

Synthesis and characterization of new complexes formed by insertion of carbon disulphide in RuL_3Cl_3 ($L=PPh_3$ and $AsPh_3$)

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Reaction of RuL_3Cl_3 ($L=PPh_3$ and $AsPh_3$) with stoichiometric amount of CS_2 in ethanol-dichloromethane mixed solvent systems at room temperature yields paramagnetic complexes of the type $[RuL_2Cl_2(S_2COEt)]$. The complexes have been characterized by conductance, IR, electronic, ESR spectral, magnetic moment measurement and thermal data as well as by elemental analysis. The appearance of three g -values in the ESR spectra reveal a highly distorted octahedral environment around ruthenium(III) ion with one bidentate $EtOCS_2^-$ ligand.

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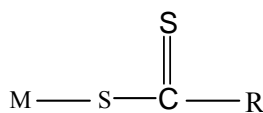
Although there are exhaustive reports on complexation of transition metals with σ -donors like phosphines, arsine and stibines, in recent years there is a resurgence of studies on carbon rich ligands with appreciable π -electron density as they have good optoelectronic property¹. Such ligands and others like cyclopentadienyls can play an important role in tuning the electronic properties and in stabilizing the complexes. In Pearson's classification, Ru(III) is a borderline acid and these donors are soft bases. The so-called bystander dithioligands in presence of 'innocent' co-ligands such as phosphine and arsine may modify the electronic properties to facilitate MLCT process due to their adjustable (with various alkyl substituents attached to dithiosystem) $\sigma+\pi$

basicity towards the metal¹. Besides, transition metal compounds with dithioligands have known antioxidant and biological activities. Such compounds can be synthesized by insertion of CS_2 into transition metal centers containing carbonyls, arsine, phosphine and cyclopentadienyls. As an unsaturated electrophile and a potentially good source of C_1 chemistry, CS_2 is a useful reagent for insertion into transition metal complexes in presence of other donor ligands². CS_2 also has a versatile coordination chemistry with η^1 -end on (**I**), η^2 -side on (**II**) and η^2 -bidentate (**III**) modes.

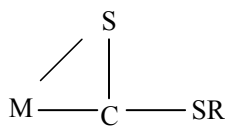
Besides, there exist some examples of CS_2 insertion reaction yielding η^3-S_2CR ligand systems. Usually CS_2 insertion takes place to a metal in a low valency state. However in our present work, we have stabilized Ru(III) in presence of CS_2 with phosphine and arsine as co-ligands. Recently, Zhao Dong *et al.*³ reported the synthesis and X-ray structure of $[(PPh_3)_2CuS_2COMe]$. The present note describes the synthesis and characterization of two new complexes formed by insertion of CS_2 into RuL_3Cl_3 [$L=PPh_3$ and $AsPh_3$] in a mixed solvent of dichloromethane and ethanol at room temperature.

Experimental

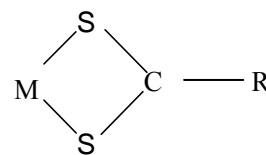
Hydrated ruthenium(III) chloride ($RuCl_3 \cdot xH_2O$, Arora-Matthey Ltd) was digested with conc. HCl (BDH, AR grade) several times before use. Triphenylphosphine (PPh_3) and triphenylarsine ($AsPh_3$) were of Fluka AG grade and used without further purification. Carbon disulphide was of E. Merck (India) while the other chemicals used in the synthesis of the complexes were of AR grade (Ranbaxy). Spectroscopic grade KBr and chloroform were used as references for spectral analyses. The IR



η^1 -end on
(**I**)



η^2 -side on
(**II**)



η^2 -bidentate
(**III**)

spectra ($4000\text{-}200\text{ cm}^{-1}$) of the compounds as KBr pellets were recorded on a Perkin-Elmer-883 spectrophotometer, while a Graphicord UV-240 (Shimadzu) was used for recording electronic spectra in chloroform with quartz cell of 1 cm thickness. Solid diffused reflectance spectra using BaSO_4 as reference were also recorded. The molar conductivity ($10^{-3}M$) measurements were made in chloroform solution at 32°C using Digital conductivity bridge (Elico India-032). Melting points were determined on an electrothermal apparatus (model Ragga), while thermograms were recorded on Perkin-Elmer DTA-TGA instrument (model Pyris Diamond). The ESR spectra of the compounds in powdered form at room temperature (RT) and at liquid nitrogen temperature (LNT) were recorded on a Varian E-line Century Series ESR spectrometer and obtained from RSIC, IIT Bombay. Tetracyanoethylene (TCNE) was used as marker with a g value of 2.00277. The magnetic moment was determined by NMR method⁴ at RRL, Jorhat.

