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Novel Tetradentate Ligand With N_2S_2 Donor Set and Its Complexes With (Ni^{II}, Pd^{II} and Pt^{II})

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Abstract

The tetradentate, nitrogen-sulfur pro-ligand [N,N-bis-(2-mercaptoethyl)oxalodiamide] (H_4L) has been synthesised, and its Ni, Pd and Pt complexes are reported. The (H_4L) pro-ligand is reacted with $Ni(NO_3)_2$, $PdCl_2$ and K_2PtCl_4 precursors at reflux in methanol and in the presence of a base to give stable anionic complexes of the general formula $[M(L)]^{2-}$ (where: M = Ni^{II}, Pd^{II}, Pt^{II}; L = $(SCH_2CH_2NCO)_2$].

All compounds have been characterised as needed by spectroscopic methods (I.R, U.V-Vis., A.A., spectroscopies), HPLC, microanalysis and molar conductivity measurements. These studies showed that, the geometry about Ni, Pd and Pt ions is a square planar.

Introduction

There has been much interest in the synthesis and characterisation of tetradentate N_2S_2 type ligands, and their complexes with Ni group. The intensive study of this field stems from the recognition of redox active M-sulfur and / or nitrogen cores.[1, 2, 3] The ability of nickel group to bind both hard and soft donor ligands allows its coordination chemistry to encompass a variety of geometries. Recently a wide range of tetradentate (N_2S_2) type ligands with a variety of substituents on the backbone and their complexes with Ni^{II} and Ni^{IV} ions have been prepared to provide small molecule mimics of the structure and function of structurally related enzymes.[4, 5] As apart of our effort in this field[6,7,8], this paper reports the synthesis and characterisation of a new ligand derived from the reaction of mercaptoethylamine and diethyloxalate and it's Ni^{II}, Pd^{II} and Pt^{II} complexes.

Experimental

Reagents were purchased form Fluka, (Hopking & Williams) & Riedel-Deltaen chemical Co. and used as received without further purification. The I.R spectra were recorded as (KBr disc) using a Pye-Unicam SP3-300. UV-Vis. spectra were recorded in DMF using a Shimadzu-160A spectrometer. Molar conductivity measurements were recorder on Philips PW 9526 in DMF (1×10^{-3}M). (C.H.N) analysis were recorded on analyzer model 1106 (Carlo-Erba) at Mousel University. Atomic absorptions were recorded on a Pye-Unicam spectrophotometer. HPLC was carried out using a Gilson S5ODSI (octadecylsilane) column, with an isocratic system and flow rate 1 cm^3 with H_2O elution and UV (254nm) detection.

Preparations

Synthesis of Ligand [H_4L]

2-mercaptoethylamonium chloride (1.54g, 13.6mmol) and triethylamine (3.8mL, 13.6mmol) were suspended in dry degassed dichloromethane (50mL), under a nitrogen atmosphere. A solution of diethyloxalate (0.98mL, 8.8mmole) in dry, degassed CH_2Cl_2 (20mL) was added dropwise. The mixture was allowed to stir for 14 hrs. under a nitrogen atmosphere. The resulting solution was washed with (2%) aqueous citric acid (2x 20 mL) and then with water (2 x 15 mL). The organic layer was separated, dried over $MgSO_4$ and then filtered. The solvent was removed under reduced pressure and the residue was dried under vacuum to give 0.7g (57%) of the title compound as a white solid. m.p = (88-90) °C.

Synthesis of $K_2[Ni(L)]$

A solution of (H_4L) (0.35g, 1.7mmole) and KOH (1.4g)] were dissolved in MeOH (30mL) with continuous stirring for 30min. Then a solution of [$Ni(NO_3)_2$ 0.5g, 1.7 mmole in (10mL) MeOH] was added slowly to the mixture. The colour of solution became red-brown in colour, and the mixture was allowed to reflux for 90min., and then allowed to cool to room temperature. A white solid (KNO_3) was removed by filtration. Solvent was partially evaporated under reduced pressure to give a red-brown precipitate. The solid was collected, washed with Et_2O and dried under vacuum. Yield 0.45g (78%). m.p. = (279-282) °C (dec).

Synthesis of $K_2[Pd(L)]$

The compound ($PdCl_2$ 0.05g, 0.36mmol) with (15mL) MeOH was heated under reflux for 30 min. The resulting solution was filtered off, and the filtrate was added dropwise under N_2 atmosphere to a flask charged with (H_4L) (0.07g, 0.36mmol) and KOH (1.45g) in (15mL) MeOH. The reaction mixture was allowed to reflux for 60min under nitrogen atmosphere. The colour of the solution became red wine. The volume of solution was concentrated under vaccum to about (8mL). A red-brown precipitate was formed upon addition of Et_2O (10mL) at room temperature. This was collected by filtration, and washed with Et_2O (5mL), and dried under vaccum to give 0.13g (86%) of the title compound. m.p. = (297-299) °C (dec).

