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Synthesis, structures and luminescent properties of metal complexes containing 4-[2-(9-anthryl)vinyl]pyridine

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Abstract

Reactions of the anthracene-containing ligand, 4-[2-(9-anthryl)vinyl]pyridine $\mathbf{L_1}$, with various metal complexes of Groups 6, 7 and 12 elements, namely, $M(CO)_6$ (M = Mo, W), $M(CO)_5Br$ (M = Mn, Re) and MCl_2 (M = Zn, Cd) readily afford new complexes of the stoichiometry $M(CO)_5(\mathbf{L_1})$ (M = Mo (**1**); W (**2**)), $M(CO)_3Br(\mathbf{L_1})_2$ (M = Mn (**3**); Re (**4**)) and $MCl_2(\mathbf{L_1})_2$ (M = Zn (**5**); Cd (**6**)) in moderate to good yields. All of these complexes have been fully characterized by FTIR, ^{1}H-NMR, UV–vis spectroscopies and fast atom bombardment mass spectrometry (FABMS). The solid-state molecular structures of **1** and **2** have been determined by X-ray crystallography and they involve the coordination of $\mathbf{L_1}$ to the $\{M(CO)_5\}$ moiety (M = Mo, W). It was found that all of these anthryl-substituted compounds are luminescent in fluid solutions at room temperature, which is attributed to the metal-perturbed anthracene emission. The emission maxima are red-shifted upon metal coordination and with the metal centers descending down the Group, suggesting some degree of electronic interactions between anthracene and the electron-withdrawing metal unit in each case. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Anthracene; Pyridine; Transition metal; Zinc; Cadmium

1. Introduction

There is a continuing and considerable current interest in the photophysics and photochemistry of supramolecular systems incorporating electronically coupled photoactive sites in molecular assemblies for intramolecular energy- or electron-transfer processes [1]. Previous reports have shown that the π-conjugated systems in a series of polyyne- or polyene-bridged anthrylporphyrins could effectively enhance the through-bond electronic coupling between the donor and the acceptor in energy- and electron-transfer processes [2]. The mechanism of intramolecular excitation energy transfer from the anthryl moiety to the porphyrin through these linkages has been discussed on the basis of the photochemical properties of the component molecules [2a]. We therefore sought to design new molecular systems featuring these characteristics. With regards to this goal, organic and inorganic molecules possessing the anthracene chromophore appear to be appealing, since it is well known that anthracene has a strong fluorescent emission and proved to be an important luminescence probe in fundamental studies of energy transfer in organized media [3]. In addition, anthracenes are unique in combining the advantages of having easily accessible absorption spectra exhibiting monomer fluorescence and high photoreactivity; they also have a fairly good solubility in organic solvents.

Studies of the photochemistry of anthracene and its derivatives are well documented in the literatures [4]. A large number of anthracene-containing ligands and complexes have been prepared and the effects of different substituents investigated [5]. Among these, 9-substituted anthracenes are the most studied [4,6]. The preparations of (9-anthracenyl)phosphanes and 9-anthryl-substituted pyridines have been reported, both of which were shown to be good ligands in the formation of metal complexes [6,7]. Recently, we have also described the synthesis and solvatochromic properties of some covalently linked anthracene-containing supramolecular complexes of triosmium carbonyl clusters in which a significant metal–anthracene interaction in the ground state via the conjugated ligand group was

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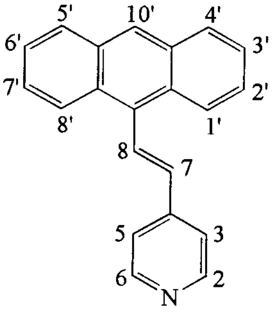
observed [7b]. The envisaged interesting feature associated with 4-[2-(9-anthryl)vinyl]pyridine $\mathbf{L_1}$ has motivated us to undertake a systematic study of the reactions between a series of transition-metal complexes and $\mathbf{L_1}$ and this study should provide a convenient entry into new anthracene-containing complexes with intriguing photophysical properties. In this report, we shall describe the synthesis and structural, spectroscopic and luminescent properties of some mononuclear metal complexes incorporating the anthracene entity.



$\mathbf{L_1}$

2. Results and discussion

2.1. Synthesis

The synthetic routes to all of the new compounds are outlined in Scheme 1. Monosubstituted metal carbonyl complexes of the Group 6 elements [M(CO)$_5$($\mathbf{L_1}$)] (M = Mo (**1**); W (**2**)) were prepared by reacting one equivalent of 4-[2-(9-anthryl)vinyl]pyridine $\mathbf{L_1}$ with Mo(CO)$_6$ or [W(CO)$_5$(THF)] prepared in situ from photolysis of W(CO)$_6$ in THF. Workup by column chromatography on silica is necessary to isolate these complexes in high purity and they are obtained as yellow solids in moderate yields (31% (**1**); 40% (**2**)). The facile displacement of two carbonyl ligands of Re(CO)$_5$X (X = Cl, Br) by pyridines to afford [Re(CO)$_3$X(NC$_5$H$_4$R)$_2$] was successfully applied to the preparation of [M(CO)$_3$Br($\mathbf{L_1}$)$_2$] (M = Mn (**3**); Re (**4**)) [8]. Treatment of two molar equivalents of $\mathbf{L_1}$ with [M(CO)$_5$Br] (M = Mn, Re) in refluxing benzene gave complexes **3** and **4** in 51 and 36% yields, respectively. The desired disubstitution products precipitate from their benzene solutions as they form and can thus be isolated and purified easily. New luminescent metal complexes of the Group 12 elements [MCl$_2$($\mathbf{L_1}$)$_2$] (M = Zn (**5**); Cd (**6**)) were readily synthesized by the reaction between anhydrous MCl$_2$ and $\mathbf{L_1}$ in absolute ethanol at room temperature [9]. The products **5** and **6** were isolated as yellow precipitates in good yields (45 (**5**); 57% (**6**)). Except for **3** and **6**, all other compounds in this study are soluble in common organic solvents. All of them are stable as solids; however, compound **1** was found to undergo slow decomposition in solution at ambient temperature.

