Coordination Chemistry Reviews, 131 (1994) 45–94

2. Ruthenium

Wing-Tak Wong

CONTENTS

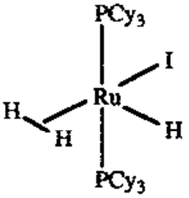
INTRODUCTION

This review covers the coordination chemistry of ruthenium for 1991 and is based upon a search of volumes 114, 115 and 116 of *Chemical Abstracts*. In addition, major inorganic chemistry journals have been searched independently from the period of January to December 1991. To avoid undesirable fragmentation of a single piece of work, the tradition of subdividing the complexes by oxidation state has been abandoned. The metal complexes are classified according to the ligand type. Most of the organometallic ruthenium complexes are not included in this article since they are periodically reviewed elsewhere, for example in *J. Organomet. Chem.*.

0010-8545/94/$26.00
SSDI 0010-8545(93)00999-9

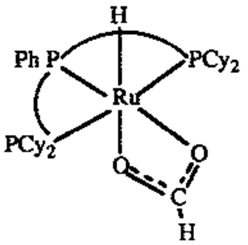
2.1 COMPLEXES WITH HYDROGEN OR HYDRIDE LIGANDS

Homoleptic ruthenium hydrides Li_4RuH_6, Na_4RuH_6 Mg_2RuH_6 and Ba_2RuH_6 have been prepared and characterised by X-ray and neutron powder diffraction. All of these compounds consist of isolated and stable $[RuH_6]^{4-}$ anion [1]. Sixteen-electron dihydrogen compounds $[RuH(H_2)X(PCy_3)_2]$ (X=Cl, **(1)**, or I, **(2)**) have been synthesised. X-ray crystallographic analysis of **(2)** revealed a slightly distorted octahedral geometry with a vacant site that is *trans* to the hydride ligand. A long H–H distance [1.03(7)Å] and a short non-bonding hydride-hydrogen distance [1.66(6)Å] are reported in **(2)** [2].

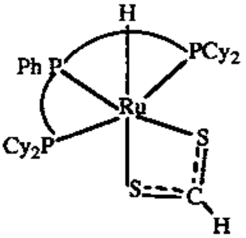


(2)

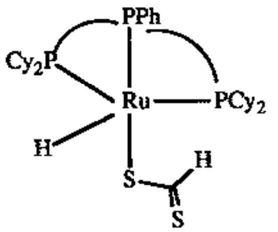
Complexes $[RuX(H_2)(dcpe_2)]BPh_4$, (dcpe = $CyPCH_2CH_2PCy_2$; X = H, **(3)**, or Cl, **(4)**) were prepared by protonation of $[RuH(X)(dcpe)_2]$ or by reaction of molecular hydrogen with the 5-coordinate $[RuX(dcpe)_2]$ BPh_4. Complexes **(3)** and **(4)** have been studied by variable-temperature ^1H and $^{31}P\{^1H\}$ NMR spectroscopies [3]. Reactions of $[RuH_2(H_2)(Cyttp)]$, **(5)**, (Cyttp = $PhP(CH_2CH_2\text{-}CH_2PCy_2)_2$) with CO_2 or CS_2 yield *mer*-$[RuH(O_2CH)(Cyttp)]$, **(6)**, or three isomers of $[(RuH(S_2CH)(Cyttp)]$, **(7a-c)**. Treatment of **(5)** with RN=C=NR (R = *p*-tolyl, Cy) gives the insertion product *mer*-[RuH(RNCHNR)(Cyttp)], with a structure similar to that of complex **(6)** [4].



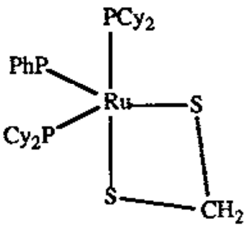
(6)



(7a)



(7b)



(7c)

Dihydrogen complexes *trans*-$[Ru(H)(H_2)L_2]BF_4$ (L = dppe, **(8)**, or depe, **(9)**) and the isotopomers *trans*-$[Ru(H)(HD)L_2]^+$, were prepared. ^1H NMR spectroscopic studies showed that the chemical shifts of the HD group for these two isotopomers are quite different due to the higher *trans* influence of D than H. The ruthenium complexes **(8)** and **(9)** have the strongest H–H interaction and the weakest metal–dihydrogen interaction compared with the iron and osmium analogues [5].

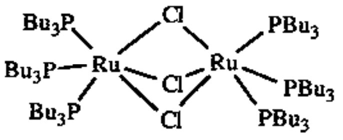
The kinetics of dissociation of H_2 for the polyhydride complexes $[RuH_3(PPh_3)_3]^-$, $[RuH_4(PPh_3)_3]$ and $[RuH_5(PPh_3)_3]^+$ were determined by either ligand substitution or 2D NMR spectroscopy. The rates of dissociation increase with increasing protonation, which does not correlate with a transition from 'classical' to 'non-classical' (η^2-H_2) structures [6]. $[RuH_4(PPh_3)_3]$ and its isotopomers have been investigated by variable-temperature ^1H, ^2H, ^{31}P NMR techniques and ^1H T_1 and T_2 and ^2H T_1 relaxation time measurements. A dynamic structure involving fast pairwise approachment-detachment of the hydrogen-ligands in these complexes is suggested by these studies [7].

The complex $RuH_2(PPh_3)_4$ **(10)** has been shown to effect regio- and stereoselective reduction of the hydroquinone all-*trans*-retinal complex [8]. In the presence of a hydrogen acceptor, complex **(10)** reacts with $H_2N(CH_2)_4OH$ and $MeNH(CH_2)_5OH$ to give the corresponding lactams [9]

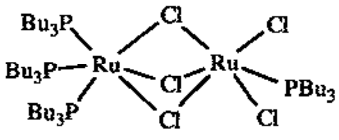
2.2 *COMPLEXES WITH HALIDE AND PSEUDOHALIDE LIGANDS*

The complexes $[Ru_2Cl_3(PBu_3)_6][RuCl_4(PBu_3)_2]$ **(11)**, $[Ru_2Cl_3(PBu_3)_6]$ $[BPh_4]$ **(12)**, $[Ru_2Cl_5(PBu_3)]$ **(13)**, $[Ru_2Cl_5(PMe_2Ph_4)]$ **(14)**, $[Ru_2Cl_5(PMe_3)_4]$ **(15)** and $[Ru_2Cl_6(PEt_3)_3]$ **(16)** have been prepared by the treatment of $RuCl_3.3H_2O$ with the corresponding phosphines under carefully screened conditions. All of these compounds have been characterised by X-ray crystallography, EPR spectroscopy, cyclic voltammetry and magnetic susceptibility measurements. There is no Ru-Ru bonding in compounds **(11)** and **(12)**; the Ru-Ru distances are 3.395(1)Å and 3.412(1)Å respectively. In **(13)**, the phosphine ligands are unsymmetrically distributed and there is no bonding interaction between the Ru(II) and Ru(III) centres. The Ru-Ru distance is 3.279(2)Å. In compounds **(14)** and **(15)** where the phosphine ligands are symmetrically distributed, the odd electron is delocalized and there is a weak bonding interaction with formal bond order of one-half.

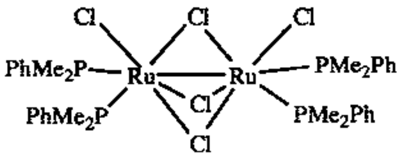
Ruthenium-ruthenium distances are 2.994(4)Å and 2.992(1)Å respectively. Compound **(16)** consists of two Ru(III) centres which are 3.20(1)Å apart and there is essentially no Ru-Ru bond [10].



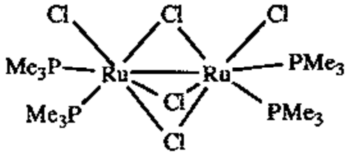
Cations of (11) and (12)



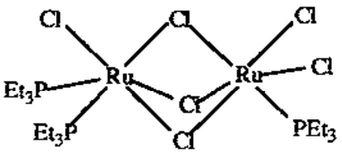
(13)



(14)

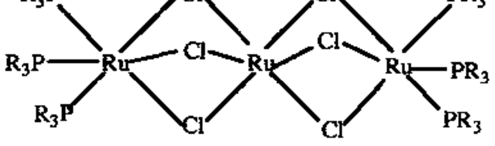


(15)



(16)

The preparation, magnetic, EPR and electrochemical properties of the complexes $[Ru_3Cl_6(PEt_3)_6][RuCl_4(PEt_3)_2]$, **(17)**, $[Ru_3Cl_6(PBu_3)_6][RuCl_4(PBu_3)_2]$, **(18)**, $[Ru_3Cl_6(PBu_3)_6][BPh_4]$,**(19)**, and $[Ru_3Cl_6(PEt_3)_6][BPh_4]$, **(20)**, have been reported [11]. They represent a new type of derivative of the $[Ru_3Cl_{12}]^{4-}$ ion where all six terminal chloride ions are replaced by phosphines. The Ru-Ru distances are in the range 3.078(1)-3.083(1)Å.

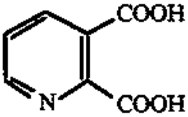


R = Et in **(17)**
= Bu in **(18)**, **(19)**

The EPR properties of $[Ru_2Cl_6(PR_3)_4]$ (R = Bu, Et) support the view that the two ruthenium atoms in these molecules are neither bonded to each other nor significantly coupled [12].

The electronic and structural characteristics of RuF_4 and RuF_5 were studied by ab initio (SCF-CI) calculations [13]. In addition, the vibrational (IR and Raman) spectra of saturated vapours of trimeric ruthenium pentafluoride, $(RuF_5)_3$ have been investigated [14]. Normal coordinate analyses for the compounds $[RuX_nY_{6-n}]^{z-}$ ($X \neq Y = F, Cl, Br$; $n = 0$-6, $z = 1$-3) were performed based on a general valence force field [15]. The variations in electrode potentials (Ru^V/Ru^{IV}, Ru(IV)/Ru(III), and Ru(III)/Ru(II)) of substituted ruthenium halide complexes ranging stepwise from $[RuX_6]^{2-}$ through $[RuX_{6-n}(RCN)_n]^z$ to $[Ru(RCN)_6]^{2+}$(X = Cl, RCN = PHCN, MeCN; X = Br, RCN = PhCN) were studied by voltammetric methods. The metal-based electrode potential is shown to be a linear function of stoichiometry, the effect of replacing each halide by nitrile on $E_{1/2}$ is consistently +0.6V for Ru(III)/Ru(II)and Ru(IV)/Ru(III) and +0.45V for Ru(V)/Ru(IV) [16].

Ruthenium trichloride has been used to catalyse the oxidation of several primary alcohols to aldehydes by NaOCl with more than 75% conversion efficiency and selectivities of 70%-90% [17]. The same system has been employed in the oxidation of quinoline to quinolinic acid **(20)** [18].

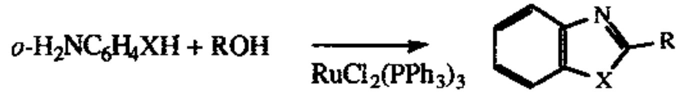


(20)

The indirect anodic oxidation of 2-methylnapthalene and naphthalene to 2-methyl-1,4-naphthoquinone and naphthoquinone, respectively, was achieved with catalysts $RuCl_3.3H_2O$, $Ru(acac)_3$ and $Ru(NH_4)_2Cl_6$ in an undivided cell using Pt electrodes. $RuCl_3.3H_2O$ and $Ru(NH_4)_2Cl_6$ increase the selectivity for quinone formation, whereas $Ru(acac)_3$ has no such effect [19]. Ruthenium trichloride efficiently catalyses the converson of β-lactams to 4-acyloxy-β-lactams in the presence of MeCHO and molecular oxygen in an acid and EtOAC under buffer conditions [20].

Cross-metathesis reactions of vinyltriethoxysilane with 1-alkenes, 2-alkenes, branched alkenes, cycloalkenes, styrene, vinylcyclohexene, vinyltrimethylsilane and some functionalised alkene catalysed by $RuCl_3.nH_2O$ and $RuCl_2(PPh_3)_3$ have been reported. Some of these reactions can be applied as novel methods for the synthesis of new silicon-containing olefins or as synthetic alternatives to well-known olefins [21]. The compound *exo exo*-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid was polymerised by aqueous ring-opening metathesis polymerisation using $RuCl_3$ to give poly (2,5-[3,4-bis(carboxylic acid)furanylene]vinylenes with 60% *cis* conformation [22]. Catalytic dehydrogenation of methanol with $RuCl_3$ under reflux conditions with excess NaOMe and small amounts of NaOH has been reported. Correlations between the coordination structure of the ruthenium centre and the catalytic activity were discussed [23]. Ruthenium trichloride also catalyses the oxidation of levulinic acid to succinic acid and formic acids by *N*-bromoacetamide in perchloric acid media in the presence of mercuric acetate as a scavenger. Kinetic data have been used to discuss the mechanistic implication of the oxidation [24].

The complex $RuCl_2(PPh_3)_3$ catalyses the reactions of *o*-$H_2NC_6H_4OH$ and *o*-$H_2NC_6H_4NH_2$ with ROH (R = Bu, aryl) giving the respective benzoxazoles, **(21)**, and benzimidazoles, **(22)**, in high yields [25].



(equ. 1)

X = O **(21)**
NH **(22)**

In the presence of NaOH cocatalyst (2.5 mol%), $RuCl_2(PPh_3)_3$ (0.1 mol%) catalyses hydrogenation of both aliphatic and aromatic ketones with rates up to 900 turnovers per hour at 82°C. However, no hydrogenation occurs in the absence of NaOH according to reference [26]. It has been shown that the selectivity of the reactions of $HOCH_2CH_2OH$ with primary amines in the presence of $RuCl_2(PPh_3)_3$ at 120°C is highly dependent on the steric nature of the amine [27]. Dehydrogenative transformation of α-hydroxyesters or nitriles into α-keto esters or nitriles by *tert*-Butyl hydroperoxide in the presence of ruthenium catalysts such as $RuCl_2(PPh_3)_3$, $RuCl_3$ and Ru/C has been described [28].

Reaction of acid chlorides with H_2 in the presence of 2,4,6-collidine and catalytic amounts of either $RuCl_2(Ph_3)_3$ or $Ru(H)Cl(PPh_3)_3$ in toluene gives estern. Acylruthenium hydrides are thought to be the intermediates involved in this reaction [29]. In the presence of a triple catalytic system consisting of $RuCl(OAc)(PPh_3)_3$/hydroquinone/Co(salophen)(PPh_3) under mild conditions at 20°C, aerobic oxidation of primary alcohols to aldehydes has been investigated [30]. Oxidation of long chain alcohols such as octanol, dodecanol and hexadecanols to the corresponding aldehydes and carboxylic acids in the presence of the catalyst $RuCl_2(PPh_3)_3$ using *N*-methylmorpholine *N*-oxide or *N*-methylmorpholine and H_2O_2 as oxidising agents has also been reported [31].

The synthesis and spectroscopic characterisation of a series of mixed halide-nitrile ruthenium complexes $[RuX_{6-n}(RCN)_n]^z$ (n = 0-6; R = Ph, Me; X = Cl, Br) have been described [32]. It has been shown that the interaction of $[RuO_2Cl_3]^-$ and $[RuO_2Cl_4]^{2-}$ with excess tert-butyl isocyanate in MeCN gives the anion $[RuN\{Bu^tNC(O)NBu^t\}Cl_2]^-$ [33]. The kinetics of the intramolecular photoinduced metal-metal charge-transfer reaction in a mixed-valence complex (equ. 2) and the reverse-electron-transfer rate coefficient have been studied by resonance Raman spectroscopy, static absorption spectroscopy and transient Stokes shift measurements [34].

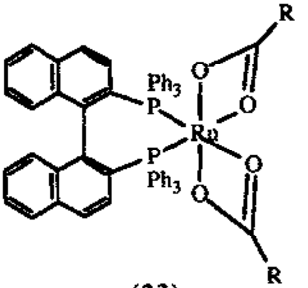
$$[(NH_3)_5Ru^{III}\text{-}NC\text{-}Fe^{II}(CN)_5]^- + h\nu \rightleftharpoons [(NH_3)_5Ru^{II}\text{-}NC\text{-}Fe^{III}(CN)_5]^- \qquad \textbf{(equ.2)}$$

Through-ligand electronic coupling in the complex cation $[(NH_3)_5Ru^{III}$-1,4-dicyanobenzene-$Ru^{II}(NH_3)_5]^{5+}$ has been calculated with different donors or acceptors grafted on the benzene. The largest electronic coupling occurs at a full 4-NO_2-substitution on the benzene

[35]. The substitution reactions of the halide ion of $[Ru(NH_3)_5X]^{2+}$ (X = Cl, Br) with $SeCN^-$ or SCN^- in aqueous medium are pseudo-first-order with respect to $SeCN^-$ [36] or SCN^- [37].

2.3 *COMPLEXES WITH PHOSPHORUS DONOR LIGANDS*

Bis(tiglato){(*R*)-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl} ruthenium(II) **(23)** is an active catalyst in the homogeneous asymmetric hydrogenation of tiglic acid. Its structure has been determined by single crystal X-ray crystallography. The tiglate ligands are η^2-carboxylate-bound. The configuration at the metal is Δ, and the formation of the seven-membered chelate ring is λ. There is no bonding interaction between the C=C bonds of the substrates and the metal centre in the solid state or in non-coordinating solvents. It is believed that if the coordination of the C=C bond to ruthenium centre is necessary for insertion into a Ru-H bond, it must occur after reaction with H_2 [38].



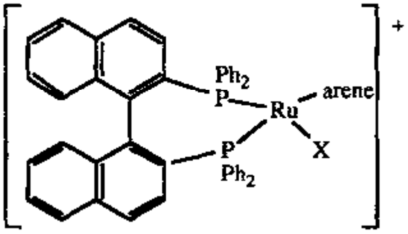
(23)

R= $C(CH_3)=CHCH_3$

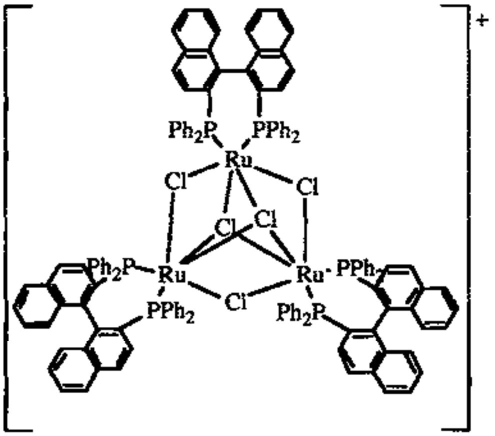
Cationic complexes [RuX((S)-BINAP)(arene)]X **(24)** (X=Cl, Br; arene= benzene, *p*-cymene) in MeOH at 60°C or under UV-irradiation at room temperature give monocationic trinuclear complexes $[Ru_3X_5((S)\text{-BINAP})_3]X$ in 40-62% yields which have been characterised by spectroscopic techniques and conductivity measurements. The molecular structure of $[Ru_3Cl_5((S)\text{-BINAP})_3][BF_4]$, **(25)**, has been established [39].

Treatment of $[RuCl_2(\eta^6\text{-benzene})]_2$ or $RuCl_2\{Sb(C_6H_5)_3\}$ with (R)- or (*S*)-BINAP produces BINAP-Ru(II) complexes which catalyse the highly enantioselective hydrogenation of functionalised ketones (equ. 3) [40]. The same catalyst has been employed in the hydrogenation β-substituted (E)-β-(acylamino) acrylic acid [41].

