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Mono and Binuclear Complexes of Heavy Metals with Diamine Derivatives of Triketones

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Abstract

A number of mono and binuclear complexes of Ru(II), Ru(III), Pd(II) and Cu(II) with Schiff base ligands *N,N'*-bis(benzoylacetylacetone) ethylenediamine ($H_4(BAA)_2en$) and *N,N'*-bis(pyvolylacetylacetone)ethylenediamine ($H_4(PAA)_2en$) have been synthesized and characterized by elemental analysis, magnetic properties, absorption and vibrational spectra. The complexes $[Ru(H_2(BAA)_2en)(PPh_3)_2]$-$[Ru(H_2(BAA)_2en)(PPh_3)Cl]$ and $[Ru(H_2(PAA)_2en)$-$Cl\cdot H_2O]\cdot H_2O$ all have an octahedral environment around the metal ions, Schiff bases behaving as tetradentate N_2O_2 donors and two ambidentate ligands occupying *trans* positions. The two binuclear species, $[Pd_2(BAA)_2en]$ and $[PdCu(BAA)_2en]$ have a square planar arrangement of ligands around the metal ions.

Introduction

The ethylenediamine derivatives of polyketones particularly those of triketones are an interesting and versatile class of ligands. The Schiff bases have been termed as compartmental ligands since these are capable of coordinating with two metal atoms (different or alike) in successive steps [1]. The complexation studies of such ligands have mostly been reported with 3d transition metals [2, 3]. However, a few complexes of these Schiff bases with heavier metals such as Pd^{2+} and uranyl (UO_2^{2+}) ion have also been reported [4–6]. These multinuclear complexes present some interesting problems such as magnetic superexchange, mixed valence metal interactions, reactivity and existence of photochemically accessible excited states for investigations. The complexes of heavier elements with such ligands are specially suited for photochemical reactivity studies. Therefore it was considered appropriate to synthesize a series of mono and binuclear complexes of heavy metals such as Ru(II), Ru(III), and Pd(II) with *N,N'*-bis(benzoylacetylacetone)ethylenediamine or *N,N'*-bis(pyvolylacetylacetone)ethylenediamine and characterize them.

We wish to report the synthesis of three mononuclear ruthenium and two binuclear (Pd_2, Pd–Cu) complexes of ethylenediamine derivatives of triketones. These complexes have been characterized by elemental analysis, magnetic and spectral studies.

Experimental

Materials and Ligand Synthesis

The ligands benzoylacetylacetone (H_2BAA) and pyvolylacetylacetone (H_2PAA) were prepared by the method of Miles *et al.* [7]. The Schiff bases, *N,N'*-bis(benzoylacetylacetone)ethylenediamine ($H_4(BAA)_2en$) and *N,N'*-bis(pyvolylacetylacetone)ethylenediamine ($H_4(PAA)_2en$) were prepared from respective triketones by an earlier reported method [8].

The complexes $Pd(H_2(BAA)_2en)$, $Ru(PPh_3)_3Cl_2$ and $Ru_2(OAc)_4Cl$ were synthesized by literature methods [6, 9, 10].

Mononuclear Chelates

N,N'-Bis(benzoylacetylacetonato)ethylenediaminebis(triphenylphosphine)ruthenium(II) [$Ru(H_2(BAA)_2en(PPh_3)_2$]

0.432 g (1 mmol) of the ligand $H_4(BAA)_2en$ was suspended in 300 ml of ethanol (95%). The mixture was stirred, brought to boiling, a slight excess (0.22 g, 2 mmol) of Et_3N was added and heating continued. When most of the ligand was dissolved, 0.95 g (1 mmol) of solid $Ru(PPh_3)_3Cl_2$ was added to the solution and stirring continued. The mixture was refluxed for nearly 3 h and then filtered while hot. The filtrate was concentrated under reduced pressure to nearly 100 ml and left overnight. The red precipitate formed was removed and washed with water to remove Et_3NHCl. The product was

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recrystallized from ethanol. Yield 56%. *Anal.* Calc. for $Ru(C_{26}H_{26}N_2O_4)(C_{18}H_{15}P)_2$: C, 70.52; H, 5.30; N, 2.65; P. 5.87. Found: C, 70.36; H, 5.46; N, 2.55; P, 5.76%.

