

Synthesis and Characterization of Multinuclear Complexes with Pyridylthiolato Selenium (IV) and their Adducts with Neutral Ligands

Nabeel H. Buttrus
Dept. of Chemistry, College of Science
University of Mosul

Wajida I. Alhamadani
Kurtiba Secondary School
Mosul-Iraq

Received 28/2/2006 Accepted 3/4/2006

الخلاصة

يتفاعل فلز السليينيوم مع ثنائي بيريداييل ثنائي الكبريتيد (Py_2S_2) في التولوين المغلي ليعطي المركب $[Se(Spy)_4]$ خلال تفاعل الاكسدة المضافة وقد تم تحضير المركبات متعددة النوى التي تمتلك الصيغ العامة $[Se(Spy)_4(MCl_2)_2]$ و $[Se(Spy)_4(MCl_2)_4]$ حيث $M = Cu(II), Ni(II), Co(II)$ من خلال التفاعل المباشر بين الاملاح $CoCl_2.6H_2O, NiCl_2.6H_2O$ or $CuCl_2.4H_2O$ مع مركب السليينيوم اعلاه.

كما تم تحضير نواتج اضافة المعقدات ثلاثية النواة مع 1,10-فينانثرولين والتي تحمل الصيغة العامة $[Se(Spy)_4(MCl_2)_2(Phen)_2]$. لقد تم تشخيص كافة المعقدات ونواتج الاضافة بواسطة الطيف الذري والاشعة تحت الحمراء والاشعة فوق البنفسجية/المرئية والتوصيلية الكهربائية والقياسات المغناطيسية.

ABSTRACT

Selenium metal react with di-pyridyl disulfide (Py_2S_2) in refluxing toluene to give the compound $[Se(Spy)_4]$ through oxidative addition reaction. Multinuclear complexes of the general formula $[Se(Spy)_4(MCl_2)_2]$ and $[Se(Spy)_4(MCl_2)_4]$ were prepared by a direct reaction of $CoCl_2.6H_2O, NiCl_2.6H_2O$ or $CuCl_2.4H_2O$ with the selenium compounds. Adducts of trinuclear complexes with 1,10-phenanthroline were also prepared and having the general formula $[Se(Spy)_4(MCl_2)_2(Phen)_2]$. The prepared complexes and their adducts were characterized by their metal analysis, IR and UV/Vis spectroscopy, conductivity and magnetic measurements.

INTRODUCTION

Complexes of both main group and transition metals with sulphur-donor ligands are a subject of current interest, but also for the presence of of the biochemical significance of such species [1-3].

The electrochemical oxidation of a metal into a non-aqueous solution of a thiol or disulfide is a convenient and direct route to the neutral thiolato complexes of such elements as zinc, cadmium, mercury [4], tin [5], gallium, indium and thallium [6].

The oxidative-addition reaction of di-2-pyridyldisulfide with tin(II) halide was studied by Masaki and Mutsunami and found to give dihalo bis(2-pyridine thiolato) tin(IV) [7]. The direct reaction between indium or tin metal with $(C_6H_5)_2E_2$, where $E = S$ or Se to give the neutral compound $[In(E(C_6H_5)_3)]$ or $[Sn(EC_6H_5)_4]$ had been studied [8]. In our recent articles, we had described the direct reaction between tin and bismuth with $(RC_6H_4S)_2$, where $R = o-NH_2, p-Me, p-Bu^t$, in refluxing toluene to give the corresponding bismuth and tin compounds, $[Bi(SC_6H_4R)_3]$ and $[Sn(SC_6H_4R)_4]$ respectively [9, 10].

In view of these interesting results and as a continuation of our comprehensive studies on transition and non-transition metal complexes with sulfur containing ligands [11-13], we have prepared multinuclear complexes through adduct's formation with selenium compound $[Se(PyS)_4]$ which was prepared by oxidative addition of di-2-pyridyl disulfide also represented the preparation of some adducts with 1,10-phenanthroline.

