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Coordination Chemistry of New Sulfur-Containing Ligands: Transition Metal Complexes of *N*-Ethoxycarbonyl-1-pyrrolecarbothioamide

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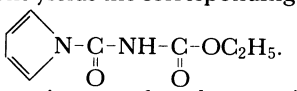
Reaction of *N*-ethoxycarbonyl-1-pyrrolecarbothioamide (Hept) with a variety of transition metal ions leads to the formation of $[M^{II}(ept)_2]$ (M=Ni, Cu, Pd, Pt), $[M^{II}(ept)_2(py)]$ (M=Co, Ni), $[Rh^{I}Cl(Hept)(PPh_3)]_2$, and $[M^{III}Cl(ept)_2(H_2O)]$ (M=Ru, Rh). Reaction of Hept with Ag(I), Cu(II), Pb(II), Hg(II), and Cd(II) under refluxing conditions yields the corresponding sulfides and an oxygenated form of the ligand (Hept), which was characterized as  . All metal complexes have been characterized on the basis of analytical, IR and electronic spectral, and magnetic measurement studies.

Over the past five years, we have been interested in the changes in both chemical reactivity and structural properties of thioamide complexes induced by alterations in the peripheral structure of the coordinated ligand.[1-4] Our work recently has centered on thioamide ligands ($R_1CSNHCOR_2$) derived from R_1=2-pyrrolyl, 2-thienyl, or 4-tolyl and R_2=OC_2H_5, NH_2, NHPh. This effort was motivated by an attempt to establish the relative importance of resonance forms (**1**, **2**, and **3**) of the ligand having terminal substituents R_1

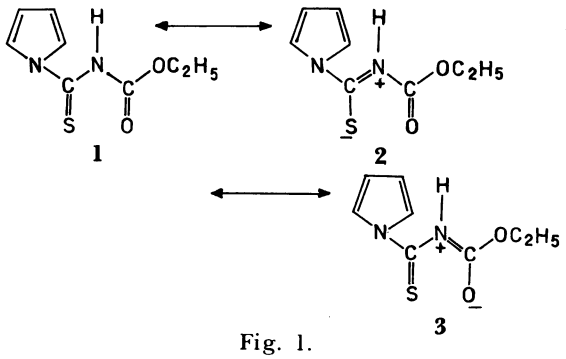


Fig. 1.

and R_2 of wide variety and their contribution to the electronic structure of resulting coordination compounds. With the above objective and as an extension of our work we report here the ligating properties of a new ligand of this class namely *N*-ethoxycarbonyl-1-pyrrolecarbothioamide (Hept). The only report[4] on the complexing behavior of the title ligand is the reaction with $[CuX(MPh_3)_3]$ (M=P or As; X=Cl or Br) in neutral media (benzene solution) resulting in the formation of tetrahedral complexes with the ligand behaving as a monodentate thione-S donor (structure **2**).

Experimental

The chemicals used were either chemically pure or AR grade. The ligand was prepared by the literature method.[5]

Preparation of Complexes. Bis(*N*-ethoxycarbonyl-1-pyrrolecarbothioamidato)copper(II). A cold solution of Hept (0.80 g, 4 mmol) in ethanol (25 ml) was added dropwise to an ice-cold solution of $CuCl_2 \cdot 2H_2O$ (0.34 g, 2 mmol) in water (25 ml). Immediate light brown precipitate results. The precipitate was centrifuged, washed with water, ethanol and ether, and then dried in vacuo.

Bis(*N*-ethoxycarbonyl-1-pyrrolecarbothioamidato)(pyridine)nickel(II). A cold solution of Hept (0.80 g, 4 mmol) in ethanol (10 ml) was added dropwise to an ice-cold solution of $NiCl_2 \cdot 6H_2O$ (0.48 g, 2 mmol) in water (25 ml) containing 10 ml of pyridine, which resulted in the precipitate of green compound. The compound was filtered off, washed with water, and dried in vacuo.

Bis(*N*-ethoxycarbonyl-1-pyrrolecarbothioamidato)nickel(II). This compound was obtained as yellow colored solid by heating the above complex at 90—100 °C.