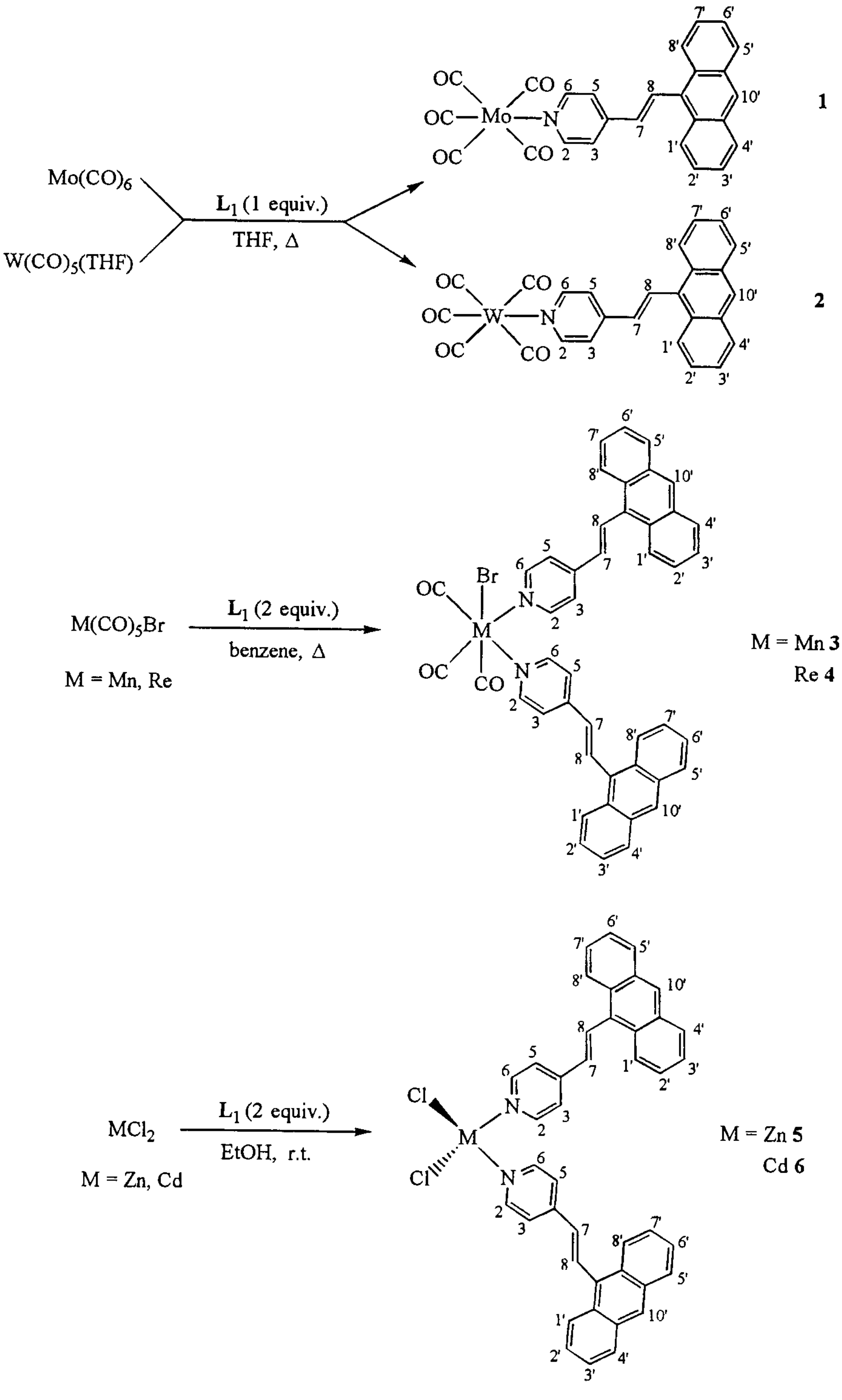
2.2. Spectroscopic properties

The spectroscopic properties (IR, ^{1}H-NMR and FABMS) of these new 4-[2-(9-anthryl)vinyl]pyridine-substituted complexes are consistent with their formulation and Table 1 summarizes the spectral data. Coordination of the dangling pyridine of $\mathbf{L_1}$ to Mo(CO)$_6$ and W(CO)$_5$(THF) was confirmed by the appearance of three medium/strong carbonyl stretching ν(CO) absorptions for **1** and **2** in the IR spectra, which are characteristic of a C_{3v} arrangement of CO ligands at the metal center. The IR spectra of **3** and **4** show three ν(CO) IR bands and this is consistent with a facial arrangement for a tricarbonyl possessing a C_s symmetry. The ^{1}H-NMR spectra of the new complexes display signals stemming from the coordinated anthryl-substituted ligand, and the fact that the chemical shifts for the α-ring protons (H$_2$ and H$_6$) of pyridine in the complexes shift to lower field than that of $\mathbf{L_1}$ indicates metal–nitrogen coordination. Such coordination-induced downfield shifts are attributed to ligand-to-metal σ-donation. The *trans* conformation of the ligands in these complexes is verified by the values of the coupling constants (ca. 16.5 Hz) associated with the vinyl protons (H$_7$ and H$_8$), which are more or less similar to that of the free ligand. Most of our compounds gave satisfactory mass spectral data. For **1**, **2**, **4** and **6**, the respective molecular ion peaks were observed in their positive fast atom bombardment mass spectrometry (FABMS). The FABMS of **5** did not show the molecular ion; however, a peak due to $[M-Cl]^+$ was detected. For **3**, a peak at *m*/*z* 725 was observed which corresponded to the fragment $[M-2CO]^+$.

2.3. Electronic absorption and luminescence spectra

Table 2 presents the absorption and emission data for the new complexes **1**–**6** in CH$_2$Cl$_2$ at room temperature together with that for the anthryl ligand $\mathbf{L_1}$. The UV–vis absorption spectrum of $\mathbf{L_1}$ displays an intense band at 389 nm, which arises from the anthracene-localized $\pi\rightarrow\pi^*$ transitions. Complexes **1**–**6** all exhibit similar structured low-energy bands in the near UV and the visible regions at ca. 391–405 nm. These strong featureless absorption bands are ascribed to the metal-perturbed intraligand $\pi\rightarrow\pi^*$ transitions of the anthracene unit, which may, however, be