(equ.3)

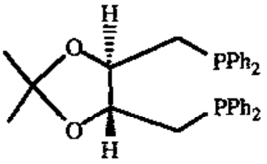


(24)

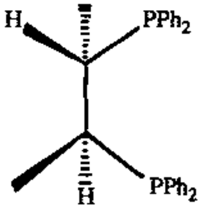


(25)

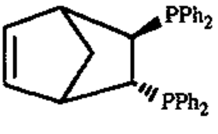
The reaction product between commercially available BINAP and $\{RuCl_2(COD)\}_n$ in the presence of triethylamine is a very active catalyst for the highly enantioselective reduction of β-keto esters under mild conditions [42].



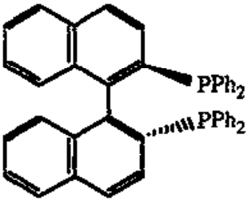
(R,R)-(-)DIOP (26)



(2S,3S)-(-)CHIRAPHOS (27)



(R R)-(-)NORPHOS (28)

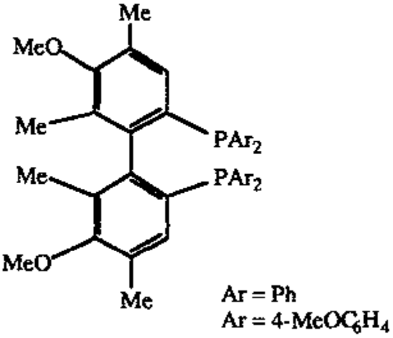


(S)-(-)BINAP (29)

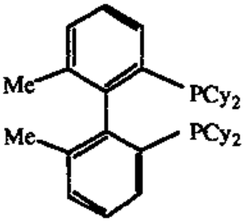
A general synthetic route to mononuclear hexacoordinate chiral ruthenium complexes containing bidentate chiral phosphine ligands (26)-(29) has been reported [43]. These chiral complexes have been used in the enantioselective synthesis of *D*- and *L*-threonine. The key step is the stereoselective hydrogenation of acetoacetates via dynamic kinetic resolution in the presence of these chiral metal complexes to give *syn* optically active alcohols [44].

A new method for the preparation of (P-P)Ru(O_2CR)$_2$ (R = CH_3 and CF_3; P-P = 6,6'-dimethyl- and 6,6'-dimethoxybiphenyl(2,2'-diyl)bis(diphenylphosphine) and 1,1'-binaphthyl-2,2'-diylbis-(diphenylphosphine and -(di-*p*-tolylphosphine) using the easily accessible starting materials $(COD)_2Ru_2(\mu\text{-}O_2CCF_3)_4$ has been described. $(COD)Ru(\eta^2\text{-}O_2CCH_3)_2$ and $(COD)_2Ru_2Cl_4(NCCH_3)$ have also been shown to be suitable precursor complexes for the *in situ* preparation of ruthenium (II) dicarboxylate and dichloro complexes of atropisomeric diphosphines, respectively. These chiral ruthenium complexes have been used in catalytic asymmetric hydrogenations of allylic alcohols, enamides and a β-keto ester [45].

Synthesis of axially disymmetric biphenylbiphosphine ligands, BIMOPS **(30)** and their ruthenium (II) complexes has been described. The ruthenium (II) complexes of (R)-BIMOPS have proven to be excellent catalysts in asymmetric hydrogenations of β-keto ester and α, β-unsaturated carboxylic acid [46].



(30)

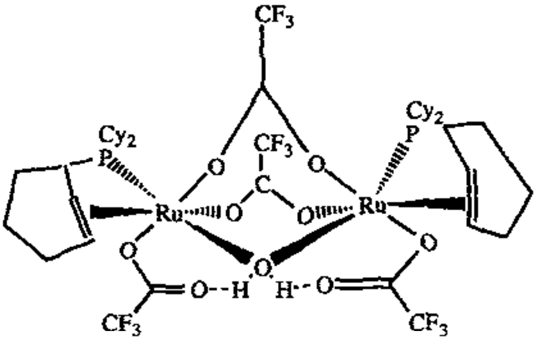


(31)

Ruthenium complexes containing chiral phosphine **(31)** were prepared as catalysts for high enantioselectivity asymmetric hydrogenation, silylation and isomerisation reactions [47].

Treatment of Ru(acac)$_3$ with PPh$_3$ and strong acid gives a ruthenium complex which is thought to be *mer*-$[HRu(PR_3)_3(S)_2]^+$ (S=solvent). The complex showed high catalytic activity and selectivity in hydrogenation of carboxylic anhydrides to the corresponding esters or lactones [48]. The catalytic oxygenation of alkenes by phosphino complexes of ruthenium has been reviewed [49].

Dehydrogenation of a cyclohexyl group in tricyclohexylphosphine complexes of ruthenium, $RuH_2(OCOCF_3)_2(PCy_3)_2$ give a novel dimeric compound $[Ru(C_6H_9PCy_2)(OCOCF_3)_2]_2(\mu\text{-}OCOCF_3)(\mu\text{-}OH_2)$ **(32)**; which contains two ruthenium(II) units bridged by two trifluoroacetato groups and one water molecule [50].

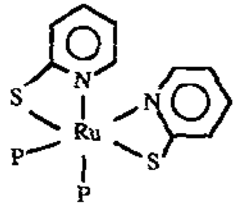


(32)

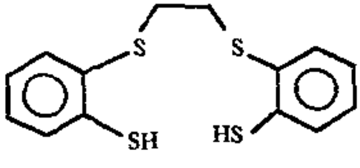
The preparation of $[RuL_5(ClO_4)]ClO_4$ (L = PPh_3, $AsPh_3$, PMe_2Ph, $AsMe_2Ph$, $AsEt_2Ph$) from $Ru(ClO_4)_3$ has been reported. Some of these complexes react with NO to give $[RuL_5(NO)](ClO_4)_2$ [51]. Ruthenium complexes of sulfonated phosphines have been used as catalysts in the selective hydrogenation of α,β-unsaturated aldehydes [52]. *trans*-$[Ru^{III}(NH_3)_4\{P(OEt)_3\}(H_2O)]^{3+}$ was obtained through chemical and electrochemical oxidation of the corresponding ruthenium(II) complex ion and was characterised by elemental analysis, spectroscopic and electrochemical methods [53].

2.4 COMPLEXES WITH SULFUR DONOR LIGANDS

The complex $[Ru(dppe)(2\text{-}Spy)_2]$, (33), has been prepared from $[Ru(PPh_3)_2(2\text{-}Spy)_2]$ and dppe. The molecular structure of (33) consists of a distorted octaheadral geometry defined by a dppe ligand and two didentate $[2\text{-}Spy]^-$ ligands. [54].



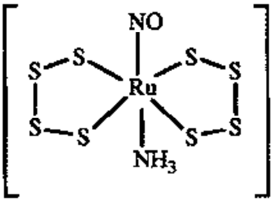
(33)



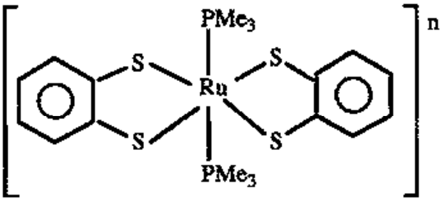
(34)

It has been shown that *Rac*-$[Ru(Cl)(H)(PPh_3)'S_4'].CH_2Cl_2$ ($'S_4'H_2$ = 1,2-bis (2-*mer*captophenylthio)ethane, (34)) react with monodentate sulfur-donor ligands L to give diastereospecifically the yellow product $[Ru(L)(PPh_3)'S_4']$. The diastereoselectivity of these compounds has been discussed [55].

The first polysulfido nitrosyl ruthenium anion [$Ru(NO)(NH_3)(S_4)_2]^-$, **(35)**, has been synthesised and structurally characterised by X-ray crystallography [56].



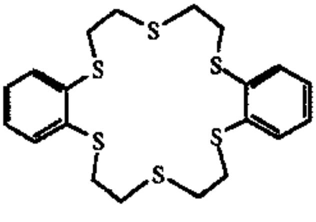
(35)



(36)

Geometric effects on the redox properties of ruthenium complexes $[RuX_2(R_2SO)_n(R_2S)_{4-n}]$ (n = 1–4) have been investigated. Using cyclic voltammetry, the oxidation potential $E_{1/2}$ *vs* n is shown to be linear with a slope of +0.22v. This suggests that the replacement of a sulfoxide ligand with a thioether donor will increase the energy of the HOMO(d_π) by ≈20.08 kJ [57]. Synthesis, structure, spectroscopic and magnetic properties of $[RuL_2(PMe_3)_2]^n$ **(36)** (n= –1, 0; H_2L= 1,2-benzenedithiol) have been reported [58].

Treating salts of $[RuQ]^{2+}$ (Q = (37)) with one equivalent of base under normal conditions has led to S–C bond cleavage and formation of the monocation $[RuL]^+$ (HL = CH_2=$CHSCH_2CH_2SCH_2CH_2S$-*o*-$C_6H_4SCH_2CH_2SCH_2CH_2S$-*o*-$C_6H_4SH$). This reaction suggests drastic C–S activation in coordinated thioethers. Its implication in the isolation of metal sulfur enzymes has been discussed [59].



(37)

The sulfide RuS_2 has been reported to be an active catalyst in both hydrogenation and hydro-desulfurisation reactions for which the active sites are anionic vacancies. The relationship between activity and acidic-basic properties of the active phase has been discussed [60]. RuS_2 catalysts supported on alumina have been used in thiophene hydrodesulfurisation, biphenyl hydrogenation and pyridine conversion reactions. The physicochemical properties of such catalysts have been investigated by XPS, high resolution electron microscopy and temperature-programmed reduction data [61].

The complex $[Ru(PPh_3)L]$ (L = *o*-$HSC_6H_4SCH_2CH_2SC_6H_4SH$-*o*) reacts with H_2S at −70°C in the absence of oxygen and water to give $[Ru(H_2S)(PPh_3)L]$, which has been characterised by X-ray crystallography and NMR spectroscopy [62].

A labile, *S*-bound isomer of the $[Ru(III)(EDTA)(DMSO)]^-$ anion is formed in the reaction of $[Ru(III)(EDTA)(H_2O)]^-$ with a large excess of DMSO. However, the corresponding Ru(II)-DMSO complex is extraordinarily stable. These two species can be interconverted within the time scale of cyclic voltammetry [63].

The reaction of $[RuCl_2(DMSO)_4]$ with excess 2,6-dimethylpyrazine (dmpz) gives a mixture of two geometrical isomers of $[RuCl_2(DMSO)_2(dmpz)_2]$, which were characterised by HPLC, cyclic voltammetry and solution spectroscopy. The more stable isomer is of *cis*-Cl_2, *cis*-$(DMSO)_2$, *trans*-$(dmpz)_2$ configuration while the second isomer is of all-*cis* configuration [64].

Resonance Raman spectra of a series of ruthenium(II) coordination polymers $[\{Ru(L\text{-}L)_xCl_2(DMSO)_{4-x}\}_n]$ (L-L = pyrazine, *p*-phenylenediamine or 1,4-diisocyanobenzene; x = 1 or 2) have been obtained. The mode of coordination and the possible structures of these polymers have been suggested based on IR and Raman data [65].

A series of ruthenium (II) bromide complexes $[RuBr_2L_4]$, $[RuBr_2(DMSO)L_2]$ (L = PPh_3, phen, bpy or *o*-phenylenediamine) have been prepared from $[RuBr_2(DMSO)_3]$. These compounds were characterised by analytical data and various physical methods [66].

The reactions of *cis*- and *trans*- $RuCl_2(DMSO)_4$ with monodentate nitrogen donor ligands such as NH_3, imidazole and benzimidazole yield a range of new derivatives which have been characterised by both spectroscopic and crystallographic methods [67]. The interaction of $[RuCl_2(DMSO)_4]$ with 2–deoxyguanosine [68] and DNA [69] has been investigated in relation to its anticancer activity.

2.5 *COMPLEXES WITH NITROGEN DONOR LIGANDS*

2.5.1 *Complexes with 2,2'-bipyridine ligands*

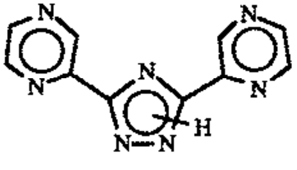
Three redox series of Ru(bpy)(L), (H_2L = 1,2-dihydroxybenzene, 2-aminophenol, 1,2-diaminobenzene) and $Ru(py)_4L$ were prepared. Their electronic, ESR spectroscopic and electrochemical properties have been discussed [70]. Four different synthetic routes can result in the immobilization of $Ru(bpy)_2(bpdc)$ (H_2bpdc = 2,2'-bipyridine-4,4'-dicarboxylic acid) upon the surface of polycrystalline SnO_2 electrodes [71]. The possibility of using the dimer $[(bpy)_2(Cl)Os(TMB)Ru(NH_3)_5]^{4+}$ (TMB = 4,4'-trimethylene-bis(pyridine)) for kinetics studies using the pulsed-accelerated-flow method has been investigated [72]. The electrochemistry of the binuclear complex $[(NC)Ru(II)(bpy)_2(CN)\text{-}Ru(II)(bpy)_2(CN)]^{2+}$ and of the trinuclear complex $[(NC)Ru^{II}(bpy)_2(CN)\text{-}Ru^{II}(bpy)_2(NC)\text{-}Ru^{II}(bpy)_2(CN)]^{2+}$ has been studied in MeCN and DMF. These polynuclear complexes give rise to very extended redox series, consisting of 2 or 3 metal-centered 1-electron reversible oxidation steps and 7 or 10 ligand-centered 1-electron reversible reductions for the binuclear and trinuclear complexes [73]. Some physical properties of the two coordination isomers of the bis(2,2'-bipyridyl)ruthenium(II) complex of 3-(pyrazin-2-yl)-1,2,4-

triazole have been reported. In particular, the acid-base properties were analysed with respect to the nature of the ligand and the coordination mode of the triazole ring [74]. A decanuclear ruthenium(II)-polypyridine complex of formula $[Ru\{(\mu\text{-}2,3\text{-}dpp)Ru[(\mu\text{-}2,3\text{-}dpp)Ru(bpy)_2]_2\}_3](PF_6)_{20}$ (dpp = 2,3-bis(2-pyridyl)pyrazine) has been prepared from the reaction of a $[Ru(2,3\text{-}dpp)_3]^{2+}$ core with three $[Ru[(\mu\text{-}2,3\text{-}dpp)Ru(bpy)_2]_2Cl_2]^{4+}$ units. Its absorption spectrum, luminescence and electro-chemical properties have also been reported [75]. A series of hexanuclear ruthenium(II)-poly-pyridine complexes of similar nature have also been studied [76]. Spectral differences between enantiomeric and racemic $[Ru(bpy)_3]^{2+}$ on layered clays and probable causes for the observation have been described in [77].

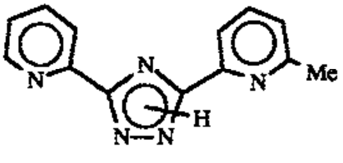
A convenient method for the preparation of ruthenium(II) polypyridine complexes within the super-cages of zeolite Y, together with their electronic absorption and Raman spectra, has been reported [78].

The complex $[(bpy)_2Ru(1,3\text{-}Me_2Lum)]^{2+}$ (1,3-Me_2Lum = 1,3-dimethyllumazine) has been prepared and characterised by spectroscopic and electrochemical methods [79]. The electrode potentials of $[Ru(bpy)_3]^{2+/1+/0}$ and $Co(Cp)_2$ redox systems have been analysed in different solvents or their mixtures. Correlation between the electrode potential for a subsequent electron transfer with the free energy of the ion transfer from one solvent to another has been sought. [80].

The synthesis, spectroscopic and electrochemical properties of mononuclear and dinuclear $Ru(bpy)_2$ complexes with bpzt (**38**) and mbpt (**39**) have been described and the structures of these complexes have been proposed [81].



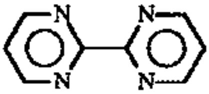
Hbpzt (**38**)



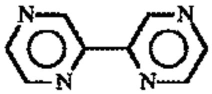
Hmbpt (**39**)

The complex cation $[Ru(II)(bpy)_2(bpy^{\cdot -})]^+$ was generated in nominally neutral aqueous solution via reduction of $[Ru\ (bpy)_3]^{2+}$ by e^-_{aq}. It reacts with the radical R• originating from the scavenging of H• and •OH by alcohol and formate ion to give $[Ru^{II}(bpy)_2(bpyR^-)]^+$ and eventually $[Ru(II)(bpy)\ (bpyRH)]^{2+}$ after protonation [82].

It has been shown that the rate constant of excited state electron transfer reactions of $RuL_3{}^{2+}$ complexes (L = 4-alkyl-4'-methyl-2,2'-bipyridyl) with aromatic amines is sensitive to the size of the ligand and the nature of the amine [83]. Electrochemical and spectroscopic properties of ruthenium bipyridyl dimers bridged by disubstituted anthraquinones such as 1,4-dihydroxy-1,5-dihydroxy- and 1-amino-4-hydroxyanthraquino have been described [84]. The one-electron reductions of ten ruthenium(II)-dimine complexes of the general formula $[Ru(bpy)_{3\text{-}m\text{-}z}(bpm)_m(bpz)_z]^{2+}$ (bpm = (**40**); bpz = (**41**); m and z = 0, 1, 2, 3 and $m+z \leq 3$) have been investigated and the relevance of the results to the use of the complexes as electron-transfer photosensitizers has been discussed [85].

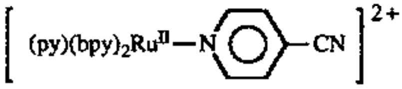


bpm **(40)**

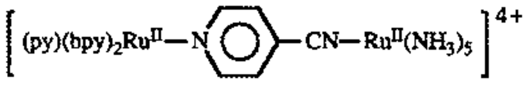


bpz **(41)**

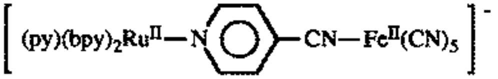
Ruthenium complexes **(42)**, **(43)** and **(44)** have been synthesised and characterised by spectroscopic techniques. Spectroscopic data suggest the existence of the pyridine-bonded isomer of 4-CNpy in **(42)** [86].



(42)



(43)



(44)

A binuclear ruthenium(II)-cobalt(II) complex, consisting of a cobalt(II)porphyrin derivative covalently bonded to a derivative of $[Ru^{II}(bpy)_3]^{2+}$, has been prepared. Cyclic voltammetry revealed seven one-electron redox process in the potential range of +1.5 to −1.8V *vs* SCE. Its emission spectrum revealed luminescene quenching but the mechanism has not been elucidated [87].

Features of the emission spectra resulting from the lowest excited state of $[Ru(bpy\text{-}H_8)_3]^{2+}$ and $[Ru(bpy\text{-}D_8)_3]^{2+}$ in $[Zn(bpy\text{-}H_8)_3](ClO_4)_2$ nave been resolved. A large number of vibronic satellites have been identified and assigned [88]. The oxidative quenching by methyl viologen of the lowest luminescent excited state of nine ruthenium(II)-diimine complexes in H_2O/CH_3CN has been studied by pulsed laser flash photolysis. There is a weak ΔG° dependence of back electron transfer within the geminate redox pairs formed in the quenching of excited Ru(II) complexes by methyl viologen [89]. Marcus theory has been applied to explain the radiation-induced electron-transfer processes in ruthenium(II)-diimine complexes of the general formula $[Ru(bpy)_{3\text{-}m\text{-}z}(bpm)_m(bpz)_z]^{2+}$ [90].