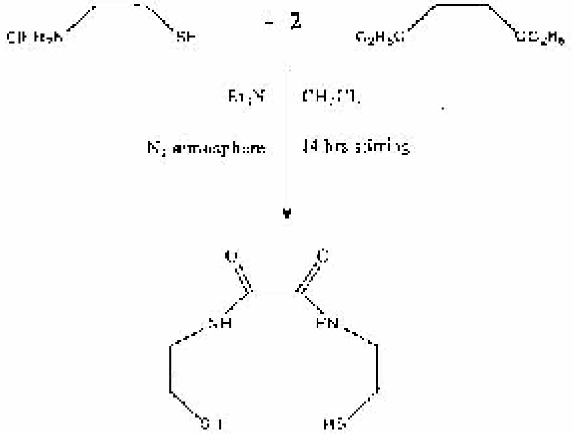
Synthesis of $[Et_3NH]_2[Pt(L)]$

The method used to prepare the complex was analogous to that given for $K_2[Ni(L)]$, but (0.037g, 0.1mmol) K_2PtCl_4 and Et_3N (0.5mL) were used in place of (0.5g, 1.7mmol) $Ni(NO_3)_2$ and (1.5g) KOH respectively. The quantities of other reagents were adjusted accordingly. An identical work-up procedure was used to give the required complex as a yellow-orange solid. Yield 0.06g (66%).

Results and Discussion

Synthesis of the Ligand

The $H_4N_2S_2$ pro-ligand was prepared according to the general method shown in **Scheme 1**. In the IR spectrum (**Figure 1A**), the double band at (1660, 1685) cm^{-1} is corresponding to ν(C=O) amide, indicating the two (C=O) amide groups are non equivalent as a result of a hydrogen bonding.[5] The (U.V-Vis) spectrum showed two absorption peaks at (254nm)(ε_{max} = 732 $L.mol^{-1}. cm^{-1}$), (328nm)(ε_{max} = 1255 $L.mol^{-1}. cm^{-1}$), which assigned for ($\pi \rightarrow \pi^*$) and ($n \rightarrow \pi^*$) transitions respectively, (**Figure 2A**).



Scheme I: The synthesis route of $[H_4L]$

Synthesis of the Complexes

The reaction of $[H_4L]$ with $[M^{2+}]$ metal ions (where: M= Ni, Pd, Pt), was carried out in MeOH under reflux. These complexes are stable in solution and electrolytes, Table (3). The analytical, physical (**Table 1**) and spectral data (**Tables 2 and 3**) are compatible with the suggested structures (**Figure 4**). The (I.R) spectral data of the complexes are presented in (**Table 2**). The strong ν(C=O) stretching bands in the free ligand at (1685 and 1666)cm^{-1} for the amide groups are shifted, and appeared at (1620), (1650) and (1635) cm^{-1} for the compounds $K_2[Ni(L)]$ (**Figure 1B**), $K_2[Pd(L)]$ (**Figure 1C**), $[Et_3NH]_2[Pt(L)]$ (**Figure 1D**), respectively, [10] indicating that, the two amide groups are equivalents in comparison with the free ligand. These bands were assigned to the ν(C=O) stretches of reduced bond order. This can be attributed to the delocalisation of metal electron density into the ligand π-system [11] The bands at ca. (550-450) and at ca. (300-370) cm^{-1} range were assigned to ν(M-N) and ν(M-S) stretches, indicating that the nitrogen amide and thiol groups were involved in coordination with metal ion.[12,13] The (U.V-Vis) spectra of the complexes $K_2[Ni(L)]$ (**Figure 2B**), $K_2[Pd(L)]$ (**Figure 2C**), $[Et_3NH]_2[Pt(L)]$ (**Figure 2D**) displayed two intense peaks in the (U.V.) region at (273-320 nm) range assigned to ligand field and charge transfer transitions. The nickel complex $K_2[Ni(L)]$ complex showed another peak at (390 nm), which is assigned to ($^1A_{1g} \rightarrow {}^1B_{1g}$) ($a_{1g} \rightarrow b_{1g}$) (d-d) transition in a square planar structure. However, the peak was shifted to lower wavelength due to the intensity stealing. The spectra of $K_2[Pd(L)]$ and $[Et_3NH]_2[Pt(L)]$ exhibited peaks in the visible region at (407 nm) and (495nm) respectively. These bands were assigned to ($^1A_{1g} \rightarrow {}^1B_{1g}$) (d - d) transition, suggesting a square planar geometry around palladium(II) and platinum(II) ions.[8,14] The molar conductance of the complexes in (DMF), (**Table 3**) lie in the (169-189) S cm^2 $mole^{-1}$ range, indicating their electrolytic nature with (1:2) mho.[15] The HPLC chromatogram for $[Pt(L)]^{2-}$ (**Figure 3**) gave a single species at (Rt = 14.85min.), showing that, the complex is pure and appears as one isomer in solution.