obscured by the other bands due to the metal-to-ligand charge transfer (MLCT) transitions and the ligand field (d–d) bands for each appropriate metal fragment. With reference to previous spectroscopic work on related metal complexes, it is apparent that there are intense low-energy absorptions from the dπ(Re)$\rightarrow\pi^*$(L) transition in rhenium(I) diimine systems [10], whereas the {$W(CO)_5(py)$}-type chromophores undergo a typical d–d transition near 400 nm [11].

As expected, all of the new anthracene-containing complexes **1**–**6** are luminescent at room temperature in solutions and strong emission peaks appear at ca. 491–528 nm (Table 2). The luminescence spectra are independent of the excitation wavelength used. Due to their similar structured peak pattern, we consider that these emission features should have the same origin in each case. Hence, these peaks are most likely caused by the metal-perturbed anthracene emission where the emission maxima are fairly red-shifted by as much as 38 nm upon metal coordination and with metal centers de-



Scheme 1.

Table 1
Spectroscopic data for complexes **1**–**6**

Complex	IR (ν(CO), cm^{-1})[a]	^{1}H-NMR (δ, J Hz)[b]	FABMS (m/z)[c]
1	2073 w, 1983 sh 1938 vs, 1896 m	8.60 (d, 2H, $J = 6.7$, $H_{2,6}$) 8.40 (s, 1H, $H_{10'}$) 8.16 (m, 3H, $H_{7,1',8'}$) 7.98 (m, 2H, $H_{4',5'}$) 7.42 (m, 6H, $H_{3,5,2',3',6',7'}$) 6.85 (d, 1H, $J = 16.3$, H_8)	517 (517)
2	2071 w, 1972 sh 1928 vs, 1894 m	8.84 (d, 2H, $J = 6.7$, $H_{2,6}$) 8.48 (s, 1H, $H_{10'}$) 8.28 (d, 1H, $J = 16.5$, H_7) 8.22 (m, 2H, $H_{1',8'}$) 8.05 (m, 2H, $H_{4',5'}$) 7.50 (m, 6H, $H_{3,5,2',3',6',7'}$) 6.94 (d, 1H, $J = 16.5$, H_8)	605 (605)
3	2026 vs, 1943 vs 1906 s[d]	[e]	725 (781)[f]
4	2025 vs, 1923 vs 1890 s	8.91 (d, 4H, $J = 6.6$, $H_{2,6}$) 8.47 (s, 2H, $H_{10'}$) 8.30 (d, 2H, $J = 16.5$, H_7) 8.22 (m, 4H, $H_{1',8'}$) 8.04 (m, 4H, $H_{4',5'}$) 7.58 (d, 4H, $J = 6.6$, $H_{3,5}$) 7.51 (m, 8H, $H_{2',3',6',7'}$) 6.96 (d, 2H, $J = 16.5$, H_8)	912 (912)
5		8.85 (d, 4H, $J = 5.8$, $H_{2,6}$) 8.46 (s, 2H, $H_{10'}$) 8.30 (d, 2H, $J = 16.5$, H_7) 8.20 (m, 4H, $H_{1',8'}$) 8.03 (m, 4H, $H_{4',5'}$) 7.74 (d, 4H, $J = 5.8$, $H_{3,5}$) 7.50 (m, 8H, $H_{2',3',6',7'}$) 6.97 (d, 2H, $J = 16.5$, H_8)	662.5 (698)[g]
6		8.62 (m, 6H, $H_{2,6,10'}$) 8.45 (d, 2H, $J = 16.6$, H_7) 8.30 (m, 4H, $H_{1',8'}$) 8.11 (m, 4H, $H_{4',5'}$) 7.79 (m, 4H, $H_{3,5}$) 7.56 (m, 8H, $H_{2',3',6',7'}$) 7.00 (d, 2H, $J = 16.6$, H_8)[h]	745 (745)