Bis(*N*-ethoxycarbonyl-1-pyrrolecarbothioamidato)(pyridine)cobalt(II). A cold solution of Hept (0.80 g, 4 mmol) in ethanol (10 ml) was added dropwise to an ice-cold solution of $CoCl_2 \cdot 6H_2O$ (0.48 g, 2 mmol) in water (25 ml) containing 10 ml of pyridine, which resulted in the precipitation of brown compound. The compound was filtered off, washed with water, and dried in vacuo.

(*N*-Ethoxycarbonyl-1-pyrrolecarbothioamidato)silver(I). A solution of Hept (0.40 g, 2 mmol) in ethanol (10 ml) was added to a stirred solution of $AgNO_3$ (0.34 g, 2 mmol) in water (10 ml) at room temperature. The resulted yellow precipitate was filtered off, washed with water, ethanol, ether, and dried in vacuo. This compound decomposes on heating or on standing for more than one day.

Aquachlorobis(*N*-ethoxycarbonyl-1-pyrrolecarboamidato)-ruthenium(III). An aqueous solution (25 ml) of hydrated ruthenium trichloride (0.26 g, 1 mmol) was added to an ethanolic solution (25 ml) of Hept (0.40 g, 2 mmol) and the resulting solution refluxed on a water bath for 1—2 h. The black-brown complex which precipitated out was separated by centrifugation, washed successively several times with water, ethanol and ether, and then dried in vacuo.

Aquachlorobis(*N*-ethoxycarbonyl-1-pyrrolecarboamidato)-rhodium(III). A solution of Hept (0.40 g, 2 mmol) in ethanol (10 ml) was added to a stirred solution of $RhCl_3 \cdot 3H_2O$ (0.26 g, 1 mmol) in water (50 ml). The resulting orange colloidal solution was digested on a water bath for 2 h and the reddish orange rhodium complex was then filtered off, washed with water, a small quantity of ethanol, and finally with ether, and then dried in vacuo.

Di-μ-chlorobis(*N*-ethoxycarbonyl-1-pyrrolecarboamidato)-bis(triphenylphosphine)dirhodium(I). A solution of Hept (0.13 g, 0.6 mmol) in dichloromethane (25 ml) was mixed with a solution of $[RhCl(PPh_3)_3]$ (0.46 g, 0.5 mmol) in dichloromethane (25 ml). The resulting mixture was heated

under reflux for 15 min, the solution was then cooled at room temperature and concentrated to 5 ml at reduced pressure. The addition of petroleum ether (40—60°) to this solution caused precipitation of a yellow complex. It was filtered, washed with petroleum ether, and dried in vacuo.

Bis(*N*-ethoxycarbonyl-1-pyrrolecarbothioamidato)palladium(II). A solution of Hept (0.40 g, 2 mmol) in ethanol (20 ml) was added to a hot solution of $PdCl_2 \cdot 2H_2O$ (0.21 g, 1 mmol) in water (50 ml). Immediately a yellow palladium complex appeared. The precipitate was separated through filtration, washed with water, ethanol and ether, and then dried in vacuo.

Bis(*N*-ethoxycarbonyl-1-pyrrolecarboamidato)platinum(II). A solution of Hept (0.40 g, 2 mmol) in ethanol (25 ml) was added to a solution of H_2PtCl_6 (0.41 g, 1 mmol) in water (25 ml). The mixture was heated under reflux for 1 h. The dark brown precipitate appeared. The precipitate was separated, washed with water, ethanol and ether, and then dried in air.

