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Synthesis and Characterization of Trinuclear Complexes and Adducts through Oxidative Addition Reaction of Thiuram Disulfide

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ABSTRACT

Selenium metal react with $(RNHC(S)S)_2$ when (R = Ph or o-EtPh) in refluxing toluene to give the compounds $[Se\{RNHC(S)S\}_4]$ in high yields. The new trinuclear complexes were prepared by the reaction of $[Se\{RNHC(S)S\}_4]$ with some transition metal chloride salts in (1:2) molar ratio giving complexes of the general formula $[M_2Se\{RNHC(S)S\}_4Cl_4]$ where M = Co(II) and Ni(II). Adducts of these complexes with triphenyl phosphine and 1,10-phenanthroline were also prepared.

The new complexes and adducts were characterized by atomic absorption, infrared, UV-visible spectroscopy, conductivity and magnetic measurements.

تحضير وتشخيص عدد من معقدات ثلاثية النوى ونواتج الإضافة من خلال تفاعل الإضافة المؤكسدة للثايورام ثنائي الكبريتيد

الملخص

تم في هذا البحث مفاعلة عنصر السيلينيوم مع الليكاند $(RNHC(S)S)_2$ عندما R = Ph و o-EtPh في التولوين ليعطي المركبات $[Se\{RNHC(S)S\}_4]$ وبنسبة ناتج عالية. كذلك تم تحضير معقدات ثلاثية النوى جديدة من خلال مفاعلة المركب $[Se\{RNHC(S)S\}_4]$ مع بعض املاح كلوريدات الفلزات الانتقالية وبنسبة مولية (1:2)، والتي تمتلك الصيغة العامة $[M_2Se\{RNHC(S)S\}_4Cl_4]$ عندما M = Co(II) ، Ni(II) ، كذلك تم تحضير مركبات الإضافة للمعقدات ثلاثية النوى باستخدام 1،10- فينانثرولين وثلاثي فنيل فوسفين.

تم تشخيص المعقدات ثلاثية النوى ومركبات الإضافة المحضرة بوساطة طيف الامتصاص الذري، طيف الأشعة تحت الحمراء، طيف الأشعة فوق البنفسجية، التوصيلية الكهربائية فضلا عن القياسات المغناطيسية.

INTRODUCTION

Many sulphur donor groups available in biological systems, the thiuram disulfide $R_2NC(S)SSC(S)NR_2$ are known on account of their biological activity, which leads to many applications as fungicides, rubber vulcanization accelerators, agents for alcoholism therapy (Kitson, 1985, Butterfield *et al.*, 1991) and as arrestors of human immuno-deficiency virus infections such as AIDS (Gessner *et al.*, 1992).

Typical reactions of thiuramdisulfides with metal species fall under three distinct categories (a) adduct formation (b) ligand reduction with concomitant degradation to dithiocarbamate (c) thiuram oxidation (Victoriano, 2000).

Contreas and Cortes (1970) have characterized the cobalt (II) chloride and chromium (III) chloride complexes of several thiuram ligands and have shown that tetramethylthiuram disulfide coordinates in a bidentate manner through both thiocarbonyl sulphur atoms resulting in formation of a seven membered ring complexes.

Complexes of Zn(II), Cd(II) and Hg(II) with N,N,N`,N`-tetramethylthiuram disulfide have been studied by Srivastava *et al.* (1983) and they showed that thiuram act as bidentate through both thiocarbonyl sulfur atoms.

Oxidation of copper powder by carbon disulfide solutions of thiuram disulfides lead to a dark solutions of $[Cu(dtc)_2]$, which are reduced by excess metal to the cuprous dithiocarbamate [Cu(dtc)] was studied using X-ray diffraction of the single crystal by Victoriano (2000).

