

Reactions of molybdenum and ruthenium carbonyls with some pyridylamine ligands

Ahmed A. Soliman*

Department of Chemistry, Faculty of Science, Cairo University, Giza, Egypt

Mohamed M. Khattab

Department of Chemistry, Faculty of Science, UAE University, Al-Ain, UAE

Ramadan M. Ramadan

Chemistry Department, Faculty of Science, Ain Shams University, Cairo, Egypt

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Abstract

The interaction of $\text{Mo}(\text{CO})_6$ and $\text{Ru}_3(\text{CO})_{12}$ with 2-aminoethylpyridine (aepy), 2-hydrazinopyridine (hzpy) and dipicolylamine (dpa) have been investigated. Molybdenum complexes were found to have either mono- or binuclear derivatives, $[\text{MoO}_2(\text{CO})_2(\text{aepy})]$ (1), $[\text{MoO}_2(\text{CO})_2(\text{hzpy})]$ (2), $[\text{Mo}_2\text{O}_6(\text{aepy})_2]$ (3), $[\text{Mo}_2\text{O}_6(\text{hzpy})_2]$ (4), and $[\text{Mo}_2\text{O}_4(\text{dpa})_2]$ (5), depending on the reactions conditions. Ruthenium complexes are shown to have a molecular formulae of a mononuclear species; $[\text{Ru}(\text{CO})_3(\text{aepy})]$ (6), $[\text{Ru}(\text{CO})_3(\text{hzpy})]$ (7) and $[\text{Ru}(\text{CO})_2(\text{dpa})]$ (8). The proposed structures of the complexes were elucidated using elemental analyses, i.r., u.v.–vis. and n.m.r. spectroscopy. The thermal stabilities of the reported complexes were also investigated using the t.g. technique.

Introduction

The coordination chemistry of numerous nitrogen donor ligands has been extensively studied and is mostly related to their relevance to biological systems [1]. Transition metal complexes of nitrogen-containing heterocyclic compounds such as pyridine, di- and poly-pyridine, azines and their derivatives are also of great interest due to their ability to undergo facile electrochemical processes. Furthermore, their abilities to absorb visible light to act as electron reservoirs are promising factors in their applications as photosensitizers [2–9]. On the other hand, transition metal carbonyl complexes are very interesting for their reactivity in homogeneous catalytic reactions such as hydrogenation, hydroformylation and carbonylation [9]. Moreover, metal carbonyl derivatives of nitrogen donor ligands are important routes to prepare interesting metal carbonyl complexes [10, 11].

Our interest in investigation of the reactions of $\text{Mo}(\text{CO})_6$ and $\text{Ru}_3(\text{CO})_{12}$ with several molecular designed nitrogen and oxygen donor ligands [12–17] has prompted us to investigate the reactions of these metal carbonyls with some pyridine derivatives; namely 2-(2-aminoethyl)-pyridine, 2-hydrazinopyridine and dipicolylamine (Scheme 1).

Experimental

Materials

$\text{Mo}(\text{CO})_6$, $\text{Ru}_3(\text{CO})_{12}$, 2-(2-aminoethyl)pyridine, 2-hydrazinopyridine and dipicolylamine were supplied by Aldrich. All solvents were of analytical grade and were purified by distillation before use.