Sulfur Abstraction from Hept by Soft Metal Ions. An aqueous solution of hydrated metal salts† (ca. 1 mmol) was mixed with an ethanolic solution of Hept (ca. 1.5 mmol). The mixture was heated under reflux for 2—4 h. The respective sulfides Ag_2S (black), CuS (black), PbS (black), Hg_2S (black), and CdS (yellow) were precipitated and characterized after separation. The filtrate obtained was evaporated to dryness and the resulting residue was crystallized from chloroform. The crystals were recrystallized from a mixture of CCl_4 and ethyl acetate (1 : 1 ratio). The resulting crystals were characterized as *N*-ethoxycarbonyl-1-pyrrolecarboamide. Abstraction of sulfur by soft metal ions from similar ligands were also reported from our laboratory.[1,3]

Results and Discussion

All compounds are air stable, insoluble in non-coordinating solvents and soluble in solvents like ethanol, DMF, DMSO, acetone etc. Analytical data (Table 1) are in good agreement with the stoichiometry proposed for the complexes. Metal ions form inner complexes (b—e) rather than simple salts (a). Hept functions both as a mono- and bidentate ligand.

The donor ability of the ligand and the shifts of various IR bands in the spectra of complexes can be best understood in terms of resonance structures (**1**, **2**, and **3**).

The positions of the major bands of interest are shifted in the spectra of complexes. The changes in IR spectra and the inferences drawn regarding site of bonding are summarized below.

The band at 3210 cm^{-1} (ν NH) in the spectrum of ligand disappears in the spectra of the complexes except the Rh(I) complex. This could most probably be explained on the assumption that during the formation of the complexes, the NH group of the ligand is

Table 1. Analytical and Magnetic Data

Compound	Color	Mp[a] θ_m/°C	Yield %	Analysis: Found (Calcd)/% M	S	Cl	C	H	N	μ_{eff}[b] (B.M.)
$[Cu(ept)_2]$	Light Brown	105	50	13.6 (13.8)	13.7 (14.0)	—	42.2 (42.0)	3.8 (4.0)	11.9 (12.2)	DM
$[Ni(ept)_2(py)]$	Green	52	50	11.3 (10.9)	11.8 (12.0)	—	47.2 (47.4)	4.5 (4.3)	13.3 (13.2)	3.14
$[Ni(ept)_2]$	Yellow	56	54	12.6 (12.8)	13.8 (14.2)	—	42.8 (42.4)	3.8 (4.0)	12.2 (12.4)	DM
$[Co(ept)_2(py)]$	Brown	82	52	11.2 (10.9)	11.5 (12.0)	—	47.1 (47.4)	4.7 (4.3)	13.1 (13.2)	2.10
[Ag(ept)]	Yellow	158d	80	35.3 (35.4)	10.2 (10.5)	—	31.4 (31.5)	2.6 (3.0)	9.3 (9.2)	DM
$[RuCl(ept)_2(H_2O)]$	Black Brown	240	56	—	12.0 (11.7)	6.8 (6.5)	35.2 (35.0)	3.2 (3.3)	10.5 (10.2)	1.64
$[RhCl(ept)_2(H_2O)]$	Reddish Brown	238d	60	—	11.7 (11.6)	6.7 (6.4)	34.8 (34.9)	3.6 (3.3)	10.5 (10.2)	DM
$[RhCl(Hept)(PPh_3)]_2$	Yellow	120	70	—	5.1 (5.3)	5.7 (5.9)	52.4 (52.1)	4.5 (4.2)	4.5 (4.7)	DM
$[Pd(ept)_2]$	Yellow	280d	65	20.8 (21.2)	12.5 (12.8)	—	38.7 (38.4)	3.4 (3.6)	10.9 (11.2)	DM
$[Pt(ept)_2]$	Dark Brown	200d	48	32.7 (33.1)	10.6 (10.9)	—	32.9 (32.6)	3.4 (3.0)	9.6 (9.5)	DM

a) Melting points are uncorrected. b) μ_{eff} was taken at room temp.

†$AgNO_3$, $CuCl_2$, $Pb(NO_3)_2$, $HgCl_2$, and $CdSO_4$.

deprotonated with the formation of a metal to nitrogen bond. Two bands at 685 and 630 cm^{-1} assigned to τ(NH) also disappear in the spectra of the complexes, confirming deprotonation of the ligand. In case of $[RhCl(Hept)(PPh_3)]_2$ the band at 3210 cm^{-1} (ν NH) becomes broad, possibly because of hydrogen bonding in the solid state of the compound. The broad bands around 3300—3500 and 1630 cm^{-1} in the spectra of Ru(III) and Rh(III) complexes are tentatively assigned, respectively to stretching (symmetric and asymmetric) and bending modes of water molecule.