Tin and bismuth metals react with N,N,N`,N`-tetraethyl thiuramdisulfide $[Et_2NC(S)S]_2$ and N,N,N`,N`-tetramethyl thiuramdisul-fide $[Me_2NC(S)S]_2$ in toluene to give the compounds $Sn(S_2CNR_2)_4$ and $Bi(S_2CNR_2)_3$(R = Et, Me) in high yield were studied by Mustafa and Taqa (2001).

In the present work, the oxidative addition of the S-S linkage of $[RNHC(S)S]_2$ (R = Ph or *o*-EtPh) to selenium metal in (2:1) molar ratio have been reported, also reported the synthesis of trinuclear complexes of the general formula $[Se(RNHC(S)S)_4(MCl_2)_2]$ (M = Co(II), Ni(II)), as well as adducts with some neutral donor ligands, i.e, triphenylphosphine (PPh_3) and 1,10-phenanthroline (Phen) were reported as a part of our continued interest in investigating this type of interaction between selenium metal and various donor ligands (Buttrus *et al.*, 2001; Buttrus and Saied, 2004).

EXPERIMENTAL

General Data:

Selenium metal (Fluka) was available in the form of 0.6 cm diameter rods. Toluene and substituted amines were used as supplied (Fluka). Thiuram disulfide were synthesized by standard methods (Victoraino, 2000).

Atomic absorption was carried out using a (PYE UNICAM SPg Atomic Absorption Spectrophotometer). Infrared spectra were recorded on a Perkin-Elmer 580 Infrared Spectrophotometer using CsI pellets. UV-visible spectra were recorded on a Shimadzu UV/Visible Recording Spectrophotometer UV/160. Conductance measurements were carried out at room temperature for 10^{-3} M solution of compounds in DMF using a Jenway 4070 conductivity meter. The metal content was estimated spectrometrically using Shimadzu AA670 Spectrophotometer. Magnetic moment measurements were carried out at (25 °C) on the solid state by Faraday's method using Bruker BM6 instrument.

Synthesis:

[Se(RNHC(S)S)$_4$] (R = Ph or o-EtPh)

A mixture of finely cut selenium metal (0.79 g, 1 mmol) and thiuram disulfide (RNHC(S)S)$_2$ (2.0 mmol) in toluene (60 cm^3) was refluxed for 14 h. The reaction mixture was filtered through celite and the result solution was reduced to ca 10 cm^3 by evaporation under reduced pressure. The solid thus obtained, after cooling in an ice-bath, was collected by filtration, washed with diethyl ether and dried in vacuum.

[M$_2$Se{RNHC(S)S}$_4$Cl$_4$], [M = Co(II), Ni(II)]

The selenium compound [Se(RNHC(S)S)$_4$] (0.75 gm, 1.0 mmol) in (10 cm^3) methanol was added to an alcoholic solution of metal (II) chloride (2 mmol in 20 cm^3 methanol). The reaction mixture was stirred under reflux for 2 h., during which time a precipitate was formed. It was collected by filtration, washed with methanol and dried in vacuum.

[M$_2$Se(RNHC(S)S)$_4$(PPh$_3$)$_4$Cl$_4$]

The complex [M$_2$Se(RNHC(S)S)$_4$Cl$_4$] (1.0 mmol) in (10 cm^3) acetone was added to a solution of the ligand PPh$_3$ (1.05 g, 4 mmol) in methanol (10 cm^3), the mixture was stirred under reflux for 2 h., during which time a precipitate was formed. It was collected by filtration, washed with methanol and dried under vacuum.

[M$_2$Se(RNHC(S)S)$_4$(Phen)$_2$Cl$_4$]

Treatment of the complex [M$_2$Se(RNHC(S)S)$_4$Cl$_4$] (1.0 mmol) in (10 cm^3) acetone with 1,10-phenanthroline (0.36 g, 2 mmol) in methanol (10 cm^3). The mixture was stirred with gentle heat for ca 2 h., 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 4 h.