[a] Recorded in CH_2Cl_2.
[b] Recorded in $CDCl_3$.
[c] Calculated values in parentheses.
[d] Recorded as KBr disc.
[e] No satisfactory data are obtained due to its extremely low solubility.
[f] Only $[M-2CO]^+$ is observed.
[g] Only $[M-Cl]^+$ is observed.
[h] Recorded in DMSO-d_6.

scending down the Group (see Fig. 3). This also corresponds to the bathochromic shift observed in the absorption spectra. Undoubtedly, we cannot rule out the possibility that the emission derived from the ^{3}MLCT excited state may interfere with the assignment as in the case of **4** [10]. Comparison of the emission spectra of $\mathbf{L_1}$ and the resulting complexes reveals a slight ground-state interaction between the anthryl moiety and the electron-withdrawing metal entities.

2.4. Crystal structure analyses

To substantiate the solid-state molecular structures of the new luminescent compounds, single-crystal X-ray analyses were performed for **1** and **2**. Suitable yellow crystals of **1** and **2** were obtained from their respective solutions in an n-hexane–CH_2Cl_2 solvent mixture at −10°C. Perspective views of their structures are shown in Figs. 1 and 2, which include the atom-numbering

Table 2
Absorption and emission data for **1**–**6** in CH_2Cl_2

Complex	Absorption (nm) [a]	Emission (nm)
L$_1$	248 (3.7), 389 (1.1)	490
1	244 (3.9), 393 (1.9)	491
2	249 (4.0), 405 (1.5)	499
3	258 (2.4), 391 (0.7)	496
4	251 (3.9), 405 (2.1)	524
5	248 (4.0), 401 (2.1)	513
6	259 (3.4), 393 br (1.0)	528 br

[a] Extinction coefficients ($\varepsilon \times 10^{-4}$ dm^3 mol^{-1} cm^{-1}) are shown in parentheses.

scheme. Pertinent structural parameters are collected in Tables 3 and 4. The essential features of both structures are very similar, so they will not be discussed separately. Structurally, both complexes **1** and **2** can be regarded as having a {$M(CO)_5N$} moiety (M = Mo, W) with the metal center covalently bonded to the nitrogen atom of the anthryl ligand **L$_1$**. In each case, the metal atom has an approximately octahedral geometry and the W–C–O linkage does not deviate significantly from linearity (173.4(6)–178.4(7)° for **1**, 173.8(6)–177.4(5)° for **2**). The average C≡O bond distances for **1** and **2** are 1.149(8) and 1.139(8) Å, respectively. The corresponding Mo–N and W–N distances are 2.290(4) and 2.274(3) Å, which compare well with literature values [11]. The carbonyl Mo–C lengths range from 1.953(6) to 2.066(9) Å, whereas the W–C lengths are from 1.975(5) to 2.063(8) Å. The apparently shorter M–C bond *trans* to the M–N bond (Mo(1)–C(2) = 1.953(6) Å for **1**, W(1)–C(3) = 1.975(5) Å for **2**) is consistent with the *trans* effect exerted by the pyridyl ligand. The orientation of the coordinated pyridyl ring with respect to the metal fragment is defined by the angle between the pyridyl plane and the $M(CO)_3N$ mean plane. After successful structure refinement, the pyridyl ring is at angles of 46.9° (**1**) and 43.0° (**2**) to the Mo(1)–C(1)–C(2)–C(4)–N(1) and W(1)–C(2)–C(3)–C(5)–N(1) mean planes. The anthracene ring is essentially coplanar in each case (mean deviation = 0.046 (**1**); 0.044 Å (**2**)). The dihedral angles between the pyridyl and anthryl mean planes are 39.6° (**1**) and 39.5° (**2**). The C(11)–C(12) vinyl bonds are 1.318(7) Å (**1**) and 1.323(7) Å (**2**) in length. Additionally, the pattern of C–C bond lengths is typical of anthracene systems [12]. However, no evidence of intermolecular stacking inter-

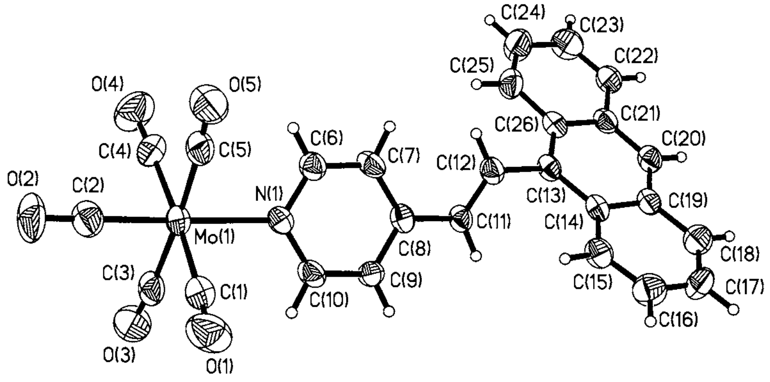


Fig. 1. Molecular structure of **1**, showing the atomic labeling scheme. Ellipsoids are shown at the 40% probability level.