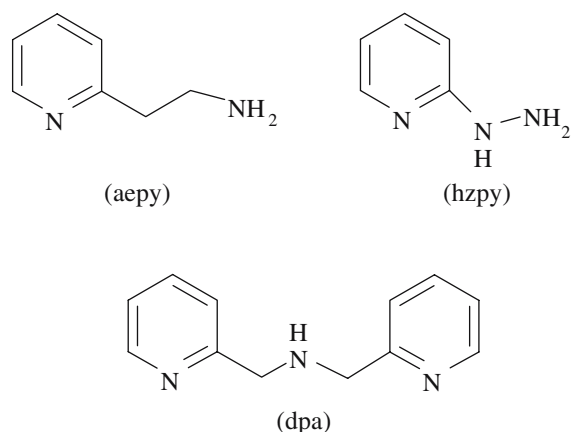
Measurements

Elemental analyses (CHN) were performed on Elemental Analyzer (Flash 1112 Analyzer, Electro Analytical). The i.r. measurements (KBr pellets) were carried out on a NEXUS 470 FT-IR spectrometer. The u.v.–vis. measurements were performed using a Cary 50 Conc spectrophotometer. ^1H -n.m.r. measurements were carried out on a Spectrospin-Bruker AC 200 MHz NMR Spectrometer. Samples were dissolved in DMSO using TMS as an internal reference. Thermal analyses of the complexes were carried out on a Shimadzu thermogravimetric analyzer TGA-50H under a nitrogen atmosphere with a heating rate of $10\text{ }^\circ\text{C min}^{-1}$.

Synthesis of $[\text{MoO}_2(\text{CO})_2(\text{hzpy})_2]$ and $[\text{MoO}_2(\text{CO})_2(\text{aepy})_2]$ complexes

A mixture of $\text{Mo}(\text{CO})_6$ (0.04 g, 0.16 mmol) and either 2-(2-aminoethyl)pyridine (0.04 g, 0.32 mmol) or 2-hydrazinopyridine (0.04 g, 0.32 mmol) in *ca.* 40 cm^3 benzene was degassed by bubbling nitrogen gas and

* Author for correspondence: E-mail: ahmedsoliman61@gmail.com



Scheme 1.

then heating the mixture to reflux for 8 h in a sealed tube. A dark brown solid residue was isolated. The reaction mixture was then cooled and the dark brown solid was separated by filtration. The residue was washed with hot benzene followed by petroleum ether and then recrystallized from hot ethanol. The complex was left to dry on a vacuum line for several hours.

Synthesis of [Mo₂O₆(hzpy)₂], [Mo₂O₆(aepy)₂] and [Mo₂O₄(dpa)₂] complexes

A mixture of Mo(CO)₆ (0.04 g, 0.16 mol) and either 2-(2-aminoethyl)pyridine (0.04 g, 0.32 mmol), 2-hydrazinopyridine (0.04 g, 0.32 mmol) or dipicolylamine (0.64 g, 0.32 mmol) in 30 cm³ dioxan was heated to reflux in air for 9 h. The reaction mixture was cooled and the resulting brown solid was isolated by filtration. The isolated brown complex was washed several times with dioxan and then recrystallized from DMSO. The complex was dried under vacuum for several hours.

Synthesis of [Ru(CO)₃(hzpy)], [Ru(CO)₃(aepy)] and [Ru(CO)₂(dpa)] complexes

Ru₃(CO)₁₂ (0.10 g, 0.16 mmol) and either 2-(2-aminoethyl)pyridine (0.04 g, 0.32 mmol), 2-hydrazinopyridine (0.04 g, 0.32 mmol) or dipicolylamine (0.64 g, 0.32 mmol) in benzene (*ca.* 40 cm³) were mixed, degassed by bubbling nitrogen gas and then heating the mixture to reflux for 8 h in a sealed tube. The reaction mixture was cooled where a brown residue was isolated, and then the solvent was evaporated under vacuum. The brown residue was washed with hot benzene followed by petroleum ether and then recrystallized from hot ethanol. The complex was left to dry on a vacuum line for several hours.

Results and discussion

I.r. and n.m.r. studies

Interaction of Mo(CO)₆ with the above-mentioned ligands (Scheme 1) resulted in the formation of two

