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STUDIES ON SPECTROSCOPIC AND CRYSTAL STRUCTURE OF DICHLORO CARBONYL DIPYRIDINE TRIPHENYLARSINE RUTHENIUM(II) COMPLEX**M. Gowri¹, T. Srinivasan², D. Velmurugan²**

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The title complex $[\text{Ru}(\text{Cl})_2(\text{CO})(\text{py})_2(\text{AsPh}_3)]$, was synthesized and characterized. The molecular structure and crystal structures are determined by X-ray crystallography. The dihedral angle between the two *cis*-pyridine rings is $73.3(2)^\circ$, which shows that they are almost orthogonal to each other. The molecular structure is stabilized by inter-molecular and intra-molecular C—H...Cl interactions. The molecular structure is further stabilized by interactions between the aromatic rings.

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INTRODUCTION

Due to the potential as versatile catalysts for organic synthesis and polymer production, ruthenium complexes have witnessed a spectacular development. Several series of organometallic complexes of ruthenium have been prepared and extensively used in variety of chemical transformations like oxidation [1, 2], hydration [3, 4], hydrogenation [5—7], isomerization [8—10], decarbonylation [11], epoxidation [12-14], Diels-Alder reaction [15, 16], cross coupling reaction [17] and other related catalytic processes. Dipyridyl Ru(II) complexes have been used in anti-tumor treatment as alternatives to *cis*-platin. The octahedral geometry of Ru(II) allows for reactivity and binding that cannot be achieved by the square-planar Pt(II) *cis*-platin system [18, 19]. Metal carbonyls are useful in organic synthesis and as catalysts or catalyst precursors in homogeneous catalysis. Pyridine is widely used as a ligand in coordination chemistry. When a pyridine ligand is part of a metal complex, it can be replaced by a stronger Lewis base. This property has the advantage in the catalysis of polymerization [20, 21] and hydrogenation reactions [22]. The pyridine ligand replaced during the reaction is restored after its completion like triphenyl phosphine/triphenyl arsine.

Based on the above discussions, we have undertaken spectroscopic and X-ray structural studies of a novel Ru(II) complex $[\text{Ru}(\text{Cl})_2(\text{CO})(\text{py})_2(\text{AsPh}_3)]$.

EXPERIMENTAL

Synthesis. A mixture of $[\text{Ru}(\text{H})(\text{Cl})(\text{CO})(\text{py})(\text{AsPh}_3)_2]$ (860 mg, 1 mmol) [23] and (Z)-4-(((2-hydroxy phenyl)imino)methylene)-3-methyl-1-phenyl-1H-pyrazol-5-one (290 mg, 1 mmole) $[\text{H}_2\text{L}]$ [24] was taken in a round bottomed flask in the solution of equal volume mixture of ethyl acetate and

chloroform and refluxed over a water bath for about 5 h. The reaction results in two types of products. They were separated and subjected to various spectroscopic analyses.

This paper describes the spectroscopic and structural details of the brown colored crystals obtained apart from the green tiny crystals as major product.

Elemental analyses. The elemental analyses were obtained from SAIF, Cochin, Kerala. Found for $[\text{Ru}(\text{Cl})_2(\text{CO})(\text{py})_2(\text{AsPh}_3)]$ (%): C 53.56, H 3.63, N 4.16. Calculated (%): C 52.37, H 3.76, N 4.21.

FTIR spectrum. The coordination mode of the central metal atom with ligands can be well understood from the absorption peaks of FTIR spectrum of the resulted complex and also on comparison with that of the ligands. The characteristic frequency of aromatic C—H stretching (3050 cm^{-1}) and C—H bending (734 cm^{-1}) are found in the expected regions. The presence of strong absorption peaks at 692 cm^{-1} , 1069 cm^{-1} , 1483 cm^{-1} confirms the presence of triphenyl arsine [25] which is coordinated to the central ruthenium through the As atom. The presence of terminally coordinated carbon monoxide as ligand is evident from the presence of a strong sharp peak at 1954 cm^{-1} [23]. Comparison of the IR spectrum of the complex with that of the pyridine indicates shifting of a strong absorption peak at 1578 cm^{-1} to 1601 cm^{-1} , in accordance with the coordination of pyridine to ruthenium through the nitrogen atom [26].

X-ray diffraction. The title complex crystallizes in monoclinic with the space group of $C2/c$ with cell parameters $a = 32.4259(6)\text{ \AA}$, $b = 10.0558(2)\text{ \AA}$, $c = 22.8155(4)\text{ \AA}$, $\beta = 133.738(1)^\circ$, $Z = 8$, $M_r = 664.40$ and $V = 5375.0(2)\text{ \AA}^3$. The structure was solved by direct methods using SHELXS-97 and refined by full-matrix least squares method using SHELXL-97 programs [27]. The final R factor value is 0.0296 with the GOOF value of 1.036 for 6642 independent reflections.

X-ray diffraction intensity data was collected on a Bruker AXS SMART APEXII single crystal X-ray diffractometer equipped with graphite monochromated $\text{MoK}\alpha$ ($\lambda = 0.7103\text{ \AA}$) radiation source and CCD detector. Crystals were cut to suitable size and mounted on a glass fibre using cyanoacrylate adhesive. The unit cell parameters were determined from 36 frames measured (0.5° ϕ -scan) from three different crystallographic zones and using the method of difference vectors. The intensity data were collected with an average four-fold redundancy per reflection and optimum resolution (0.75 \AA). The intensity data collection, frames integration, Lorentz and polarization correction and decay correction were done using SAINT-NT (version 7.06a) software. Empirical absorption correction (multi-scan) was performed using SADABS (Bruker, 2008) program [28].