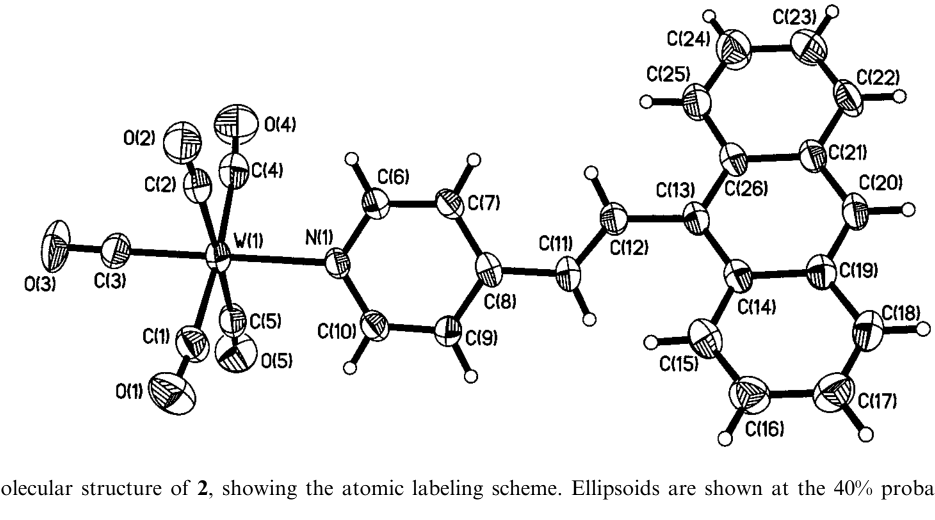


Fig. 2. Molecular structure of **2**, showing the atomic labeling scheme. Ellipsoids are shown at the 40% probability level.

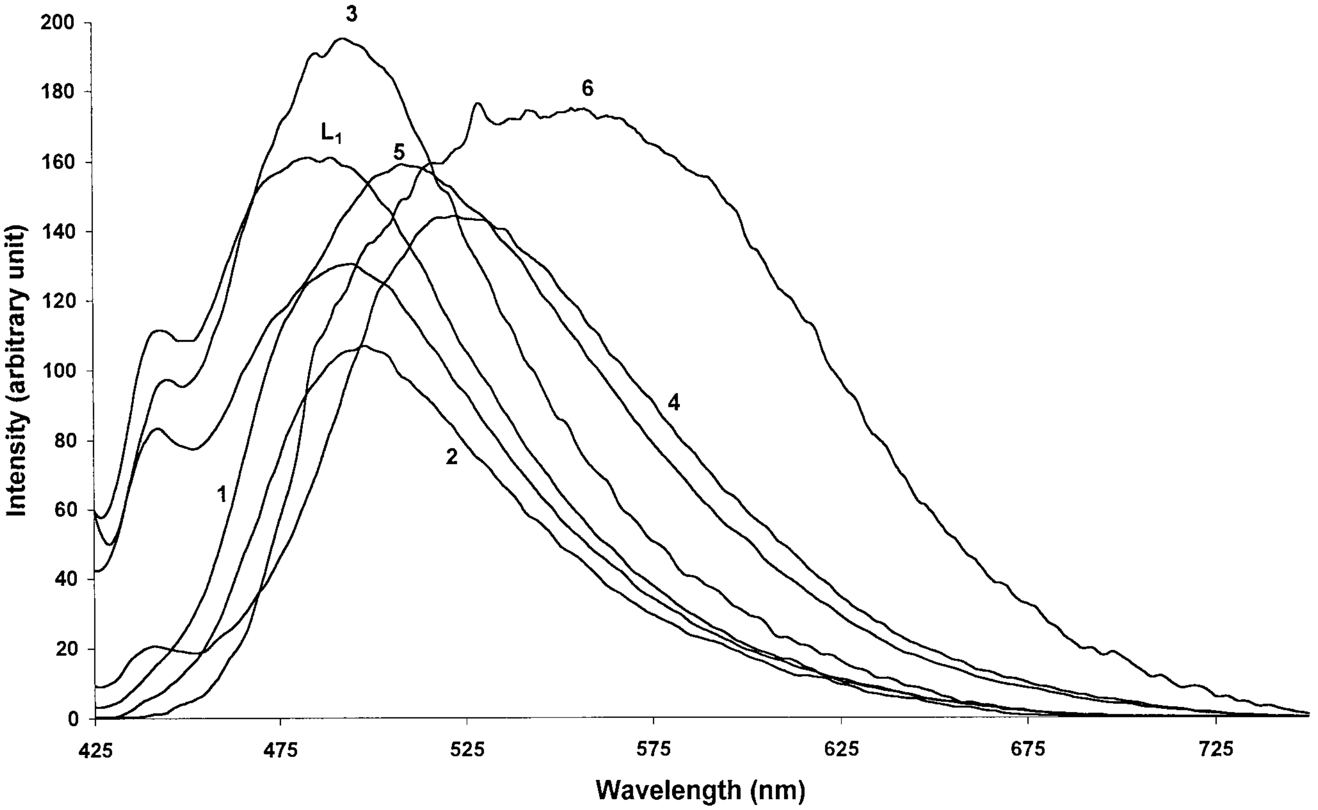


Fig. 3. The room temperature emission spectra of ligand $\mathbf{L_1}$ and complexes **1**–**6**.

action between individual anthracene units in the crystal lattice was observed in both cases.

