Tikrit Journal of Pure Science Vol. 13 No.(3) 2008

Synthesis and characterization of some Co(II), Ni(II) and Cu(II) complexes with bis-(1,4-benzyl thio) butane and selected N,P-ligands

Omer M. Al-Ramadane

Department of Chemistry, College of Science, University of Mosul, Mosul, Iraq

(Received 8 / 4 / 2007, Accepted 27 / 5 / 2007)

Abstract:

The new cobalt(II), nickel(II) and copper(II) complexes with bis-(1,4-benzyl thio) butane and their adducts with ethylene diamine and triphenyl phosphine in the coordination sphere were prepared. All the complexes and adducts were characterized by IR, UV-vis. spectroscopy, conductivity and magnetic measurements and some of them by metal content. Electronic spectral data and magnetic measurements showed that the complexes have tetrahedral geometry with the adduct have octahedral environments.

Introduction:

The alkyl and arylthiolato derivatives of main group metals have not been studied as have those of the transition elements, but there is never the less there is a significant literature on these compounds, the chemistry of $Sn(SR)_4$ and $RnSn(SR`)_{4-n}$ and of the corresponding lead compounds has been reviewed [1-3].

Recently some literature[4] formation regarding cobalt and nickel with 1,2-dithiolates has been made available. These compounds exhibit interesting properties and technical applications as super conductors, pesticides, Q-swithing dyes for IR spectroscopy and, moreover, they are able to stabilize higher oxidation states of the central atom. Most papers deal with the compounds containing 1,2-dithiolates and N,P-ligands in the coordination sphere [5,6]. As to aliphatic dithiolate complexes, the compounds containing malenonitril dithiolates as ligands were studied preferably [7].

The new cobalt and nickel complexes with 1,2-ethane dithiol containing tridentate ligand 1,1,1-tris (diphenyl phosphinomethyl) ethane and bidentate ligand (2,2`-biquinoline) in the coordination sphere have been isolated and characterized physico-chemically by Kamenicek et al. [8].

Buttrus et al. [9, 10] reported the preparation of multinuclear complexes of general formula $[Se(Spy)_4(MCl_2)]$ and $[Se(Spy)_4(MCl_2)_4]$ were Spy=pyridenthiolate, M=Co(II), Ni(II), Cu(II), Pd(II) and Pt(II) and their physico-chemical characterization.

The aim of this work was the synthesis and physico-chemical study of new nickel(II), cobalt(II) and copper(II) coordination complexes with bis-(1,4-benzyl thio) butane and their adducts with ethylene diamine and triphenyl phosphine.

Experimental:

General:

$CoCl_2.6H_2O$, $NiCl_2.6H_2O$ and $CuCl_2.2H_2O$ and the remaining reagents were products from Fluka and used as supplied. IR spectra were recorded on a Perkin-Elmer 580B spectro-photometer in the 4000-200cm^{-1} range using Nujol or CsI discs. UV-vis. Spectra were recorded on a Shimadzu UV-vis spectrophoto-meter of type UV-160 for 10^{-3}M solution of the complexes in dimethyl sulfoxide (DMSO) at 25°C using 1cm quartz cell. The metal content of some of the complexes was estimated spectrophotometrically using Shimadzu AA670.

Conductivity measurements were made on 10^{-3}M solution of the complexes in (DMSO) solvent at 25°C using conductivity nutral model 4070 Jenway. The magnetic measurements were carried out at 25°C on the solid state by Faradays method using Bruker BM6 instrument.

1. Preparation of the ligand bis(1,4-benzyl thio) butane (L).:

Benzyl mercaptan (2.28g-0.02mmol) and NaOH (0.80g-0.02mmol) in ethanol (30ml) were mixed with 1,4-dichlorobutane (2.16g-0.01mmol) in ethanol (10ml). The mixture was boiled under reflux for (4h). After cooling to room temperature, NaCl was removed by filtration. The solution was reduced in volume ca 15ml and on cooling to ca 5 °C, a precipitate was obtained the product can be recrystallized from ethanol.

2. Preparation of $[M(L)Cl_2]$ and $[M(L)_2Cl_2]$ complexes (M=Co(II)), Ni(II) and Cu(II)).:

The complexes was prepared according to the following procedure. An alcoholic solution of metal salt (0.01mol) in ethanol (10ml) was mixed with a solution of the ligand (0.01mol) or (0.02mol) dissolved in acetone (10ml). The mixture was stirred with reflux for (2-3h), to ensure completion of the reaction. The solid thus obtained were filtered off, washed with ethanol, diethyl ether and dried in vacuum for several hours.