Chlorine and sulphur were estimated gravimetrically as AgCl and BaSO_4 , respectively. The analyses of carbon and hydrogen were made microanalytically at RRL, Jorhat.

Synthesis of the complexes

The digested $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ (1.91 mmol) was dissolved in ethanol (30 ml) to which triphenylphosphine (5.73 mmol) also dissolved in ethanol (30 ml) was added dropwise with constant stirring. A brown coloured precipitate was obtained after stirring for about 2 h, which was filtered off and washed with ethanol. It was later recrystallised from 1:1 dichloromethane-chloroform mixture to obtain⁵ $(\text{PPh}_3)_3\text{RuCl}_3$.

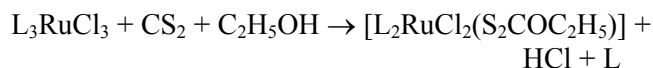
$(\text{PPh}_3)_3\text{RuCl}_3$ (0.4 mmol) was added to a mixture of dichloromethane (20 ml), carbon disulphide (0.23 ml) and ethanol (10 ml). The mixture was stirred for 24 h at room temperature. The resulting solution was exposed to air for slow evaporation at room temperature to reduce the volume to 10-15 ml. The blackish-brown crystalline precipitate of $[(\text{PPh}_3)_2\text{RuCl}_2(\text{S}_2\text{COEt})]$ obtained was filtered off, washed with a mixture of ethanol and water (2:1), recrystallised from dichloromethane and dried. [Yield: ~70%. Anal: Calc. for $\text{C}_{39}\text{H}_{35}\text{RuOP}_2\text{S}_2\text{Cl}_2$: C:56.64; H:4.35; S:7.95; Cl:8.82%. Found: C:56.02; H:4.10; S:7.50; Cl:8.94%].

A similar preparative procedure was adopted for the synthesis of $[(\text{AsPh}_3)_2\text{RuCl}_2(\text{S}_2\text{COEt})]$. [Yield: ~60%. Anal: Calc. for $\text{C}_{39}\text{H}_{35}\text{RuOAs}_2\text{S}_2\text{Cl}_2$ C:50.40; H:3.86; S:7.07; Cl:7.84%. Found: C:50.26; H:4.11; S:6.58; Cl:7.61%].

Repeated attempts to get good quality crystals suitable for X-ray crystallography ended in failure.

Results and discussion

At room temperature, reaction of carbon disulphide with the compound of the type $[\text{L}_3\text{RuCl}_3]$ ($\text{L}=\text{PPh}_3, \text{AsPh}_3$) in mixed solvent of dichloromethane and ethanol results in the formation of a new compound of the type $[\text{L}_2\text{RuCl}_2(\text{S}_2\text{COEt})]$. The mechanism of the reaction is attributed to the insertion of carbon disulphide in the O-H bond of ethanol to give HS_2COEt , which in a subsequent reaction with $[\text{L}_3\text{RuCl}_3]$ yields in the Ru(III) complex, $[\text{L}_2\text{RuCl}_2(\text{S}_2\text{COEt})]$ ($\text{L}=\text{PPh}_3, \text{AsPh}_3$).



The elemental analysis of the complexes agrees well with their formulation. Conductance data ($10^{-3}M$ chloroform solution: $0.05\text{ mol}^{-1}\text{cm}^2$) shows that the complexes are non-electrolyte, confirming its mononuclear nature and the coordination character of PPh_3 and AsPh_3 . Both the complexes are air-stable, readily soluble in chloroform, dichloromethane and dimethylsulphoxide, sparingly soluble in benzene and insoluble in water and toluene. The complexes are found to be thermally stable with melting points of 168°C and 244°C for phosphine and arsine derivatives, respectively.