EXPERIMENTAL

General

IR spectra were recorded on Perkin-Elmer 580B IR spectrophotometer in the $(4000-200\text{ cm}^{-1})$ range using Nujol mulls or CsI discs. The metal content was estimated spectrophotometrically using Shimadzu AA 670. Conductivity measurements were made on $10^{-3}M$ solution of the complexes in dimethyl sulfoxide (DMSO) solvent at ambient temperature using conductivity meter model 4070 Jenway. Electronic spectra were recorded on Shimadzu UV/Vis. Spectrophotometer UV-160 for $10^{-3}M$ solution of complexes in DMSO using 1cm quartz cell. The magnetic measurements were carried out at $25^\circ C$ on the solid state by Faradays method using Bruker BM6 instrument.

Materials

The compound $[Se(PyS)_4]$ was prepared according to a literature method [12]. The metal chlorides were used as supplied by Fluka.

Preparation of $[Se(Spy)_4(MCl_2)_2]$ complexes, $M = Co, Ni, Cu$

A clear solution of $[Se(Spy)_4]$ (1 mmol) in methanol (10cm^3) was added to a solution of $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$ or $CuCl_2 \cdot 4H_2O$ (2 mmol) in distil water (10cm^3). The mixture was stirred under reflux for Ca 2h., the precipitate formed,

was filtered off washed with methanol, water and diethyl ether then dried under vacuum for several hours.

Preparation of $[\text{Se}(\text{Spy})_4(\text{MCl}_2)_4]$ complexes

These complexes were prepared using similar procedure as above except using (4mmol) of metal salts.

Preparation of $[\text{Se}(\text{Spy})_4(\text{MCl}_2)_2(\text{Phen})_2]$ adducts

The complex $[\text{Se}(\text{Spy})_4(\text{MCl}_2)_2]$ in (10cm³) dimethyl formamide was added to a solution of the ligand 1,10-phenanthroline (0.36g, 0.02mol) in methanol (10cm³). The mixture was stirred with gentle heat for ca. 2h., during which time a precipitate started to deposit. This was cooled to room temperature and the solid filtered off, washed with methanol then dried under vacuum for several hours.

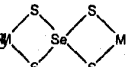
RESULTS AND DISCUSSION

The direct reaction of the ligand di-2-pyridyl disulfide with selenium metal in refluxing toluene using a 1:2 metal to ligand molar ratio afforded the compound $[\text{Se}(\text{PyS})_4]$ through an oxidative addition reaction [12]. Treatment of the selenium compound in alcohol with an aqueous solution of metal(II) chloride in (1:2) and (1:4) molar ratio gave the tri and pentanuclear complexes of the type $[\text{Se}(\text{Spy})_4(\text{MCl}_2)_n]$ n = 2 or 4. The nucleophilicity of the thiolate sulfur atom in the selenium compound is responsible for the formation of these new complexes.

The physical properties of the complexes are listed in Table (1). The complexes are quite stable in dry air and melt or decompose at above 200°C. They are insoluble in most organic solvents but soluble in DMSO.

The most important IR assignment of the selenium compound and complexes are listed in Table 2. The most important band which appeared at 1580cm⁻¹ due to $\nu(\text{C}=\text{N})$ stretching of the free disulfide is shifted either to higher field (1595cm⁻¹) or lower field (1560cm⁻¹) in the prepared complexes. This is usually indicates that C=N group is involved in the coordination with metal atom through nitrogen of the pyridine ring [4]. The bands appeared at 450-500cm⁻¹ are tentatively assigned to $\nu(\text{M}-\text{N})$ M=Co, Ni, Cu, indicating that nitrogen atom is involvement in the coordination with the metal [15].