3. Preparation of $[M(L)_2X_n]Cl_2$, X=ethylene diamine n=1, X=triphen-yl phosphine n=2.:

The complex $[M(L)_2Cl_2]$ (0.01mol) in (10ml) dimethyl formamide (DMF) was added of the ligand ethylene diamine (0.06g-0.01mol) in ethanol (10ml) or triphenyl phosphine (0.52g-0.02mol) in ethanol (10ml). 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 ethanol and dried under vacuum for several hours.

Results and Discussion:

The reaction of the ligand bis(1,4-benzylthio) butane with metal chloride in (1:1) or (2:1) ligand to metal molar ratio afford the complexes of the general formula $[M(L)Cl_2]$ and $[M(L)_2Cl_2]$. Treatment of the complexes of the type $[M(L)_2Cl_2]$ with ethylene diamine (1:1) or triphenyl phosphine (1:2) molar ratio gave the adduct complexes of general formula $[M(L)_2en]Cl_2$ and $[M(L)_2(PPh_3)_2]Cl_2$.

The physical properties of the complexes and adducts are tabulated in Table (1). They are quite stable in air and melt or decompose above 121°C. They are insoluble in most organic solvent but soluble in DMF and DMSO.

The most important IR assignment of the complexes and adducts are listed in Table (2). The most important band which appeared at 1058cm^{-1} due to ν(C-S) stretching in the free ligand is shifted to the lower field in the prepared complexes. This is usually indicates that the C-S groups of the ligands are involved in coordination with metal atom through sulphur atom [11]. Further support for the formation of the complexes is provided by the appearance of a new band within 370-359cm^{-1} range characteristic of bidentate form of the ligand and tentatively attributed to ν(M-S) [12] M=Co, Ni or Cu. Furthermore, the IR spectra of the complexes (1-6) showed another band within 283-352cm^{-1} range which may be due to ν(M-Cl) [13].

Furthermore the IR spectra of the adducts (7-12), show similar observation for ν(C-S) indicating that the ligand coordinated through sulphur. Further support for this was obtained from the appearance of new bands at 390-418cm^{-1} which assigned to ν(M-S).

The ν(M-N) and ν(M-P) bands were observed at (440-452) and (478-490)cm^{-1} indicating that the coordination occur through nitrogen and phosphorus atom, similar results was found some where else [14].

The values of magnetic moment of Co(II) complex (No. 1) is (4.02) B.M. The electronic spectrum (Table 2) of Co(II) complex shows abroad band at 11612 and 13327cm^{-1} due to $^4A_2 \rightarrow {}^4T_1P$ (ν_3) transition, due to spinorbitcoupling similar to those reported for $[CoCl_4]^{-2}$ and $[CoI_4]^{-2}$ suggesting a tetrahedral geometry of Co(II) complex [13].

The Ni(II) complex (No.2) show a magnetic moment of (3.20) B.M. which agree well with high-spin configuration and indicates the presence of tetrahedral environment [15].

The electronic spectra of the complex show a band at 12019-12232cm^{-1} which correspond to the transition $^3T_1(F) \rightarrow {}^3T_1(P)$ (ν_3) in tetrahedral environment.

The Cu(II) complex (No. 3) show a magnetic moment (2.14) B.M., the electronic spectrum showed a band at 12988cm^{-1} which correspond to the transition $^2B_1g \rightarrow {}^2A_2g$ or $^2B_1g \rightarrow {}^2Eg$ and another band at 28900 cm^{-1} correspond to charge transfer. This show that the Cu(II) complex has tetrahedral geometry [15].

The electronic spectra of the complexes (4-6) and adducts (7-12) with ethylene diamine and triphenyl phosphine in DMSO are listed in Table (2).

The Co(II) complexes (4, 7 and 10) shows the presence of three bands in the region 10469-10610, 13112-15070 and 26185- 27981cm^{-1} are assigned to $^4T_1g(F) \rightarrow {}^4T_2g(F)$, $^4T_1g(F)(\nu_1) \rightarrow {}^4A_2g(F)(\nu_2)$ and $^4T_1g(F) \rightarrow {}^4T_1g(P)(\nu_3)$ transitions respectively. This shows that the positions of the electronic spectral bands have change from tetrahedral to octahedral environment.

The Ni(II) complexes (5, 8 and 11) shows the presence of three bands in the region 10561-12506, 12116-13151 and 27030-28600cm^{-1} which are assigned to $^2A_2g \rightarrow {}^3T_1g(P)(\nu_3)$, $^2A_2g \rightarrow {}^3T_1g(F)(\nu_2)$ and $^2A_2g \rightarrow {}^3T_2g(F)$ (ν_1) transitions respectively. This shows that the Ni(II) complexes have an octahedral geometry.