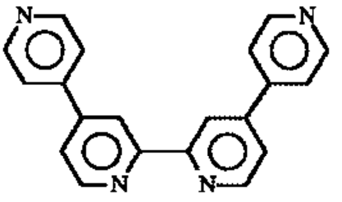
A new technique for the detection of amino acids has been developed. The method is based on their chemiluminescence reaction with $[Ru(bpy)_3]^{3+}$. The key experimental parameter in the application of this method is the pH [91]. Spectroelectrochemical studies of both the oxidised and reduced forms of $[Ru(bpy)_2CN]_2CN$ have revealed evidence of valence delocalisation of the single oxidised complex [92].

Upon Nd-YAG laser irradiation of a LB film containing $[Ru(bpy)_3]^{2+}$ derivative metal complex, strong second-harmonic radiation at 532nm has been observed [93]. Kinetic data and mechanisms of the photo-induced oxidation of ascorbic acid by molecular oxygen, catalysed by $[Ru(bpy)_3]^{2+}$ or $[Ru(bpz)_3]^{2+}$, have been reported [94]. Transfer of $[RuL_3]^{2+}$ (L = bpy, 2,2'-bipyrimidine or 2,2'-bipyrazine) in their ground states across the water/1,2-dichloroethane interface has been classified as the reversible transfer of a divalent cation. Photoexcitation of these complexes leads to the photoinduced charge transfer across the water/1,2-dichloroethane interface [95].

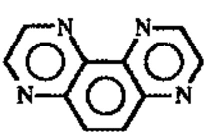
It has been reported that the quenching rate the excited $[RuL_3]^{2+*}$ complexes (L = 4,4'-dialkyl-2,2'-bipyridine) by substituted styrylpyridines is neither influenced by an increase in size of the alkyl group of the photo-sensitiser nor by the substituent in the quencher. Energy transfer seems to be dominant [96].

Complexes containing the $[Ru(bpy)(terpy)]^{2+}$ moiety as a photosensitiser, 4-CN-py as a bridging ligand, and $[Ru(NH_3)_5]^{n+}$ as an electron donor (n = 2) or acceptor (n = 3) capping group have been synthesised and characterised by electrochemical and spectroscopic techniques [97]. The interligand electron transfer dynamics in the excited metal-to-ligand charge transfer state of $[Ru(bpy)_3]^{2+}$ in several solvents have been investigated by using pico-second time-resolved absorption polarisation spectroscopy [98]. Luminescence from the excited state of $[Ru(bpy)_3]^{2+}$, which is incorporated into a silk fibroin membrance has been studied. The emission lifetime is longer (1700 ns) compared to the value (598 ns) in aqueous solution, which suggests the presence of a rigid binding site for the complex [99].

Photocurrent deriving from $[Ru(bpy)_3]^{2+}$, oxygen and triethanolamine in a hydrogen matrix has been observed [100]. Syntheses, photophysical and electrochemical properties of three new ruthenium(II) complexes based on the ligand **(45)** have been described [101].



qpy **(45)**

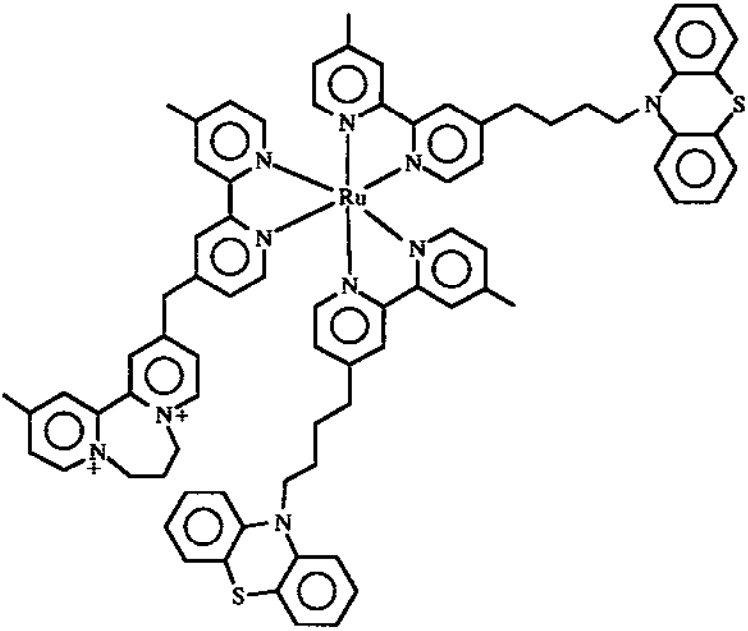


tap **(46)**

The photoelectrochemistry of a series of complexes $[Ru(bpy)_i(tap)_{3-i}]^{2+}$ (tap = **(46)**) has been examined on a transparent SnO_2 electrode under pulsed laser illumination [102].

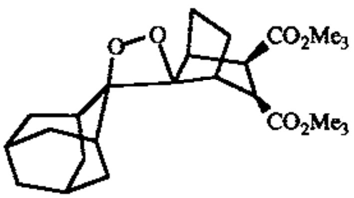
Time-resolved emission studies have been performed on a series of covalently linked Ru(bipyridine)$_3$-donor-acceptor complexes. A representative example of these complexes is **(47)**.

It has been observed that excitation to the Ru(bipyridine)$_3$ metal-to-ligand charge-transfer state led to a long-lived charge-separated state [103].

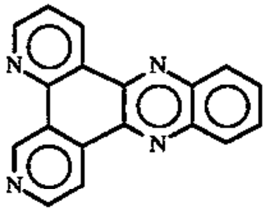


(47)

The cation [Ru(bpy)$_3$]$^{2+}$ has been used to enhance the chemi-luminescent intensity in the thermolysis of **(48)** [104].



(48)



dppz **(49)**

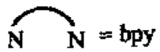
The oxidative quenching of excited $[Ru(bpy)_3]^{2+}$ and its derivatives by nitroaromatics, quinones and methylviologen has been studied in MeCN. The relationship between the quenching rate constant, electron-transfer distance and exoergicity has been discussed [105].

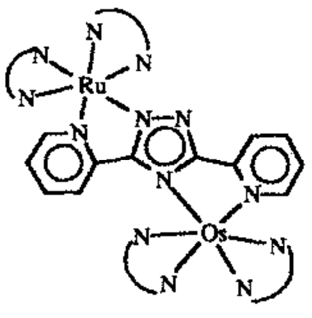
The quenching of excited $[Ru(bpy)_3]^{2+}$ by $O_2^{\cdot-}$, generated from KO_2/18-crown-6 ether, in MeCN has been studied. The products are $[Ru(bpy)_3]^{+}$ and O_2. There was no evidence for O_2 being formed as singlet molecular oxygen even though sufficient energy exists [106]. Both $[Ru(bpy)_3]^{2+}$, (a photo-chromophore), and methyl viologen, (a quencher), can be immobilised within a carrageenan hydrogel matrix at an electrode surface. The electrochemistry and photocurrents of this system have been established [107].

The luminescence of $[Ru(bpy)_3]^{2+}$ has been studied in the sol-gel reaction system of $(EtO)_4Si$. The spectrum showed a blue shift during the sol-gel stage, suggesting that $[Ru(bpy)_3]^{2+}$ was entangled by siloxane polymers [108].

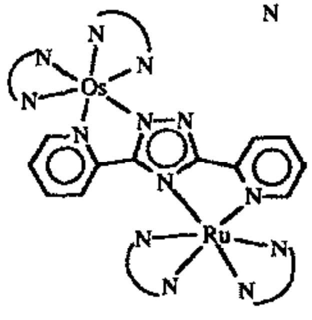
It has been observed that the quenching of excited $[Ru(bpy)_3]^{2+}$ and $[Ru(bpz)_3]^{2+}$ by ferrocene derivatives occurred competitively by both energy-transfer and electron-transfer reactions [109]. The luminescence properties of $[Ru(bpy)_2(dppz)]^{2+}$, (dppz = **(49)**), in sodium dodecyl sulfate aqueous solutions above the critical micellar concentration has been investigated. Shielding of the dipyridophenazine ligand (at which quenching of the emission occurs) from water molecules by the micellar core was used to explain the photochemical observation [110].

The luminescene and photochemical properties of the two isomeric heterobimetallic complexes $[(bpy)_2Ru(bpt)Os(bpy)_2]^{3+}$, **(50)**, and $[(bpy)_2Os(bpt)Ru(bpy)_2]^{3+}$, **(51)**, have been studied. The properties of **(50)** and **(51)** were compared with those of the corresponding dinuclear homometallic complexes. The latter is inert, and exhibits luminescence only from the Os-based component [111].



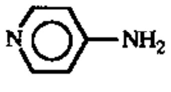


(50)

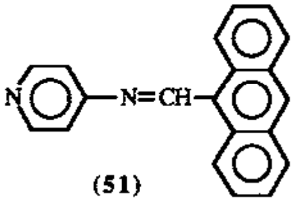


(51)

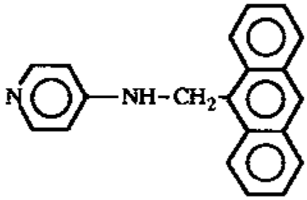
Ruthenium (II) complexes of formula $[Ru(bpy)_2(py\text{-}L)_2]^{2+}$ (py-L = **(52)**, **(53)** and **(54)**) have been subjected to detailed photochemical studies [112].



(52)



(51)

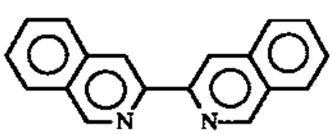


(54)

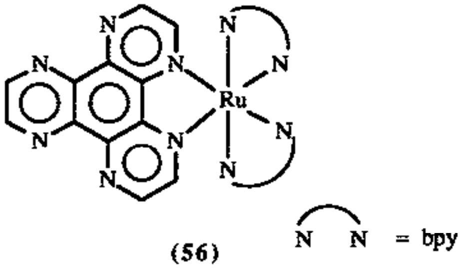
The isolation and characterisation of the intermediate complex cation $[Ru(bpy)_2(MeCN)L]^{2+}$, which is produced on the photolysis of $[Ru(bpy)_2L](PF_6)_2$ in MeCN (L= 4-methyl-2-(pyridin2-yl)-1,2,4-triazole, has been reported. The triazole ligand is coordinated to the ruthenium centre in a monodentate fashion [113]. Continuous and pulsed laser flash photolysis techniques have been applied to determine the efficiency with which the redox products are released upon the oxidative quenching of excited $[Ru(bpy)_3]^{2+}$ methyl viologen in the presence and absence of triethanolamine as a sacrifical electron donor in aqueous solution [114]. A system for electrogenerated chemilumine-scence based on the reaction of electrogenerated $[Ru(bpy)_3]^{2+}$ with tryptophan has been established. This system will be useful for the selective and sensitive detection of tryptophan. [115].

It has been shown that $[Co(EDTA)]^{-}$ can be reduced to $[Co(EDTA)]^{2-}$ by quenching oxidatively the photoexcited cation $[Ru(bpy)_3]^{2+}$ in the presence of a sacrificial donor such as EDTA, *trans*-1,2-cyclohexanediaminetetraacetic acid or oxalic acid [116].

Oxidative electron transfer was a main mechanism of quenching the fluorescence of $[Ru(bpy)_3]^{2+}$ by Pt(IV) complexes $[Pt(NH_3)_nX_{6-n}]^{z\pm}$ ($n = 0$-6; X = Cl, Br) [117]. The photosensitised decomposition rate of $[Co(ox)_3]^{3-}$ using $[Ru(bpy)_3]^{2+}$ and $[Ru(i\text{-}biq)_2(bpy)]^{2+}$ (i-biq = **(55)**), has been shown to be zero-order and first order respectively [118].

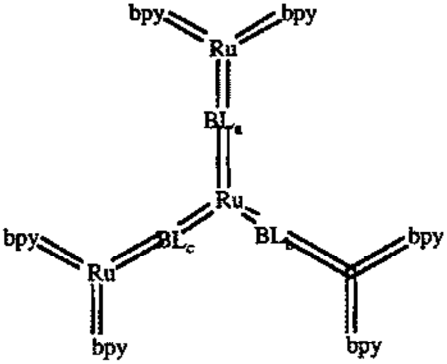


i-biq **(55)**



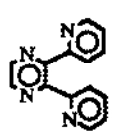
(56)

The effects of solvent, pH, and binding to poly-electrolytes on the spectroscopic and photophysical properties of $[Ru(bpy)_2(HAT)]^{2+}$, **(56)**, have been discussed [119]. The synthesis and photophysical properties of ruthenium(II) complexes **(57)** and **(58)** have been described [120].



BL$_a$= 2,5-dpp
BL$_b$= BL$_c$= 2,3-dpp **(57)**

BL$_a$=BL$_b$= BL$_c$= 2,3-dpp **(58)**

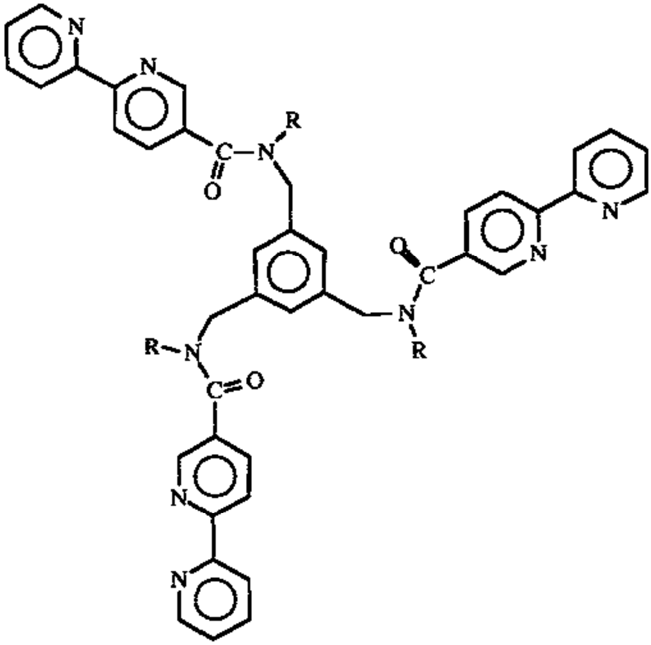


2,3-dpp

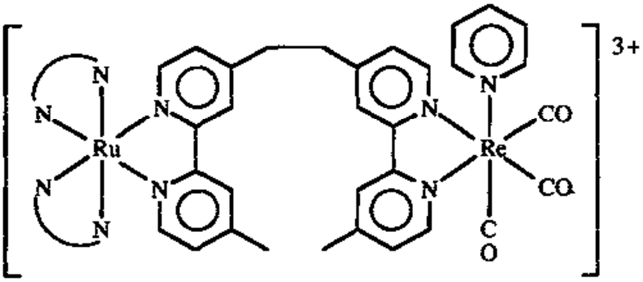
2,5-dpp

The positive-ion fast-atom bombardment (FAB) mass spectra of the binuclear $[CN-Ru(L)_2-CN-R(L')_2-CN]^+$ and trinuclear $[CN-Ru(L)_2-CN-Ru(L)_2-CN-Ru(L_2)-CN]^{2+}$ complexes L = bpy; L' = bpy or 1,10-phenanthroline) have been compared with those of the mononuclear NC-Ru(L')$_2$-CN species [121]. In polychromophoric ruthenium complexes $[NC-Ru(L)_2-CN-Ru(L')_2-CN]^+$, $[NC-Ru(L)_2-CN-Ru(L'')_2-NC-Ru(L)_2]^{2+}$ (L = bpy, L' = bpy or 1,10-phenandroline, L" = bpy or 4,4'-dicarboxy -2,2'-bipyridine) photoinduced energy transfer from *C*- to *N*-bonded Ru-units has been observed [122]. Ruthenium and osmium bipyridine complexes containing the ligand **(59)** have been synthesised and their absorption spectra and luminescence properties have been studied [123].

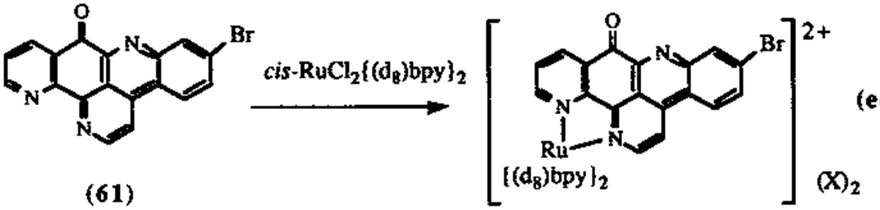
The synthesis, electrochemistry and photophysical properties of the dinuclear complex **(60)** have been described and compared with the properties of $[(bpy)_2Ru(Mebpy\text{-}Mebpy)]^{2+}$ and $[(Mebpy\text{-}Mebpy)Re(CO)_3py]^+$ (Mebpy = 1,2-bis(4'-methyl-2,2'-bipyridyl-4-yl) ethane) [124]. Bidentate chelating ligand **(61)**, isolated from an ascidian, forms a complex with *cis*-$[RuCl_2\{(d_8)bpy\}_2]$ as shown in equ. 4. The product has been isolated as the $[PF_6]^-$, **(62)**, and Cl^-, (63), salts. Intercalation of (63) in calf-thymus DNA as well as photoactivated cleavage of double-stranded supercoiled DNA PBR322 under visible-light irradiation were observed [125].



(59)



(60)

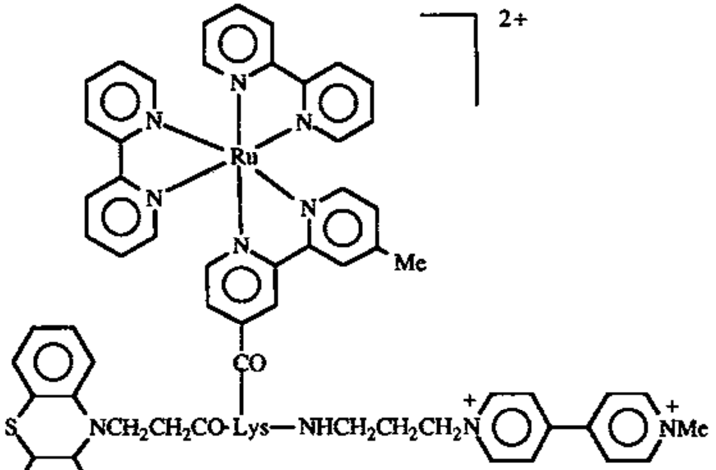


(61)

X= PF$_6^-$ **(62)**
X= Cl$^-$ **(63)**

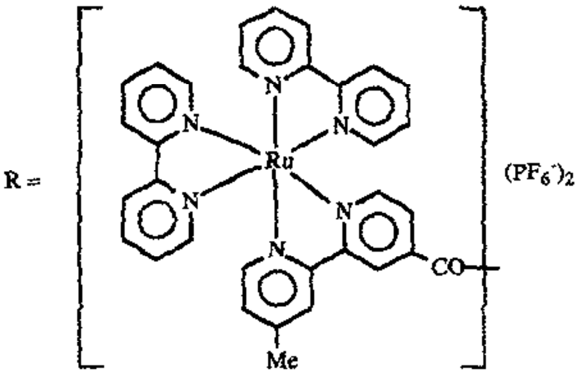
(equ.4)

Irradiation of the synthetic amino acid **(64)** in MeCN with 460 nm, 6 ns laser pulses resulted in net electron transfer between the bipyridinium group and phenothiazine group, mediated by the ruthenium chromophore, as observed by transient absorption spectroscopy [126]. The lysine derivative Boc-Lys(R)-OH (Boc = Me3COOC, R = **(65)**) has been prepared and its redox properties have been studied [127].