Chloro-N,N'-bis(benzoylacetylacetonato)ethylenediamine-triphenylphosphineruthenium(III) [Ru-(H_2(BAA)$_2$en)(PPh$_3$)Cl]

Equimolar quantities of $H_4(BAA)_2en$ and $Ru(PPh_3)_3Cl_2$ (1 mmol) were reacted in 25 ml of benzene. The solution was brought to boiling and a slight excess of Et_3N (2.1 mmol) was added. The resulting mixture was refluxed for 5 h and filtered. About 100 ml of methanol was added to the filtrate and refluxing continued for another 4 h. A dark red precipitate formed upon cooling to room temperature, was separated, washed with portions of ethanol, acetone and dried. This red complex analyzed for $Ru(H_2(BAA)_2en)(PPh_3)_2 \cdot HCl$. *Anal.* Calc. for $Ru(C_{26}H_{26}N_2O_4)(C_{18}H_{15}P)_2 \cdot HCl$: C, 68.16; H, 5.22; N, 2.56; P, 5.67; Cl, 3.25; Ru, 9.26. Found: C, 67.76; H, 5.22; N, 2.45; P, 5.38; Cl, 3.00; Ru, 9.57%.

The red compound was dissolved in 25 ml of dry benzene and slowly evaporated in an open beaker. The residue was again dissolved in benzene and evaporated at room temperature. This process was repeated four times till the red complex was completely converted into a green product. The green complex was recrystallized from benzene. *Anal.* Calc. for $Ru(C_{26}H_{26}N_2O_4)(C_{18}H_{15}P)Cl$: C, 63.73; H, 4.95; N, 3.38; P, 3.74; Cl, 4.28. Found: C, 63.62; H, 4.9; N, 3.24; P, 4.35; Cl, 4.75%.

Chloro-N,N'-bis(pyvolylacetylacetonato)ethylenediamine-aquoruthenium(III) hydrate [Ru(H_2(PAA)$_2$en)Cl(H_2O)]H_2O

Equimolar quantities of $H_4(PAA)_2en$ and $Ru_2(OAc)_4Cl$ (1 mmol) were placed in a three neck 500 ml reaction flask equipped with nitrogen inlet, condensor and a dropping funnel. About 300 ml of methanol was added and the mixture slowly brought to boiling under nitrogen atmosphere. A clear red solution was obtained in a short time. The solution was refluxed with stirring for 60 h when it was changed to greenish black. The solution was cooled to room temperature and filtered. The filtrate was evaporated to dryness at room temperature. The dark residue was dissolved in $CHCl_3$ and loaded on a silica gel column saturated with $CHCl_3$. The column was first washed with chloroform and then eluted with methanol. The complex slowly moved down the column as a dark band and was collected. A brown black solid was obtained after removal of the solvent. Yield 80%. *Anal.* Calc. for $[Ru(C_{22}H_{34}N_2O_4)Cl \cdot H_2O] \cdot H_2O$: C, 46.93; H, 6.75; N, 4.98; Cl, 6.30; Ru, 17.97. Found: C, 46.45; H, 6.10; N, 4.58; Cl, 6.15; Ru, 17.96%.

Binuclear Chelates

N,N'-Bis(benzoylacetylacetonato)ethylenediamine-dipalladium(II) acetic acid hydrate [Pd$_2$(BAA)$_2$-en]$CH_3COOH \cdot H_2O$

The mononuclear complex $Pd(H_2(BAA)_2en)$ (0.536 g, 1 mmol) was dissolved in 250 ml acetone under reflux conditions. An equimolar quantity of $Pd(OAc)_2$ (0.244 g) dissolved in a minimum volume of acetone water (2:1) was slowly added to a boiling solution of the complex. The solution turned to red. It was refluxed for 6 h during which time an orange precipitate (small amount) was formed. The precipitate was separated and rejected. The filtrate was allowed to concentrate at room temperature when a reddish orange complex separated. This was filtered, washed with ether and dried in air. Yield 62%. *Anal.* Calc. for $Pd_2(C_{26}H_{24}N_2O_4) \cdot CH_3COOH \cdot H_2O$: C, 46.74; H, 4.17; N, 3.90; Pd, 29.60. Found: C, 46.85; H, 4.09; N, 3.98; Pd, 29.53%.

