Synthesis, structure and properties of α,β-unsaturated carboxylic acid adducts of arene ruthenium(II) Schiff-base complexes: X-ray crystal structure of [(η⁶-p-cymene)Ru(O₂CCH=CMe₂)(O⁻₂-C₆H₄CH=NC₆H₄-p-Me)].H₂O

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Arene ruthenium(II) Schiff-base complexes of formulations [(η⁶-p-cymene)Ru(O₂CCH=CMe₂)(O⁻₂-C₆H₄CH=NC₆H₄-p-Me)].H₂O (Ia–e) and [(η⁶-p-cymene)Ru(O₂CCH=CHR')(O⁻₂-C₆H₄CH=NC₆H₄-p-Me)].H₂O (Ia,b) (R₁=H, R₂=Ph (a), R₁=R₂=Me (b), R₁=H, R₂=Me (c)) have been prepared by reacting the chloro adducts with the silver salts of the α,β-unsaturated carboxylic acids in methanol or tetrahydrofuran and characterised by analytical and spectroscopic methods. The molecular structure of [(η⁶-p-cymene)Ru(O₂CCH=CMe₂)(O⁻₂-C₆H₄CH=NC₆H₄-p-Me)].H₂O (1b.H₂O) has been determined by X-ray crystallography. The crystal belongs to the monoclinic space group P2₁/n with the following cell dimensions for the C₇₇H₇₁NO₅Ru (M = 562.65): a = 8.509 (5) Å, b = 21.123 (4) Å, c = 14.824 (4) Å, β = 93.88 (3)°, V = 2658 (2) Å³, Z = 4. D = 1.406 g cm⁻³, μ(Mo-Kα) = 6.64 cm⁻¹, λ(Mo-Kα) = 0.7107 Å, T = 293 K, R₁ = 0.0478 (wR₂ = 0.1111) for 3056 reflections with 1 > 2σ(I) and 316 parameters. The complexes 1 and 2 have ruthenium(II) centre bonded to an η⁶-c-p-cymene group, a unidentate carboxylate and a bidentate chelating Schiff-base ligand. The carboxylate ligand is involved in hydrogen-bonding interaction with the lattice water molecule.

The half-sandwich (η⁶-arene)ruthenium(II) complexes are of current interest considering their utility in asymmetric transformation reactions and in the development of the chemistry of optically active enantioselective catalytic systems. Earlier we have reported the chloride adducts of the (p-cymene)ruthenium(II) species containing achiral N,N'- and N,O-donor Schiff-base ligands. Herein we report the synthesis, structure and properties of the α,β-unsaturated carboxylate complexes 1 and 2. The molecular structure of [(η⁶-p-cymene)Ru(O₂CCH=CMe₂)(O⁻₂-C₆H₄CH=NC₆H₄-p-Me)].H₂O (1b.H₂O) is determined by X-ray crystallographic study.

Materials and Methods

All reactions were done in dry solvent under a dinitrogen atmosphere. The carboxylic acids were of reagent grade and used as received. The solvents were purified following standard procedures. The preparative procedures for the Schiff-bases and the precursor complexes were reported earlier. Elemental analyses were carried out on a Perkin-Elmer 2400 CHN analyser. The infrared spectra were recorded on a BIO-RAD FTS-7 spectrometer. ¹H NMR spectra were obtained on a Bruker Ac(F/A)200 MHz spectrometer using CDCl₃ as a solvent and tetramethylsilane (TMS) as an internal standard.

Preparation of [(η⁶-p-cymene)RuCl(O₂CCH=CHR')(O⁻₂-C₆H₄CH=NC₆H₄-p-Me)](CI0₄) (R₁=H, R₂=Ph, a; R₁=R₂=Me, b; R₁=H, R₂=Me, c).

The complexes were prepared using a general procedure in which [(η⁶-p-cymene)RuCl(O₂-C₆H₄CH=NC₆H₄-p-Me)](140 mg, 0.3 mmol) was reacted with the silver salt of the α,β-unsaturated carboxylic acid in dry tetrahydrofuran (15 cm³) at -5°C for 2 hr under stirring conditions. The solution was filtered through celite to remove the precipitated AgCl and the solid residue of the complex was obtained on evaporating the solvent followed by trituration with n-hexane. The product which was isolated as an air-
stable orange solid in ~90% yield was crystallized from ethyl acetate and n-heptane mixture. [Found: C, 71.4; H, 5.9; N, 2.4. Calc. for C_{29}H_{33}NO_3Ru (1a): C, 70.9; H, 5.9; N, 2.5%. Found: C, 61.4; H, 6.3; N, 2.0. Calc. for C_{29}H_{33}NO_3Ru (1b): C, 61.9; H, 6.3; N, 2.6%. Found: C, 63.9; H, 5.8; N, 2.4. Calc. for C_{28}H_{31}NO_3Ru (1c): C, 63.4; H, 5.9; N, 2.6%]