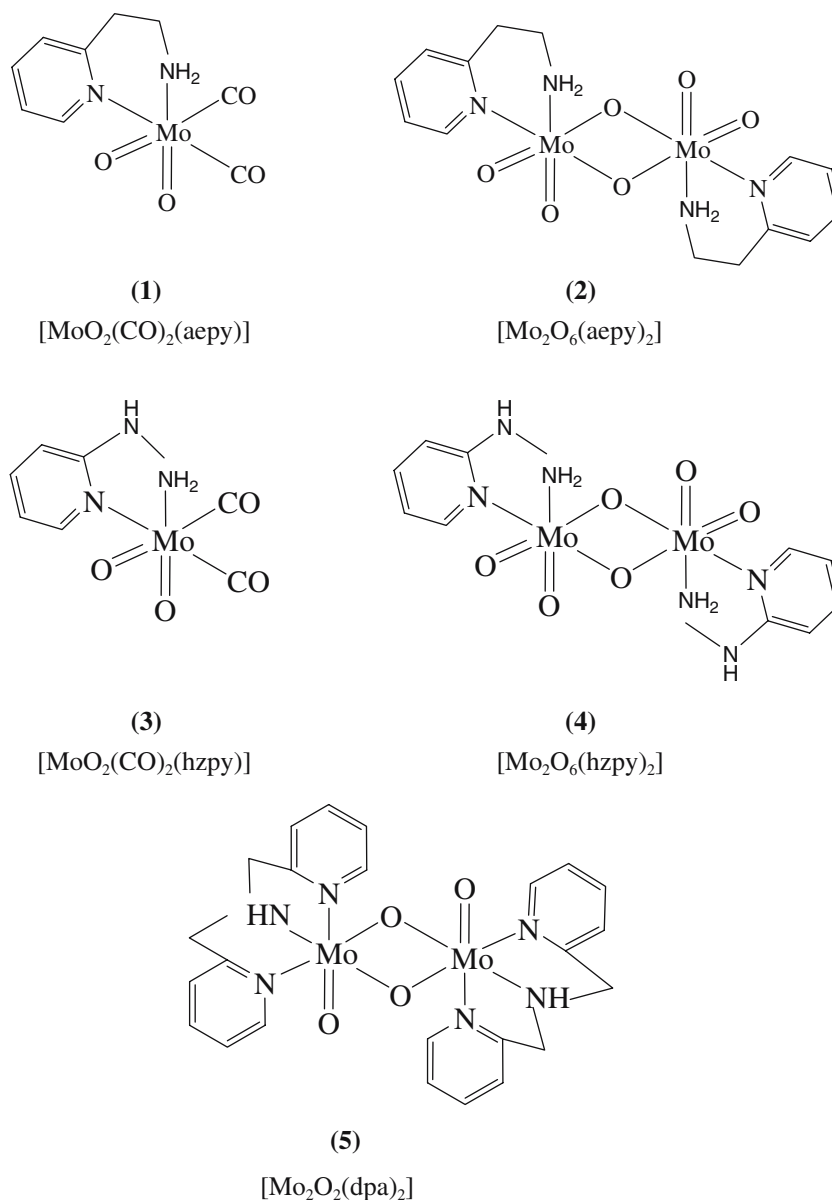
different types of complexes depending on the experimental conditions. When the reactions were carried out in benzene and in an inert atmosphere, the oxo carbonyl derivatives [MoO₂(CO)₂(aepy)] (1) and [MoO₂(CO)₂(hzpy)] (3) were produced. Although these reactions were performed in an inert atmosphere, complete exclusion of oxygen was not possible [18]. We were not able to isolate a bicarbonyl molybdenum complex with dpa under similar conditions. The i.r. spectra of the pyridine ligands showed medium to strong bands at 3420–3363 cm⁻¹, 3308–3287 cm⁻¹ and 3308–3100 cm⁻¹ which are assigned to the stretching vibration of the NH₂ (aepy and hzpy) or NH (dpa) groups, Table 1. These bands have been found shifted to lower frequencies in the spectra of all complexes which indicate the coordination of these groups to metals [19]. The coordination of the NH₂ or NH groups is also confirmed from the shift of their deformation vibration found at 1285–1207 cm⁻¹ (ρ_t NH₂), 1150–1048 (ρ_w NH₂) and 769–759 (ρ_r NH₂) to higher frequencies in the spectra of complexes at 1300–1249 cm⁻¹, 1158–1048 cm⁻¹ and 774–764 cm⁻¹ [19]. The pyridine (py) vibrations in the higher frequency region are not shifted appreciably upon complexation, whereas those at 610–604 cm⁻¹ (in-plane ring deformation) and 415–406 cm⁻¹ (out-of-plane ring deformation) are found to be shifted in the spectra of complexes to higher frequencies; 686–614 cm⁻¹ and 479–438 cm⁻¹, respectively, Table 1. The i.r. spectra of [MoO₂(CO)₂(aepy)] and [MoO₂(CO)₂(hzpy)] exhibited two bands in the terminal metal carbonyl range due to symmetric and asymmetric stretching frequencies of two CO groups in *cis*-position [19–21]. Also, the i.r. spectra of the two displayed two medium to strong bands at 934–923 cm⁻¹ and 898–894 cm⁻¹, which are assigned to asymmetric and symmetric stretching frequencies of two Mo=O bonds for a *cis*-MO₂ fragment [22–25].