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الخلاصة

تضمن البحث تحضير الليكند الجديد ذي الرمز [N, N' L)$_2$ (H] – *bis*-(2 - mercaptoethyl) oxalodiamide ومعقداته مع النيكل و البلاديوم و البلاتين. تم معاملة الليكند مع المواد الاولية $PdCl_2$, $NiCl_2$ و K_2PtCl_4 مع KOH وباستخدام الميثانول وسطاً للتفاعل وبوجود القاعدة المناسبة و تحت التصعيد الارجاعي لاعطاء معقدات ايونية جديدة ذات الصيغة العامة $[M(L)]^{2-}$ حيث ان M = Ni, Pd, Pt, L = $(SCH_2CH_2NCO)_2$ شخصت جميع المركبات المحضرة بالطرق الطيفية التالية [الاشعة تحت الحمراء و الاشعة فوق البنفسجية المرئية و مطيافية الذرية] . كذلك شخصت المركبات بواسطة HPLC (السائل الكفوء) و التحليل الكمي الدقيق للعناصر مع التوصيلية المولارية الكهربائية . من النتائج اعلاه الشكل الفراغي المقترح لمعقدات النيكل و البلاديوم و البلاتين هو المربع المستوي.

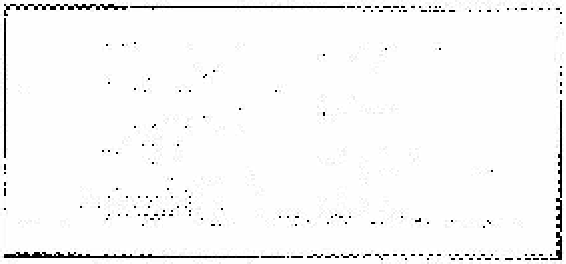

Figure (1A) The IR Spectrum of Ligand [H$_2$L]

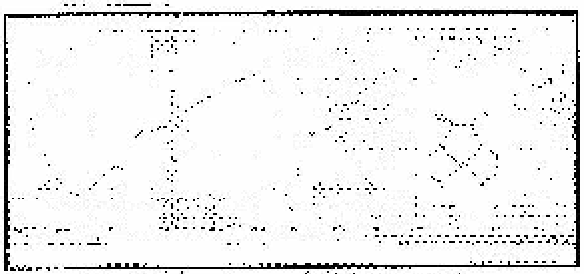

Figure (1B) The IR Spectrum of [Ni L]$^{-2}$

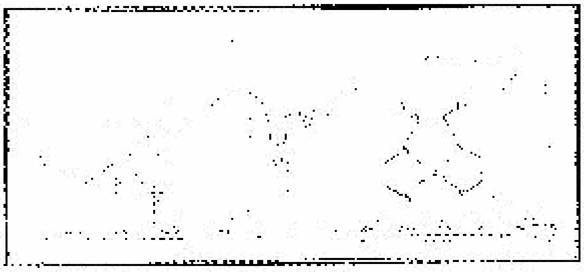

Figure (1B) The IR Spectrum of Pd L]$^{-2}$

Figure (1B) The IR Spectra of [Pt L]^{2}

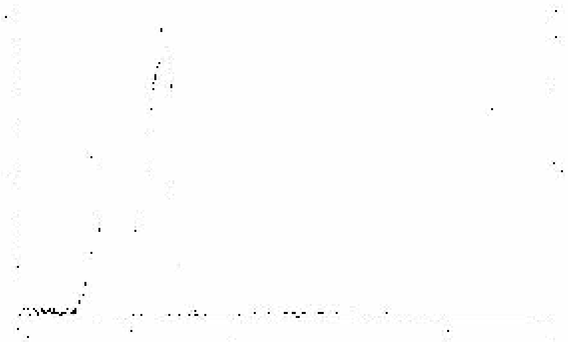

Figure (2 –A) The UV spectrum of [H$_2$L^1]