N,N'-Bis(benzoylacetylacetonato)ethylenediamine-palladium(II) copper(II) [PdCu(BAA)$_2$en]

$Pd(H_2(BAA)_2en)$ (0.536 g, 1 mmol) was suspended in 150 ml of methanol and brought to boiling under reflux and constant stirring for an hour. A methanol solution of $Cu(OAc)_2 \cdot 4H_2O$ (1 mmol) was slowly added to the boiling suspension of the mononuclear complex. The reaction mixture was refluxed with stirring for nearly 20 h, then slowly cooled to room temperature and a greenish yellow product was removed. It was further purified by boiling with three 400 ml portions of acetone and filtering the solvent away from the solid. Yield 85%. *Anal.* Calc. for $PdCu(C_{26}H_{24}N_2O_4)$: C, 52.18; H, 4.01; N, 4.68; Pd, 17.79; Cu, 10.62. Found: C, 52.83; H, 4.21; N, 4.77; Pd, 17.44; Cu, 10.03%.

Physical Measurements

The elemental analyses were obtained from Galbraith Laboratories, Inc. Knoxville, TN. Melting points were taken with a Thomas-Hoover Unimelt by capillary method and reported uncorrected. Infrared spectra of the solid compounds were recorded on a Perkin-Elmer model 283 B spectrophotometer using KBr discs. Each spectrum was calibrated with polystyrene. The solution spectra were recorded on Carry model 17B spectrophotometer using a matched pair of 1 cm quartz cuvettes. The concentrations of complexes in THF or chloroform solution were of the order of 10^{-3} M. Magnetic measurements were made on solid complexes using Faraday's method. Crystalline $Hg[Co(SCN)_4]$ was used as a calibrant. The molecular susceptibility values were corrected for diamagnetic effects of various atoms and bonds.

TABLE 1. Colour, Decomposition Temperature, Solubility, Magnetic Moments and Absorption Spectra of Mono and Binuclear Chelates

Complex	Colour	Decomposition/ melting point (°C)	Magnetic moments (BM)	Absorption spectra (nm)	Solubility[a]
$[Ru(H_2(BAA)_2en)(PPh_3)_2]$	dark red	210	diamagnetic	460(sh) 370 290	EtOH
$[Ru(H_2(BAA)_2en)PPh_3 \cdot Cl]$	dark green	180	1.91		benzene
$[Ru(H_2(PAA)_2en)Cl \cdot H_2O] \cdot H_2O$	dark brown	190	2.27 (295 K) 2.31 (77 K)		MeOH, $CHCl_3$
$[Pd_2(BAA)_2en)]CH_3CO_2H \cdot H_2O$	orange, micro-crystalline	213	diamagnetic	400 295	acetone (sp) $CHCl_3$ (sp)
$[PdCu(BAA)_2en)]$	greenish yellow powder	243	1.89 (295 K) 1.84 (77 K)		acetone (sp) $CHCl_3$ (sp)

[a] sp = sparingly soluble.

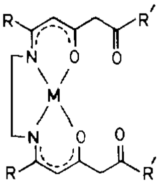
Results and Discussion

Three new mononuclear and two binuclear complexes of ruthenium(II), ruthenium(III), palladium(II) and copper(II) with ethylenediamine derivatives of two triketones H_2BAA and H_2PAA have been synthesized. These compounds have been characterized by their elemental analyses, magnetic measurements, infrared and solution spectra. The elemental analyses fit well to the proposed formulae of these compounds. Their characteristic colours, decomposition points, solubility, magnetic and spectral data are reproduced in Table 1.

The complex $[Ru(H_2(BAA)_2en)(PPh_3)_2]$ was synthesized from two different solvents and one of these preparations is associated with a molecule of hydrogen chloride as solvent of crystallization. Both compounds have the same infrared and absorption spectra. The dark red $[Ru(H_2(BAA)_2en)(PPh_3)_2] \cdot HCl$ is slowly oxidized in air to a green Ru(III) complex and chloride ion takes the position of the PPh_3(TPP) ligand in its coordination sphere. Similar behaviour has already been observed for another Ru(II) complex by Murray *et al.* [11], who reported that $Ru(Salen)(PPh_3)_2$ in methanol solution instantaneously converted to a green oxidized form. However, our studies reveal that air oxidation of this complex occurs slowly and complete oxidation is achieved only after repeating the evaporation process several times.

