

Cobalt, Nickel and Copper Complexes of Bis (vanillidene) phthaloloylhydrazide

Issam J. Sallomi , Wijdan A. Al-Zeadan

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

Abstract

A series of neutral and anionic mixed metal complexes of cobalt(II), nickel (II), and copper (II) have been synthesized by the reactions of their metal salts with the Schiff base ligand bis(vanillidene) phthaloloylhydrazide (VPH₄), derived from vanillin and phthaloloyl hydrazide. Structural features of the complexes were obtained from their elemental microanalysis, magnetic susceptibility, molar conductance, UV-visible and IR spectral studies. The data showed that these complexes have compositions of the type:

$[M_3(VPH_4)_2X_6]$, $[M_2M^*(VPH_4)_2X_6]$, $[MM^*M^{**}(VPH_4)_2X_6]$ for the neutral complexes (type I), and $K_2[M_3(VP)_2]$, $[MM^*(VP)_2]$, $[MM^*M^{**}(VP)_2]$ for the anionic complexes (type II), where M, M*, M** represent Co⁺², Ni⁺², Cu⁺²; VPH₄ and VP are the neutral and tetra-basic forms of the ligand and X= Cl or NO₃. Neutral complexes were obtained from neutral reaction medium where the ligand acts as neutral hexadentate forming octahedral structure. In alkaline reaction medium, anionic complexes were obtained where the ligand acts as tetrabasic hexadentate giving tetrahedral and square planar structures. The study of the nature and stability of the complexes was carried out by Job method and revealed the formation of 1:1 metal to ligand species in neutral solution which have similar stability constants.

Introduction

Reflecting their unusual relative ease of synthesis and versatile metal complexation properties, Schiff base complexes have been extensively investigated for more than a century and have been employed in areas that include magnetochemistry [1,2], non-linear optics [3-5], photo physical studies [6,7], catalysis [8-10] and material chemistry [11,12]. Polynuclear metal complexes of transition metals with Schiff bases have also been of continuing interest because of their roles as biological models, catalysts for organic reactions and their usefulness as structural components for the synthesis of new metallo-supermolecular structures [13-16]. Several Schiff base macroligands have been synthesized to study their selectivity towards complexation of different metallic ions [17,18]. Schiff base ligands with structural similarity to phthalocyanines (N₄ macrocycles) and other related compounds are currently used as modifiers of active surface of electrodes to improve their catalytic activity in the selective detection of organic pollutants and entrainment of metals [14,17-21].

Most Schiff bases have often been used in the field of coordination chemistry and their metal complexes are of great interest for many years [22-24]. It is well known that S and N atoms play a key role in the coordination of metals to the active sites of many metallo-biomolecules [25-27]. Schiff bases and their complexes are also very useful and found many medical applications as antifungal, antibacterial and anticancer [28,29]. Recently, chemists as well as physicists used multinuclear Schiff base complexes to study the interaction between the paramagnetic ions and the bridging ligands and to develop the magneto-structural correlations enabling the design of interesting magnetic materials [30]. In this paper, the synthesis of a new series of cobalt, nickel and copper complexes with the Schiff base ligand bis (vanillidene) phthaloloylhydrazide is reported. Two

types of complexes were obtained and characterized by different techniques.

Experimental

Preparation of the Schiff base ligand:

Phthaloloylhydrazide was prepared by the reaction of hydrazine hydrate with diethylphthalate. 2:1 ratio for the hydrazine hydrate and the ester was used as reported for the hydrazide synthesis [31]. Reaction of the resulting phthaloloylhydrazide with vanillin by refluxing an ethanolic mixture containing 0.01 mol of the ester and 0.02 mol of vanillin for 5-6 hours gave a pale yellow precipitate of bis (vanillidene) phthaloloylhydrazide. The resulting ligand was filtered off, washed with cold ethanol and dried. The product has the following elemental analytical data:

Found: C, 62.02; H, 4.88; N, 12.30%

C₂₄H₂₂N₄O₆ required: C, 62.34; H, 4.67; N, 12.12%

Preparation of the complexes:

One general procedure was used for the preparation of the complexes. In this procedure, 3:2 metal to ligand ratio was used in both neutral and basic media, as follows:

1-The neutral complexes were obtained by refluxing a mixture containing 0.01 mol of the ligand and 0.015 mol of the metal salt in 80 ml of ethanol. The reflux was continued for 2-3 hours. On cooling, the separated complexes were filtered off, washed with ethanol and dried.