(64)

Single crystals and powder of the layered, wide bandgap semiconductor, $Cd_2P_2S_6$, were intercalated with $[Ru(bpy)_3]^{2+}$ by a cation exchange mechanism. The luminescence of the intercalated material has been examined in the range 1.8–77K and compared with the luminescence properties of the host lattice and the free intercalate [128]. The intercalation of $[Ru(bpy)_3]^{2+}$ into the interlayer region of $V_2O_5.nH_2O$ gel by the reaction of the complex with undried V_2O_5 gel has been demonstrated [129].

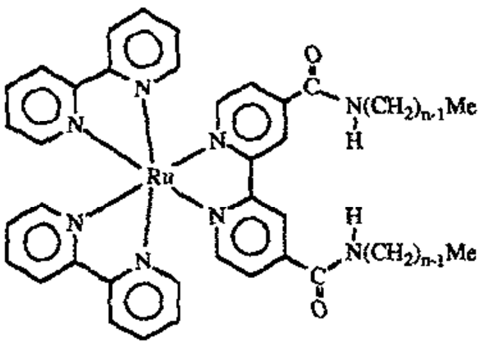


(65)

The nature of the hydrophobic binding of $[Ru(bpy)_3]^{2+}$ and methyl viologen to Nafion was investigated by measuring steady-state emission of $[Ru(bpy)_3]^{2+}$ in Nafion aqueous solutions. The effects of both quenchers and chemically inert ions on the emission have been established [130].

A water insoluble copolymer pendant Ru-Hg complex {poly-$Ru(bpy)_3{}^{2+}$-$[Hg_2Cl_6]^{2-}$} was prepared from a water soluble $[Ru(bpy)_3]^{2+}$ pendant complex of the copolymer of 4-methyl-4'-vinyl-2,2'-bipyridine and *N*-vinylpyrrolidone, and was characterised by IR, visible absorption, emission spectroscopies and emission decay measurments [131]. Luminescence of acrylic acid-4-methyl-4'-vinyl-2,2'-bipyridine copolymer containing $[Ru(bpy)_3]^{2+}$ complex was quenched by methylviologen and propylviologen sulfonate. A strong pH dependence of the cage escape quantum yield for both quenchers has been observed [132].

Second harmonic generation and very weak two-photon emission were observed for the alkylated ruthenium-bipyridine complexes **(66)**, **(67)**, and **(68)**, whereas only two-photon emission was observed for $[Ru(bpy)_3]^{2+}$. The presence of two amide bonds in one bipyridine ligand for **(66)** - **(68)** most probably enhanced the molecular hyperpolarisability as compared to $[Ru(bpy)_3]^{2+}$ [133].

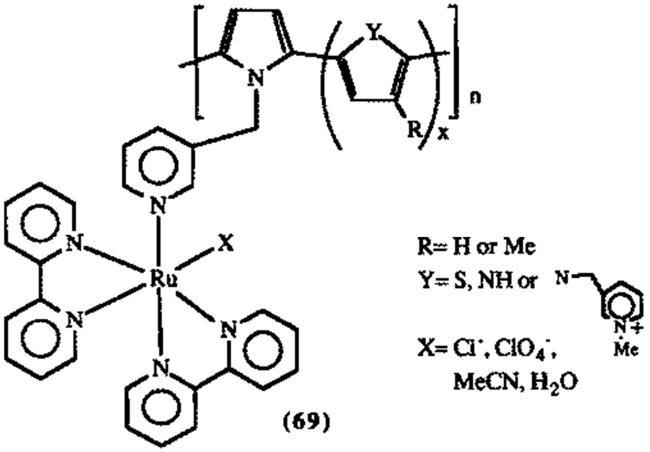


n= 12 **(66)**

n= 16 **(67)**

n= 18 **(68)**

Photoinduced electron transfer kinetics, with respect to photoelectron conversion of $[Ru(bpy)_3]^{2+}$ in heterogeneous LB films has been studied by nanosecond laser photolysis [134]. Conducting films containing ruthenium complexes (69) have been synthesised by copolymerisation of the Ru complex monomer with pyrrole, 3-methylthiophene, 1-methyl-3-(pyrrol-1-ylmethyl)-pyridinium(1+) or 2,2'-bithiophene. The immobilised complexes show rapid and reversible electrochemistry in MeCN [135].

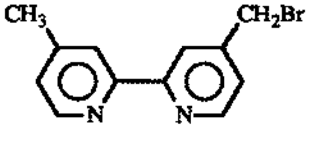


R= H or Me
Y= S, NH or
X= Cl⁻, ClO_4^-,
MeCN, H_2O

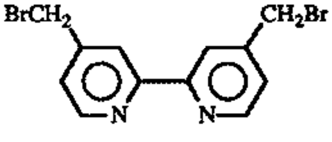
(69)

A surfactant such as $[Ru(bpy)_2(bpy\text{-}C_{19})]^{2+}$ ($C_{19} = CH_2NHOC(CH_2)_{16}CH_3$) has been used to identify insoluble electroactive species in films at the air/water interface. The effects of several parameters, such as electrode surface hydrophobicity and transfer conditions, have been discussed [136].

Ruthenium complexes containing ligands (70) and (71) have been prepared. Upon electrochemical reduction of the complexes, coupling reactions occur to ligands which give thin, metal-complex-containing polymeric films on electrode surfaces [137].

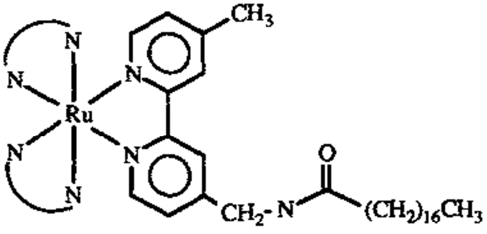


(70)

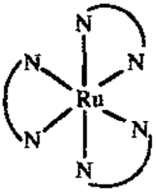


(71)

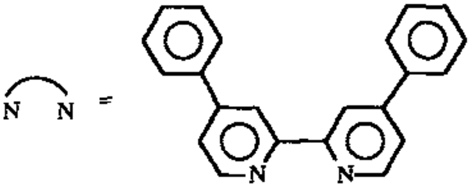
Monolayer films of **(72)** and **(73)** on a Langmuir trough contacted by the horizontal touch method with an InSn oxide coated glass or a highly oriented pyrolytic graphite electrode have been characterised by imaging of their electrogenerated chemiluminescent emission [138].



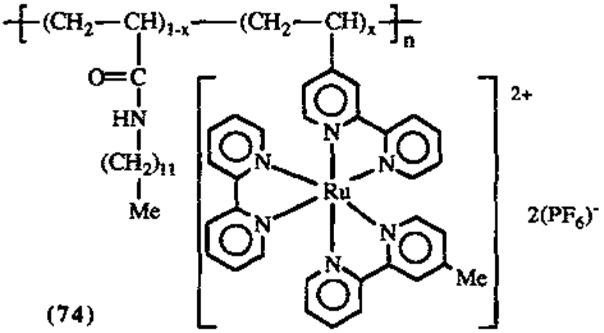
(72)



(73)



The electron-transfer process at electrodes coated with [Ru(bpy)$_2$Cl(PVP)]Cl (PVP= 1-ethenyl-2-pyrrolidinone polymer), polyaniline and poly(1-hydroxyphenazine) has been analysed from the optical probe-beam deflection signals, together with cyclic voltammograms. With this technique, it is possible to determine whether cations or anions are used as the charge-compensating ions in the electron-transfer process [139].

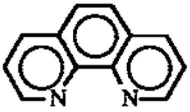


(74)

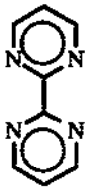
A series of copolymers of styrene and 4-vinylpyridine and their corresponding $[Ru(bpy)_3]^{2+}$ containing metallopolymers have been synthesised and characterised using IR, UV-visible, emission spectroscopy and microanalysis [140]. Treatment of *N*-Dodecylacrylamide-4-vinyl-4'-methyl-2,2'-bipyridine copolymer with $[Ru(bpy)_3]Cl_2$ yielded a polymeric ruthenium complex **(74)**. Complex **(74)** formed a stable condensed monolayer on H_2O, and the monolayer could be transferred to a solid support to give a bilayer ruthenium-containing film [141].

2.5.2 Complexes with phenanthroline ligands

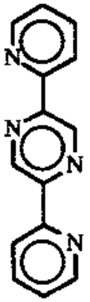
Dinuclear complexes of the type $[\Lambda\text{-}Ru(phen)_2\text{-}\mu\text{-}X\text{-}\Lambda\text{-}Ru(phen)_2]^{4+}$ (phen = **(75)**; X=**(76)** or **(77)**] have been synthesised in high yield using the chiral building block Λ-$[Ru(phen)_2(py)_2]^{2+}$. The stereochemistry of the products has been studied by ^1H NMR spectroscopy and one of the dinuclear complexes (X=**(76)**) has been characterised by 2-D COSY ^1H NMR spectroscopy [142].



(75)

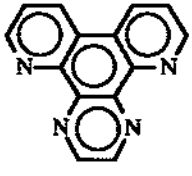


(76)



(77)

A new method has been established for the enantiomeric resolution of $[Ru(phen)_3]^{2+}$ and $[Ru(bpy)_2(ppz)]^{2+}$ (ppz = **(78)**) by passing an aqueous solution through a column containing DNA adsorbed onto hydroxylapatite. A single pass results in a fraction of > 95% enantiomerically pure isomers [143].



(78)

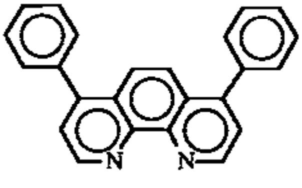
The kinetics of aqua ligand substitution of phen and bpy in *cis*-$[Ru(bpy)_2(H_2O)_2]^{2+}$ has been studied by a spectrophotometric method in the 35-50°C temperature range. A rate law operating within pH 3.65-5.5 has been proposed [144].

The binding structures of enantiomeric and racemic $[Ru(phen)_3]^{2+}$ with sodium montmorillonite have been investigated by means of X-ray diffraction and electric dichroism measurements. The electron density curves along the *c* axis of a clay layer have been established for the powder samples of clay-chelate adducts [145].

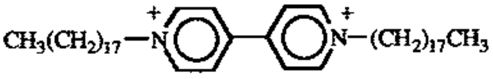
The complex cations $[Ru(phen)_3]^{2+}$ and $[Ru(bpy)_3]^{2+}$ photoinitiated the grafting of acrylamide, acrylic acid, acrylonitrile, methyl acrylate, methacrylamide and glycidyl methacrylate onto cellulose triacetate in the presence of $[S_2O_8]^{2-}$. It is believed that excited ruthenium(II) complexes interact with $[S_2O_8]^{2-}$ to form sulfate anion-radicals, and their reaction with cellulose triacetate gives radicals which react with vinyl monomers to yield a copolymer [146].

The photo-induced electron-transfer of ruthenium complex **(79)** to stearyl viologen **(80)** in barium stearate LB film assembly systems has been studied by a steady-state quenching technique. The electron-transfer from the excited state of **(79)** to **(80)** across two barium stearate monolayers was found to be impossible by electron tunnelling during the lifetime of excited **(79)** [147]. Electron-transfer quenching of excited **(79)** by octahecanethiol in a barium stearate LB assembly matrix has also been studied by steady-state fluorescence spectroscopy [148]. The complexes $[Ru(phen)_3]Cl_2$ and $[Ru(bpz)_3]Cl_2$ (bpz = **(41)**) have been used to sensitise photopolymerisation of acrylamide in aqueous solution [149].

$[Ru(dpphen)_3]^{2+}$ **(79)**



dpphen

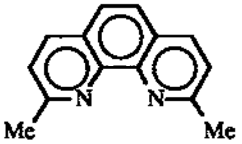


(80)

The binding interactions of enantiomers of $[Ru(phen)_3]^{2+}$ and $[Ru(dppz)_3]^{2+}$ (dppz = dipyridophenazine) with Z-form poly-d(GC) have been investigated by photophysical studies. Parallel enhancements in the steady-state luminescent intensity and lengthening of the luminescent lifetime have been observed for ruthenium enantiomers with Z-DNA as well as for B-DNA, but with enantioselectivities reversed [150]. Molecular modelling and potential energy minimization calculations which incorporate solvent effects have been used to investigate the complexation of Δ-and Λ-[Ru(phen)$_3$]$^{2+}$ to DNA. The most stable binding geometry for both enantiomers is the one in which a phenanthroline ligand is positioned in the major groove [151].

In the presence of double helical polynucleotides, the efficiency of oxidative or reductive electron-transfer between photoexcited [Ru(phen)$_3$]$^{2+}$ and cationic quenchers such as methylviologen increases 1-2 orders of magnitudes compared to the efficiency of the same quenching in microhomogeneous aqueous medium. The role of the nucleic acid double helix in these reactions has been discussed [152]. Molecular mechanics calculations and molecular dynamics simulations have been used to investigate the binding of the partially inserted major groove complex of Λ-[Ru(phen)$_3$]$^{2+}$ with DNA. Energy refinements of this ruthenium complex showed a clear preference for binding at purine-3',5'-pyrimidine sites [153].

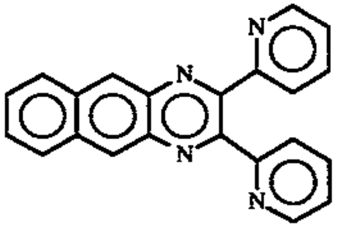
The sterically crowded *cis*-[Ru(dmp)$_2$S$_2$](PF$_6$)$_2$ (dmp = (**81**); S= MeCN or H_2O) has been shown to hydroxylate methane under mild conditions utilising H_2O_2 as the primary oxidant. Ruthenium(VI) has been suggested as the active oxidant from spectroscopic data [154].



dmp (**81**)

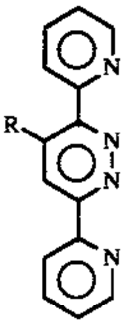
2.5.3 *Complexes with other N-heterocyclic ligands*

The synthesis, electrochemical and spectroscopic properties of [Ru(dpb)$_3$](PF$_6$)$_2$ (dpb= (**82**)) have been reported. The principal features controlling the electrochemistry and spectroscopic properties are the ligand reduction potential and the steric crowding around the metal centre. The metal complex also shows a low energy emission spectrum which is consistent with predictions based on the energy gap law [155].

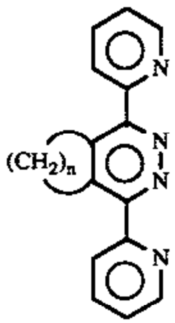


dpb (**82**)

Ruthenium complexes $[RuL_3]^{2+}$ (L = **(83)**, **(84)** and **(85)**) have been characterised by UV-visible spectroscopy and cyclic voltammetry. The possibility of using these complexes in solar energy conversion has been evaluated [156].

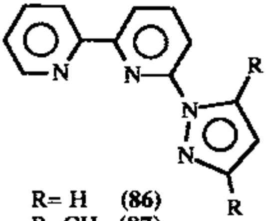


R= H **(83)**
R=Ph **(84)**

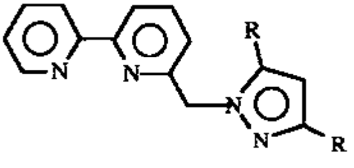


(85) n= 3-6, 10

Photoaquation using near-UV-visible radiation of *cis*-$[Ru(NH_3)_4L_2]$ (L = pyridine, 4-picoline, isonicotinamide (isn), or 4-acetylpyridine) and *cis*-$[Ru(NH_3)_4(isn)(L)]$ in acidic medium has been studied. The *cis* metal complexes have ligand-field and metal-to-ligand charge-transfer states as the lowest energy excited states [157]. Synthesis, spectroscopic and electrochemical properties of homoleptic ruthenium complexes containing ligands **(86)**, **(87)**, **(88)** and **(89)** have been described. Complete assignments of the ^{13}C and ^{1}H NMR spectra of the ligands and their complexes are available [158].



R= H **(86)**
R=CH_3 **(87)**

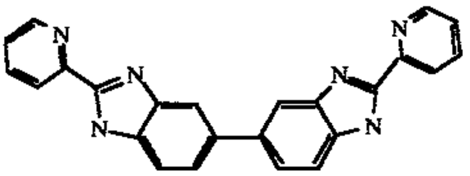


R= H **(88)**
R= CH_3 **(89)**

Ruthenium(II) complexes $[Ru(NH_3)_5L](PF_6)_2$ (L = isonicotinamide or pyrazine) and ruthenium(III) complexes $[Ru(NH_3)_5L](PF_6)_3$ (L = 4-*N*,*N*-dimethylamino pyridine or 4-aminopyridine) have been shown to form adducts with 18-crown-6 ether in MeCN. A red shift in the metal-to-ligand charge-transfer band for the ruthenium(II) complexes is observed, and this compares with a blue shift in the ligand-to-metal charge-transfer band for ruthenium(III) complexes. A negative shift of the Ru(III)/Ru(II) redox potential for these complexes has also been observed [159].

The cage escape efficiency, (a measure of the competition between back electron transfer and diffusional separation of the geminate redox pair formed within the solvent cage), for the sacrifical reductive quenching of the excited states of homo-and heteroleptic ruthenium(II)-diimine complexes of bpy, bpm, **(40)**, and bpz, **(41)**, has been determined [160].

Binuclear complexes $[Ru(L)_2(bpbimH_2)Ru(L)_2]^{4+}$ (L = bpy, phen; $bpbimH_2$= **(90)**) have been prepared. Both the oxidation potentials and absorption spectra are strongly dependent on the solution pH, which is responsible for the deprotonation of the N-H group on the coordinated ligand **(90)**. It has been shown that the metal-metal interaction of the deprotonated binuclear complexes is 4-6 times longer than that of protonated complexes [161]. Electronic excited states of these binuclear complexes have been studied by laser photolysis kinetic spectroscopy [162].



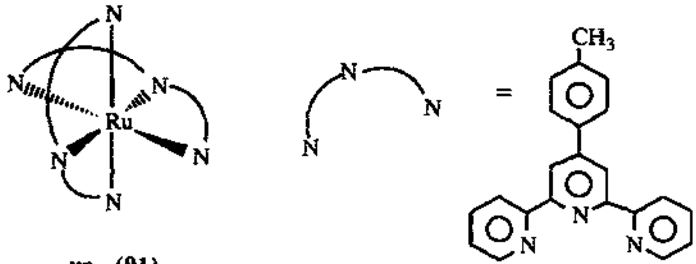
$bpbimH_2$ **(90)**

Generation of cathodic and anodic currents based on photoexcited $[Ru(bpz)_3]^{2+}$ (bpz= **(41)**) in aqueous solution in the presence of $[S_2O_8]^{2-}$ and EDTA has been described. A theoretical analysis has been developed to account for the dependences of the photocurrent on applied potential, concentration of $[Ru(bpz)_3]^{2+}$, $[S_2O_8]^{2-}$ and EDTA, pH and light intensity [163]. The oxidation rate of $[C_2O_4]^{2-}$ by $[S_2O_8]^{2-}$ in an aqueous solution containing $[Ru(bpz)_3]^{2+}$ is greatly increased by irradiation with visible light. The mechanism may involve a chain reaction initiated by a reductive quenching of photoexcited $[Ru(bpz)_3]^{2+}$ with $[C_2O_4]^{2-}$ [164].