The expression for the equivalent isotropic thermal parameter is

\[ U_{eq} = \frac{1}{3} \sum_{i=1}^{3} a_i \sum_{j=1}^{3} a_j \]
solution of the complex in ethyl acetate and n-heptane mixture under dinitrogen atmosphere. A red prismatic crystal of dimensions 0.1x0.2x0.4 mm was mounted on a glass fibre with epoxy cement. Unit cell parameters were obtained from least-squares treatment of 25 reflections in the range 18<2θ<32°. Intensity data(±hkl) were collected for reflections (-10 ≤ h ≤ 10; 0 ≤ k ≤ 25; 0 ≤ l ≤ 17) within the range 3.4≤ 2θ ≤ 50° using ω-scan technique on an Enraf-Nonius CAD4 diffractometer equipped with a graphite-monochromatised Mo-Kα radiation. The data were corrected for Lorentz, polarisation and absorption effects.

Out of 4656 unique reflections collected, 3056 data with I > 2σ(I) were used for structure solution and refinement. The structure was solved by Patterson’s heavy atom method which revealed the position of the metal in the crystallographic asymmetric unit. The remaining atoms were located from the difference Fourier maps and refined by least-squares techniques. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms attached to the atoms in the complex were generated and assigned isotropic thermal parameters, riding on their parent atoms and used for structure factor (F²) calculation only. There was one molecule of water as solvent of crystallization. The source of water could be the solvent used for crystallizing the complex. The final refinement converged to R=0.0478 and wR²=0.1111 with 3056 reflections having I ≥ 2σ(I) and 316 parameters with a weighting scheme w = 1/[σ²(F²) + (0.0625P)² + 3.97P], where P=[Max (F², 0) + 2F²]/3 and using 316 parameters [R indices (all data):R=0.0882, wR²=0.1370; F(000)=1168]. The final difference Fourier map showed the largest peak and hole as 0.950 and -1.194 eÅ⁻³. The goodness-of-fit on F² was 1.067. All calculations were carried out using VAX88 and IBM computer systems at the Indian Institute of Science using SHELX programs. The positional parameters along with equivalent isotropic thermal parameters are given in Table 1, and selected bond distances and angles are given in Table 2. The hydrogen atom coordinates, full lists of bond distances and angles, anisotropic thermal parameters, and the structure factor tables are available with the authors on request.

Crystal data

The cell constants and crystallographic data are: mol. formula C₂₉H₃₁NO₃Ru; mol. wt. 562.65; monoclinic, P2₁/n; a = 8.509 (5) Å, b = 21.123 (4) Å, c = 14.824 (4) Å, β = 93.88 (3)°, V = 2658 (2) Å³, Z = 4. Dc = 1.406 g cm⁻³, μ(Mo-Kα) = 6.24cm⁻¹, λ=0.7107 Å, T = 293 K, transmission coeff.: 0.743-1.209.

Results and Discussion

The complexes are isolated in good yield by reacting the chloride complex with the silver salt of the α,β-unsaturated carboxylic acids. The complexes are fairly stable in air in the solid state but are unstable in the solution phase. They are characterised from elemental analysis, infrared and ¹H-NMR spectral data (Table 3). The infrared spectra of the