When the reactions of Mo(CO)₆ with the pyridylamine ligands were carried out in dioxan and in air, the binuclear oxo derivatives [Mo₂O₆(aepy)₂] (2), [Mo₂O₆(hzpy)₂] (4) and [Mo₂O₄(dpa)₂] (5), were isolated. The binuclearity of the complexes was confirmed from their mass spectra. The i.r. spectra of the former two complexes exhibited the two *cis* Mo=O vibrations at 1005–945 cm⁻¹ and 933–898 cm⁻¹ (Table 1). On the other hand, [Mo₂O₄(dpa)₂] showed only one Mo=O vibration (950 cm⁻¹). This observation is consistent with the bonding of the two oxo in *trans* position and the dpa ligand coordinated in a tridentate fashion. In addition, the three complexes exhibited bands in the range 730–723 cm⁻¹ which are assigned to Mo–O–Mo bridging vibration [26, 27]. This observation is in agreement with several findings with complexes having the Mo₂O₆, Mo₂O₅ or Mo₂O₄ cores which have been recently reported, where molybdenum atom bonded to a *cis* dioxo or one *trans* dioxo group, and the two Mo atoms were bridged by one or two oxygen atoms [22–28]. Scheme 2 gives the proposed structures of molybdenum complexes.

Table 1. Important i.r. data of the ligands and their complexes

Compound	I.r. data (cm ⁻¹) ^a ν(NH)	ν(C=O)	ρ(NH)	ν(Mo=O)	ν(Mo–O–Mo)	δ(py)	ν(M–N)
aepy	3363 s, 3287s	–	1207 m, 1150 m, 760 s	–	–	604 w, 415 w	–
hzpy	3420 b, 3306 b	–	1285 m, 1020 m, 769 s	–	–	608 w, 406 w	–
dpa	3400 s, 3308 s	–	1225 m, 1048 m, 759 s	–	–	610 w, 412 w	–
[MoO ₂ (CO) ₂ (aepy)]	3191 b, 3130 b	1962 s, 1861 s	1263 m, 1052 m, 770 m	934 s, 898 s	–	633 m, 487 s	531 m
[Mo ₂ O ₆ (aepy) ₂]	3204 b, 3109 b	–	1263 m, 1152 m, 770 m	945 s, 933 s	730 m	630 m, 479 m	550 w
[MoO ₂ (CO) ₂ (hzpy)]	3210 b, 3100 b	1973 s, 1840 s	1279 m, 1155 m, 771 m	923 s, 894 s	–	664 m, 452 w	521 m
[Mo ₂ O ₆ (hzpy) ₂]	3240 b, 3200 b	–	1281 m, 1158 m, 774 m	1005 m, 898 s	723 m	614 m, 465 w	571 m
[Mo ₂ O ₄ (dpa) ₂]	3270 b, 3094 s	–	1249 m, 1114 m, 770 m	950 s, 894 s	728 m	644 m, 438 m	508 m
[Ru(CO) ₃ (aepy)]	3248 m, 3140 m	2035 s, 1989 s, 1956 s	1267 m, 1048 m, 764 s	–	–	686 w, 450 w	520 w
[Ru(CO) ₃ (hzpy)]	3204 b, 3100 b	2043 s, 2022 s, 1963 s	1300 w, 1153 m, 770 s	–	–	683 w, 457 w	574 w
[Ru(CO) ₂ (dpa)]	3218 b, 3094 m	2037 s, 1941 s	1280 m, 1056 w, 767 s	–	–	686 w, 472 w	528 w

^as, strong; m, medium; mb, medium broad; w, weak.