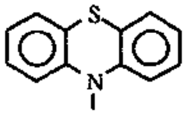
Electroabsorption spectra for the charge-transfer transitions of $[Ru(NH_3)_5L]^{2+}$ and $[\{Ru(NH_3)_5\}_2L]^{4+/5+}$, (L = pyrazine or 4,4'-bipyridine) have been recorded. Experimental estimates of the susceptibility of the transition dipole moment to an electric field, the change in polarisability and the magnitude of the change in permanent electric dipole moment associated with most of the metal-to-ligand and metal-to-metal charge-transfer transitions in these complexes have been made [165].

Dibenzo-24-crown-8 ether was used to encapsulate donor and acceptor charge-transfer sites in a ligand-bridged mixed-valence complex $[\{Ru(NH_3)_5\}_2(4,4'\text{-bpy})]^{5+}$ in order to investigate the molecular aspect of solvent reorganisation in electron transfer reactions. The energetic effects of crown encapsulation have been monitored directly by intervalence charge-transfer absorption measurements in nitromethane solutions. Complete crown binding has only a modest negative effect on the energetics of solvent reorganisation [166].

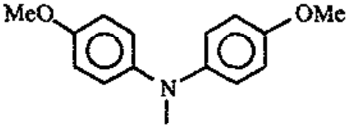
Five supramolecular systems containing $[Ru(ttp)_2]^{2+}$ (ttp = (**91**)) photosensitiser covalently linked to an electron acceptor such as methylviologen and/or an electron donor such as PTZ, (**92**), or DPAA, (**93**), have been synthesised. The spectroscopic and electrochemical properties of these systems have been investigated [167].



ttp (**91**)

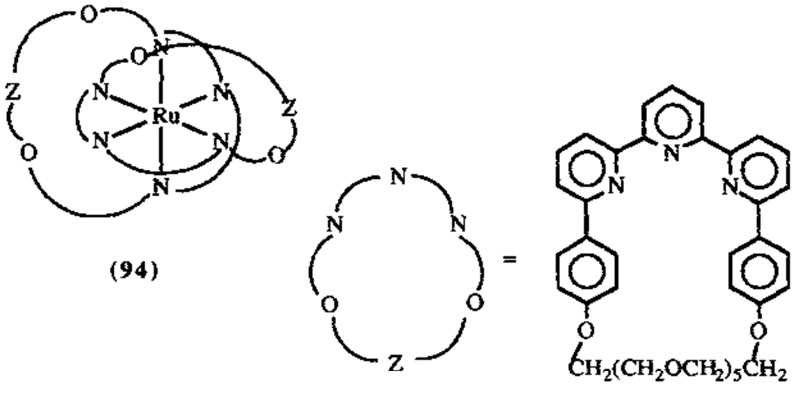


PTZ (**92**)



DPAA (**93**)

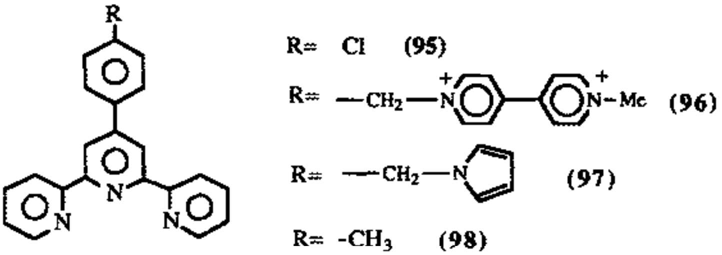
A bis(terpyridine)ruthenium(II) catenate, (**94**), which contains a pseudooctahedral coordination geometry has been synthesised. The catenate obtained consists of two interlocking 38-membered rings and is nonluminescent [168].



(**94**)

The absorption spectrum of the excited state of $[Ru(Cl\text{-}ptpy)_2]^{2+}$ (Cl-ptpy = **(95)**) in ethanol has been measured by laser flash spectroscopy at room temperature and assigned to the metal-to-ligand charge-transfer triplet state [169].

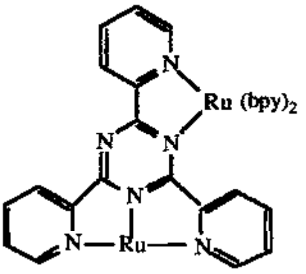
Photophysical data and spectroscopic data of some para-substituted phenylterpyridine Ru(II) complexes along with molecular orbital studies of the iron(II), ruthenium(II) and osmium(II) compounds $[M(R\text{-}ptpy)]^{2+}$, (R = H, CH_3, OH, OCH_3 and Cl) have been reported. The visible charge-transfer absorption of $[Ru(R\text{-}ptpy)]^{2+}$ is almost twice as intense as observed for $[Ru(bpy)_3]^{2+}$ with a red shift of about 50 nm [170].



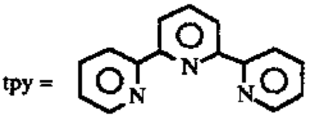
Ruthenium(II) complexes with modified terpy ligands **(96)** **(97)** and **(98)** have been prepared. For the system consisting of two different ligands bonded to the metal centre, one bearing an electron acceptor (viologen) and the other being end-linked to a pyrrole ring via its N atom, electro polymerisation to give an electrically conductive film on the surface of a platinium electrode has been achieved. The modified electrode thus obtained can act as a photoelectrode [171].

The large difference in the affinity of *N*-methylpyrazinium cations for the $[Ru^{III}(EDTA)(H_2O)]^-$ and $[Ru^{II}(EDTA)(H_2O)]^{2-}$ gives a pattern of irreversibility in the electro-chemical responses exhibited by these complexes. Estimates of the equilibrium constants, rate constants and formal potentials have been made from the spectral and electrochemical measurements [172].

An unsymmetrical binuclear ruthenium(II) complex, **(99)**, has been synthesised and characterised by ^1H NMR spectroscopy [173].

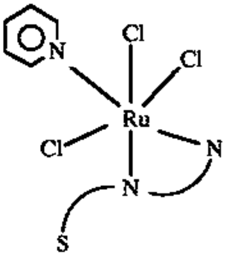


(99)

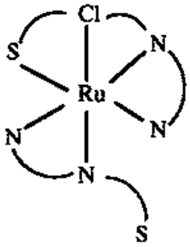


Ruthenium(II) complexes **(100)** and **(101)** containing the ligand 6-(2-thienyl)-2,2'-bipyridine have been characterised by ^1H NMR spectroscopy and X-ray crystallography [174].

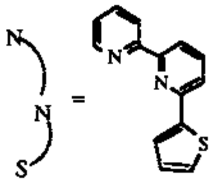
Ruthenium(II) complexes $[Ru(NH_3)_4(bptz)]^{2+}$ and $[\{Ru(NH_3)_4\}_2(bptz)]^{4+}$ (bptz = **(102)**) have been synthesised and characterised. Reversible metal oxidations for the binuclear complex are at +1.56V and +0.72V *vs* SCE and ΔE (2-1) = 840mV, which suggest that a large degree of Ru-Ru communication occurs through the bptz bridging ligand [175].

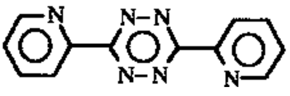


(100)

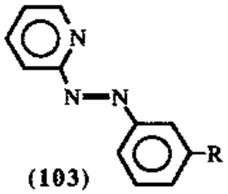


(101)



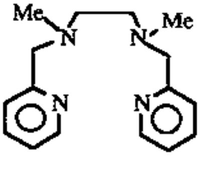


bptz **(102)**



(103)

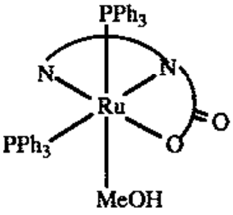
Direct synthetic routes to isomeric $[RuCl_2L_2]$ and $[RuL_3](ClO_4)_2.H_2O$ (L = **(103)**) complexes, based on the reaction of $RuCl_3.3H_2O$ and $[AgL_2]ClO_4$, have been sought. The complexes have been characterised by elemental analysis, as well as by spectroscopic and electrochemical methods [176]. The complex *cis*-$[Ru^{III}L(Cl)(H_2O)]$ (L = **(104)**) has been characterised by spectroscopic and crystallographic methods. A cyclic voltammogram of the complex shows three reversible/quasi-reversible couples at 1.29, 0.93 and 0.23V *vs* SCE assigned to the couples Ru(V)/Ru(IV), Ru(IV)/Ru(III) and Ru(III)/Ru(II). It has been shown that the complex is an active catalyst for the electrochemical oxidation of alcohols and tetrahydrofuran [177].



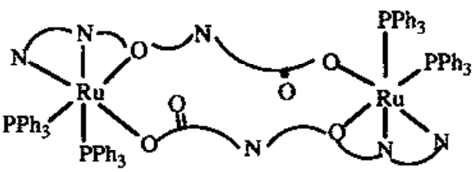
L^1 **(104)**

Octahedral ruthenium metal complexes $K[RuQ_2L^1{}_2]$, $K[RuQ_2L^2]$ and $K_2[RuQL^3]$ (H_2Q = phthalic acid; L^1 = quinoline, isoquinoline, α- and β-picoline, py; L^2 = 2-aminopyrrolidine, *o*-phenanthroline, 3-aminopyridine, bpy and L^3 = 8-hydroxyquinodine) have been prepared and characterised based on elemental analyses, magnetic and conductivity measurements, IR and electronic spectroscopies [178].

The complexes $[Ru(glygly)(PPh_3)_2(CH_3OH)]$, **(105)**, and $[Ru(glyglygly)(PPh_3)_2]_2$, **(106)**, (glygly = diglycine; glyglygly = triglycine) have been characterised by X-ray analysis and electrochemical methods [179].

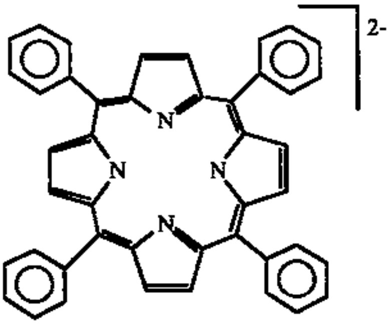


(105)



(106)

The tumour-inhibiting complex *trans*-imidazolium bis(imidazole)tetrachlororuthenate(III) has been shown to bind DNA and inhibit DNA synthesis catalysed by *E. Coli* DNA polymerase I. The kinetics of the reaction with DNA are reminiscent of those for cisplatin [180]. The photo-induced intramolecular electron transfer in cytochrome *c* ruthenium polypyridine derivatives with other metalloproteins has been reviewed [181].

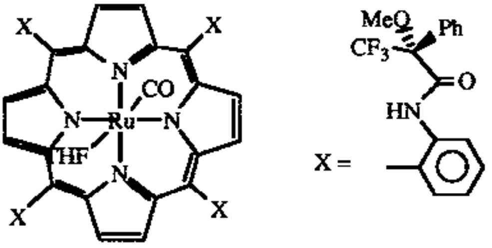


(107)

2.5.4 *Complexes with macrocyclic ligands*

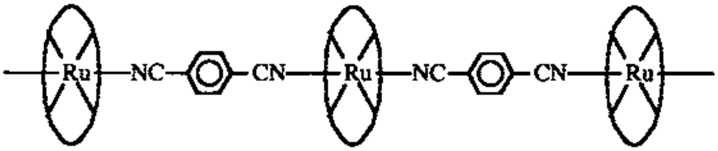
Reactions of $[Ru(TPP)]_2$ (TPP = **(107)**) with HBr, HCl or I_2 give paramagnetic complexes $[Ru(TPP)X_2]$ (X = Br, Cl or I). $[Ru(TPP)Br_2]$ has been structurally characterised. The Ru-Br distance, 2.425(2)Å, is the shortest reported for any Ru-Br bond. Treatment of [Ru(TTP)Br$_2$] with PhLi yields diamegnetic [Ru(TPP)Ph$_2$], which can be thermally decomposed to [Ru(TPP)Ph] [182].

The synthesis of ruthenium 'picket-fence' porphyrins (**108**) which bear optically active α-methoxy-α-(trifluoromethyl)phenylacetyl residue on both sides of the porphyrin plane, and the chiral recognition in the complexation of racemic benzylmethyphenylphosphine to the α,β,α,β-isomer of (**108**) to give one of three possible product diastereoisomers with high stereoselectivity have been described [183].

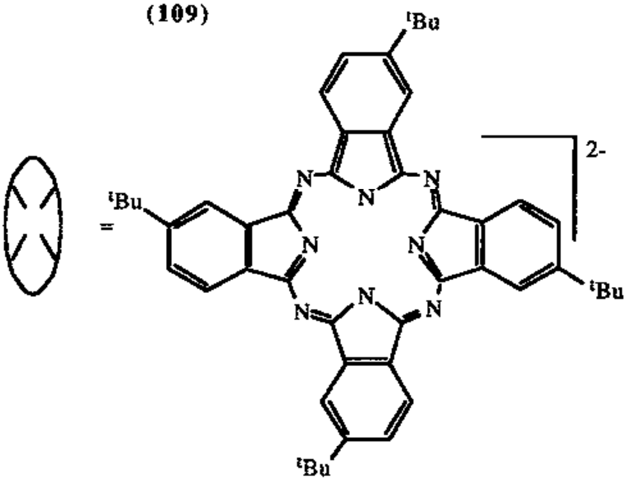


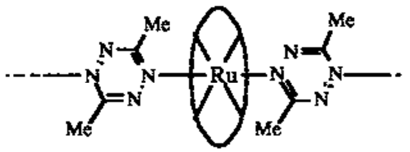
(108)

The photophysical properties of a soluble oligomeric ruthenium phthalocyanine, (**109**), containing bidentate bridging ligands have been compared with those of a monomeric analogue. The triplet states have been characterised by time-resolved absorption spectroscopy [184].

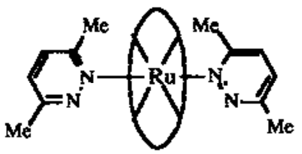


(109)

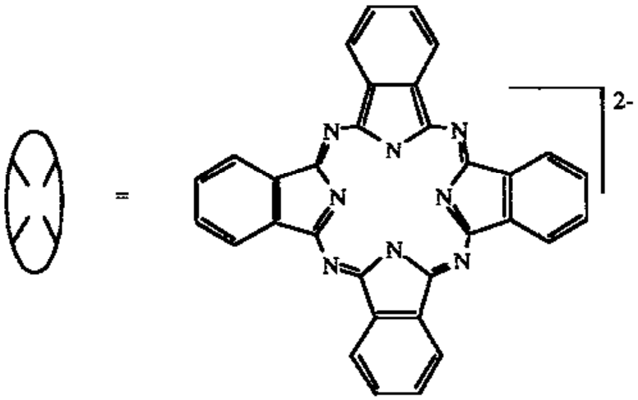




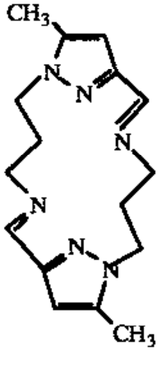
(110)



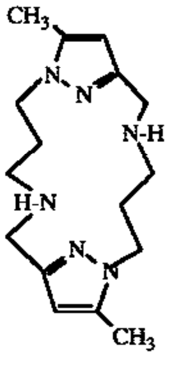
(111)



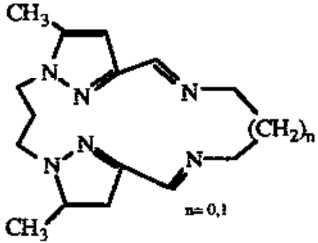
The synthesis and semiconducting properties of the tetrazine-bridged phthalocyaninato ruthenium complex **(110)** and the monomeric complex **(111)** have been reported [185]. (Phthalocyaninato)ruthenium complexes with biaxially coordinated azanaphthalenes or pyridine have been prepared and characterised by IR, ^{1}H NMR, and UV-visible spectroscopy, and by TG/DTA and FD-MS techniques [186, 187]. Ruthenium(II) complexes with macrocyclic ligands **(112)**–**(118)** have been prepared and characterised by ^{1}H NMR and UV spectroscopies, and electrochemical techniques [188].



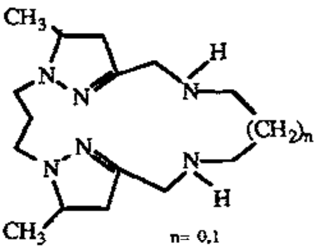
(112)



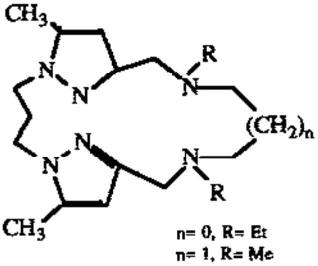
(113)



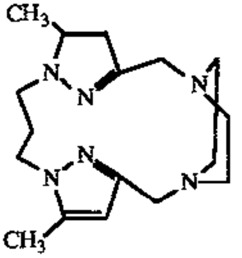
(114)



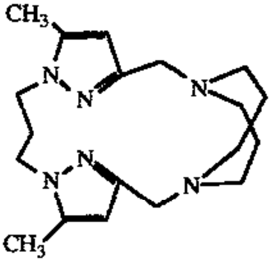
(115)



(116)



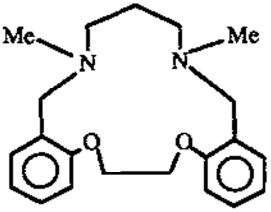
(117)



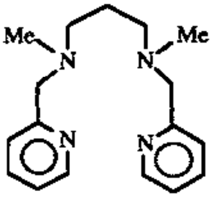
(118)

2.5.5 Complexes with other mixed donor ligands

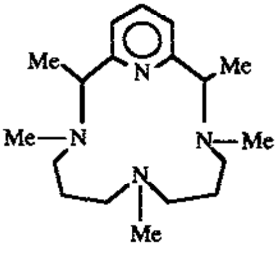
The kinetics of oxidation of aromatic hydrocarbons and tetrahydrofuran by *trans*-$[Ru(VI)(L)O_2]^{2+}$ (L = bpy, **(119)**, **(120)** and **(121)**) have been studied. A hydrogen-atom abstraction mechanism has been suggested for the oxidation of C-H bonds by *trans*-dioxo ruthenium(VI) complexes [189]. The synthesis and spectroscopic characterisation of chiral $K[RuLCl_2(H_2O)]$ **(122)** have been reported [190].



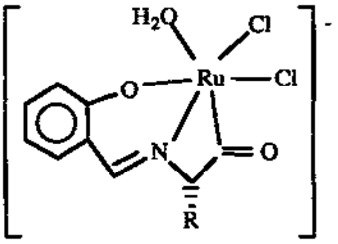
(119)



(120)



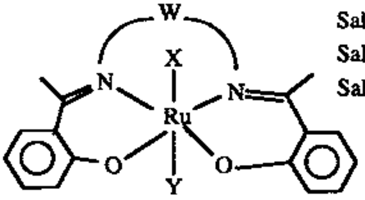
(121)



$R = CH_3, CH_2\text{-}Ph$
$CH_2OH, CH\text{-}(CH_3)_2$
$CH_2\text{-}S\text{-}CH_2$
$CH_2C_6H_4OH$
$CH_2\text{-}C_3H_4N_2$
$(CH_2)_3C(NH_2)\text{=}NH$
CH_2COOH
CH_2SH

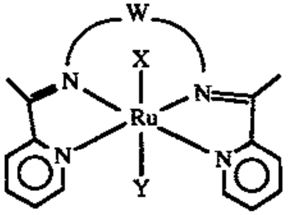
(122)

Ruthenium(III) Schiff base complexes of the structural types **(123)** and **(124)** have been prepared and characterised by various physical methods. The reversible binding of CO to these complexes in DMF, MeCN, MeOH and Me_2CO has been demonstrated [191].