2-The anionic complexes were obtained after treating a similar solution, prepared as in 1, with 0.1N KOH until pH 9-9.5 where complete precipitation of the complexes occurred. The reaction mixture was then digested on a water bath for few minutes and left to cool down. The separated complexes were filtered off, washed with ethanol and dried.

Analysis and physical measurements:

Elemental microanalysis, molar conductance, infrared, Uv-vis. Spectra and magnetic susceptibility were performed as reported previously [32].

Determination of stability constant:

Job method was used for the determination of the conditional stability constants for a number of complexes reported in this paper as in the following procedure: several solutions of 3:2 metal salts and the ligand were prepared in absolute ethanol. The low absorbance (E_s) of these solutions was then measured. Another series of similar solutions were also prepared with the same amount of the metal salts but with excess ligand. For such solutions, the complexes are largely associated and therefore have higher absorbance (E_m). The difference between the two absorbencies represents a measure of the degree of dissociation (α) [33] which is given by:

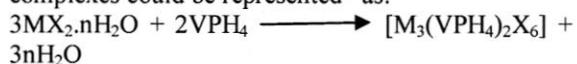
$$\alpha = E_m - E_s/E_m$$

And K , the stability constant was calculated from the equation:

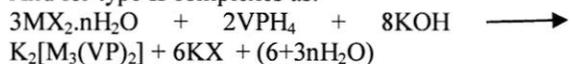
$$K = 1 - \alpha/4\alpha^3C^2 \quad (C \text{ is the concentration}).$$

Results and Discussion

The reactions of the prepared ligand, bis (vanillidene) phthaloloylhydrazide with different metal salts in neutral and alkaline ethanolic media gave two types of complexes. The chemical equations for type I complexes could be represented* as:



And for type II complexes as:



All the complexes are stable in dry air, having relatively high melting points and their elemental microanalyses are in good agreement with the suggested formulations showed in the above equations (Table 1). They are soluble in dimethylformamide (DMF) and the electrical conductivity measurements, in this solvent, for type I complexes give Λ_M values of 26-40 $\Omega^{-1}cm^{-1}mol^{-1}$ confirming that they are neutral and non-electrolytes, and for type II complexes give Λ_M values of 132-156 $\Omega^{-1}cm^{-1}mol^{-1}$ confirming that they are ionic and 1:2 electrolytes [34]. The stability constants of few representatives of the neutral complexes (type I) were measured in solution. For type II the measurements could not be possible because of the precipitate formation during the addition of KOH. The nature and stability constants measurements indicate that only 1:1 metal to ligand identities are possible, while 3:2 ratio is found for the solid complexes. This is might be due to the weakness of HO-M bridges which could not maintain the tri-nuclear framework present in solid complexes. All the studied complexes showed similar stability constants of $1.10-1.20 \times 10^4 l.mol^{-1}$. The similarity in the stability constants might be due to the similar environments around the metal ions.

The main stretching frequencies of the IR spectra for the ligand and its complexes are tabulated in Table 2. The IR spectra of the ligand and its corresponding complexes are found to be very similar to each other. Hence, significant frequencies are selected by

comparing the IR spectrum of the ligand with those of its cobalt, nickel and copper complexes.