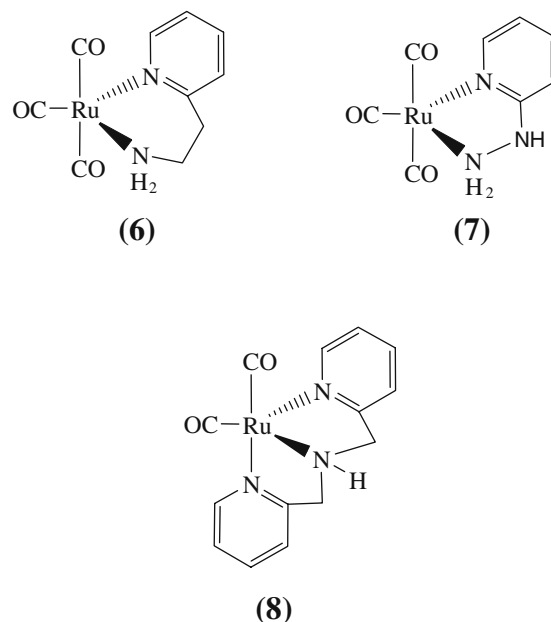


Scheme 2. Proposed structures of the molybdenum complexes.

It is interesting to speculate that the oxo complexes reported here were prepared through intermediate (I), Scheme 3 [28, 29]. Upon reaction with oxygen, such an intermediate would result in the formation of carbonyl derivatives (1) and (3). Dimerization and further reaction with oxygen will give the binuclear products (2), (4) and (5) (Scheme 3).

Interaction of $\text{Ru}_3(\text{CO})_{12}$ with 2-aminoethylpyridine (aepy), 2-hydrazinopyridine (hzpy) and dipicolylamine (dpa) in benzene results in the formation of the mononuclear carbonyl derivatives: $[\text{Ru}(\text{CO})_3(\text{aepy})]$, (6) $[\text{Ru}(\text{CO})_3(\text{hzpy})]$, (7) and $[\text{Ru}(\text{CO})_2(\text{dpa})]$, (8). The $[\text{Ru}(\text{CO})_3(\text{aepy})]$ and $[\text{Ru}(\text{CO})_3(\text{hzpy})]$ complexes showed three vibration bands in the terminal metal carbonyl region due to three CO groups (Table 1). From the number and pattern of the CO bands, it can be indicated that ruthenium existed in a trigonal bipyramidal environment and coordinated to two axial and one equatorial CO groups. The other two equatorial sites are bound to the bidentate ligand. In $[\text{Ru}(\text{CO})_2(\text{dpa})]$ complex, the dpa coordinates to ruthenium as a tridentate ligand. The i.r. spectrum of the complex exhibited two symmetric and asymmetric CO vibrations in the terminal metal carbonyl range (2043–1941) due to two CO groups in *cis* position, Scheme 4. These findings are in agreement with the proposed formula based on the elemental and mass spectral analyses.

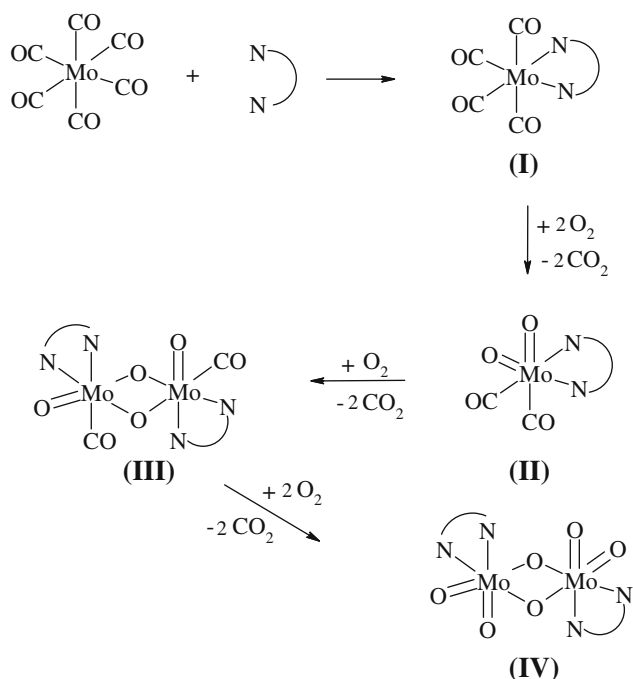
Similar findings were previously observed in the case of reactions of $\text{Ru}_3(\text{CO})_{12}$ with several ligands. For example, interaction of $\text{Ru}_3(\text{CO})_{12}$ with 2-(2'-pyridyl)benzimidazole (HPBI) in the presence of either pyridine (py) or bipyridine (bpy) resulted in the forma-