RESULTS AND DISCUSSION

The method described in this work clearly represents a simple and efficient one-pot synthesis of Se(RNHC(S)S)$_4$ compounds where (R = Ph or o-EtPh) by a direct oxidative addition reaction of thiuram disulfide to selenium metal (Buttrus *et al.*, 2001) as in the following equations.

$$2M + (RNHC(S)S)_2 \longrightarrow 2M\{RNHC(S)S_2\} \quad .\ .\ .\ .\ 1$$

$$2M\{RNHC(S)S_2\} + 2\{RNHC(S)S\}_2 \longrightarrow 2M\{RNHC(S)S\}_4 \quad .\ .\ .\ .\ 2$$

Reduction of thiuram disulfide and scission of the S-S bond results in incorporation of the dithiocarbamate fragments into the selenium coordination sphere. The oxidative insertion process of equation (2) is clearly analogous to the known reactions involving the conversions, In° → In^{+3} or Sn^{+2} → Sn^{+4} (Buttrus, 1998).

The trinuclear complexes were prepared by adding an alcoholic solution of metal(II) chloride to the alcoholic solution of [Se{RNHCS(S)}$_4$]. The nucleophilicity of the sulfur atoms in the selenium compounds are responsible for this adduct formation.

The physical properties of the solid complexes are listed in Table (1). The complexes are quite stable in dry air and stable to heat, they are insoluble in most organic solvents with exception of dimethylformamide (DMF) and dimethylsulfoxide (DMSO).

The most important IR assignment of the selenium compounds are listed in Table 2. The characteristic IR bands that are sensitive to molecular structure are the stretching modes of the N-C, C-S and Se-S bonds. In particular, the ν(C-N) band in the region 1460 and 1468 cm^{-1} and the ν(C-S) band in the region 850 and 880 cm^{-1} while ν(C=S) in the region 991-1046 cm^{-1}, these bands are known to depend on the nature of coordination of dithiocarbamate ligand to metal ion (Sharma *et al.*, 2003). The dithiocarbamate ligand in [Se{RNHC(S)S}$_4$] compounds act as monodentate, through sulfur atoms of ν (C-S) band only, Table 2. Further support of the coordination of these derivatives was provided by the appearance of the band about 340 and 365 cm^{-1} which are assigned to ν(Se-S) (Buttrus, 2004).

Table 1: Colours, melting point, elemental analysis, conductance and magnetic measurements of the complexes

No.	Complex	Colour	m.p. °C	Analysis found/calc.		Λ 10^{-3} M ohm^{-1}.cm^2.mol^{-1}	μ_{eff} (B.M)
				Se%	M%		
1	[Se{PhNHCS$_2$}$_4$]	Pale yellow	119	10.48 (10.51)	-	14	-
2	[Se{o-EtPhNHCS$_2$}$_4$]	Orange	160	8.97 (9.14)	-	17	-
3	[Co$_2$Se{PhNHCS$_2$}$_4$Cl$_4$]	Greenish yellow	126	7.60 (7.81)	11.57 (11.60)	31	4.61
4	[Co$_2$Se{o-EtPhNHCS$_2$}$_4$Cl$_4$]	Violet	137	7.04 (7.03)	10.41 (10.49)	5	2.06
5	[Ni$_2$Se{PhNHCS$_2$}$_4$Cl$_4$]	Green	147	7.76 (7.81)	11.59 (11.62)	8	3.85
6	[Ni$_2$Se{o-EtPhNHCS$_2$}$_4$Cl$_4$]	Gray	225	6.97 (7.03)	10.38 (10.46)	12	3.87
7	[Co$_2$Se{PhNHCS$_2$}$_4$Cl$_4$(PPh$_3$)$_4$]	Orange	123	3.79 (3.83)	5.66 (5.72)	9	4.62
8	[Co$_2$Se{o-EtPhNHCS$_2$}$_4$Cl$_4$(PPh$_3$)$_4$]	Dark green	139	3.49 (3.63)	5.38 (5.42)	6	4.82
9	[Co$_2$Se{PhNHCS$_2$}$_4$Cl$_4$(Phen)$_2$]	Brown	150	5.21 (5.61)	8.19 (8.37)	8	4.94
10	[Co$_2$Se{o-EtPhNHCS$_2$}$_4$Cl$_4$(Phen)$_2$]	Pale brown	126	4.91 (5.19)	7.73 (7.75)	18	4.81
11	[Ni$_2$Se{PhNHCS$_2$}$_4$Cl$_4$(PPh$_3$)$_4$]	Dark green	113	3.62 (3.83)	5.65 (5.70)	8	3.10
12	[Ni$_2$Se{o-EtPhNHCS$_2$}$_4$Cl$_4$(PPh$_3$)$_4$]	Pale brown	158	3.58 (3.63)	5.32 (5.40)	11	3.08
13	[Ni$_2$Se{PhNHCS$_2$}$_4$Cl$_4$(Phen)$_2$]	Green	103	5.54 (5.61)	8.29 (8.34)	5	3.28
14	[Ni$_2$Se{o-EtPhNHCS$_2$}$_4$Cl$_4$(Phen)$_2$]	Pale gray	130	4.97 (5.19)	7.68 (7.73)	19	3.46