| Table 3—¹H-NMR spectroscopic data for complexes 1a-1c, 2a and 2b |
|------------------|------------------|------------------|
| Complex | p-Cymene | Schiff-base | Carboxylate |
| 1a | 1.11, 1.18 (each d, J=7Hz, 6H); 2.09 (s, 3H); 2.43 (s, 3H); 2.46 (s, 3H); 2.5 (m, 1H); 3.55 (s, 3H); 5.47 (each d, J=6Hz, 1H) | 6.37-7.0 (m, 2H); 7.21-7.27 (m, 5H) | 6.37-7.0 (m, 2H); 7.21-7.27 (m, 5H) |
| 1b | 1.09, 1.15 (each d, J=7Hz, 6H); 2.03 (s, 3H); 2.43 (s, 3H); 2.46 (s, 3H); 2.5 (m, 1H); 3.45 (s, 3H); 5.43 (s, 3H); 6.37-7.56 (8H) | 6.37-7.56 (8H) | 6.37-7.56 (8H) |
| 1c | 1.01, 1.08 (each d, J=7Hz, 6H); 2.09 (s, 3H); 2.43 (s, 3H); 2.46 (s, 3H); 2.5 (m, 1H); 3.55 (s, 3H); 5.47 (each d, J=6Hz, 1H) | 6.37-7.56 (8H) | 6.37-7.56 (8H) |
| 2a | 1.08-1.21 (m, 6H); 2.07 (s, 3H); 2.5 (m, 1H); 5.50 (d, J=6Hz, 1H); 5.8 (m, 3H); 6.3 (d, J=16Hz, 1H); 7.2 (d, J=8Hz, 1H); 8.05-8.17 (m, 2H); 8.6 (s, J=16Hz, 1H); 9.57 (d, J=6Hz, 1H) | 6.3 (d, J=16Hz, 1H); 7.2 (d, J=16Hz, 1H); 8.05-8.17 (m, 2H); 8.6 (s, J=16Hz, 1H); 9.57 (d, J=6Hz, 1H) | 6.3 (d, J=16Hz, 1H); 7.2 (d, J=16Hz, 1H); 8.05-8.17 (m, 2H); 8.6 (s, J=16Hz, 1H); 9.57 (d, J=6Hz, 1H) |
| 2b | 1.06-1.21 (m, 6H); 2.07 (s, 3H); 2.53 (m, 1H); 5.48 (d, J=6Hz, 1H); 5.65 (d, J=6Hz, 1H); 7.81 (d, J=8Hz, 1H); 8.0-8.2 (m, 2H); 8.56 (d, J=6Hz, 1H) | 1.6 (s, 3H); 1.7 (s, 3H); 5.5 (s, 1H) | 1.6 (s, 3H); 1.7 (s, 3H); 5.5 (s, 1H) |

* spectra recorded in CDCl₃, s-singlet, d-doublet, m-multiplet.
complexes show a medium-intensity band near 1640 cm⁻¹ assignable to the νasym(OCO) unidentate mode of bonding of the carboxylate ligand. Complex 2 displays strong band at 1100 cm⁻¹ due to the perchlorate anion. While 1 is a non-electrolyte in nitromethane solution, complex 2 is 1:1 ionic in nature. In presence of halides, the metal-carboxylate bond readily undergoes substitution to form the precursor halide adducts.

The ¹H-NMR data suggest a 1:1:1 ratio of the p-cymene, Schiff-base and the ω,ω-unsaturated carboxylate ligand in 1 and 2 (Fig. 1). The p-cymene ligand displays a singlet for the methyl and a pair of doublets and a septet for the CHMe₂ in the range δ 1-3. The arene ring protons exhibit four doublets within δ 4-6. The Schiff-base methyl group appears as a singlet near δ 2.4. A singlet near δ 7.7 is assignable to the imine CH proton of the Schiff-base ligand in 1. The same proton in 2 is observed near δ 8.6. The aryl group protons appear in the range δ 6-8. The ω,ω-unsaturated carboxylate ligands show the methyl group(s) signals in the range δ 1.5-1.7 for the crotonate and dimethylacrylate adducts. The olefinic protons appear in the range δ 5-8. The olefinic proton adjacent to the carboxyl group shows a downfield shift of its proton resonance compared to the other olefinic proton in the carboxylate ligand.

The complex [(η⁶-p-cymene)Ru(O₂CCH=CHPh) (C₅H₄N-2-CH=NCH₂Me)]ClO₄ (2a) in CDCl₃ (S = solvent; TMS = tetramethylsilane).

Fig.1—¹H-NMR spectrum of [(η⁶-p-cymene)Ru(O₂CCH=CHPh) (C₅H₄N-2-CH=NCH₂Me)]ClO₄ (2a) in CDCl₃ (S = solvent; TMS = tetramethylsilane).

The coordination geometry of ruthenium is essentially octahedral in which the η⁶-bonded p-cymene ligand occupies one face of the octahedron. The Schiff-base displays a bidentate chelating N, O-bonding mode. The C—C olefinic bond distance in the carboxylate ligand of 1.311Å indicates the double bond nature of this moi-
19 Sheldrick G M, SHELX-86 and SHELXL-93, Programs for X-ray crystal structure solution and refinement (University of Göttingen, Germany) 1986 & 1993.