The IR spectra (in KBr) of $[(\text{PPh}_3)_2\text{RuCl}_2(\text{S}_2\text{COEt})]$ and $[(\text{AsPh}_3)_2\text{RuCl}_2(\text{S}_2\text{COEt})]$ exhibit the expected bands due to the ligands PPh_3 and AsPh_3 . A medium strong band at 341 cm^{-1} is observed, which can be assigned to $\nu_{\text{Ru-S}}$ ⁵. A medium strong band observed at 1084 cm^{-1} and 1095 cm^{-1} for the complexes $[(\text{AsPh}_3)_2\text{RuCl}_2(\text{S}_2\text{COEt})]$ and $[(\text{PPh}_3)_2\text{RuCl}_2(\text{S}_2\text{COEt})]$, respectively, can be assigned to C-S stretching vibration⁵. However, due to instrumental limitations $\nu_{\text{Ru-As}}$ and $\nu_{\text{Ru-P}}$ could not be observed, which generally appear^{6,7} around 245 cm^{-1} and 280 cm^{-1} , respectively.

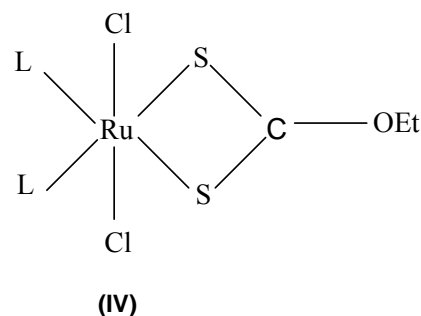
The ligand field bands observed at $18,518\text{ cm}^{-1}$ for $[(\text{PPh}_3)_2\text{RuCl}_2(\text{S}_2\text{COEt})]$ and at $20,161\text{ cm}^{-1}$ for $[(\text{AsPh}_3)_2\text{RuCl}_2(\text{S}_2\text{COEt})]$ have been assigned⁸

to ${}^2T_{2g} \rightarrow {}^2A_{2g}$, ${}^2T_{1g}$. The electronic spectra, (in chloroform solution, $10^{-4}M$) of the complexes show one strong absorption at $\sim 40,000\text{ cm}^{-1}$ ($\epsilon_{\text{max}}=13,200\text{ L mol}^{-1}\text{cm}^{-1}$) followed by two weaker bands at $\sim 28,000\text{ cm}^{-1}$ ($\epsilon_{\text{max}}=3891\text{ L mol}^{-1}\text{cm}^{-1}$) and $\sim 24,000\text{ cm}^{-1}$ ($\epsilon_{\text{max}}=3026\text{ L mol}^{-1}\text{cm}^{-1}$) which may be assigned to intraligand $\pi \rightarrow \pi^*$ and spin forbidden $d-d$ transitions (${}^2T_{2g} \rightarrow {}^4T_{2g}$ and ${}^2T_{2g} \rightarrow {}^4T_{1g}$) respectively^{9,10}.

The compound, $[(\text{PPh}_3)_2\text{RuCl}_2(\text{S}_2\text{COEt})]$ shows three g values at liquid nitrogen temperature ($g_1=2.25$, $g_2=2.14$, $g_3=2.03$), indicating large distortion from octahedral symmetry. Similarly, three g values at LNT ($g_1=2.26$, $g_2=2.17$, $g_3=1.84$) and at room temperature (RT) ($g_1=2.29$, $g_2=2.10$, $g_3=1.82$) for Ru(III) complex of triphenylarsine are also in agreement with highly distorted octahedral structure for the complex¹¹.

Magnetic moment value (1.81 BM) exhibited by the complex $[(\text{PPh}_3)_2\text{RuCl}_2(\text{S}_2\text{COEt})]$ was found to be slightly higher than the spin only value, which may be due to orbital contribution from ${}^2T_{2g}$ ground term of Ru(III) ion.

Compared to phosphine derivative, the arsine derivative melts at a higher temperature, reflecting more basic character of arsine. Thermogravimetric study of the complex, $[(\text{AsPh}_3)_2\text{RuCl}_2(\text{S}_2\text{COEt})]$ indicates that weight loss starts at 231.44°C and occurs gradually up to 462.42°C with four major inflexions indicated by DTG curve. After that, the weight remains constant (27.72%) indicating the existence of a mixture of ruthenium metal and arsenic. At 231.44°C the compound loses one chloride ion (expt. 3.3%, calc. 3.9%), while at 288.48°C , 12.1% weight loss (expt.) indicates the release of $-\text{OC}_2\text{H}_5$ group and the remaining Cl^- ion. At 361.21°C (weight loss: 20.9%; calc. 21.2%) and 462.42°C , the respective weight loss of 72.2%



(calc. 72.3%) correspond to the loss of $>\text{S}_2\text{C}-$ and six $-\text{C}_6\text{H}_5$ groups.

On the basis of the above results, distorted octahedral structure has been tentatively proposed for the complexes (IV).

Acknowledgement

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