The trinuclear complexes display bands (Table 2) characteristic of coordinated dithiocarbamate ligand, strong absorption in the 1475-1547 and 991-1046 cm^{-1} region due to ν(C-N) and ν(C=S) modes, indicate bidentate bridging nature of dithiocarbamate (Singh and Prassad, 1998). A shift to higher frequency in the ν(C-N) band of the binuclear complexes comparable to the dithiocarbamate ligands, indicate an increase in the double bond character of the C-N bond (Nakamato, 1986). The shift to lower frequency in the ν(C=S) band of the dithiocarbamate ligand in the complexes indicating the involvement of sulphur atom of the ligand in the coordination with the metal ions, the bands occurring near 370-392 cm^{-1} and 242-309 cm^{-1} have been assigned to the ν(M-S) and ν(M-Cl) modes (Singh and Prassad, 1998). Furthermore, the IR spectra of the adduct of the above complexes with (PPh_3) or (Phen), Table 2 show that the ν(C-S) bands appears around 819-842 cm^{-1} supporing the bridging dithiocarbamate ligands, as well as the band at 425-498 cm^{-1} correspond to ν(M-N) (Manohar *et al.*, 1998).

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

No.	Complex	UV-Vis.	Selected IR bands (cm^{-1})						
			ν(C-S)	ν(C=S)	ν(C-N)	ν(Se-S)	ν(M-S)	ν(M-Cl)	ν(M-N)
1	$[Se\{PhNHCS_2\}_4]$	49505, 33120, 20618	850	1011	1460	340	-	-	-
2	$[Se\{o\text{-}EtPhNHCS_2\}_4]$	49261, 33222, 21142	880	991 1046	1468	365	-	-	-
3	$[Co_2Se\{PhNHCS_2\}_4Cl_4]$	16339, 14859	804	1002	1547	347	380	285	-
4	$[Co_2Se\{o\text{-}EtPhNHCS_2\}_4Cl_4]$	18430, 17942, 10050	825	984 1007	1491	350	375	259	-
5	$[Ni_2Se\{PhNHCS_2\}_4Cl_4]$	12898, 11001	815	1005	1492	337	370	277	-
6	$[Ni_2Se\{o\text{-}EtPhNHCS_2\}_4Cl_4]$	13175, 12610	830	1000	1535	340	372	293	-
7	$[Co_2Se\{PhNHCS_2\}_4Cl_4(PPh_3)_4]$	21413, 15748	835	976 1005	1495	330	370	276	-
8	$[Co_2Se\{o\text{-}EtPhNHCS_2\}_4Cl_4(PPh_3)_4]$	20080, 15974	848	985	1494	325	365	242	-
9	$[Co_2Se\{PhNHCS_2\}_4Cl_4(Phen)_2]$	21052, 15873	842	996	1483	334	375	253	450
10	$[Co_2Se\{o\text{-}EtPhNHCS_2\}_4Cl_4(Phen)_2]$	19379, 13889	819	994	1527	347	392	283	499
11	$[Ni_2Se\{PhNHCS_2\}_4Cl_4(PPh_3)_4]$	23980, 19607, 10235	840	970 1000	1475	340	388	283	-
12	$[Ni_2Se\{o\text{-}EtPhNHCS_2\}_4Cl_4(PPh_3)_4]$	21929, 15898, 10351	838	975 1005	1495	328	380	259	-
13	$[Ni_2Se\{PhNHCS_2\}_4Cl_4(Phen)_2]$	24096, 19608, 10384	835	955 1002	1495	344	372	298	425
14	$[Ni_2Se\{o\text{-}EtPhNHCS_2\}_4Cl_4(Phen)_2]$	24115, 17543, 10162	837	994 1026	1523	349	381	309	473