For Ni(II), Co(II), Cu(II), and Rh(I) structures **1** and **3** seem to predominate and the band at 1730 cm^{-1} (ν C=O) of Hept shifts towards lower wave numbers (see Table 2). A band at 1125 cm^{-1} of Hept (ν C=S) either remains stationary or goes up and thioamide band IV having major contribution of ν(C=S) (ca. 880 cm^{-1}) undergoes blue shifts in the spectra of complexes. These shifts are indicative of non-involvement of thiocarbonyl sulfur in bond formation, indicating strong interaction of the metal ion with carbonyl oxygen.

For Ag(I), Rh(III), Pt(II), and Pd(II) and Ru(III) complexes structures **1** and **2** of the ligand appear to be operative and the band due to ν(C=O) at 1730 cm^{-1} in the ligand either remains stationary or shifts towards higher wavenumber. This indicates the non-involvement of carbonyl oxygen in the bond formation with the metal ion. The ν(C=S) band of the ligand at 1125 cm^{-1} shifts to lower frequencies whereas in case of $[RuCl(ept)_2(H_2O)]$ the band disappears probably merging with 1095 cm^{-1} band of the ligand. The red shift observed for thioamide band IV further supports the bonding through thiocarbonyl sulfur.

The band at 1500 cm^{-1} in the ligand is assigned to thioamide band I (ν(C-N)+δ(C-H)).[6] In most of the complexes this band shifts to higher wave numbers (see Table 2). Only in the case of $Cu(ept)_2$ the band remains stationary.

A band at 1320 cm^{-1} of Hept assigned to thioamide band II (ν(C=S)+ν(C-N)+δ(C-H)) shifts to lower frequencies (ca. 10—12 cm^{-1}) in the spectra of all the complexes with the exception of $[Rh(Hept)(PPh_3)Cl]_2$ in which Hept is bonded to rhodium(I) through carbonyl oxygen only, as expected, this band shifts to higher wavenumber (1330 cm^{-1}).

Thioamide band III (mainly due to ν(C=S) and ν(C-N) at 1015 cm^{-1} of Hept undergoes red shift on complexation in all the cases.

The new band at 1580 cm^{-1} of $[Cu(ept)_2]$ which has been tentatively assigned to ν(C=N), will have significant contribution of ν(C=O) also as in this complex ν(C=O) of the ligand at 1730 cm^{-1} disappears. Large red shift is indicative of relatively stronger interaction of the Cu(II) ion with carbonyl oxygen. In case of $[Ni(ept)_2(py)]$ band at 1580 cm^{-1} has major contribution of ν(C=N) because there is a band at 1620 cm^{-1} which is assigned as ν(C=O) in the complex. The bands at 1450 and 1490 cm^{-1} for $[Cu(ept)_2]$ and

Table 3. Electronic Spectra of Ligand and Complexes in 95% Ethanol

Compound	Band position λ_{max}/nm
Ligand [Hept]	262
	300
$[Cu(ept)_2]$	285
$[Ni(ept)_2(py)]$	285
	320
$[Ni(ept)_2]$	280
	360
$[Co(ept)_2(py)]$	285
	320
[Ag(ept)]	280
	350
$[RuCl(ept)_2(H_2O)]$	265
	320
	425
$[RhCl(Hept)(PPh_3)]_2$	280
	320
$[RhCl(ept)_2(H_2O)]$	280
	320
$[Pd(ept)_2]$	250
	285
	325
	400
$[Pt(ept)_2]$	295
	450

Table 2. Major IR Bands of Interest. Comparison of IR Spectra of the Complexes with Ligand