Scheme 4. Proposed structures of the ruthenium complexes.

tion of the tricarbonyl derivatives $[\text{Ru}(\text{CO})_3(\text{HPBI})\text{py}]$ and $[\text{Ru}(\text{CO})_3(\text{HPBI})\text{dpy}]$ [30]. Also, the tricarbonyl derivatives $[\text{Ru}(\text{CO})_3(\text{LH}_2)]$, LH_2 = maleic hydrazide [31], $[\text{Ru}(\text{CO})_3(\text{dpq})]$, dpq = 2,3-*bis*(2'-pyridyl)quinoxaline [32] and $[\text{Ru}(\text{CO})_3(\text{H}_2\text{L})]$, H_2L = 4-(2,4-dichlorophenylhydrazono)-5-trifluoromethyl-2,4-dihydropyrazol-3-one, 4-(3-fluorophenylhydrazono)-5-trifluoromethyl-2,4-dihydropyrazol-3-one, 4-(3-trifluoromethylphenylhydrazono)-5-trifluoromethyl-2,4-dihydropyrazol-3-one and 4-(3-nitrophenylhydrazono)-5-trifluoromethyl-2,4-dihydro-pyrazol-3-one complexes [33] were isolated. These complexes showed three CO stretching frequencies ($2a' + a''$) in the range 2024–1940 cm^{-1} and assigned to two axial and one equatorial CO groups in trigonal bipyramidal geometry.

The diamagnetism of the isolated molybdenum and ruthenium complexes has been further confirmed from their ^1H -n.m.r. spectral measurements. All ligands displayed multiplets at 8.62–7.23 p.p.m. (Table 2) with 4 protons (aepy, hzpy) and 8 protons (dpa) assigned for the aromatic protons of the pyridine ring. In addition, aminoethylpyridine (aepy) showed two doublets at 3.14 p.p.m. and 2.98 p.p.m. with an integration of 4 protons, assigned to the two CH_2 protons. It also displayed singlet at 2.0 assigned to NH_2 protons. The 2-hydrazinopyridine displayed two additional singlets at 4.0 p.p.m. and 2.0 p.p.m. with integration corresponding to one and two protons which can be assigned to NH and NH_2 protons, respectively. The dpa displayed the NH singlet at 2.0 ppm and another singlet at 4.0 p.p.m. with an integration of 4 protons assigned for the two CH_2 protons. The above mentioned peaks are also observed in the spectra of the complexes but are downfield shifted to higher p.p.m. values. The NH_2 protons of aepy and hzpy were found in the



Scheme 3. Proposed mechanism for the formation of the oxomolybdenum complexes.

