (6H) and δ 2.5 (6H).[42] Comparison of the NMR spectra of these three compounds promoted us to assign δ 2.33 ppm signal to the CH_3 group adjacent to the imine moiety, the δ 2.5 ppm signal to the CH_3 group of the *p*-tolyl fragment, and δ 2.73 ppm signal to the

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methyl group of the acetyl moiety. In complex **1**, where the ligand behaves in the tetradentate manner, the δ 2.33 ppm signal is shifted upfield to δ 1.9 ppm, whereas the δ 2.5 and 2.73 ppm signals of the free ligand merge into a single signal δ 2.32 (6H). Both these observations indicate the involvement of the imine nitrogen and the carbonyl oxygen atom in coordination to the Ru(II) center. All the complexes exhibit proton signals in the aromatic region (δ 6.6−7.8 ppm), and for complexes containing triphenylphosphine the signals of the aromatic proton of L_2 cannot be distinguished from the aromatic proton signals of triphenylphosphine due to their extensive overlap. Thus the ligand L_2 occupies the square plane containing the ruthenium center with the two PPh_3 groups trans to each other. Such a trans disposition of the two PPh_3 groups places each of them cis to the coordinated carbonyl oxygen of the ligand. This relative positioning of the PPh_3 molecules and the carbonyl group is manifested in the reactions of compound **1** with both bipy and ophen, when one PPh_3 and the coordinated carbonyl group is detached from the Ru(II) center leading to the formation of compounds **4** and **5**.

Conclusion

The mono(thiosemicarbazone) of 2,6-diacetylpyridine is reported for the first time in the literature. The ligand is found to behave in a flexidentate manner, coordinating either as a monoanionic tetradentate ONNS donor or as neutral/monoanionic tridentate NNS^- donor. Structural data suggest that there is extensive conjugation within the ligand framework that induces it to occupy a square or a meridonal plane. Besides, this is probably the first report of the structural characterization of a complex containing a ketone moiety of an α-carbonyl heterocyclic ligand coordinated to a Ru(II) center.

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Supporting Information Available: ORTEP diagrams and complete tables of X-ray crystallographic parameters, bond lengths and angles, atomic coordinates and equivalent isotropic temperature factors, anisotropic thermal parameters, and hydrogen atom coordinates and assigned isotropic temperature factors for complex **1** (12 pages). Ordering information is given on any current masthead page.

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