The UV-visible spectra of selenium compounds and trinuclear complexes were recorded as 10^{-3} M solutions in DMSO and the results are presented in Table 2. The broad bands observed in the range 33120-49505 cm^{-1} are due to π-π^* or n-π^* within the dithiocarbamate group, while new additional band was observed in the range 20618-21142 cm^{-1}. This can be attributed to the charge transfer from filled ligand orbital to the vacant selenium orbitals.

The electronic spectra of Co(II) complexes show a band observed in the visible region 14859-16366 cm^{-1} is generally considered to correspond to the transition from singlet level of F state ($^2A_2$) to the P state ($^4T_2$) which is consistent with tetrahedral geometry, while the Co(II) complex (No. 4) show two bands at 18340 and 17942 cm^{-1} may be assigned to $^2A_1g \rightarrow {}^2Eg`$ in square planer geometry (Bhargava *et al.*, 1983). In the Ni(II) complexes the observed band at 11001 cm^{-1} in tetrahedral geometry are due to a transition from F state $^3T_1(F) \rightarrow {}^3T_1(P)$ state.

The electronic spectra of the adducts of the trinuclear complexes with PPh_3 and Phen are listed in Table 2. Adducts of Co(II) show the presence of two bands in the region 19379-21413 and 13889-15974 cm^{-1} which are assigned to ^4T_1g (F) → ^4T_1g (P) (ν_3) and ^4T_1g (F)→^4A_2g (F) (ν_2) transition respectively. This shows that the positions of the electronic spectral band have changed from tetrahedral to octahedral region. The adducts of Ni(II) show the presence of three bands in the region 21929-24115, 15898-19608 and 10162-10384 cm^{-1} which are assigned to $^3A_2g \rightarrow {}^3T_1g$ (P) (ν_3) and $^3A_2g \rightarrow {}^3T_1g$ F (ν_2) transition $^3A_2g \rightarrow {}^3T_2g$ (ν_1) respectively. This show that the geometry of the adducts are octahedral (Victoriano, 2000).