Table 2. Important ¹H-n.m.r. data for the ligands and their complexes

Compound	¹ H-n.m.r. data (p.p.m.)
aepy	7.67–7.23 m (4H, pyridine), 3.14–2.98 (4H, ethyl), 2.0s (2H, NH ₂)
hzpy	8.11–6.60 m (4 H, pyridine), 4.0 s (1 H, NH), 2.0 s (2 H, NH ₂)
dpa	8.64–7.29 m (8 H, pyridine), 4.14 s (4 H, 2CH ₂), 2.0 s (1 H, NH)
[MoO ₂ (CO) ₂ (aepy)]	8.52–7.26 m (8 H, 2 CH ₂ , 4 PyH), 3.04 s (2 H, NH ₂)
[Mo ₂ O ₆ (aepy) ₂]	8.52–7.26 m (8 H, 2 CH ₂ , 4 PyH), 3.06 s (2 H, NH ₂)
[MoO ₂ (CO) ₂ (hzpy)]	8.58–7.06 m (4 H, PyH), 6.74 m (3 H, NH, NH ₂)
[Mo ₂ O ₆ (hzpy) ₂]	8.59–7.67 m (8 H, PyH), 7.42–7.39 m (6 H, 2NH, 2NH ₂)
[Mo ₂ O ₄ (dpa) ₂]	8.81–6.94 m (24 H, PyH, CH ₂), 4.1 (2 H, NH)
[Ru(CO) ₃ (aepy)]	8.46–7.16 m (10 H, pyridine H), 3.0–2.80 d (4 H, 2 NH ₂)
[Ru(CO) ₃ (hzpy)]	8.56–7.36 m (8 H, pyH), 5.8 m (6 H, 2NH, 2NH ₂)
[Ru(CO) ₂ (dpa)]	7.91–7.10 m (20 H, pyridine), 4.80–4.20 m (8 H, 4CH ₂), 6.4 d (2 H, 2NH)

ligand spectra at 2.0 p.p.m. and are found downfield shifted in a wide range of 7.42–2.80 p.p.m. The same observation is withdrawn to the dpa NH proton which is found shifted to 6.4–4.1 p.p.m. The aromatic pyridine protons are found shifted to higher p.p.m. values due to the downfield shift of the pyridine CH=N proton upon coordination. The shifts in the positions of the NH and NH₂ indicate the coordination of the two groups to ruthenium or molybdenum without proton displacement and confirm the diamagnetic d⁶ ruthenium, d⁰ and d² molybdenum configurations [2, 33].

U.v.–vis. studies

The u.v.–vis. spectra of the ligands displayed two main absorption bands at 370–312 n.m. and 279–266 n.m. (Table 3) which may be assigned to n-π* and π-π* transitions within the pyridine nuclei. These two bands are shifted in the spectra of all complexes, especially the n-π* band which is directly affected by the coordination of the pyridine nitrogen to ruthenium or molybdenum. In addition, the complexes displayed a new absorption band at 433–420 n.m. which may be assigned to a charge transfer band (Table 3). The E_{CT} value of this charge transfer band was calculated from the λ_{CT} in the electronic spectra of the complexes and was found to be in the range 2.95–2.86 eV. This may

be attributed to the metal to ligand charge transfer (MLCT). These values are low compared with the E_{CT} of the charge transfer of the other molybdenum and ruthenium carbonyl complexes or their solvated complexes (DMSO) which amount to 4.83 eV [2, 34, 35]. The low E_{CT} values observed for the reported complexes may be attributed to the weak ligand field contribution of the nitrogen donor ligands compared with the strong ligand field carbonyl ligands which may reduce the energy gap between the eg* and the t_{2g}* states.

Thermal analyses

The thermal studies of the ruthenium and molybdenum complexes were carried out using the thermogravimetric t.g. and the differential thermogravimetric d.t.g. The decomposition temperature ranges of along with the corresponding mass loss of species for each step are given in Table 4. The decomposition of [MoO₂(CO)₂(aepy)] and [MoO₂(CO)₂(hzpy)] started with the removal of either the amine or CO ligands leaving the metal oxide (MoO) as the metallic residue. On the other hand, [Mo₂O₆(aepy)₂], [Mo₂O₆(hzpy)] and [Mo₂O₄(dpa)₂] decomposed in a more simple manner starting with the removal of the amine ligands and ending with the formation of the MoO as metallic residue. [Ru(CO)₃(aepy)], [Ru(CO)₃(hzpy)]