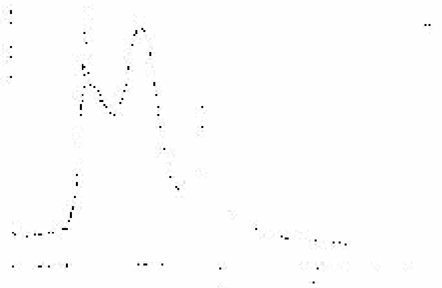

Figure (2 –B) The UV spectrum of [NiL^1]$^{-2}$

Figure (2 –C) The UV spectrum of [PdL^1]$^{-2}$

Figure (2 –D) The UV spectrum of [PtL^1]$^{-2}$

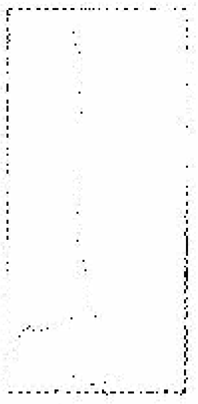

Figure (3) The HPLC Chromatogram of [Pt L^1]$^{-2}$

Table (1) The Physical properties of complexes

Formula	Colour	m.p. °C (dec)	M.Wt	Yield%	Microanalysis Found, (calc.) % C%	H%	N%	Metal%
$K_2[Ni(SCH_2CH_2NCO)_2]$	Deep brown	279-281	341.14	78	(21.12) 21.09	(2.36) 2.33	(8.21) 8.17	(17.20) 16.89
$K_2[Pd(SCH_2CH_2NCO)_2]$	Brown	297-299	388.84	86	(18.56) 18.50	(2.07) 1.98	(7.20) 7.19	(27.36) 26.22
$(Et_3NH)_2[Pt(SCH_2CH_2NCO)_2]$	Yellow- orange	298-300	603.74	66	(35.80) 34.90	(6.67) 6.06	(9.32) 8.89	(32.31) 31.02

Table (2) I.R Spectral data of the ligand and its complexes (cm^{-1})

Symbol	Formula	ν(N – H)	ν(C – H)	ν(S – H)	ν(C = O)	δ(N – H)	δ(CH$_2$)	ν(C – N)	ν(C – S)	Additional peaks
$[H_4L^1]$	$(HSCH_2CH_2NHCO)_2$	3310 (S)	2920 (w)	2525 (w)	1660 (vs) 1690 (vs)	1530 (S)	1450 (m)	1220 (S)	1030 (m)	770m (N- H) out of plane
$[Ni(L^1)]^{-2}$	$K_2[Ni(SCH_2CH_2NCO)_2]$	-	2950 (w)	-	1620 (S)	-	1440 (m)	1210 (vw)	1030 (S)	480ν(Ni – N) 440ν(Ni – N) 320ν(Ni – S) 290 ν(Ni – S)
$[Pd(L^1)]^{-2}$	$K_2[Pd(SCH_2CH_2NCO)_2]$	-	2920 (vw)	-	1650 (S)	-	1490 (m)	1220 (w)	1010 (w)	450 ν(Pd – N) 370 ν(Pd – S)
$[PtL^1]^{-2}$	$(Et_3NH)_2[Pt(SCH_2CH_2NCO)_2]$	3300 2690 (S)	2920 (S)	-	1635 (S)	1510 (w)	1490 (S)	1180 (m)	1030 (w)	550 ν(Pt – N) 490 ν(Pt – N) 440 ν(Pt – S) 390ν(Pt – S)

S = strong , w = weak , vs = very strong , m = medium , vw = very weak

Table (3): Electronic spectral data* and conductivity measurement of $[H_4L]$ and its metal complexes

Compound	λ nm	υ cm^{-1}	€ max S.cm^{-1}.mol^{-1}.	Assignment	Medium	Conductivity $\Lambda_M(\Omega^{-1}\ cm^2mol^{-1})$	Ratio
$[H_4L]$	264	37878	732	$\pi \rightarrow \pi^*$			
	326.6	30617	1755	$n \rightarrow \pi^*$			
$[Ni(L)]^{-2}$	273	36360	1297	Ligand field	DMF	169	2:1
	324	30864	1701	Ligand field			
	390	25641	676	d→d transition $^1A_{1g} \rightarrow {}^1B_{1g}$			
$[Pd(L)]^{-2}$	275	36363	624	Ligand field	DMF	173	2:1
	315	31746	222	Ligand field			
	407	24570	175	d→d transition $^1A_{1g} \rightarrow {}^1B_{1g}$			
$[Pt(L)]^{-2}$	203	49309	1304	Ligand field	DMF	188	2:1
	297	33870	95	Ligand field			
	495	20202	80	d→d transition $^1A_{1g} \rightarrow {}^1B_{1g}$			