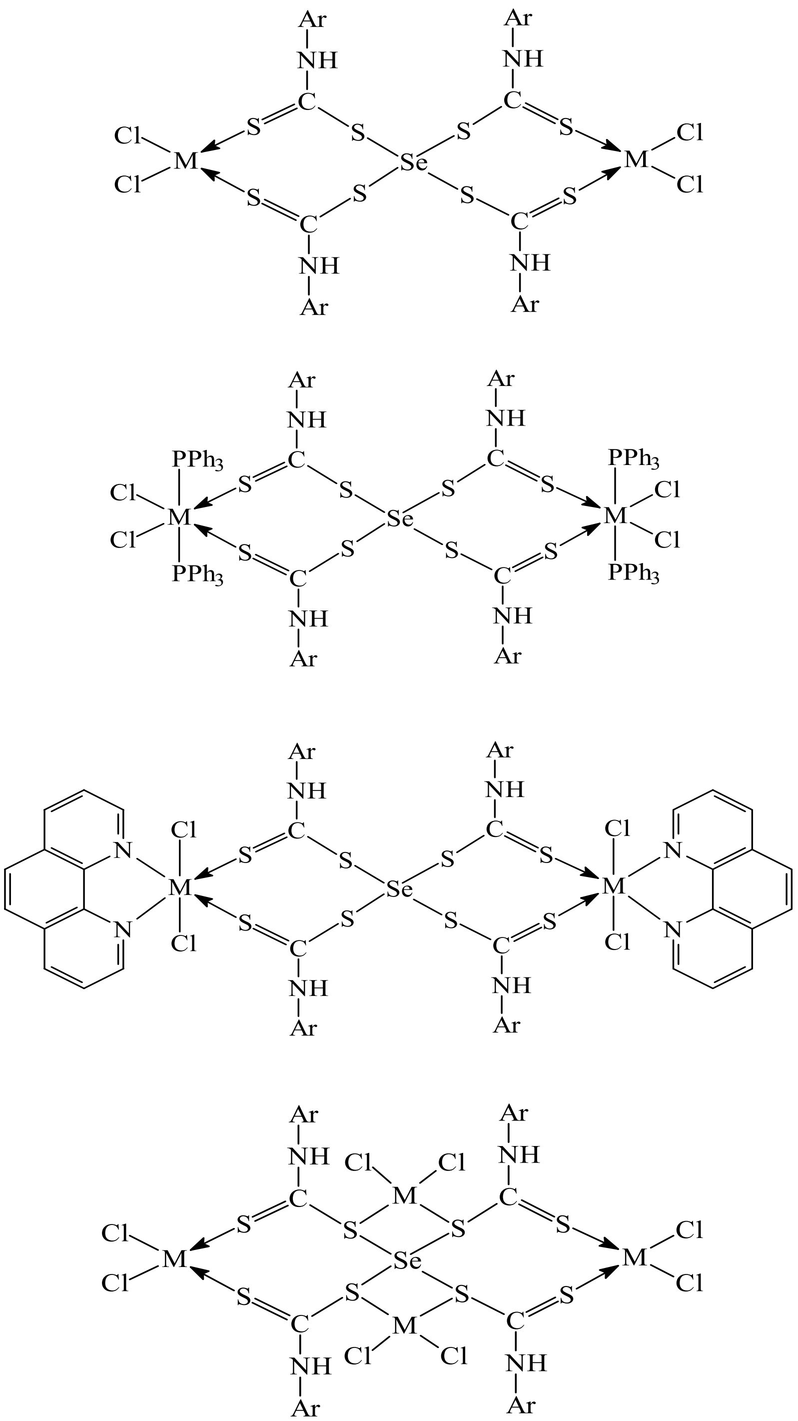
The results of the magnetic measurements presented in Table 1 throw light on the stereochemistry of these complexes. The Co(II) complexes the magnetic moments were found to be 4.61 and 2.06 B.M correspond to high spin tetrahedral (sp^3) and the other as low spin square planer configuration.

The magnetic moment value of the Ni(II) complexes are 3.85 and 3.87 B.M suggest a tetrahedral geometry for the complexes.

Adducts of Co(II) and Ni(II) complexes have a magnetic moments of (3.08-4.94) B.M so that the adducts of the complexes may have octahedral geometry (Bhargava *et al.*, 1983).

The molar conductivities of 10^{-3} M solutions of the complexes and their adducts, Table 1, indicates that they are non-electrolytes in DMSO (Geary, 1971).

As a conclusion the ligands (L) used in this study coordinate to the metal ions in a tetera coordinate fashion from s sides of the ligand forming the trinuclear and pentanuclear complexes and atoms as shown in Figure (1).



M = Co(II), Ni(II)

Fig. 1: The suggested structures of some complexes and others.

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