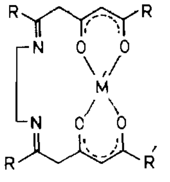
The Ru(II) complexes are diamagnetic while those of Ru(III) are paramagnetic with magnetic moments between 1.91–2.27 BM. These values are higher than expected for systems with an unpaired electron. The higher values of magnetic moments in these systems may be due to a contribution from orbital angular momentum which becomes appreciable in 4d and 5d transition elements.

A number of mononuclear complexes of other metal ions such as Cu(II), Ni(II) and Pd(II) with these ligands have been reported. The metal ions in such systems have a square planar arrangement of N_2O_2 donor atoms of ligands (**I**). Such complexes have two more oxygen donor atoms in appropriate positions to accommodate a second metal ion forming binuclear species. In certain cases, metals prefer to coordinate with four oxygen donor atoms of the ligand leaving a vacant N_2O_2 site on the ethylenediamine side of the molecule (**II**). The O_2–O_2 bonding is observed for complexes of VO^{2+}, Cu^{2+}, and UO_2^{2+} ions with such ligands while both types of mononuclear complexes have been isolated for $[Pd(H_2(BAA)_2en)]$.



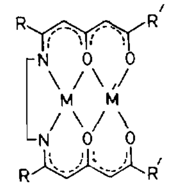
$M = Ni^{2+}, Cu^{2+}, Pd^{2+}$

I



$M' = VO^{2+}, Cu^{2+}, UO_2^{2+}$

II



$M' = VO^{2+}, Fe^{2+}, Co^{2+}, Cu^{2+}, UO_2^{2+}$, etc

III

The prominent infrared absorption bands assigned to various vibrational modes for these complexes are reproduced in Table 2. The general features of spectra of these mononuclear chelates are very much similar to those of the ligands and quite different

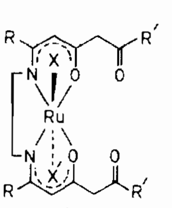
TABLE 2. Prominent Infrared Bands (cm^{-1}, KBr Disc) for Mono and Binuclear Complexes of Schiff Base–Triketone Ligands

Complex	Stretching OH due to H_2O	Asymmetric stretching CH_3 due to t-butyl	$\nu(C=O)$ uncoordinated	$\nu(\mathrm{C}\overset{---}{-}\mathrm{O})$	$\nu(\mathrm{C}\overset{---}{-}\mathrm{O})$ + $\nu(\mathrm{C}\overset{---}{-}\mathrm{C})$	$\nu(\mathrm{C}\overset{---}{-}\mathrm{N})$	$\nu(C=C)$	$\nu(P-\phi)$	Aromatic C–H bend	Others
$[Ru(H_2(BAA)_2en)(PPh_3)_2]$			1650	1610	1552	1455	1110	1090	780	3020, 1435, 745, 700 due to phenyl group in TPP
$[Ru(H_2(BAA)_2en)\cdot PPh_3Cl]$			1645	1600	1560	1450	1100	1080	785	3010, 1440, 750, 700 due to phenyl group in TPP
$[RuH_2(PAA)_2en)Cl\cdot H_2O]H_2O$	3400(b)	2960(t)	1670	1590	1557(w)	1500(b, m)	1070		780	
$[Pd_2(BAA)_2en]CH_3CO_2H\cdot H_2O$	3440(b)			1600	1555	1460	1110		780	
$[PdCu(BAA)_2en]$				1587	1575	1480	1052		780	

b = broad, m = medium, w = weak, t = triplet.

from those of binuclear species. One can easily identify the mono and binuclear complexes by comparing their infrared spectra. It is also possible to differentiate these N_2–O_2 and O_2–O_2 bonded mononuclear chelates from their infrared spectra. The N_2–O_2 bonded mononuclear complexes have two uncoordinated carbonyl groups which exhibit a strong and sharp band near 1700 cm^{-1}. This band either shifts to lower energy or completely disappears in O_2–O_2 bonded mononuclear or binuclear species. This carbonyl band is invariably observed near 1650–80 cm^{-1} in the IR spectra of Ru(II) and Ru(III) chelates, indicating uncoordinated carbonyl (–C=O) sites. The three strong bands in the regions 1455–1500, 1052–1110 and 3410–20 cm^{-1} may be assigned to stretching vibrations of ketoimine and N–H groups bonded to metal atoms. In addition, a number of bands observed at 3010, 1440, 750 and 700 cm^{-1} have been assigned to phenyl groups present in the coordinated TPP molecule. The P–ϕ stretching is observed at 1080–1090 cm^{-1}. The complex $[Ru(H_2(PAA)_2en)Cl\cdot H_2O]\cdot H_2O$ has an additional medium intensity triplet band at 2960 cm^{-1} due to the t-butyl group and a broad band at 3400 cm^{-1} indicative of coordinated water. These spectral studies indicate the ruthenium atoms in these mononuclear complexes are bonded through N_2O_2 donor atoms of the ligands.