The Cu(II) complexes (6, 9 and 12) shows the presence of a bands at 11588-11622, 12096-15346 and 27027-28601cm^{-1} which may assigned to $^2B_1g \rightarrow {}^2A_1g$, $^2B_1g \rightarrow {}^2B_2g$ and $^2B_1g \rightarrow {}^2Eg$ transitions, this shows that the Cu(II) complexes have distorted octahedral geometry.

The molar conductivites of 10^{-3}M solution of the complexes (1-6) are non electrolyte in DMSO while those for adducts (7-12) are 1:2 electrolyte in DMSO [16].

On the basis of spectral and magnetic studies the following structure could be assigned to the metal complexes and adducts as in Fig. (1).

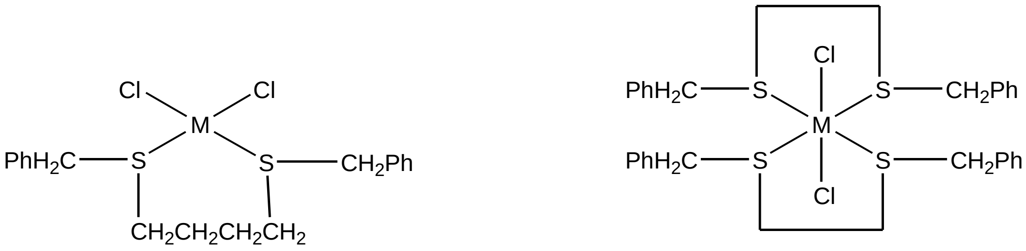
Table 1: Physical properties of the complexes and adducts

Seq.	**Compounds**	**Colour**	**m.p. °C**	**Cond. Λ_M ohm^{-1}.cm^{2}mol^{-1}**	**μeff B.M**	**%(M)**
1	$[C_{18}H_{22}S_2)CoCl_2]$	Dark brown	149	16.7	4.02	(13.84) 13.56
2	$[C_{18}H_{22}S_2)NiCl_2]$	Green	152	11.9	3.20	-
3	$[C_{18}H_{22}S_2)CuCl_2]$	Yellowish brown	142	10.2	2.14	-
4	$[C_{18}H_{22}S_2)_2CoCl_2]$	Dark green	176	18.0	3.72	-
5	$[C_{18}H_{22}S_2)_2NiCl_2]$	Pale green	121	20.2	2.96	(8.12) 7.82
6	$[C_{18}H_{22}S_2)_2CuCl_2]$	Pale brown	133	14.6	1.44	-
7	$[C_{18}H_{22}S_2)_2Co(en)]Cl_2$	Dark brown	190	72.1	4.90	-
8	$[C_{18}H_{22}S_2)_2Ni(en)]Cl_2$	Yellowish green	201	80.4	3.01	-
9	$[C_{18}H_{22}S_2)_2Cu(en)]Cl_2$	Green	164	76.6	1.48	(7.97) 7.61
10	$[C_{18}H_{22}S_2)_2Co(PPh_3)_2]Cl_2$	Dark brown	231*	73.7	4.71	-
11	$[C_{18}H_{22}S_2)_2Ni(PPh_3)_2]Cl_2$	Yellow	186	82.1	3.08	-
12	$[C_{18}H_{22}S_2)_2Cu(PPh_3)_2]Cl_2$	brown	253*	77.4	1.80	(5.02) 4.92

* Decomposition

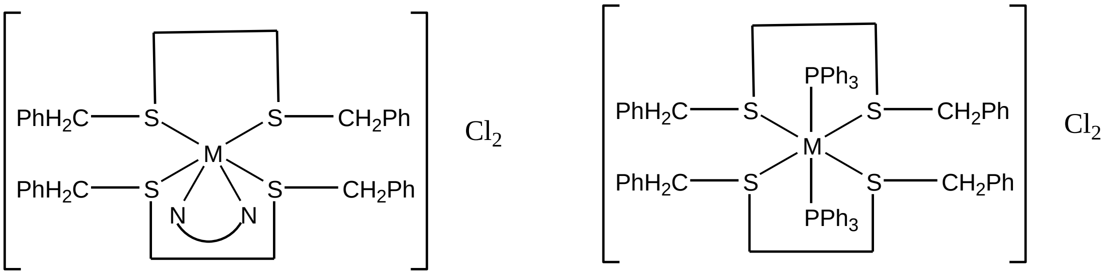
Table 2: IR spectra (cm^{-1}) and electronic spectra of the ligand and their metal compounds and adducts