3. Conclusions

Our present study provides an entry into a new class of luminescent anthracene-containing molecules by complexation of 4-[2-(9-vinyl)anthryl]pyridine $\mathbf{L_1}$ with suitable transition metals. A series of metal complexes of Groups 6, 7 and 12 elements incorporating $\mathbf{L_1}$ have been prepared in moderate to good yields and characterized spectroscopically. These new compounds are found to be emissive in fluid solutions at room temperature and the anthracene-based emission peaks could be fine-tuned by modification of the electronic properties associated with the coordinated metal centers. Down the Group in the Periodic Table, we observe a noticeable red-shift of emission wavelengths. Work is currently in progress to investigate further the extent of electron delocalization and other photophysical properties in these systems. The effect of other transition metals on the luminescent behavior will also be the subject of a future study.

Table 3
Selected bond lengths (Å) and angles (°) for complex **1**

Bond lengths			
Mo(1)–N(1)	2.290(4)	Mo(1)–C(1)	2.034(8)
Mo(1)–C(2)	1.953(6)	Mo(1)–C(3)	2.066(9)
Mo(1)–C(4)	2.038(8)	Mo(1)–C(5)	2.018(8)
C(8)–C(11)	1.454(7)	C(11)–C(12)	1.318(7)
C(12)–C(13)	1.503(6)		
Bond angles			
C(1)–Mo(1)–N(1)	91.5(2)	C(2)–Mo(1)–N(1)	177.6(3)
C(3)–Mo(1)–N(1)	92.3(2)	C(4)–Mo(1)–N(1)	93.4(2)
C(5)–Mo(1)–N(1)	91.2(2)	C(8)–C(11)–C(12)	124.9(5)
C(11)–C(12)–C(13)	128.3(5)		

Table 4
Selected bond lengths (Å) and angles (°) for complex **2**

Bond lengths			
W(1)–N(1)	2.274(3)	W(1)–C(1)	2.033(7)
W(1)–C(2)	2.012(7)	W(1)–C(3)	1.975(5)
W(1)–C(4)	2.038(7)	W(1)–C(5)	2.063(8)
C(8)–C(11)	1.453(6)	C(11)–C(12)	1.323(7)
C(12)–C(13)	1.470(6)		
Bond angles			
C(1)–W(1)–N(1)	91.3(2)	C(2)–W(1)–N(1)	91.0(2)
C(3)–W(1)–N(1)	177.8(2)	C(4)–W(1)–N(1)	93.0(2)
C(5)–W(1)–N(1)	92.2(2)	C(8)–C(11)–C(12)	126.7(5)
C(11)–C(12)–C(13)	129.6(5)		

4. Experimental

4.1. General procedures

All operations were carried out under an atmosphere of dinitrogen with the use of standard Schlenk techniques, but no special precautions were taken to exclude oxygen during work-up. Solvents were predried and distilled from appropriate drying agents [13]. All chemicals, unless otherwise stated, were from commercial sources and used as received. The ligand 4-[2-(9-vinyl)anthryl]pyridine was prepared by literature methods [7b,14] and $ZnCl_2$ was dried from thionyl chloride. Infrared spectra were recorded as CH_2Cl_2 solutions in a CaF_2 cell (0.5 mm path length) or KBr disc on a Perkin–Elmer Paragon 1000 PC or Nicolet Magna 550 Series II FTIR spectrometer. Proton NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 on a JEOL GX270 FT NMR spectrometer. Chemical shifts were quoted relative to $SiMe_4$ ($\delta = 0$). FAB mass spectra were recorded on a Finnigan MAT 95 mass spectrometer. Electronic absorption spectra were obtained with a Hewlett–Packard 8453 UV–vis spectrophotometer whilst luminescence spectra were recorded using Perkin–Elmer LS50B luminescence spectrometer. Column chromatography was carried out in air on Kieselgel 60 (230–400 mesh) silica gel.

4.2. Preparations of complexes **1**–**6**

4.2.1. Synthesis of [Mo(CO)$_5$(**L$_1$**)] (**1**)

A mixture of $Mo(CO)_6$ (50 mg, 0.19 mmol) and 4-[2-(9-vinyl)anthryl]pyridine **L$_1$** (53 mg, 0.19 mmol) was dissolved in dry THF (30 cm^3). The solution mixture was refluxed under N_2 for 4 h, during which time it changed from yellow to reddish brown. Completion of the reaction was confirmed by TLC. The solvent was then removed under vacuum. The residue was dissolved in CH_2Cl_2 and purified by column chromatography on silica. Elution with 4:1 hexane–CH_2Cl_2 (v/v) gave a yellow band ($R_f = 0.50$) from which compound **1** was isolated in 31% yield (30 mg) after removal of solvent. $C_{26}H_{15}NO_5Mo$ requires C, 60.36; H, 2.92; N, 2.71. Found: C, 60.16; H, 2.85; N, 2.50%

4.2.2. Synthesis of [W(CO)$_5$(**L$_1$**)] (**2**)

$W(CO)_6$ (50 mg, 0.14 mmol) was suspended in dry THF (30 cm^3) in a flask fitted with a condenser jacket. The stirred mixture was then irradiated with a 450 W mercury lamp. After 0.5 h, a yellow solution of [W(CO)$_5$(THF)] was obtained and one equivalent of the ligand **L$_1$** (40 mg, 0.14 mmol) was subsequently added. The resulting mixture was refluxed for 3 h and the solvent was then removed. The desired yellow product **2** was isolated from the first major yellow band ($R_f =$ 0.75) in 40% yield (34 mg) after column chromatography on silica, eluting with 3:2 hexane–CH_2Cl_2 (v/v). $C_{26}H_{15}NO_5W$ requires C, 51.60; H, 2.50; N, 2.31. Found: C, 51.52; H, 2.40; N, 2.18%.