The $\nu(\text{C}-\text{S})$ band was observed at 1062cm⁻¹ in the free ligand which upon coordination with metals was found to shift either to upper or lower frequency values (Table 2). Further support for the formation of new complexes is provided by the appearance of a new band within the 360-380 or 400 cm⁻¹ range

characteristic of the bidentate tetrathio selenium complexes  [16] and are

tentatively attributed to $\nu(\text{M}-\text{S})$, M=Se, Co, Ni or Cu [13]. Furthermore, the IR spectra of the multinuclear complexes showed another band within the 325-290 cm⁻¹ range which may be are $\nu(\text{M}-\text{Cl})$ [16].

The values of magnetic moments of Co(II) complexes (2 and 5) are 3.9 and 4.1 B.M. respectively. The electronic spectrum (Table 2) of Co(II) complexes shows a broad band at 16400-17000 cm^{-1} due to ${}^4A_2 \rightarrow {}^4T_1P(\nu_3)$ transition due to spin orbit coupling [17] similar to those reported for $[\text{CoCl}_4]^{-2}$ and $[\text{CoI}_4]^{-2}$ suggesting a tetrahedral geometry for Co(II) complexes.

The Ni(II) complexes (No 3 and 6) show a magnetic moment of 3.80 and 3.87 B.M. these values agree well with a higher-spin configuration and indicates the presence of tetrahedral environment [18]. The electronic spectra of Ni(II) complexes show a band at 13000-14400 cm^{-1} which correspond to the transition ${}^3T_1(F) \rightarrow {}^3T_1(P)(\nu_3)$ in tetrahedral environment.

The Cu(II) complexes (No 4 and 7) shows a magnetic moment 1.90 and 1.98 B.M. the electronic spectrum showed bands at 13300-15797 cm^{-1} which correspond to the transition ${}^2B_{1g} \rightarrow {}^2A_{2g}$ and after transition at 28000 cm^{-1} correspond to charge transfer respectively. This shows that the Cu(II) complexes have tetrahedral geometry [19].

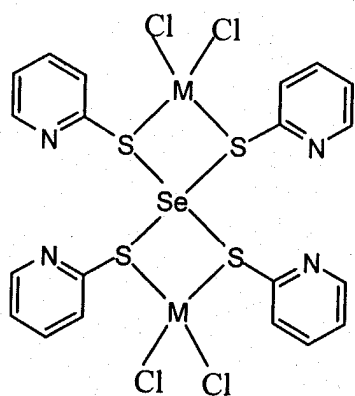
The electronic spectra of the isolated adduct (8-10) with 1,10-phenanthroline recorded in DMSO are listed in Table (2). The Co(II) complex (8) shows the presence of two bands in the region 17600 and 21230 cm^{-1} are assigned to ${}^4A_{2g} \rightarrow {}^4T_{1g}(F)(\nu_3)$ and ${}^4A_{2g} \rightarrow {}^4T_{1g}(P)(\nu_2)$ transitions respectively. This shows that the positions of the electronic spectral bands have changed from tetrahedral to octahedral environment [20]. The Ni(II) complex (9) shows the presence of three bands in the region 11230-26230 cm^{-1} which are assigned to ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)(\nu_3)$, ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)(\nu_2)$ and ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)(\nu_1)$ transition respectively. This show that the structure have an octahedral environment.

The Cu(II) complex (10) shows the presence of the bands at 14300, 16000 and 27600 cm^{-1} which may assigned to ${}^2B_{1g} \rightarrow {}^2A_{1g}$, ${}^2B_{1g} \rightarrow {}^2B_{2g}$ and ${}^2B_{1g} \rightarrow {}^2E_g$ transitions respectively. This shows that the Cu(II) complex have distorted octahedral geometry.