Compound	ν(NH)	ν(C=O)	ν(C=S)	Thioamide bands				Possible coordination
				I	II	III	IV	
[Hept]	3210m	1730s	1125s	1500s	1320s	1015s	880s	—
$[Cu(ept)_2]$	—	1580s[a]	1125m	1500s	1320s	990m	880m	N and O
$[Ni(ept)_2(py)]$	—	1620s	1160m	1550s	1310s	980m	900m	N and O
$[Ni(ept)_2]$	—	1610s	1140s	1540s	1310s	980s	900m	N and O
$[Co(ept)_2(py)]$	—	1600s	1160m	1550m	1310	990m	910s	N and O
[Ag(ept)]	—	1750s	1120m	1550s	1300s	980s	850s	N and S
$[RuCl(ept)_2(H_2O)]$	—	1750s	—	1540s	1300s	980s	850s	N and S
$[RhCl(Hept)(PPh_3)]_2$	3300br	1650s	1140m	1540s	1330s	980s	890s	O
$[RhCl(ept)_2(H_2O)]$	—	1750s	1110s	1550s	1300s	990s	850s	N and S
$[Pd(ept)_2]$	—	1760s	1120s	1540s	1300s	980s	860s	N and S
$[Pt(ept)_2]$	—	1765s	1115s	1550s	1300s	985s	860s	N and S

a) This band has significant contribution from both ν(C=N) and ν(C=O).

[Ni(ept)$_2$(py)], respectively have been assigned to ν(N-C=S).[7] The weak broad band at ca. 3500 cm^{-1} in the spectra of [Ni(ept)$_2$(py)] and [Co(ept)$_2$(py)] are characteristic of pyridine, ca. 80 cm^{-1} towards higher frequency (pyridine band ca. 3420 cm^{-1}). In both the complexes bands in free pyridine at 604 cm^{-1} (in plane ring deformation) and 405 cm^{-1} (out-of-plane ring deformation) shift to higher frequencies (ca. 35 cm^{-1}).[8-10]

The appearance of new medium intensity bands in the region 500—300 cm^{-1} is strong evidence of coordination by both nitrogen and oyxgen or sulphur. They have been tentatively assigned to coupled vibrations of ν(M-N), ν(M-O), and ν(M-S). Bands of a few representative compounds in this region are as given below: 330, 345 cm^{-1} [Cu(ept)$_2$]; 335, 360 cm^{-1} [RuCl(ept)$_2$-H$_2$O]; 340, 450, 490 cm^{-1} [Ni(ept)$_2$]; and 300, 390, 440 cm^{-2} [Co(ept)$_2$(py)].

All compounds except Ni(II), Co(II), and Ru(III) complexes were found diamagnetic at room temperature. The magnetic moment of Ni(II) complex corresponds to two unpaired electrons whereas those of Co(II) and Ru(III) indicate the presence of one unpaired electron in each.

The electronic spectrum of Hept in ethanol exhibits two strong transitions at 300 and 262 nm which are assigned to n→π* and π→π* intraligand transitions, respectively. Usually n→π* transitions involving N and S occur at lower energy and are less intense than π→π*.[11,12] The spectra of almost all the compounds show the presence of these two bands with the hypsochromic blue shift. The high intensity of these bands suggest that they should be charge-transfer or intraligand and not d-d transition bands. The absence of band around 300 nm (n→π*) from the spectra of some complexes may be due to stabilization of the energy of the lone pair of electrons on complex formation,[13] and similarly the hypsochromic shift in bands in the spectra of complexes may be explained as that metal ions are bonded through thiocarbonyl sulfur, carbonyl oxygen, and nitrogen.[14] The bond formations lower the energy of non-bonding orbitals as well as π-levels, thus now more energy will be required to promote the electron from the n or π level to π* orbital hence the observed hypsochromic shift (Fig. 2).