For type I complexes, the very strong and sharp band located at 1600 cm^{-1} is assigned to $\nu_{(C=N)}$ stretching vibration of azomethine of the ligand. This band is shifted 20-40 cm^{-1} to lower wave number. The shift to lower wave number support the participation of the azomethine group of the ligand in binding to the metal ions [35,36]. Infrared spectra of the complexes display the characteristic bands associated with the N-H and C=O bonds of the amide functionality present in the free Schiff base [37,38]. The N-H band located in the free ligand at 3205 cm^{-1} is found at nearly the same position in complexes. Thus, in each complex of this type the amide functionality exists and is not deprotonated. The IR spectrum of the ligand display a band at 1660 cm^{-1} which assigned to the C=O of amide functionality. After complexation, this band shifted to lower wave numbers 1635-1645 cm^{-1} and this finding support the involvement of C=O in coordination to the metal ions [39]. The phenolic OH band occurred in the IR spectrum of the free ligand at 3480 cm^{-1} is shifted 45-100 cm^{-1} in the IR spectra of the complexes. This shift of O-H bands suggested additional coordination through both hydroxyl oxygen atoms [40]. In addition, the complexes containing nitrate groups showed three bands at 995-1000, 1380-1385 and 1495-1520 cm^{-1} . The positions of these bands and the difference between the two with the highest frequencies ($\sim 120 \text{ cm}^{-1}$) are suggesting monodentate coordination of nitrate groups to the metal ions in these complexes [38]. On the other hand, the band due to the chloride ions could not be observed because they occurred below 300 cm^{-1} in the IR spectra of the complexes which is out of our spectrophotometer range.

Type II complexes showed different IR spectra due to the deprotonation of N-H and O-H groups in basic medium with the formation of azine chromophore, $-C=N-N=C-$. For these complexes, the position of the C=N band is found at similar location as for those of type I complexes. The N-H, O-H and C=O bands are disappeared due to the deprotonation process, instead new band is found at 1590-1605 cm^{-1} and assigned to the azine chromophore [39,40]. For both type of complexes the shift of $\delta_{(O-H)}$ and $\nu_{(C-O)}$ stretching bands to lower values support the suggested coordination through phenolic and enolic oxygen atoms [40,41]. For all the complexes new bands, not found in the ligand spectrum, are observed at 460-490 and 420-430 cm^{-1} . These bands are assigned to M-O and M-N stretching vibrations [38] confirming the formation of metal-oxygen and metal-nitrogen bonds. According to measurements of magnetic susceptibilities, the isolated complexes are paramagnetic. With account of obtained values of μ_{eff} , type I complexes has octahedral environments, while type II has tetrahedral environments for cobalt and nickel ions and square planar structure for copper ion. These characters correlate well with the positions of

absorption bands in their electronic absorption spectra [42].

The data of the electronic spectral measurements are given in Table 3. For type I, the three bands observed in the visible region for cobalt and nickel complexes are correspond to the allowed d-d transitions for these ions in an octahedral environment [42]. The combined single broad asymmetric band located below 15000 cm^{-1} in the electronic spectra of copper complexes suggests a distortion of Jahn-Teller type in the octahedral structure of these complexes [43]. The presence of charge-transfer (CT) bands in the spectra indicate certain degree of π -bond character in the coordination bonds between the metal and the donor sites of the ligand, as these bands result from π - π^* transitions [44]. The values of β (Table 3) give an indication for the covalent character in the coordination bonds and thus suggesting relatively higher covalence for cobalt complexes than that for the analogous nickel complexes [44]. For type II complexes where the metal ions are tetra-coordinated, only ν_3 band is observed, as ν_1 and ν_2 bands fall in the electronic spectral regions below the range limits of our spectrophotometer. From the positions of these bands, tetrahedral structural environment is suggested for cobalt and nickel complexes. The position of the band in the region of 19000 cm^{-1} suggests square planar environment for copper complexes. Both types of complexes containing mixed metal ions showed several bands in their electronic spectra and assigned as due to octahedral and tetrahedral arrangements around these ions [42].