(123)

Complex	W	X	Y
Saloph	$(C_2H_4)^-$	Cl^-	Cl^-,Im,2MeIm
Salen	$(CH_2)_2$	Cl^-	Cl^-,Im,2MeIm
Saldien-	$(C_2H_4)NH(C_2H_4)$	N of W	Cl^-



(124)

Complex	W	X	Y
Picoph	$(C_6H_4)^-$	Cl^-	Cl^-,Im,2MeIm
Picen	$(CH_2)_2$	Cl^-	Cl^-,Im,2MeIm
Picdien	$(C_2H_4)NH(C_2H_4)$	N of W	Cl-

2.5.6 Complexes with ammonia or amine ligands

The activation and subsequent interaction with absorbates of $[Ru(NH_3)_6]^{3+}$ in HX zeolite have been investigated by ESR, electron spin echo modulation, XPS, and IR spectroscopic methods [192]. The $[Ru(NH_3)_6]^{3+}$ complex cation has been reported to be a two-electron catalyst for homogeneous and heterogeneous water oxidation to give O_2. A mechanism involving a peroxo-bridged intermediate $[Ru(V)(NH_3)_6]^{5+}$ has been proposed for this reaction [193]. The overall charge-transfer reaction at $[Ru(NH_3)_6]^{3+/2+}$-containing montmorillonite clay film-coated graphite electrodes has been studied by cyclic voltammetry, chronocoulometry and normal pulse voltammetry. Kinetic parameters such as standard rate constant, cathodic transfer coefficient and apparent diffusion coefficient have been obtained [194].

Crystal and molecular structure of $[RuCl(NH_3)_5]_2(BF_4)Cl_3$ have been determined. The average Ru-N bond length, (2.108Å) and the Ru-Cl bond length (2.343(1) Å) are not significantly different from values reported for the chloride salt [195].

The kinetics of long-range electron transfer have been measured in $Ru(NH_3)_4L$(His39) derivatives (L = NH_3, pyridine or isonicotinamide) of zinc-substituted *Candida krusei* cytochrome c and $Ru(NH_3)_4L$(His62) derivatives (L = NH_3 or pyridine) of zinc-substituted *Saccharomyces cerevisiae* cytochrome *c* [196].

Treatment of $[Ru(NH_3)_5(H_2O)]^{2+}$ with cobalt *meso*-tetrakis(4-pyridyl)porphyrin, [CoP-$(py)_4$], on graphite electrodes coated with Nafion gives $[CoP\text{-}(PyRu(NH_3)_5)_4]^{8+}$. The latter acts as a catalyst for the four-electron reduction of O_2. Under the same condition, the same porphyrin with uncoordinated $[Ru(NH_3)_6]^{2+}$ or $[Ru(NH_3)_5py]^{2+}$ shows no such catalytic activity [197]. The kinetics and mechanism of acid-dependent oxidation of RNH_2 (R=Me, Et, Pr or Bu), Me_2NH and Me_3N by Ce(IV) in the presence of ruthenium(III) catalyst have been described [198]

2.5.7 *Complexes with nitrosyl ligands*

Potential curves of NO group dissociation from ruthenium complexes in their ground states and in a series of singlet- and triplet-excited states have been calculated by multiconfigurational SCF method. The lowest excited state in $[Ru(NO)Cl_5]^{2-}$ and $[Ru(NO)(NH_3)_2Cl_3]$ complexes was $d \rightarrow \pi^*$ (NO) charge-transfer state which dissociates to form NO. In $[Ru(NO)(NH_3)_5]^{3+}$, the lowest excited state was of the $d \rightarrow d$ type, and it dissociates to give NO^+ [199]. CNDO/2 MO calculations have been applied on the system $[Ru(NX)Cl_5]^{2-}$ and $[Ru(NX)Cl_4(H_2O)]^-$ (X = O or S) to investigate the nature and energetics of the interaction between ruthenium and isoelectronic NO and NS ligands. The result suggests that the strength of the Ru-NS bond is greater than that of the Ru-NO bond; the NS ligand withdraws electron density more effectively from the central ruthenium atom than does NO [200].

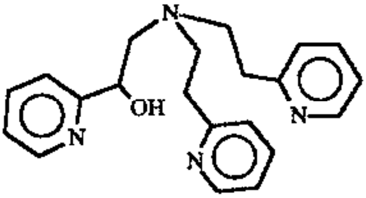
The complexes $[RuX_3(NO)L]$ (X = Cl or Br; L = 8-quinolinol or its derivatives) have been prepared and characterised by elemental analysis and spectroscopic methods. X-ray analysis of $[RuBr_3(NO)$(2-methyl-8-quinoline)] revealed that all the bromide ions are coordinated *cis* to NO and the 8-quinolinolate oxygen is *trans* to NO; this reflects the fact that NO is the stronger π-acceptor [201]. The kinetics of the nucleophilic addition of OH^- to $[Ru(CN)_5(NO)]^{2-}$ has been studied by spectroscopic techniques [202]. Reactions of $[Ru(NO)Cl_3]$ with $M[B(R\text{-}pz)_3]$ (M = alkali metal, Tl; pz =1-pyrazolyl) give $[RuCl_2\{B(R\text{-}pz)_3\}(NO)]$ which exhibits NO^+ coordinated to the metal centre in a linear fashion [203]. The diazotization of primary aromatic amines with a strongly electrophilic mononitrosyl ruthenium complex, $[Ru(NO)(NO_2)L_2](ClO_4)_2$ (L = 2-(phenylazo) pyridine), in CH_2Cl_2 and acetone has been studied by following the reaction sequence through the isolation of products at various stages of the reaction [204]. $[Ru(NO)(NO_2)_4(OH)]^{2-}$

and [Ru(NO)(NO$_2$)$_2$(H$_2$O)(OH)] have been studied by ^{99}Ru, ^{17}O, ^{14}N and ^{15}N NMR spectroscopies [205].

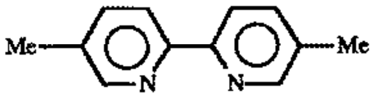
2.6 COMPLEXES WITH OXYGEN DONOR LIGANDS

2.6.1 Complexes with oxo ligands

The complex [Ru(V)L(O)]$^{2+}$, (HL= **(125)**), is a very active oxidant towards hydrocarbons. Stoichiometric oxidation of saturated alkanes in MeCN gives tertiary alcohols exclusively or ketones when only methylene groups are present. The mechanism of C-H bond oxidation by this mono-oxoruthenium compound has been discussed [206].



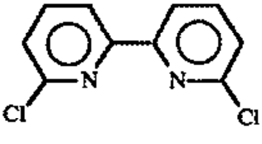
(125)



(126)

Oxidation of *trans*-[Ru(III)(L)$_2$(OH)(H$_2$O)]$^{2+}$ (L = phen or **(126)**) by Ce(IV) in water gives *trans*-[Ru^{VI}(L)$_2$O$_2$]$^{2+}$. It has been shown that the latter complex oxidised alcohols to ketones/aldehydes, tetrahydrofuran to γ-butyrolactone, and alkenes to epoxides [207].

The cation [Ru(IV)(terpy)(dcbipy)O]$^{2+}$ (dcbipy = **(127)**) has been prepared by the oxidation of the aquo precursor complex with cerium(IV). It is a powerful oxidant (E° Ru(IV)/Ru(III) = 1.13V *vs* SCE) and can selectively oxidise the tertiary C-H bond of adamantane. The mechanism of alkene oxidation by this complex has been investigated [208].



dcbiby **(127)**

The redox potentials for several *cis*-diaquaruthenium complexes with bipyridine and related ligands have been determined. The catalytic oxidations of benzylalcohol, iso-propanol, THF and Cl^- have been studied in the presence of ruthenium complexes [209].

Oxo-ruthenium(VI) carboxylato complexes $[RuO_2(OCOR)Cl_2]^-$ (R=Me, Et, Pr, CF_2H) and their uses as oxidants and catalysts for the oxidation of alcohols to aldehydes or ketones in the presence of a cooxidant such as *N*-methylmorpholine *N*-oxide have been described [210]. The electrochemistry of *trans*-$[Ru(IV)Cl(O)(py)_4]^+$ and its related complexes, *trans*-$[Ru(III)Cl(OH)(py)_4]^+$ and *trans*-$[Ru(II)Cl(H_2O)(py)_4]^+$, has been studied in both MeCN and water. The oxo complex undergoes a one-electron oxidation to give a very reactive complex cation *trans*-$[Ru(V)Cl(O)(py)_4]^{2+}$, which is the species capable of oxidising organic substrates [211]. Chemical oxidation of *trans*-$[Ru(NO_2)_2(py)_4]$ gives *trans*-$[Ru(NO_2)(O)(py)_4]^+$, via the formation of a precursor *trans*-$[Ru(NO_2)(H_2O)(py)_4]^+$. The process has been confirmed by electrochemical studies [212].

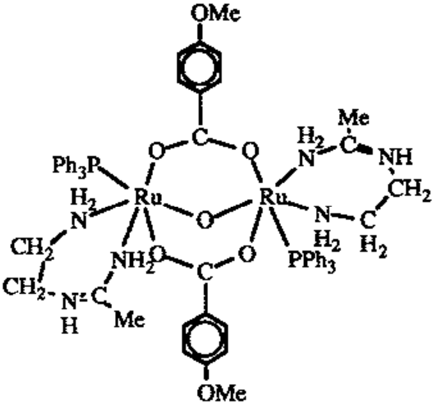
The kinetics and possible mechanisms of reactions of $[Ru(EDTA)(O)]^-$ with PPh_3 [213], [214], L-ascorbic acid [215], [216], amine [217], [218] and alkane [219], [220] have been investigated. The compounds $[Ru(O)_2(py)_2\{SCH_2CH(R)C(O)O\}]$ (R = H, NHCOMe) and $[Ru(O)_2(bpy)\{SCH_2CH_2CH(R)C(O)O]$ (R = NCHO, NHCOMe) have been synthesised from $[Ru(O)_2(OH)_2(py)_2]$ and $[Ru(O)_2Cl_2(bpy)]$ respectively, and characterised by ^1H and ^{13}C NMR, UV-visible spectroscopies and cyclic voltammetry [221].

Evidence from elemental analysis and spectroscopic studies including ^{17}O NMR spectroscopy have been obtained in support of the formulation of the tetranuclear ruthenium(IV) aqua ion as $H_n[Ru_4O_6(H_2O)_{12}]^{(4+n)+}$ (n = 0-4). Possible structures for this ion have been suggested [222]. The synthesis and NMR spectroscopic properties of oxo-Ru(IV) complexes, as well as reaction kinetics of inorganic substrates oxidation by these complexes, have been reviewed [223].

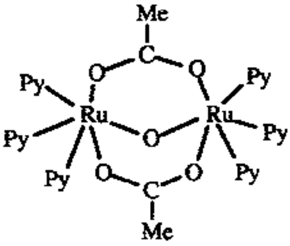
2.6.2 *Complexes with carboxylate ligands*

The complex $[Ru_2O(O_2CR)_2(MeCN)_4(PPh_3)_2](ClO_4)_2$, reacts with 1,2-diaminoethane in MeOH at 25°C. Nucleophilic attack occurs at the carbon of two facial MeCN ligands to give $[Ru_2O(O_2CR)_2\{NH_2CH_2CH_2NHC(Me)NH_2\}_2(PPh_3)_2](ClO_4)_2$, **(128)**. The Ru-Ru and average Ru-O_{oxo} distances are 3.280(2)Å and 1.887Å, respectively. The spectroscopic and electrochemical properties of **(128)** have been discussed [224].

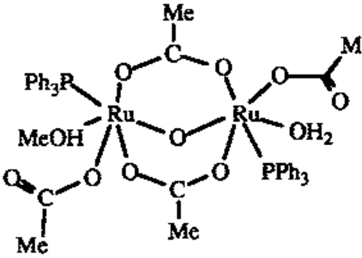
Two ruthenium(III) dimers $[Ru_2(\mu\text{-}CH_3COO)_2(\mu\text{-}O)(py)_6]^{2+}$, **(129)**, and $[Ru_2(\mu\text{-}CH_3COO)_2(\mu\text{-}O)(bpy)(py)_2]^{2+}$, each with a core structure similar to the methemerythrin active centre, have been synthesised and characterised by spectroscopic and electrochemical methods. The molecular structure of **(129)** has been established. There is no direct metal-metal bond between two ruthenium centres, and the Ru-Ru distance is 3.251(2)Å [225]. It has been shown by X-ray structural analysis that $[Ru_2(CH_3COO)_4(\mu\text{-}O)(H_2O)\ (CH_3OH)(PPh_3)_2]$ **(130)** contains a '$Ru_2(\mu\text{-}CH_3COO)_2(\mu\text{-}O)$' core and unidentate acetate ligands. ^1H NMR spectra in $CDCl_3$ revealed that a unidentate-chelate equilibrium of acetate ligands between the bis(chelate) and mono(chelate)-mono(unidentate) of **(130)** was established in solution [226].



(128)



(129)



(130)

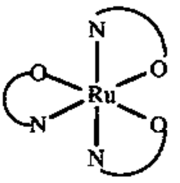
Reaction between $[Ru_2(\mu\text{-}O_2CCH_3)_4(THF)_2]BF_4$ and PPh_3 in THF or toluene gives $[Ru(O_2CCH_3)_2(PPh_3)(CH_3C_6H_5)]$ and $[Ru_2(\mu\text{-}O_2CCH_3)(\mu\text{-}O)(O_2CCH_3)_2(PPh_3)_2]$. The latter has been characterised by spectroscopic techniques and X-ray crystallography. A possible mechanism for the reaction with some supporting spectroscopic evidence has been presented [227].

The binuclear ruthenium(II, III) compound $[Ru_2(O_2CC_6H_4\text{-}p\text{-}OMe)_4(H_2O)_{0.25}]$ has been synthesised and characterised by X-ray crystallography. The $\{Ru_2(O_2CC_6H_4\text{-}p\text{-}OMe)_4{}^+\}$ units are bridged by chloride ion into an infinite zigzag chain [228].

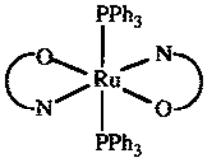
The synthesis and structural properties of Ru(II, III) complexes containing long-chain carboxylates, $Ru_2(O_2CR)_4X$ ($R = C_8H_{17}, C_{11}H_{23}$; $X = Cl, O_2CR$), were reported. The carboxylato species exhibits a thermotropic columnar mesophase, and is the first example of a mixed-valent liquid-crystalline material [229].

The salt $[Ph_4As][Ru(acac)_2Cl_2]$, **(131)**, with the first *trans*-bis(acetylacetone) complex, has been prepared and characterised by X-ray analysis and spectroscopic methods. A number of related Ru(II), Ru(III), and Ru(IV) complexes have been prepared from **(131)** [230].

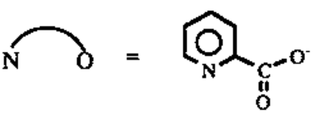
Reaction of $[Ru_2(CH_3COO)_4]^+$ by oxalatotitanium(III) has been studied in $LiCF_3SO_3$ media. The magnitude of the rate constant indicates an outer-sphere mechanism for this reaction [231]. The reaction of $[Ru_2(O_2CMe)_4Cl]$ with pyridine-2-carboxylic acid (Hpyca) in $MeOH/H_2O$ (1:1) yields $[Ru(pyca)_3]$, **(132)**, and $[Ru_2(pyca)_4]$ **(133)**. Both **(132)** and **(133)** react with PPh_3 to give $[Ru(pyca)_2(PPh_3)_2]$, **(134)**. The structures of **(132)** and **(134)** have been determined by X-ray analysis [232].



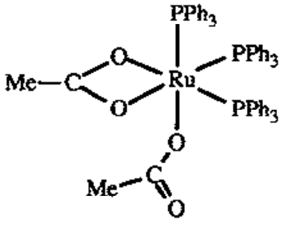
(132)



(134)

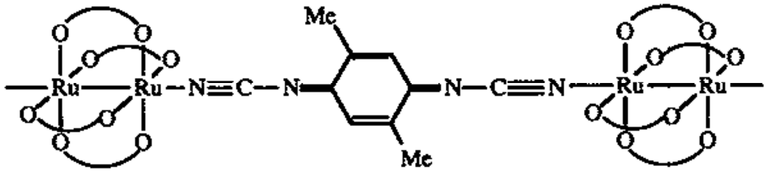


$[Ru_2(\mu\text{-}O_2CCH_3)_4(O_2CCH_3)]$ reacts with excess PPh_3 in acetic acid to give *fac*-$[Ru(O_2CCH_3)(PPh_3)_3]$, **(135)**, which contains both unidentate and chelating acetate ligands. Complex **(135)** shows slight catalytic activity for the ring-opening polymerisation of bicyclo[2.2.1]hept-2-ene [233].



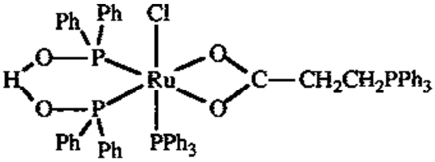
(135)

Kinetic studies of the complexation of oxalate with $[Ru(H_2O)_6]^{2+}$ shows that the rate-determining reaction involves the monoanion of oxalic acid [234]. $[Ru_2(O_2CR)_4]$ (R= H, Me Et, Pr, Ph) reacts with bis(2,5-dimethyl-*N*,*N*'-dicyanoquinonediimine, (DMDCNQI), to give $[Ru_2(O_2CR)(DMDCNQI)]$, **(136)**, which exhibits a polymeric chain with $\{Ru_2(O_2CR)_4\}$ dimeric units bridged by DMDCNQI [235].



(136)

Reaction of $[RuCl_2(PPh_3)_4]$ with 1 equivalent of $Ph_2PO_2CCH=CR'R''$ produces $[RuCl_2(PPh_3)_2(Ph_2PO_2CCH=CR'R'')]$ (R', R'' = H or Me). However, the major product of these reactions is $[RuCl\{Ph_2PO)_2H\}(PPh_3)(O_2CCH_2CHR''PPh_3)]$ **(137)** for R' = H, R'' = H or Me. The structure of **(136)** (R'' = H) has been determined by X-ray crystallography [236].



(137)

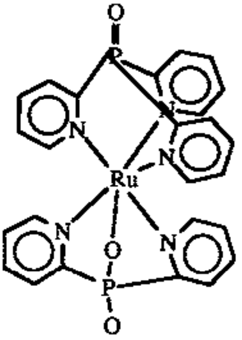
2.6.3 *Complexes with ligands derived from H_4EDTA*

Efficient photocatalytic reduction of CO_2 to MCOOH and HCHO occurs when K[Ru(H-EDTA)Cl].$2H_2O$ is used as the homogeneous catalyst and particulate Pt-CdS-RuO_2 as the photon absorber at 505 nm. The rates of formation of HCOOH and HCHO exhibit a first-order dependence on the catalyst and dissolved CO_2 concentrations. A mechanism for the formation of HCOOH and HCHO has been proposed [237]. The reaction of $[Ru(H\text{-}EDTA)(H_2O)]$ with $[Fe(CN)_6]^{3-}$ ion was studied spectrophotometrically as a function of $[Fe(CN)_6]^{3-}$ ion concentration, pH (1.5-8.5) and temperature (30-45°C) at ionic strength 0.2M ($NaClO_4$). Kinetic and activation parameters obtained are consistent with the proposed mechanism of the reaction [238]. Similar techniques have been employed in the study of kinetics and mechanism of substitution reaction of $[Ru(H\text{-}PDTA)(H_2O)]$ with sulfur containing ligands such as thiourea and 2-mercaptopyrimide [239].