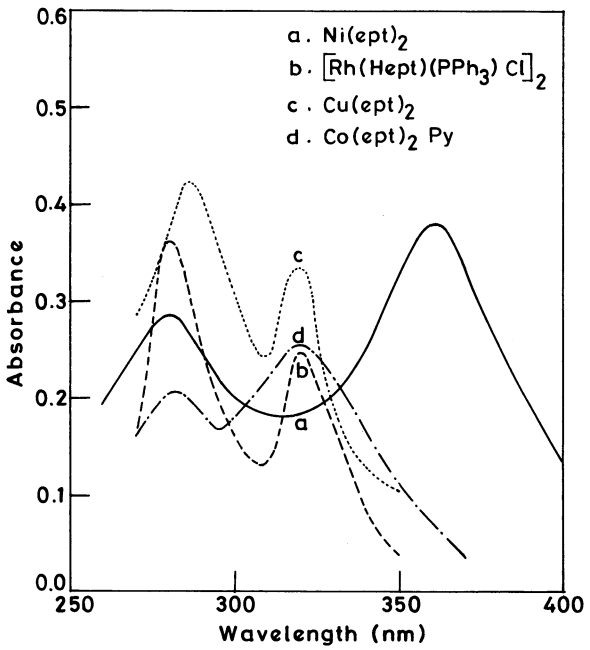


Fig. 2. Electronic spectra.

The IR evidence clearly indicates that the ligand acts as an NO/NS donor in these complexes. Square planar geometry is assigned to Ni(II), Pd(II), Pt(II), Rh(I), and Cu(II) complexes. Ru(III) and Rh(III) complexes are octahedrally coordinated whereas [Ni(ept)$_2$-(py)] and [Co(ept)$_2$(py)] are proposed to have square pyramidal geometry and the Ag(ept) complex is linear one. In case the ligand functions as a bidentate to one metal ion, it will result in a four membered chelate ring (structure b) and this will involve undue strain specially in case when the ligand acts as a NO donor. In view of the above fact and the insolubility of the complexes in most of the non-coordinating solvents the complexes may have open polymeric structures with the nitrogen and oxygen atoms of one ligand being bound to two different metal atoms (structure c).

It is known that OS donor β-thioxoketonates form exclusively cis-complexes with square planar coordinated metal ions and facial complexes with octahedrally coordinated metal ions.[15] Consequently, it is suggested that the Pd(II) and Pt(II) complexes (in which the ligand in NS donor) have the cis square

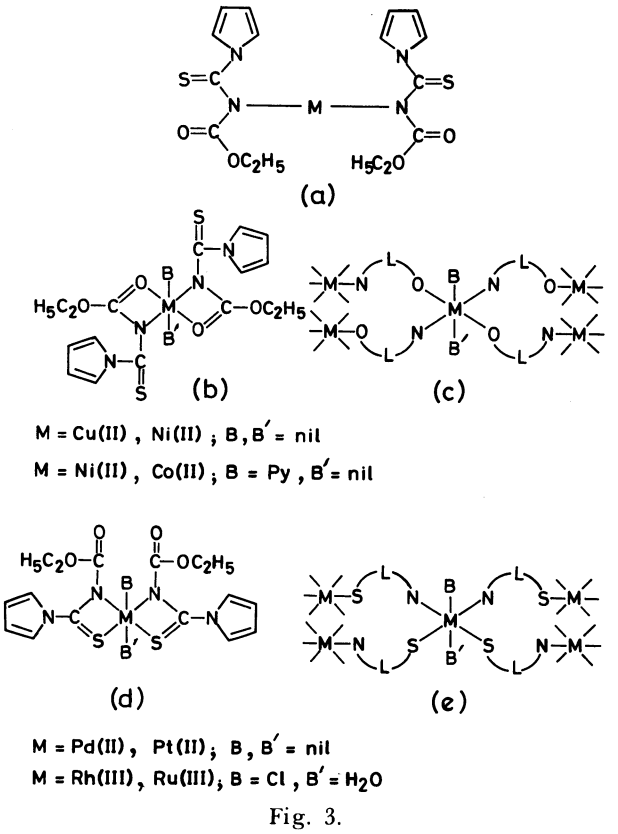


Fig. 3.

planar configuration and those of Ru(III) and Rh(III) are octahedral. Although these structures contain a four membered ring, they do not involve undue strain because of the large size of the sulfur atom. Four membered chelate rings are known with NS ligands.[16] Hence, inspite of insolubility of compounds, in case of NS donor situation, both chelate and open polymeric structures (structures d and e) are equally probable.

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