4.2.3. Synthesis of Mn(CO)$_3$Br(**L$_1$**)$_2$ (**3**)

$Mn(CO)_5Br$ (28 mg, 0.10 mmol) and ligand **L$_1$** (56 mg, 0.20 mmol) were mixed in benzene (10 cm^3) and the mixture was heated under reflux for 2 h. A yellow–brown suspension was formed. After filtration, the dark yellow precipitate obtained was washed with benzene and characterized to be **3**. The yield was 51% (40 mg). $C_{45}H_{30}N_2BrO_3Mn$ requires C, 69.15; H, 3.87; N, 3.58. Found: C, 69.05; H, 3.79; N, 3.40%.

4.2.4. Synthesis of [Re(CO)$_3$Br(**L$_1$**)$_2$] (**4**)

$Re(CO)_5Br$ (20 mg, 0.05 mmol) and ligand **L$_1$** (28 mg, 0.10 mmol) in benzene (10 cm^3) were heated to reflux under N_2. After stirring for 2 h, the yellow suspension was filtered and washed with a small volume of benzene to afford a yellow–orange solid **4** in 36% yield (16 mg). $C_{45}H_{30}N_2BrO_3Re$ requires C, 59.21; H, 3.31; N, 3.07. Found: C, 59.30; H, 3.20; N, 2.95%.

Table 5
Summary of crystal structure data for complexes **1** and **2**

	1	**2**
Empirical formula	$C_{26}H_{15}NO_5Mo$	$C_{26}H_{15}NO_5W$
Molecular weight	517.33	605.24
Crystal size (mm)	0.36 × 0.26 × 0.24	0.33 × 0.29 × 0.28
Crystal system	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$ (No. 19)	$P2_12_12_1$ (No. 19)
Unit cell dimensions		
a (Å)	7.457(2)	7.427(1)
b (Å)	15.941(3)	15.882(2)
c (Å)	19.402(4)	19.322(3)
α (°)	90	90
β (°)	90	90
γ (°)	90	90
U (Å^3)	2306.3(8)	2279.3(5)
D_{calc} (g cm^{-3})	1.490	1.764
Z	4	4
μ (Mo–K$_\alpha$)/cm^{-1}	6.05	51.05
F(000)	1040	1168
θ range (°)	1.65–27.47	1.66–27.53
Reflections collected	13 616	13 372
Unique reflections	5080	5107
R_{int}	0.076	0.032
Observed reflections [$I > 2.0\sigma(I)$]	5080	5107
No. of parameters	298	298
R_1	0.051	0.030
wR_2	0.090	0.073
Goodness-of-fit	0.996	1.025
Residual extrema in final diff. map (e Å^{-3})	0.48 to −0.58	2.00 to −1.53 (close to w)

4.2.5. Synthesis of $ZnCl_2(\mathbf{L_1})_2$ (**5**)

Anhydrous $ZnCl_2$ (50 mg, 0.37 mmol) and ligand $\mathbf{L_1}$ (210 mg, 0.74 mmol) were mixed in absolute ethanol (20 cm^3) as the solvent. The mixture was stirred at room temperature (r.t.) for 2 h, after which the yellow precipitate formed was centrifuged to give the desired product **5** in 45% yield (120 mg). $C_{42}H_{30}N_2Cl_2Zn$ requires C, 72.17; H, 4.33; N, 4.01. Found: C, 72.20; H, 4.35; N, 3.95%.

4.2.6. Synthesis of $CdCl_2(\mathbf{L_1})_2$ (**6**)

A mixture of $CdCl_2$ (50 mg, 0.27 mmol) and ligand $\mathbf{L_1}$ (150 mg, 0.54 mmol) was stirred in absolute ethanol at room temperature After 2 h, a yellow precipitate was obtained after centrifugation, followed by washing with ethanol. The product identified as **6** had a yield of 57% (120 mg). $C_{42}H_{30}N_2Cl_2Cd$ requires C, 67.62; H, 4.05; N, 3.75. Found: C, 67.52; H, 3.98; N, 3.50%.

5. Crystallography

Single crystals of **1** and **2** suitable for X-ray crystallographic analyses were chosen and mounted on a glass fiber using epoxy resin. Crystal data and other experimental details are summarized in Table 5. The diffraction experiments were carried out at r.t. on a Bruker Axs SMART 1000 CCD area-detector diffractometer using graphite-monochromated Mo–K_α radiation ($\lambda = 0.71073$ Å). Cell parameters and orientation matrix for both complexes were obtained from the least-squares refinement of reflections measured in three different sets of 15 frames each. At the end of data collection, no crystal decay was observed. The collected frames were processed with the software SAINT [15a], and an absorption correction was applied (SADABS) [15b] to the collected reflections. The space groups for all crystals were determined from a combination of Laue symmetry check and their systematic absences, which were then confirmed by successful refinement of the structures. Both structures were solved by direct methods, and expanded by difference Fourier syntheses using the software SHELTXL [16]. Structure refinements were made on F^2 by the full-matrix least-squares technique. In each case, all the non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed in their ideal positions and not refined.

6. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Centre, CCDC nos. 138535–138536. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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References

[1] (a) E.C. Constable, R. Martinez-Manez, A.M.W. Cargill-Thompson, J.V. Walker, J. Chem. Soc. Dalton Trans. (1994) 1585. (b) J.-P. Sauvage, J.-P. Collin., J.-C. Chambron, S. Guillerez, C. Coudret, V. Balzani, F. Barigelletti, L. De Cola, L. Flamigni, Chem. Rev. 94 (1994) 993. (c) D. Astruc, New J. Chem. 16 (1992) 305. (d) J.-P. Collin, S. Guillerez, J.-P. Sauvage, J. Chem. Soc. Chem. Commun. (1989) 776. (e) S. Boyde, G.F. Strouse, W.E. Jones, Jr., T.J. Meyer, J. Am. Chem. Soc. 111 (1989) 7448.

[2] (a) S. Kawabata, I. Yamazaki, Y. Nishimura, Bull. Chem. Soc. Jpn. 70 (1997) 1125. (b) A. Osuka, N. Tanabe, S. Kawabata, I. Yamazaki, Y. Nishimura, J. Org. Chem. 60 (1995) 7177. (c) K. Maruyama, S. Kawabata, Bull. Chem. Soc. Jpn. 63 (1990) 170. (d) S. Kawabata, N. Tanabe, A. Osuka, Chem. Lett. (1994) 1797.

[3] (a) J.P. Konopelski, F. Kotzyba-Hibert, J.-M. Lehn, J.-P. Desvergne, F. Fages, A. Castellan, H. Bouas-Laurent, J. Chem. Soc. Chem. Commun. (1985) 433. (b) L. Fabbrizzi, A. Poggi, Chem. Soc. Rev. 24 (1995) 197. (c) N. Kimizuka, T. Kunitake, J. Am. Chem. Soc. 111 (1989) 3758. (c) V. Ramamurthy (Ed.), Photochemistry in Organized and Constrained Media, VCH, New York, 1991.

[4] H. Bouas-Laurent, A. Castellan, J.-P. Desvergne, Pure Appl. Chem. 52 (1980) 2633.

[5] D.O. Cowan, R.L. Drisko (Eds.), Elements of Organic Photochemistry, Plenum Press, New York, 1976.

[6] J. Wesemann, P.G. Jones, D. Schomburg, L. Heuer, R. Schmutzler, Chem. Ber. 125 (1992) 2187.

[7] (a) C.-W. Chan, T.-F. Lai, C.-M. Che, S.M. Peng, J. Am. Chem. Soc. 115 (1993) 11245. (b) W.-Y. Wong, W.-T. Wong, J. Chem. Soc. Dalton Trans. (1996) 1853.

[8] (a) P.J. Giordano, M.S. Wrighton, J. Am. Chem. Soc. 101 (1979) 2888. (b) D.R. Gamelin, M.W. George, P. Glyn, F.-W. Grevels, F.P.A. Johnson, W. Klotzbücher, S.L. Morrison, G. Russell, K. Schaffner, J.J. Turner, Inorg. Chem. 33 (1994) 3246.

[9] (a) K.-Y. Ho, W.-Y. Yu, K.-K. Cheung, C.-M. Che, J. Chem. Soc. Dalton Trans. (1999) 1581. (b) P. Ghosh, M. Wood, J.B. Bonanno, T. Hascall, G. Parkin, Polyhedron 18 (1999) 1107.

[10] (a) M.S. Wrighton, D.L. Morse, J. Am. Chem. Soc. 96 (1974) 998. (b) M.S. Wrighton, D.L. Morse, L. Pdungsap, J. Am. Chem. Soc. 97 (1975) 2073. (c) V.W.W. Yam, V.C.Y. Lau, K.K. Cheung, Organometallics 14 (1995) 2749. (d) V.W.W. Yam, S.H.F. Chong, K.K. Cheung, Chem. Commun. (Cambridge) (1998) 2121. (e) V.W.W. Yam, K.Z. Wang, C.R. Wang, Y. Yang, K.K. Cheung Organometallics 17 (1998) 2440.

[11] (a) J.T. Lin, S.-S. Sun, J.J. Wu, L. Lee, K.-J. Lin, Y.F. Huang, Inorg. Chem. 34 (1995) 2323. (b) S. Sakanishi, D.A. Bardwell, S.

Couchman, J.C. Jeffery, J.A. McCleverty, M.D. Ward, J. Organomet. Chem. 528 (1997) 35. (c) W.Y. Wong, S.H. Cheung, S.M. Lee, S.Y. Leung, J. Organomet. Chem. 596 (2000) 36.

[12] F.H. Allen, O. Kennard, D.G. Watson, L. Brammer, A.G. Orpen, R. Taylor, J. Chem. Soc. Perkin Trans. 2 (1987) S1.

[13] W.L.F. Armarego, D.D. Perrin, Purification of Laboratory Chemicals, 4th ed., Butterworth–Heinemann, Guildford, UK, 1996.

[14] Y.Y. Choi, W.Y. Wong, W.T. Wong, Chin. J. Chem. 17 (1999) 100.

[15] (a) SAINT, Reference manual, Siemens Energy and Automation, Madison, WI, 1994–1996. (b) G.M. Sheldrick, SADABS, Empirical Absorption Correction Program, University of Göttingen, 1997.

[16] G.M. Sheldrick, SHELXTL™, Reference manual, ver. 5.1, Madison, WI, 1997.