The values of the effective magnetic moments shown in Table 1 are in good agreement with the suggested high-spin octahedral and tetrahedral geometries for cobalt and nickel ions with d^7 and d^8 configurations, respectively. These values, also, agree well with the presence of 3 and 2 odd electrons. The presence of some anti-ferromagnetism is believed to be responsible for the lowering of effective magnetic moments. This effect results from the super exchange mechanism among the adjacent metallic centers in these complexes [45].

Conclusion

Two types of complexes are obtained by the reactions of metal salts with the ligand in neutral and basic media, all have 3:2 metal-ligand composition. In the neutral complexes, the ligand acts as neutral hexadentate and the coordination occurred by both carbonyl oxygen, azomethine nitrogen and phenoxyl oxygen atoms. The inorganic ligands nitrate and chloride ions are also coordinated as monodentate ligands giving hexa-coordinated metal ions having the most probable octahedral structure. On the other hand, for the anionic complexes, the ligand coordinated through both enolic oxygen, azomethine nitrogen and phenoxyl oxygen atoms. The metal ions in this case are tetra-coordinated with tetrahedral structure for cobalt and nickel complexes, while copper complexes showed square planar arrangement. The solid complexes for these metal ions are trinuclear for both types as shown in figures 1 and 2. The study of the reaction between the metal ions and the ligand in solution revealed the formation of 1:1 metal-ligand species.

Table 1- Analytical data and some physical properties

Compound	λ_{max} (nm) in DMF	Colour	MP $^{\circ}\text{C}$	μ_{eff} (BM)	Analysis %, Found (Calculated)				
					C	H	N	M	Cl
$[\text{Co}_3(\text{VPH}_4)_2(\text{NO}_3)_6]$	40	Pale yellow	306					11.96 (11.87)	
$[\text{Ni}_3(\text{VMH}_4)_2\text{NO}_6]$	39	Pale green	302	2.62	39.12 (39.43)	2.98 (3.20)	13.31 (13.10)	11.99 (11.91)	
$[\text{Cu}_3(\text{VPH}_4)_2(\text{NO}_3)_6]$	35	Pale brown	290	2.46				12.80 (12.76)	
$[\text{Co}_3(\text{VPH}_4)_2\text{Cl}_6]$	36	deep yellow	242	3.84				13.41 (13.48)	16.20 (16.14)
$[\text{Ni}_3(\text{VPH}_4)_2\text{Cl}_6]$	31	Yellow-green	310					14.0 (13.92)	16.20 (16.14)
$[\text{Cu}_3(\text{VPH}_4)_2\text{Cl}_6]$	26	Dark yellow	293					14.36 (14.36)	16.02 (16.13)
$[\text{Co}_2\text{Ni}(\text{VPH}_4)_2(\text{NO}_3)_6]$	38	Pale green	300	3.53	39.11 (39.46)	2.98 (3.11)	13.31 (13.10)	Co,8.00(7.80) Ni,3.99(3.96)	
$[\text{Ni}_2\text{Co}(\text{VPH}_4)_2(\text{NO}_3)_6]$	31	Pale green	294	3.44	39.12 (39.02)	2.98 (2.88)	13.31 (13.45)	Ni,7.97(7.86) Co,4.00(3.96)	