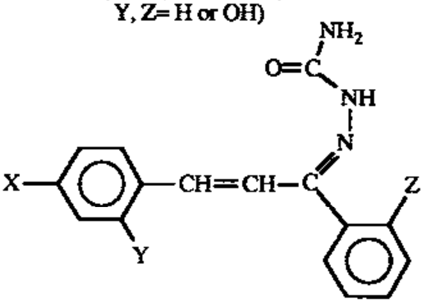
2.6.4 *Complexes with other O-donor ligands*

The reaction of $K_2RuCl_5{\cdot}H_2O$ with $(C_5H_4N)P(O)(OEt)_2$ **(138)** yields $K[RuCl_2\{OP(O)(OEt)(C_5H_4N)\}_2]$ **(139)**. One ethyl group of **(138)** has been eliminated in an Arbuzov-type reaction. The reaction of **(139)** with Zn, Al or $Na[BH_4]$ does not lead to reduction of the metal centre but to further dealkylation of **(138)**. The reaction of **(138)** with $RuCl_3.3H_2O$ gives $[RuCl_3\{(C_5H_4N)P(O)(OEt)_2\}_2]$ [240].

During the synthesis of $[Ru(py_3P=O)_2]^{2+}$, **(140)**, the species $[Ru\{py_3P=O\}\{py_2P(O)O\}]^+$, **(141)**, was also isolated. X-ray structural analysis of **(141)** revealed a tridentate phosphinate anion coordinated to the ruthenium centre [241].



(141)



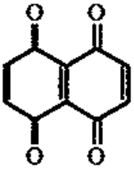
(X= H, OMe or Cl;
Y, Z= H or OH)

(142)

Nineteen *trans*-$[Ru(R\text{-}py)_2L_2]^n$ (R-py= substituted pyridines, n = 0, ±1; L=non-innocent 1,2-dioxolene ligands) were prepared. Their electrochemical and spectroscopic properties were reported and discussed in terms of their electronic structures [242].

The reactions of $RuCl_3$ with neutral chalcone semicarbazones **(142)** have been studied by spectroscopic and electrochemical methods. Some possible products of these reactions were suggested [243].

Resonance Raman and electronic spectral studies of $[Ru_2(bpy)(tetrox)]^{n+}$ and $[Ru_2(py)_8(tetrox)]^{n+}$ (tetrox = **(143)**; n = 2, 3, 4) were reported. Electronic structures of these complexes were determined and their spectra were assigned [244].



(143)

Acid-catalysed dissociation reactions of tris-β-diketonato-ruthenium(III) complexes in the presence of HNO_3 and p-$MeC_6H_4SO_3H$ were studied spectrophotometrically in acetone/water mixtures. Kinetic parameters and a possible mechanism for substitution the β-diketonatoruthenium dericatives have been deduced [245].

Ruthenium semiquinone complexes $[Ru(PPh_3)_2(SQ)Cl_2]$ (SQ=3,5-di-tert-butylsemiquinone) and $[Ru(PPh_3)_2(DBSQ)_2]$ (DBSQ=tetrachloro-1,2-semiquinone) were synthesised and structurally characterised. The charge distribution in these complexes has been deduced from structural and electrochemical data [246].

REFERENCES

1. M. Kritikos, Chem. Commun., Univ. Stockholm, 2 (1991) 52; [*Chem. Abstr.* 115; 221716h].
2. B. Chaudret, G. Chung, O. Eisenstein, S.A. Jackson, F.J. Lahoz and J.A. Lopez, *J. Am. Chem. Soc.*, 113 (1991) 2314.
3. A. Mezzetti, A Del Zotto, P. Rigo and E. Farnetti, *J. Chem. Soc., Dalton Trans.*, (1991) 1525.
4. G. Jia and D.W. Meek, *Inorg. Chem.*, 30 (1991) 1953.
5. M.T. Bautista, E.P. Cappellani, S.D. Drouin, R.H. Morris, C.T. Schweitzer, A. Sella and J. Zubkowski, *J. Am. Chem. Soc.*, 113 (1991) 4876.
6. J. Halpern, L. Cai, P. J. Desrosiers and Z. Lin, *J. Chem. Soc., Dalton Trans.*, (1991) 717.
7. D.G. Gusev, A.B. Vymenits and V.I. Bakhmutov, *Inorg. Chim. Acta*, 179 (1991) 195.
8. G.Allmang, F. Grass, J.M. Grosselin and C. Mercier, *J. Mol. Catal.*, 66 (1991) L27.
9. T. Naota and S. Murahashi, *Synlett*, 10 (1991) 693.
10. F.A. Cotton and R.C. Torralba, *Inorg. Chem.*, 30 (1991) 2196.
11. F.A. Cotton and R.C. Torralba, Inorg. *Chem.*, 30 (1991) 4386.
12. F.A. Cotton and R.C. Torralba. *Inorg. Chem.*, 30 (1991) 4392.
13. A. Jarid, M. Aaid, Y. Legoux, J. Merini, M. Loudet, D. Gonibau and G. Pfister-Guillouzo, *Chem. Phys.*, 150 (1991) 353.
14. N.I. Giricheva and G.V. Girichev, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim.Tekhnol.*, 34 (1991) 3; [*Chem. Abstr.* 115: 242768S].
15. K. Irmer and W. Preetz, *Z. Naturforsch, B: Chem, Sci.*, 46 (1991) 1200.
16. C.M. Duff and G.A. Heath, *Inorg. Chem.*, 30 (1991) 2528.
17. Y.N. Ogibin, A.I. Ilovaiskii and G.I. Nikishin, *Izv. Akad. Nauk SSSR, Ser. Khim*, 1 (1991) 115; [*Chem. Abstr.* 115: 77185].
18. Y. Furukawa, *Chem. Abstr.* 115: 232093d.
19. S. Chocron and M. Michman, *J. Mol. Catal.*, 66 (1991) 85.
20. S. Murahashi, T. Saito, T. Naota, H. Kumobayashi and S. Akutagawa, *Tetrahedron Lett.*, 32 (1991) 5991.
21. Z. Foltynowicz, B. Marciniec and C. Pietraszule, *J. Mol. Catal.*, 65 (1991) 113.
22. W.J. Feast and D.B. Harrison, *Polymer*, 32 (1991) 558.
23. T. Fujii and Y. Saito., *J. Mol. Catal.*, 67 (1991) 185.
24. B. Singh and S. Sahai, *J. Indian Chem. Soc.*, 68 (1991) 208 [*Chem. Abstr.* 115: 231530g].
25. Kondo, S. Yand, K.T. Huh, M. Kobayashi, S. Kotachi and Y. Watanabe, *Chem. Lett.*, 7 (1991) 1275
26. R.L. Chowdhury and J.E. Baeckvall, *J. Chem. Soc., Chem. Commun.*, (1991) 1063.
27. J.A. Marsella, *J. Organomet. Chem.*, 407 (1991) 97.
28. F. Abe, T. Kobayashi, T. Sakakura and M. Tanaka, *Kagaku Gijutsu Kenkyusho Hokoku*, 86 (1991) 151; [*Chem. Abstr.* 116: 58337v].
29. V.V. Grushin and H. Alper, *J. Org. Chem.*, 56 (1991) 5159.
30. J.E. Baeckvall, R.L. Chowdhury and U. Karlsson, *J. Chem. Soc., Chem. Commun.*, (1991) 473.
31. A. Behr and K. Eusterwiemann, *J. Organomet. Chem.*, 403 (1991) 215.
32. D.J. Irvine, S.A. Preston, D.J. Cole-Hamilton and J.C. Barnes, *J. Chem. Soc., Dalton Trans.*, (1991) 2413.
33. W.-H. Leung, G. Wilkinson, B. Hussain-Bates and M.B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, (1991) 2791.

34. G.C. Walker, P.F. Barbara, S.K. Doorn, Y. Dong and J.T. Hupp, *J. Phys. Chem.*, 95 (1991) 5712.
35. C. Joachim, *Chem. Phys. Lett.*, 185 (1991) 569.
36. B. Chakravarty and S. Adhikari, *Transition Met. Chem. (London)*, 16 (1991) 58.
37. B. Chakravarty and S. Adhikari, *Indian J. Chem. Sect. A: Inorg., Bio-inorg. Phys. Theor. Anal. Chem.*, 30 (1991) 692.
38. M.T. Ashby, M.A. Khan and J. Halpern, *Organometallics*, 10 (1991) 2011.
39. K. Mashima, T. Hino and H. Takaya, *Tetrahedron Lett.*, 32 (1991) 3101.
40. D.F. Taber and L.J. Silverbery, *Tetrahedron Lett.*, 32 (1991) 4227.
41. M. Kitamura, M. Tokunaga, T. Ohkuma and R. Noyori, *Tetrahedron Lett.*, 32 (1991) 4163.
42. W.D. Lubell, M. Kitamura and R. Noyori, *Tetrahedron: Asymmetry*, 2 (1991) 543.
43. J.P. Genet, C. Pinel, S. Mallart, S. Juge, S. Thormbert and J.A. Laffitte, *Tetrahedron: Asymmetry*, 2 (1991) 555.
44. J.P. Genet, S. Mallart, C. Pivel, S. Juge and J.A. Laffitte, *Tetrahedron: Asymmetry*, 2 (1991) 43.
45. B. Heiser, E.A. Broger and R. Crameri, *Tetrahedron: Asymmetry*, 2 (1991) 51.
46. N. Yamamoto, M. Murata, T. Morimoto and K. Achiwa, *Chem. Pharm. Bull.*, 39 (1991)1085.
47. H. Nohira, H. Takaya and A. Miyashita, *Chem. Abstr* 115: 256381.
48. Y. Hara and K. Wada, *Chem. Lett.*, 4 (1991) 553.
49. M. Bressan, *Bull. Soc. Chim. Belg.*, 100 (1991) 677; [*Chem. Abstr.* 115: 231383m].
50. T. Arliguie, B. Chaudret, G. Chung and F. Dahan, *Organometallics*, 10 (1991) 2973.
51. T.M.M. Khan and M.S. Reddy, *Indian J. Chem. Sect. A: Inorg. Bio- inorg., Phys., Theor. Anal. Chem.*, 30A (1991) 278; [*Chem. Abstr.* 114: 220131f].
52. J.M. Grosselin, C. Mercier, G. Allmang and F. Grass, *Organometallics*, 10 (1991) 2126.
53. N.M.S. De Rezende, S.C. Martins, L.A. Marinho, J.A. Viana dos Santos, M. Tabak, J.R. Perussi and D.W. Franco, *Inorg. Chim. Acta*, 182 (1991) 87.
54. E.R.T. Tiekink, S.Tarick and R. Singh, *J. Crystallogr., Spectrosc. Res.*, 21 (1991) 205.
55. D. Sellmann, P. Lechner and M. Moll, *Z. Naturforsch. B: Chem. Sci.*, 46 (1991) 1459.
56. A. Muller, M. Ishaque Khan, E. Krickemeyer and H. Bogge, *Inorg. Chem.*, 30 (1991) 2040.
57. D. Riley and J. Lyon III, *J. Chem Soc., Dalton Trans.*, (1991) 157.
58. D. Sellmann, M. Geck, F. Knoch and M. Moll, *Inorg. Chim. Acta*, 186 (1991) 187.
59. D. Sellmann, H.P. Neuner, M. Moll and F. Knoch, *Z. Naturforsch., B: Chem. Sci.*, 46 (1991) 303.
60. M. Breysse, J. Afonso, M.Lacroix, J. L. Portefaixz and M. Vrinat, *Bull. Soc. Chim. Belg.*, 100 (1991) 923.
61. J. A. De Los Reyes, M. Vrinat, C. Geantet and M. Breysse, *Catal. Today*, 10 (1991) 645.
62. D. Sellmann, P. Lechner, F. Knoch and M. Moll, *Angew. Chem., Int. Ed. Engl.*, 30 (1991) 552.
63. H. E. Toma and K. Araki, *J. Coord. Chem.*, 24 (1991) 1.
64. H. E. Toma and D. de Olivena, *Polyhedron*, 10 (1991) 1699.
65. J. A. Crayston, D. C. Cupertino and T. J. Dines, *J. Chem. Soc., Dalton Trans.*, (1991) 1603.
66. B. C. Paul, U. C. Sarma abd R.K. Poddar, *Inorg. Chim. Acta*, 179 (1991) 17.
67. M. Henn, E. Alessio, G. Mestroni, M. Calligaris and W. M. Attia, *Inorg. Chim. Acta*, 187 (1991) 39.
68. S. Cauci, P. Viglino, G. Esposito and F. Quadrifoglio, *J. Inorg. Biochem.*, 43 (1991) 739.
69. F. Loseto, E. Alessio; G. Mestroni, G. Lacidogna, A. Nassi and D. Giordano, *Anticancer Res.*, 11 (1991) 1549.
70. H. Masui, A.P.B. Lever and P.R. Aubrun, *Inorg. Chem.*, 30 (1991) 2402.
71. P.G. Pickup and K.R. Seddon, *J. Chem. Soc., Dalton Trans.*, (1991) 489.
72. J.A. Roberts, *J. Electrochem. Soc.*, 138 (1991) 40C.
73. S. Roffia, R. Casadei, F. Paolucci, C. Paradisi, C.A. Bignozzi and F. Scandola, *J. Electroanal. Chem. Interfacial Electrochem.*, 302 (1991) 157.
74. R. Hage, J.G. Haasnoot, H.A. Nieuwenhuis, J Reedijk, R. Wang and J.G. Vos, *J. Chem. Soc., Dalton Trans.*, (1991) 3271.
75. S. Serroni, G. Denti, S. Campagna, M. Ciano and V. Balzani, *J. Chem. Soc., Chem. Commun.*, (1991) 994.
76. S. Campagna, G. Denti, S. Serroni, M. Ciano and V. Balzani, *Inorg. Chem.*, 30 (1991) 3728.
77. P.V. Kamat, K.R. Gopidas, T. Mukherjee, V. Joshi, D. Kotkar, V.S. Pathak and P.K. Ghosh, *J. Phys. Chem.*, 95 (1991) 10009.
78. K. Maruszewski, P.D. Strommen, K. Handrich and J.R. Kincaid, *Inorg. Chem.*, 30 (1991) 4579.
79. G. Juriga, M. Sattgast and M.E. McGuire, *Inorg. Chim. Acta*, 183 (1991) 39.

80. N.M. Alpatova, E.V. Ovsyannikova and L.I. Krishtalik, *Elektrokhimiya*, 27 (1991) 931; [*Chem. Abstr.* 115; 168932x].
81. R. Hage, J.G. Haasnoot, J. Reedijk, R. Wang and J.G. Vos, *Inorg. Chem.*, 30 (1991) 3263.
82. Q.G. Mulazzani, M. D'Angelantonio, N. Camaioni and M. Venturi, *J. Chem. Soc., Faraday Trans.*, 87 (1991) 2179.
83. S. Rajagopal and N. Vijaylakshmi, *Indian J. Chem., Sect. A: Inorg. Bio-inorg., Phys., Theor. Anal. Chem.*, 30A (1991) 604; [*Chem. Abstr.* 115; 113870v].
84. G.G. Sadler and N.R. Gordon, *Inorg. Chim. Acta*, 180 (1991) 271.
85. M. D'Angelantonio, Q. G. Mulazzani, M. Venturi, M. Ciano and M.Z. Hoffman, *J. Phys. Chem.*, 95 (1991) 5121.
86. E.H. Cutin and N.E. Katz, *Polyhedron*, 10 (1991) 653.
87. B. Steiger, E. Eichenberger and L. Walder, *Chimia*, 45 (1991) 32; [*Chem. Abstr.* 114: 256088m].
88. H. Yersin and D. Braun, *Chem. Phys. Lett.*, 179 (1991) 85.
89. T. Ohno, A. Yoshimura, D.R. Prasad and M.Z. Hoffman, *J. Phys. Chem.*, 95 (1991) 4723.
90. M. Venturi, Q.G. Mulazzani, M. D'Angelantonio, M. Ciano and M.Z. Hoffman, *Radiat. Phys. Chem.*, 37 (1991) 449.
91. S.N. Brune and D.R. Bobbit, *Talanta*, 38 (1991) 419.
92. J.B. Copper, T.M. Vess, W.A. Kalsbeck and D.W. Wertz, *Inorg. Chem.*, 30 (1991) 2286.
93. H. Sakaguchi, T. Nagamura and T. Matsuo, *J. Appl. Phys., Part 2*, 30 (1991) L377.
94. K. Tsukahara, Y. Wada and M. Kimura, *Bull. Chem. Soc. Jpn.*, 64 (1991) 908.
95. J. Hanzlik and A.M. Camus, *Collect. Czech. Chem. Commun.*, 56 (1991) 120; [*Chem. Abstr.* 114: 17381f].
96. S. Rajagopal, T. Rajendran and C. Srinivasan, *Indian J. Chem., Sect. A: Inorg., Bio-inorg., Phys. Theor. Anal. Chem.*, 30A (1991) 13.
97. A. Ben Altabet, S.B. Ribotta de Gallo, M.E. Folquer and N.E. Katz, *Inorg. Chim. Acta*, 188 (1991) 67.
98. R.A. Malone and D.F. Kelley, *J. Chem. Phys.*, 95 (1991) 8970.
99. M. Kaneko, S. Iwahata and T. Asakura, *J. Photochem. Photobiol.*, 61 (1991) 373.
100. A.K. Edwards and D.P. Rillema, *J. Electroanal. Chem. Interfacial Electrochem.*, 314 (1991) 165.
101. K.Bierig, R.J. Morgan, S. Tysoe, H.D. Gafuey, T.C. Strekas and B.A. David, *Inorg. Chem.*, 30 (1991) 4898.
102. K. Karlsson and A. Kirsh-De Mesmaeker, *J. Phys. Chem.*, 95 (1991) 10681.
103. L.F.Cooley, S.L. Larson, C.M. Elliott and D.F. Kelley, *J. Phys. Chem.*, 95 (1991) 10694.
104. A.I. Voloshin, G.L. Sharipov, V.P.Kazakov and G.A. Tolstikov, *Izv. Akad. Nauk SSSR, Ser. Khim*, 6 (1991) 1316; [*Chem. Abstr.* 115: 279187c].
105. S. Rajagopal, S. Rajendran , R. Suthakaran and C. Srinivasan, *Indian J. Chem., Sect. A: Inorg., Bio-inorg., Phys., Theor. Anal. Chem.*, 30A (1991) 765; [*Chem. Abstr.* 115: 255425c].
106. Q.G. Mulazzani, M. D'Angelantonio, M. Venturi and M.A.J. Rodgers, *J. Phys. Chem.*, 95 (1991) 9605.
107. D.P. Rillema, A.K. Edwards, S.C. Perine and A.L. Crumbliss, *Inorg. Chem.*, 30 (1991) 4421.
108. K. Matsui, K. Sasaki and N. Takahashi, *Langmuir*, 7 (1991) 2866.
109. E.J. Lee and M.S. Wrighton, *J. Am. Chem. Soc.*, 113 (1991) 8562.
110. J.C. Chambron and J. P. Sauvage, *Chem. Phys. Lett.*, 182 (1991) 603.
111. L. De cola, F. Barigelletti, V. Balzani, R. Hage, G. Jaap, J. Reedijk and J.G. Vos, *Chem. Phys. Lett.*, 178 (1991) 491.
112. G. Giuffrida, G. Guglidlmo, V. Ricevuto and S. Campagna, *Chem. Phys. Lett.*, 180 (1991) 78.
113. B.E. Buchanan, H. Hughes, J.H. Van Diemen, R. Hage, J.G. Haasnoot, J. Reedijk and J.G. Vos, *J. Chem. Soc., Chem. Commun.*, (1991) 300.
114. M. Georgopoulos and M.Z. Hoffman, *J. Phys. Chem.* 95 (1991) 7717.
115. K. Uchikura and M. Kirisawa, *Chem. Lett.*, 8 (1991) 1373.
116. S. Yamazaki-Nishida, A. Nagai, N. Mouri, S. Kawashima and M. Kinura, *Bull. Chem. Soc. Jpn.*, 64 (1991) 1866.
117. K.P. Balashev and A.M. Zimnyakov, *Koord. Khim.*, 17 (1991) 523; [*Chem. Abstr.* 115: 60579y].
118. M. Kato, Y. Ohonishi and M. Kimura, *Bull. Chem. Soc. Jpn.*, 64 (1991) 1401.
119. F. De Buyl, A. Kirsh-De Mesmaeker, A. Tossi and J.M. Kelly, *J. Photochem. Photobiol. A*, 60 (1991) 27.
120. G. Denti, S. Serroni, S. Campagna, V. Ricevuto and V. Balzani, *Inorg. Chim. Acta*, 182 (1991) 127.
121. C.A. Bignozzi, O. Bortolini and P. Traldi, *Rapid Commun. Mass Spectrom.*, 5 (1991) 600.