In ruthenium complexes, the metal atom is usually surrounded by six donor atoms and maintains an octahedral geometry. This trend is retained in the present series of complexes as well. In these complexes the Schiff base multidentate ligands occupy four planar positions on the octahedron while two ambidentate ligands such as TPP, chloride or water occupy two *trans* positions as shown in **IV**. The Schiff base diamine still has two more uncoordinated oxygen atoms. It should be possible to incorporate another metal ion in the remaining donor sites of these mononuclear complexes as has been observed for analogous Ni(II) and Pd(II) chelates of this series.



1. X=X′ = TPP
2. X=TPP, X′=Cl
3. X=Cl, X′=H_2O

IV

The two binuclear chelates have been synthesized by interaction of metal acetates with mononuclear $[Pd(H_2(BAA)_2en)]$ in methanol. $[Pd_2(BAA)_2en)]$ can also be prepared by reacting 2 mol of $Pd(OAc)_2$

with 1 mol of $H_4(BAA)_2en$. These are insoluble in a number of organic solvents. At room temperature, $[Pd_2(BAA)_2en]$ is diamagnetic while $[PdCu(BAA)_2en]$ is paramagnetic with a magnetic moment of 1.89 BM which is slightly decreased to 1.84 BM at 77 K. A similar decrease in magnetic moment with temperature has been reported for an analogous compound $[NiCu(BAA)_2en]$ [3]. These values are explainable by assuming that the Pd(II) ion is coordinated in a square planar environment and should be diamagnetic. The paramagnetism in $[PdCu(BAA)_2en]$ may be arising from the Cu(II) ion also present in a square planar environment.

The infrared spectra of these two chelates are typical of binuclear complexes and comparable to that of other reported systems of this series. The carbonyl stretching vibrational bands present in the mononuclear precursor disappear upon coordination of a second metal atom.

These two metal ions (*i.e.* Pd(II) and Cu(II)) prefer to coordinate with four donor atoms in a square planar environment. It seems that both of the binuclear complexes have a square planar array of donor atoms around these metal ions as in **III**. $[Pd_2(BAA)_2en]$ is also associated with an acetic acid and a water molecule outside its coordination sphere.

The two analogous complexes $[NiH_2(BAA)_2en]$ and $[Pd(H_2(BAA)_2en)]$ greatly differ in their reactivity towards other bivalent metal ions. The complex $[Ni(H_2(BAA)_2)]$ readily accommodates a number of metals such as VO^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+} or UO_2^{2+} ions forming heterobinuclear species. On the other hand, attempts to incorporate a number of ions like VO^{2+}, Mn^{2+}, Co^{2+} or Ni^{2+} in $[Pd(H_2(BAA)_2en)]$ completely failed. However, this complex easily reacts with Cu^{2+}, UO_2^{2+} or Pd^{2+} ions to form binuclear species. The difference in reactivity of these two mononuclear species may be due to different ionic radii of the metal ions. It is interesting to note that Pd^{2+}, Mn^{2+} and U^{6+} have the same ionic radii (0.8 Å) yet $[Pd(H_2(BAA)en]$ reacts with Pd^{2+} and UO_2^{2+} ions forming binuclear species but not with Mn^{2+} ion. On the other hand Co^{2+}, Cu^{2+} (0.72 Å) and Ni^{2+} (0.69 Å) have nearly the same radii, considerably smaller than that of Pd^{2+} ion but Cu^{2+} reacts to form $[PdCu(BAA)_2en]$ while Co^{2+} and Ni^{2+} do not react. It seems that the radii of the metallic ions play a less important role in these binucleation reactions. There should be some other yet unknown factors responsible for metal addition in these systems. The reasons for the difference in reactivity of the two mononuclear complexes $[Ni(H_2(BAA)_2en]$ and $[Pd(H_2(BAA)_2en]$ are not well understood.

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