In the title complex, $[\text{Ru}(\text{Cl})_2(\text{CO})(\text{py})_2(\text{AsPh}_3)]$, the dihedral angle between the two pyridine rings ((N1/C1—C5) and (N2/C6—C10)) is $73.3(2)^\circ$, which shows that they are almost orthogonal to each other. The angles around As1 atom (C11—As1—C23 = $105.88(11)^\circ$, C11—As1—C17 = $102.28(10)^\circ$ and C23—As1—C17 = $97.18(11)^\circ$) deviates from the ideal tetrahedral values which may be a steric interaction between benzene rings and Ru atom. The molecular structure is stabilized by C24—H24...C12 (H...C1 = 2.70 and the angle C24—H24...C12 = 133°) intra-molecular halogen interaction, which results in pseudo six membered ring structure. The crystal packing features intermolecular C13—H13...C11 halogen bond interactions with the distance of H...C1 = $2.862(2)\text{ \AA}$ and the angle C13—H13...C11 = 145° (Symmetry code: $-x+1/2, -y+1/2+1, -z$). The molecular structure is further stabilized by Cg1...Cg2 interactions with the distance of $3.7127(19)\text{ \AA}$, where Cg1 is the center of gravity of (N1/C1—C5) and Cg2 is the center of the gravity of (C11—C16). The molecular structure of the title complex, the crystal packing of the title compound viewed down c axis showing the hydrogen bonds are given in Figs. 1 and 2 respectively.

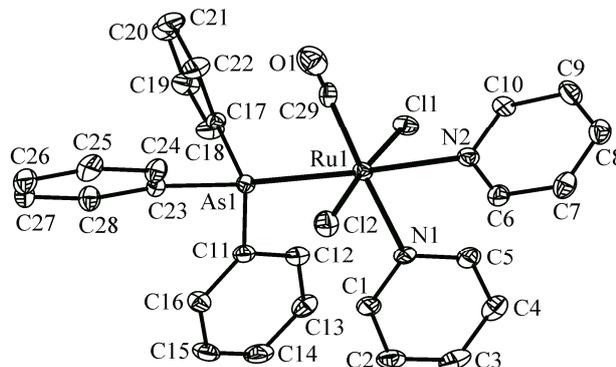


Fig. 1. The molecular structure of the title complex, showing displacement ellipsoids drawn at the 30% probability level. H atoms are removed for structure clarity

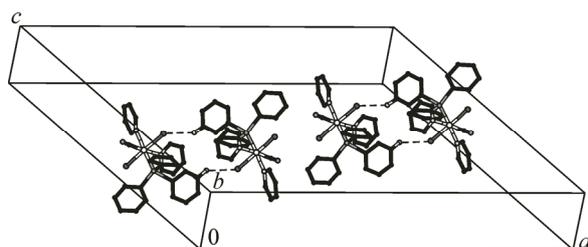
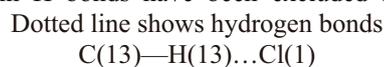


Fig. 2. The crystal packing of the title compound viewed down *c* axis, showing the hydrogen bonds; H atoms not involved in H bonds have been excluded for clarity.



The main details of the X-ray diffraction of the title complex $[\text{Ru}(\text{Cl})_2(\text{CO})(\text{py})_2(\text{AsPh}_3)]$ are given in Table 1. The crystallographic data has been deposited in Cambridge Crystallographic Data Centre (CCDC No. 894858) deposit@ccdc.cam.ac.uk. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.

CONCLUSION

This research article describes the spectroscopic and X-ray determination of the new novel crystal which is obtained as byproduct in the synthesis of ruthenium(II) complex which is coordinated to di-basic tridentate Schiff base ligand. During the reaction, it is expected that certain ligands like pyridine, chloride, triphenyl arsine and hydride gets detached from the starting precursor complex. These detached ligands from the precursor complex, reacts with the same precursor complex and results in the formation of the titled complex and this conversion may be expected to be catalyzed by the main product obtained in the same reaction. Synthesis of various metal complexes and its evaluation of catalytic activities are ongoing project in our laboratory. The results will be published in due course.

T a b l e 1

Crystal data and structure refinement for $[\text{Ru}(\text{Cl})_2(\text{CO})(\text{py})_2(\text{AsPh}_3)]$

Empirical formula	C ₂₉ H ₂₅ As Cl ₂ N ₂ O Ru
Formula weight	664.40
Temperature, K	293(2)
Wavelength, Å	0.71073
Crystal system; space group	Monoclinic; <i>C</i> 2/ <i>c</i>
Unit cell dimensions <i>a</i> , <i>b</i> , <i>c</i> , Å; β, deg.	32.4259(6), 10.0558(2), 22.8155(4); 133.738(10)
Volume, Å ³	5375.0(2)
Z; Calculated density, g/cm ³	8; 1.642
Absorption coefficient, mm ⁻¹	2.030
<i>F</i> (000)	2656
Crystal size, mm	0.20×0.20×0.20
θ range for datacollection, deg.	1.74 to 28.32
Limiting indices	-42 ≤ <i>h</i> ≤ 42, -13 ≤ <i>k</i> ≤ 12, -29 ≤ <i>l</i> ≤ 30
Reflections collected / unique	24815 / 6642 [<i>R</i> (int) = 0.0251]
Completeness to θ = 28.32 %	99.3
Absorption correction	None
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	6642 / 0 / 325
Goodness-of-fit on <i>F</i> ²	1.036
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0296, <i>wR</i> ₂ = 0.0713
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0404, <i>wR</i> ₂ = 0.0762
Largest diff. peak and hole, e/Å ³	0.652 and -0.581
CCDC No.	894858

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