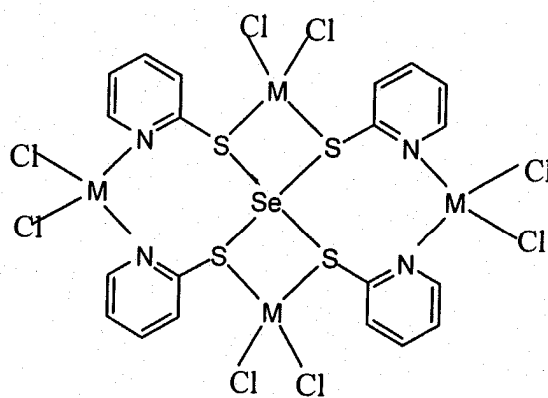
The molar conductivities of 10^{-3}M solution of the complexes and their adducts indicates that all complexes and adducts are non electrolyte in DMSO [21].

The magnetic moment data of these adducts calculated from the corrected magnetic susceptibilities determined at room temperature are given in Table (1).

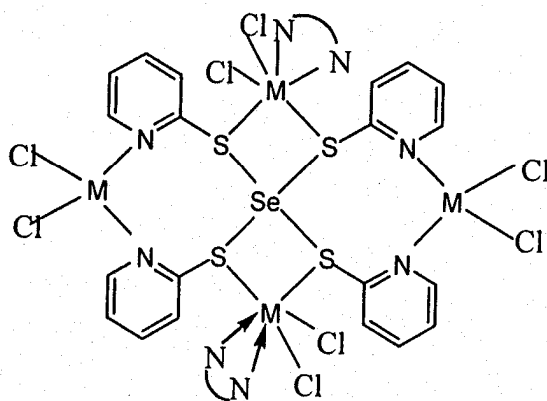
On the basis of spectral, magnetic and other studies the following structures could be assigned to the metal complexes and adducts as in Fig.1.



Complex No= (2-4)



(5-7)



(8-10)

M= Co, Ni, Cu


 N = 1,10-phenanthroline

Fig. 1: Suggested structure of the prepared complexes and adducts

Table 1: Physical properties, magnetic moments and conductance data for complexes and adducts

No.	Complex	Colour	m.p. (°C)	Yield %	Analysis % found (calcd) Se (M)	Λ $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$	μ_{eff} (B.M.)
1	[Se(PyS) ₄]	Pale blue	358*	93	15.20 (15.22)	14	-
2	[Se(PyS) ₄ Co ₂ Cl ₄]	Dark brown	286	85	10.10 (10.14) 15.09 (15.15)	20	3.9
3	[Se(PyS) ₄ Ni ₂ Cl ₄]	Gray	294	88	10.08 (10.15) 15.00 (15.04)	18	3.80
4	[Se(PyS) ₄ Cu ₂ Cl ₄]	Dark, green	300*	83	10.00 (10.03) 16.09 (16.16)	21	1.90
5	[Se(PyS) ₄ Co ₄ Cl ₈]	Dark kakhi	350*	75	8.79 (8.81) 26.30 (26.31)	15	4.1
6	[Se(PyS) ₄ Ni ₄ Cl ₈]	Greenish yellow	280- 282	79	8.75 (8.82) 26.15 (26.21)	17	3.87
7	[Se(PyS) ₄ Cu ₄ Cl ₈]	Dark brown	320- 322	72	8.61 (8.63) 27.59 (27.76)	14	1.98
8	[Se(PyS) ₄ Co ₂ Cl ₄ (Phen) ₂]	Brown	285*	80	6.89 (6.94) 10.31 (10.36)	12	4.60
9	[Se(PyS) ₄ Ni ₂ Cl ₄ (Phen) ₂]	Green	299- 301	79	6.58 (6.60) 10.28 (10.31)	10	3.20
10	[Se(PyS) ₄ Cu ₂ Cl ₄ (Phen) ₂]	Pale brown	289- 291*	83	6.83 (6.89) 11.01 (11.08)	18	1.83