Compounds	**ν(C-S)**	**ν(M-S)**	**ν(M-Cl)**	**ν(M-N)**	**ν(M-P)**	**M_{max} (U.V)**
$C_{18}H_{22}S_2$	1058(m)	-	-	-	-	-
1	1042(w)	370(m)	352(w)	-	-	11612, 13327
2	1039(w)	396(m)	306(w)	-	-	12019, 12232
3	1051(w)	405(w)	295(m)	-	-	12988, 15216, 28900
4	1040(s)	359(m)	283(m)	-	-	10469, 11596, 11618, 13112
5	1036(m)	412(s)	321(m)	-	-	11996, 12116, 12124, 15529, 27466
6	1045(w)	396(s)	342(m)	-	-	11588, 11622, 12114, 15331, 27981, 28601
7	1049(m)	390(w)	-	442(m)	-	10610, 11039, 12096, 15070, 28825
8	1051(s)	410(w)	-	452(m)	-	12506, 12529, 14942, 15483, 27030
9	1048(m)	418(w)	-	440(m)	-	12999, 13215, 15112, 27027
10	1053(m)	391(m)	-	-	485(s)	10509, 14660, 26185
11	1046(w)	400(s)	-	-	490(w)	10561, 13151, 27480, 28600
12	1038(m)	408(s)	-	-	478(s)	12096, 15346, 27027, 28502



Complexes (1-3)

Complexes (4-6)



Complexes (7-9)

Complexes (10-12)

M=Co(II), Ni(II), Cu(II)

Fig. 1: Suggested structures for complexes and adducts

References:

1. R.K. Chadha, P.C. Hayes, H.E. Mabrouk and D.G. Tuck, can. J. Chem. 65, 804 (1987).
2. E.W. Abel and D.A. Armitage, Adv. Organomet. Chem. 5, 1 (1967).
3. P. Solichova; Diploma thesis, Palacky University, Olomonc, (2001).
4. P.W. Bunce and D.O. Hare; Inorganic materials, Wiley J. and Sons (1997).
5. R.K. Agrwal and S. Prasad, Turk. J. Chem. 29, 289 (2005).
6. J. Kamnicek and J. Kroutitikov, J. Acta Univ. Palack. Olom. 36, 11 (1997).
7. J. Kamnicek and K. Mirkvova, Acta. Univ. Palack. Olom. 39, 39 (2000).
8. J. Kamnicek, P. Solichova and Z. Sindelar, Acta Univ. Palack. Olom. Chemica. 40, 35 (2001).
9. N.H. Buttrus, S.M. Mohammed and F.T. Said, J. Edu. Sci. 18, 32 (2006).
10. N.H. Buttrus and A.F. Al-Omari, Raf. J. Sci. 16(3), 138(2005).
11. E.M. Shoukry, H.A. Bayoumi and M.M. Mostafa, Trans. Met. Chem. 25 (1), 73 (2000).
12. N.H. Buttrus, National, J. Chem. 8, 611, (2002).
13. H.A. Bayoumi, E.M. Shoukry and M.M. Mostafa, Synth. React. Inorg. Met. Org. Chem. 31(4) 579 (2001).
14. N.H. Buttrus and W.I. Al-hamdani. J. Edu. Sci. 18(2), 51, (2006).
15. P. Comba, W.I. Hambley, P. Hifenhans and D.T. Richens. J. Chem. Soc. Dalton Trans, 533(1996).
16. W.J. Geary, Coord. Chem. Rev. 7, 81 (1971).

تحضير وتشخيص بعض معقدات الكوبلت والنيكل والنحاس مع ليكندات ثنائي (١، ٤-بينزل ثايو) بيوتان والحاوية على النتروجين والفسفور

عمر موفق الرمضاني

قسم الكيمياء، كلية العلوم، جامعة الموصل، الموصل، جمهورية العراق

الملخص:

يتضمن البحث تحضير معقدات Co(II) و Ni(II) و Cu(II) جديدة مع ثنائي (١و٤-بنزيل ثايو) بيوتان ومركبات الاضافة مع اثيلين ثنائي امين وثلاثي فنيل فوسفين. تم تشخيص جميع المعقدات ومركبات الاضافة بوساطة طيف الاشعة تحت الحمراء وفوق البنفسجية وكذلك القياسات الموصلية والمغناطيسية. كذلك تم تحليل المحتوى الفلزي لبعض المعقدات. وقد بينت القياسات المغناطيسية واطياف الاشعة فوق البنفسجية بان المعقدات تمتلك بنية رباعي السطوح، بينما مركبات الاضافة تمتلك بنية ثماني السطوح.