Table 3. Elemental analysis and u.v.–vis. spectral data of complexes

Compound	Mol. wt.	Yield %	Found (Calcd.) (%)			U.v.–vis. (λ _{max}) ^a
			C	H	N	
[MoO ₂ (CO) ₂ (aepy)]	306.11	54	35.4(35.3)	3.4(3.3)	9.2(9.2)	420, 346 sh, 264
[Mo ₂ O ₆ (aepy) ₂]	532.22	77	31.4(31.6)	3.6(3.8)	10.7(10.5)	433, 347 sh, 261
[MoO ₂ (CO) ₂ (hzpy)]	295.96	59	28.7(28.5)	3.1(3.1)	14.2(14.2)	423, 350 sh, 265
[Mo ₂ O ₆ (hzpy) ₂]	506.13	72	23.6(23.7)	2.8(2.8)	16.7(16.6)	433, 345 sh, 263
[Mo ₂ O ₄ (dpa) ₂]	654.38	69	43.9(44.1)	4.0(4.0)	12.5(12.8)	421, 351 sh, 261
[Ru(CO) ₃ (aepy)]	307.27	52	38.9(39.1)	3.1(3.3)	9.1(9.1)	432, 351 sh, 263
[Ru(CO) ₃ (hzpy)]	294.23	61	32.0(32.7)	2.4(2.4)	14.2(14.3)	433, 348 sh, 261
[Ru(CO) ₂ (dpa)]	356.34	48	46.7(47.2)	3.5(3.7)	11.1(11.8)	429, 349 sh, 264

^aaepy: 342, 279, hzpy: 312 (sh), 266, dpa: 370, 279 (sh, shoulder).

Table 4. Thermoanalytical (t.g.) data for the molybdenum and ruthenium complexes

Complex	F. wt	T.g. range (°C)	D. I _{max} (°C)	Mass loss found (Calcd. %)	Assignment of the removed species (loss of)	Metallic residue found (Calcd. %)
[MoO ₂ (CO) ₂ (aepy)]	306.11	90–180, 550–750, 780–900	118, 665, 800	18.3 (18.3), 39.8 (39.9), 5.4 (5.2)	2 CO, aepy, 1/2 O ₂	MoO, 36.5, (36.6)
[Mo ₂ O ₆ (aepy) ₂]	532.22	100–250, 580–820	179, 740	23.0 (22.9), 34.8 (35.0)	aepy, aepy + 2O ₂	2 MoO, 44.1, (44.0)
[MoO ₂ (CO) ₂ (hzpy)]	295.96	150–240, 590–680, 690–730	211, 650, 710	36.7 (36.9), 18.7 (18.9), 5.4 (5.4)	hzpy, 2 CO, 1/2 O ₂	MoO, 38.3, (37.8)
[Mo ₂ O ₆ (hzpy) ₂]	506.13	150–230, 300–350, 550–950	211, 329, 643	21.7 (21.6), 6.3 (6.3), 27.8 (27.9)	hzpy, O ₂ , hzpy + O ₂	2MoO, 44.2, (44.2)
[Mo ₂ O ₆ (dpa) ₂]	654.38	200–300, 810–880	262, 850	61.0 (60.9), 4.9 (4.9)	2 dpa, O ₂	2MoO, 34.1, (34.2)
[Ru(CO) ₅ (aepy)]	307.27	90–120, 140–180, 250–330	110, 163, 286	9.0 (9.1), 18.0 (18.2), 35.6 (35.5)	CO, 2 CO, aepy	Ru, 37.4, (36.8)
[Ru(CO) ₅ (hzpy)]	294.23	90–130, 210–260, 310–370, 430–510	125, 246, 332, 485	9.4 (9.5), 18.7 (18.5), 9.6 (9.5), 27.8 (28.1)	CO, 1/2 Hzpy, CO, CO + 1/2 Hzpy	Ru, 34.5, (34.3)
[Ru(CO) ₂ (dpa)]	356.34	90–132, 220–270, 450–530	119, 255, 496	7.7 (7.8), 31.6 (31.9), 32.0 (31.9)	CO, 1/2 CO + 1/2 dpa, 1/2 CO + 1/2 dpa	Ru, 28.4, (28.3)

and [Ru(CO)₂(dpa)] decomposed by the initial removal of a carbonyl ligand first followed by mutual removal of CO and or amine ligands in the subsequent steps leaving the metal(Ru) at the end as the metallic residue.

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