* decomposition temperature

Table 2: Electronic and infrared bands (cm^{-1}) for the complexes and adducts

No.	UV/Vis	Selected IR bands							
		$\nu(\text{C}=\text{N})$	$\nu(\text{C}-\text{S})$	$\nu(\text{Se}-\text{S})$	$\nu(\text{M}-\text{S})$	$\nu(\text{M}-\text{N})$	$\nu(\text{M}-\text{Cl})$		
1	34246, 25000	1581m	1045m	334m	-	-	-	-	
2	16400, 16900	1580m	1083m	337w	380m	-	-	276w	
3	13000, 14200	1582m	1036m	334m	372m	-	-	293m	
4	14300, 15797	1579m	1085s	340w	375m	-	-	285m	
5	16800, 17000	1598s	1037s	324w	380m	450s	-	325w	
6	13600, 14400	1560s	1075m	333w	375m	480s	-	295w	
7	13300, 15700	1595s	1025s	342m	370m	465s	-	290w	
8	17600, 21230	1562s	1030m	336m	375m	500m	-	320m	
9	11230, 18500, 26230	1598s	1080s	340m	380m	485m	-	310m	
10	14300, 16000, 27600	1595s	1035s	342w	370m	490m	-	325m	

m= medium, s= strong, w= weak

REFERENCES

1. K.J. Stanger, J.W. Wiench, M. Prusji, J.H. Espenson, G.A. Krans and R.J. Angelici, *J. Molecular Cat.A.* 243(2), 158, (2006).
2. R. Balamurugan, M. Palaniandavar, H.S. Evans and M. Neuburger, *Inorg. Chim. Acta*, 464, 210(2005).
3. G.E. Cami, M. L.Gonzalez, F. SanzRusiz and J.C. Pedregosa, *J. Phys, Chem. Of Solids*, 66(6), 936 (2005).
4. J.L. Hencher, M.A. Khan, F.F. Said and D.G. Tuck *Polyhedron*, 4(7) 1263, (1985).
5. R. Kumar, H.E. Mabrouk, and D.G. Turk, *J. Chem. Soc. Dalton Trans*, 1045 (1988).
6. J.L. Hencher, M.A. Khan, F.F. Said, R. Selier and D.G. Turk, *Inorg. Chem.* 21, 2787 (1982).
7. M. Masaki and S. Mutsunami, *Bull. Chem. Soc. Japan* 49(11), 3274 (1976).
8. R.K. Chadha, R. Kumar and D.G. Turk, *Can. J. Chem.*, 65, 1336(1987).
9. N.H. Buttrus, *Synth. React. Inorg. Met. Org. Chem.*, 28(10), 1643, (1998).
10. N.H. Buttrus, M.M. Suliman and T.A.K. Al-Allaf, *Synth. React. Inorg. Met. Org. chem.* 31(5), 837 (2001).
11. N.H. Buttrus and A.F. Al-Omari, *raf. J. Sci*, 16(3), 138 (2005).
12. N.H. Buttrus, Z.M. Jasim and T.A.K. Al-Allaf, *J.J. Appl. Sci*, 7(2) 92 (2005).
13. L.J. Al-Hayaly, N.H. Buttrus, F. Tarq. And T.A.K.-Al-Allaf, *J.J. Appli. Sci.*, 7(1) 64, (2005).
14. N. Ohkaka and K. Nakamoto, *Inorg. Chem.* 12, 2440 (1973).
15. N.H. Buttrus, *National J. Chem.* 8, 611 (2002).
16. T.A.K. Al-Allaf, I.A. Mustafa and S.E. Al-Mukhtar, *Transition. Met. Chem.* 18, 1 (1993).
17. H.A. Bayoumi, E.M. Shonkry and M.M. Mostafa, *Synth. React. Inorg. Met. Org. chem.* 31, 94), 579 (2001).
18. I.A. Mustafa and L. Al-Saady, *Nationa J. Chem.*, 13, 65, (2004).
19. P. Comba, W.T. Hambley, P. Hifenhans and D.T. Richens, *J. Chem. Soc. Dalton. Trans*, 533, (1996).
20. S. Gandra and K. Gupta, *Synth. React. Inorg. Met. Org. Chem.* 31(4), 661 (2001).
21. W.J. Geary, *Coord. Chem. Rev.* 7, 81, (1971).