122. C.A. Bignozzi, R. Argazzi, C. Chiorboil, S. Roffia and F. Scandola, *Coord. Chem. Rev.*, 111 (1991) 261.
123. L. De Cola, F. Barigelletti, V. Balzani, P. Belser, A. Von Zelewasky, C. Seel, M. Frank and F. Voegtle, *Coord. Chem. Rev.*, 111 (1991) 255.
124. S.Van Wallendael and D.P. Rillema, *Coord. Chem. Rev.*, 111 (1991) 297.
125. V. Goulle, J.M. Lehn, B. Schoentjes and J.F. Schmitz, *Helv. Chim. Acta*, 74 (1991) 1471.
126. S.L. Mecklenburg, B.M. Peak, B.W. Erickson and T.J. Meyer, *J. Am. Chem. Soc.*, 113 (1991) 8540.
127. B.M. Peak, G.T. Ross, S.W. Edwards, G.J. Meyer, T.J. Meyer and B.W. Erickson, *Int. J. Pept. Protein Res.*, 38 (1991) 114.
128. E. Lifshitz, R. Clement, L.C. Yu-Hallada and A.H. Francis, *J. Phys. Chem. Solids*, 52 (1991) 1081.
129. T. Nakato, T. Ise, Y. Sugahara, K. Kurodo and C. Kato, *Mater. Res. Bull.*, 26 (1991) 309.
130. J. Rabani, M. Kaneko and A. Kira, *Langmuir*, 7 (1991) 941.
131. R. Ramaraj, A. Kira and M. Kaneko, *J. Photochem. Photobiol., A*, 56 (1991) 287.
132. M.S. Barrie, J.A. Delaire and M. Kaneko, *New J. Chem.* 15 (1991) 65.
133. H. Sakaguchi, T. Nagamura and T. Matsuo, *Appl. Organomet. Chem.*, 5 (1991) 257.
134. T. Kondo, M. Yanagisawa and M. Fujijira, *Electrochim. Acta*, 36 (1991) 1793.
135. J. Ochmanska and P.G. Pickup, *Can. J. Chem.*, 69 (1991) 653.
136. C.J. Miller and A.J. Bard, *Anal. Chem.*, 63 (1991) 1707.
137. S. Gould, G.F. Strouse, T.J. Meyer and B.P. Patrick, *Inorg. Chem.*, 30 (1991) 2942.
138. C.J. Miller, P. McCord and A.J. Bard, *Langmuir*, 7 (1991) 2781.
139. O. Haas, J. Rudnicki, F.R. McLarnon and E.J. Cairns, *J. Chem. Soc., Faraday Trans.*, 87 (1991) 939.
140. D. Leech, R.J. Forster, M.R. Smyth and J.G. Vos, *J. Mater. Chem.*, 1 (1991) 629.
141. T. Miyashita, H. Saito and M. Matsuda, *Chem. Lett.*, 5 (1991) 859.
142. X. Hua and A. Von Zelewsky, *Inorg. Chem.*, 30 (1991) 3796.
143. A.D. Baker, R.J. Morgan and T.C. Strekas, *J. Am. Chem. Soc.*, 113 (1991) 1411.
144. D. Mallick and G.-S. De, *Transition Met. Chem. (London)*, 16 (1991) 289.
145. M. Taniguchi, A. Yamagishi and T. Iwamoto, *Inorg. Chem.*, 30 (1991) 2462.
146. H.D. Burrows, P.J.S.C. Eliseu, M.H. Gil and R.M.S. Freire, *J. Photochem. Photobiol., A*, 59 (1991) 81.
147. T. Miyashita, Y. Hasegawa and M. Matsuda, *J. Phys. Chem.*, 95 (1991) 9403.
148. T. Miyashita, Y. Hasegawa and M. Matsyda, *Langmuir*, 7 (1991) 1491.
149. K. Iwai, Y. Uesugi, T. Sekabe, C. Hazama and F. Takemura, *Polym. J. (Tokyo)*, 23 (1991) 757.
150. A.E. Friedman, C.V. Kumar, N.J. Turro and J.K.Barton, *Nucleic Acids Res.*, 19 (1991) 2595.
151. I.S. Haworth, A.H. Elcock, J. Freeman, A. Rodger and W.G. Richards, *J. Bimol. Struct. Dyn.*, 9 (1991) 23.
152. G. Orellana, A. Kirsch-De Mesmaeker, J.K. Barton and N.J. Turro, *Photochem. Photobiol.*, 54 (1991) 499.
153. I.S. Haworth, A.H. Elcock, A. Rodger and W.G. Richards, *J. Bimol. Struct. Dyn.*, 9 (1991) 553.
154. A.S. Goldstein and R.S. Drago, *J. Chem. Soc., Chem. Commun.*, (1991) 21.
155. D.L. Carlson and W.R.Jr., Murphy, *Inorg. Chim. Acta*, 181 (1991) 61.
156. A. Atfah, A.H. Tuhl and T.S. Akasheh, *Polyhedron*, 10 (1991) 1485.
157. L.A. Pavanin, Z. Novais da Rocha, E. Giesbrecht and E. Tfouni, *Inorg. Chem.*, 30 (1991) 2185.
158. A.J. Downard, G.E. Honey and P.J. Steel, *Inorg. Chem.*, 30 (1991) 3733.
159. I. Audo, H. Fujimoto, K. Nakayama, K. Ujimoto and H. Kurihara, *Polyhedron*, 10 (1991) 1139.
160. H. Sun, G. Neshvad and M.Z. Hoffman, *Mol. Cryst. Liq. Cryst.*, 194 (1991) 141.
161. M. Haga, T. Auo, K. Kano and S. Yamabe, *Inorg. Chem.*, 30 (1991) 3843.
162. T. Ohno, K. Nozaki, N. Ikeda and M. Haga, *Adv. Chem. Ser.*, 228 (1991) 215.
163. S. Yamazaki-Nishida, Y. Harima and K. Yamashita, *J. Chem. Soc. Dalton Trans.*, (1991) 3401.
164. S. Yamazaki-Nishida and M. Kimura, *Bull. Chem. Soc. Jpn.*, 64 (1991) 1840.
165. D.H. Oh, M. Sano and S.G. Boxer, *J. Am. Chem. Soc.*, 113 (1991) 6880.
166. M.D. Todd, Y. Dang and J.T. Hupp, *Inorg. Chem.*, 30 (1991) 4685.
167. J.P. Collin, S. Guillerez, J.-P. Sauvage, F. Barigelletti, L. De Cola, L. Flamigni and V. Balzani, *Inorg. Chem.*, 30 (1991) 4230.
168. J.-P. Sauvage and M. Ward, *Inorg. Chem.*, 30 (1991) 3869.
169. E. Amouyal, M. Mouallem-Bahout and G. Calzaferri, *C.R. Acad. Sci. Ser. II*, 313 (1991) 1129; [*Chem. Abstr.* 116: 71043r].

170. E. Amouyal, M. Mouallem-Bahout and G. Calzaferri, *J. Phys. Chem.*, 95 (1991) 7641.
171. J.P. Collin, A. Deronzier and M. Essakalli, *J. Phys. Chem.*, 95 (1991) 5906.
172. K. Araki, C.-F. Shu and F.C. Anson, *Inorg. Chem.*, 30 (1991) 3043.
173. S. Chirayil, V. Hegde, Y. Jahng and R.P. Thummel, *Inorg. Chem.*, 30 (1991) 2821.
174. E.C. Constable, R.P.G. Henney and D.A. Tocher, *J. Chem. Soc., Dalton Trans.*, (1991) 2335.
175. J.E.B. Johnson, C. De Groff and R.R. Ruminski, *Inorg. Chim. Acta*, 187 (1991) 73.
176. A.K. Deb, M. Kakoti and S. Goswami, *J. Chem. Soc., Dalton Trans.*, (1991) 3249.
177. C.-K.Li, W.-T. Tang, C.-M. Che, K.-Y. Wong, R.-J. Wong and T.C.W. Mak, *J. Chem. Soc., Dalton Trans.*, (1991) 1909.
178. M.S. Islam, M.A.L. Kabir and M.A. Ali, *Pak. J. Sci, Ind. Res.*, 34 (1991) 7; [*Chem. Abstr.* 115: 246048a].
179. W.S. Sheldrick and R. Exner, *Inorg. Chim. Acta*, 184 (1991) 119.
180. E. Holler, W. Schaller and B. Keppler, *Arzneim.-Forsch.*, 41 (1991) 1065; [*Chem. Abstr.* 115: 270152e].
181. F. Millett and B. Durham, *Met. Ions Biol. Syst.*, 27 (1991) 223.
182. M. Ke, C. Sishta, B.R. James, D. Dolphin, J.W. Sparapany and J.A. Ibers, *Inorg. Chem.*, 30 (1991) 4766.
183. P. Le Maux, H. Bahri and G. Simonneaux, *J. Chem. Soc., Chem. Commun.*, (1991) 1350.
184. D. Markovitsi, M. Hanack and P. Vermehren, *J. Chem. Soc., Faraday Trans.*, 87 (1991) 455.
185. M. Hanack, A. Lange and R. Grosshans, *Synth. Met.*, 45 (1991) 59.
186. M. Hanack and Y.-G. Kang, *Chem. Ber.*, 124 (1991) 1607.
187. M, Hanack and P. Vermehren, *Chem. Ber.*, 124 (1991) 1733.
188. G. Tarrago, S. El Kadiri, C. Marzin and C. Coquelet, *New J. Chem.*, 15 (1991) 677.
189. C.-M. Che, W.-T. Tang, K.-Y. Wong and C.-K. Li, *J. Chem. Soc., Dalton Trans.*, (1991) 3277.
190. M.M.T. Khan, R.I. Kursehy and N.H. Khan, *Tetrahedron: Asymmetry*, 2 (1991) 1015.
191. M.M.T. Khan, R.I. Kureshy and N.H. Khan, *Inorg. Chim. Acta.*, 181 (1991) 119.
192. G.D. Lei and L. Kevan, *J. Phys. Chem.*, 95 (1991) 4506.
193. R. Ramaraj, M. Kaneko and A. Kira, *Bull. Chem. Soc. Jpn.*, 64 (1991) 1028.
194. T. Okajima, T. Ohsaka and N. Oyama, *J. Electroanal. Chem. Interfacial Electrochem.*, 315 (1991) 175.
195. T.W. Hambley, P. Keyte, P.A. Lay and M.N. Paddon-Row, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 147 (1991) 941.
196. M.J. Therien, B.E. Bowler, M.A. Selman, H.B. Gray, I.J. Chang and J.R. Winkler, *Adv. Chem. Ser.*, (1991) 228.
197. C. Shi and F.C. Anson, *J. Am. Chem. Soc.*, 113 (1991) 8564.
198. N.N. Rao and M.A. Rao, *Indian J. Chem, Sect. A: Inorg., Bio-inorg., Phys., Theor. Anal. Chem.*, 30A (1991) 620; [*Chem. Abstr.* 115:135305s].
199. N.V. Ivanova, V.I. Baranovskii, O.V. Sizova and A.B. Nikol'skii, *Koord. Khim.*, 17 (1991) 273 [*Chem. Abstr.* 115: 60550g].
200. K.K. Pandey, *J. Coord. Chem.*, 22 (1991) 307.
201. E. Miki, K. Harada, Y. Kamata, M. Umehara, K. Mizumachi, T. Ishimori, M. Nakahara, M. Tanaka and T. Nagai, *Polyhedron*, 10 (1991) 583.
202. A.A. Chevalier, L.A. Gentil and J.A. Olabe, *J. Chem. Soc., Dalton Trans.*, (1991) 1959.
203. M. Onishi, *Bull. Chem. Soc. Jpn.*, 64 (1991) 3039.
204. A.K. Deb and S. Goswami, *Polyhedron*, 10 (1991) 1799.
205. M.A. Fedotov, *Koord. Khim.*, 17 (1991) 103; [*Chem. Abstr.* 114: 177237f].
206. C.-M. Che, C. Ho and T.-C. Lau, *J. Chem. Soc., Dalton Trans.*, (1991) 1259.
207. C.-M. Che, W.-H. Leung, C.-K. Li and C.-K. Poon, *J. Chem. Soc., Dalton Trans.*, (1991) 379.
208. C.-M. Che, C. Ho and T.-C. Lau, *J. Chem. Soc., Dalton Trans.*, (1991) 1901.
209. C.-M. Che, K.-Y. Wong, W.-O. Lee and F.C. Anson, *J. Electroanal. Chem. Interfacial Electrochem.*, 309 (1991) 303.
210. W.P. Griffith and J.M. Jolliffe, *Stud. Surf. Sci. Catal.*, (1991) 66.
211. H. Nagao, M. Shibayama, Y. Kitanaka, F.S. Howell, K. Shimizu, M. Masako and H. Kakihana, *Inorg. Chim. Acta*, 185 (1991) 75.
212. K. Satoh, H. Kuroda, H. Nagao, K. Matsubara, F.S. Howell, M. Mukaida and H. Kakihana, *Chem. Lett.*, 3 (1991) 529.
213. M.M.T. Khan, M.A. Moiz, S.D. Bhatt, R.R. Merchant and O. Chatterjee, *J. Mol. Catal.*, 67 (1991) 1.
214. M.M.T. Khan, R.R. Merchant and D. Chatterjee, *J. Mol. Catal.*, 66 (1991) 23.
215. M.M.T. Khan and R.S. Shukla, *J. Mol. Catal.*, 70 (1991) 129.
216. M.M.T. Khan, D. Chatterjee and R.S. Shukla, *J. Mol. Catal.*, 69 (1991) 33.

217. M.M.T. Khan, D. Chatterjee, S.D. Bhatt, H.C. Bajaj and S.A. Mirza, *React. Kinet. Catal. Lett.*, 44 (1991) 505.
218. M.M.T. Khan, D. Chatterjee, S.S. Kumar, R.R. Merchant and K.N. Bhatt, *J. Mol. Catal.*, 67 (1991) 317.
219. M.M. Khan, *Stud. Surf. Sci. Catal.*, 66 (1991) 31.
220. M.M. Khan, D. Catterjee, R.R. Merchant, A. Bhatt and S.S. Kumar, *J. Mol. Catal.*, 66 (1991) 289.
221. W.S. Bigham and P.A. Shapley, *Inorg. Chem.*, 30 (1991) 4093.
222. A. Patel and D.T. Richens, *Inorg. Chem.*, 30 (1991) 3789.
223. W.K. Seok, *Hwahak Kwa Kongop Ui Chinbo*, 31 (1991) 154; [*Chem. Abstr.* 115: 125456c].
224. A. Syamala and A. R. Chakravarty, *Inorg. Chem.*, 30 (1991) 4699.
225. Y. Sasaki, M. Suzuki, A. Nagasawa, A. Tokiwa, M. Ebihara and T. Ito, *Inorg Chem.*, 30 (1991) 4903.
226. T. Ochi, Y. Sasaki, T. Tamaguchi and T. Ito, *Chem. Lett.*, 11 (1991) 2019.
227. M.C. Barral, R. Jimenez-Aparicio, E.C. Royer, F.A. Urbanos, A. Monge and C. Ruiz-Valero, *Polyhedron*, 10 (1991) 113.
228. B.K. Das and A.R. Chakravarty, *Polyhedron*, 10 (1991) 491.
229. F.D. Cukiernik, P. Makdivi, A. M. Girond-Godquin, J.C. Machon, M. Ibn-Elhaj, D. Guillon and A. Skoulios, *Liq. Cryst.*, 9 (1991) 903.
230. T. Hasegawa, T.-C. Lau, H. Taube and W.P. Schaefer, *Inorg. Chem.*, 30 (1991) 2921.
231. A.O. Oyetunji, O. Olubuyide, J.F. Ojo and J.E. Earley, *Polyhedron*, 10 (1991) 829.
232. M.C. Barral, R. Jimenez-Aparicio, E.C. Royer, M. Jose Sauceds and F.A.Urbanos, *J. Chem. Soc., Dalton Trans.*, (1991) 1609.
233. E. Lindner, R. Fawzi, W. Hiller, A. Carvill and M. Mc Cann, *Chem. Ber.*, 124 (1991) 2691.
234. A Patel, P. Leitch and P.T. Richen, *J. Chem. Soc., Dalton Trans.*, (1991) 1029.
235. S.C. Huckett, C.A. Arrington, C.J. Burns, D.L. Clark and B.I. Swanson, *Synth. Met.* 42 (1991) 2769.
236. D.J. Irvine, S.A. Preston, D.J. Cole-Hamilton and J.C. Barnes, *J. Chem. Soc., Dalton Trans.*, (1991) 2413.
237. M.M.T. Khan, N. N. Rao and D. Chatterjee, *J. Photochem. Photobiol., A*, 60 (1991) 311.
238. D. Chatterjee and A.K. Ghosh, *Transition Met. Chem. (London)*, 16 (1991) 481.
239. D. Chatterjee and A.K. Ghosh, *Transition Met. Chem. (London)*, 16 (1991) 484.
240. Y.S. Huang, B. Chaudret, J. Bellan and M.R. Mazieres, *Polyhedron*, 10 (1991) 2229.
241. F.R. Keene, P.J. Stephenson and E.R.T. Tiekink, *Inorg. Chim. Acta.*, 187 (1991) 217.
242. P.R. Auburn, E.S. Dodsworth, M. Haga, W. Liu, W.A. Nevin and A.B.P. Lever, *Inorg. Chem.*, 30 (1991) 3502.
243. V.K. Sharma, O.P. Pandey and S.K. Sengupta, *Synth. React. Inorg. Met.-Org. Chem.*, 21 (1991) 793.
244. S. Bruni, F. Cariati, A. Dei and D. Gatteschi, *Inorg. Chim. Acta*, 186 (1991) 157.
245. B. Chakra varty and S. Adhikari, *Transition Met. Chem. (London)*, 16 (1991) 586.
246. S. Bhattacharya and C. Pierpont, *Inorg. Chem.*, 30 (1991) 1511.