[Co ₂ Cu(VPH ₄) ₂ (NO ₃) ₆]	31	Brown	305	3.23					Co,8.57(8.46) Cu,3.97(3.89)
[Cu ₂ Ni(VPH ₄) ₂ (NO ₃) ₆]	29	Brown	301						Cu,8.57(8.60) Ni,3.96(4.20)
[CoNiCu(VPH ₄) ₂ (NO ₃) ₆]	37	Brown	280	2.86					Co,3.99(3.94) Ni,3.97(3.86) Cu,4.30(4.32)
K ₂ [Co ₃ (VP) ₂]	151	dark brown	329	3.61					15.09 (15.10)
K ₂ [Ni ₃ (VP) ₂]	140	Pale green	282	2.80	49.21 (49.36)	3.07 (3.00)	9.57 (9.32)		15.04 (15.12)
K ₂ [Cu ₃ (VP) ₂]	136	dark green	301	1.91					16.02 (16.21)
K ₂ [Co ₂ Ni(VP) ₂]	132	Yellowish green	316	3.41					Co,10.05(10.15) Ni,5.01(5.00)
K ₂ [Ni ₂ Co(VP) ₂]	139	Yellowish green	302	3.64					Ni,10.03(10.23) Co,5.03(4.98)
K ₂ [Co ₂ Cu(VP) ₂]	156	Light brown	316						Co,10.02(10.05) Cu,5.04(5.09)
K ₂ [Cu ₂ Co(VP) ₂]	148	Dark green	299	3.47					Cu,10.77(10.76) Ni,4.99(5.20)
K ₂ [Ni ₂ Cu(VP) ₂]	151	Light green	320	2.16	49.01 (48.89)	3.02 (2.90)	9.53 (9.68)		Ni,9.99(10.13) Cu,5.41(5.38)
K ₂ [Cu ₂ Ni(VP) ₂]	156	Green	336						Cu,10.77(10.65) Ni,4.97(4.89)
K ₂ [CoNiCu(VP) ₂]	148	Dark green	330						Co,5.01(4.96) Ni,4.99(5.13) Cu,5.41(5.42)

Table 2- Some important infrared spectral data (cm⁻¹)

Neutral compound	v(OH)	(NH)	vC=O	v(C=N)	δ(OH)	v(N-N)	v(M-N)	v(M-O)	v(NO ₃)
VPH ₄	3480	3205	1660	1600	1290	995	-----	-----	-----
[Co ₃ (VPH ₄) ₂ (NO ₃) ₆]	3380	3200	1640	1555	1260	1020	490	430	1000,1380,1495
[Ni ₃ (VPH ₄) ₂ (NO ₃) ₆]	3380	200	1635	1555	260	1020	70	425	980,1380,1495
[Cu ₃ (VPH ₄) ₂ (NO ₃) ₆]	3410	240	1645	1575	252	1024	60	30	1000,1385,1495
[Co ₃ (VPH ₄) ₂ Cl ₆]	3420	3205	1640	1560	1260	1030	465	430	-----
[Ni ₃ (VPH ₄) ₂ Cl ₆]	3405	3205	1645	1580	1260	1025	465	425	-----
[Cu ₃ (VPH ₄) ₂ Cl ₆]	3425	3220	1645	1570	1260	1025	465	430	-----
[Co ₂ Ni(VPH ₄) ₂ (NO ₃) ₆]	3420	3205	1645	1560	1265	1030	465	425	1000,1385,1505
[Ni ₂ Co(VPH ₄) ₂ (NO ₃) ₆]	3410	3225	1645	1575	1250	1025	465	425	995,1385,1505
[Co ₂ Cu(VPH ₄) ₂ (NO ₃) ₆]	3410	3220	1645	1575	1250	1020	460	420	1000,1385,1495
[Cu ₂ Ni(VPH ₄) ₂ (NO ₃) ₆]	3400	3205	1635	1550	1265	1030	460	420	1000,1385,1520
[CoNiCu(VPH ₄) ₂ (NO ₃) ₆]	3400	3200	1635	1580	1265	1030	460	425	990,1385,1520
Anionic complexes	v(C=N)	v(azine) -C=N-N=C-	v(C-O)	v(N-N)		v(M-O)		v(M-N)	
K ₂ [Co ₃ (VP) ₂]	1580	1600	1160	1020		460		425	
K ₂ [Ni ₃ (VP) ₂]	1580	1595	1160	1023		460		420	
K ₂ [Cu ₃ (VP) ₂]	1580	1600	1160	1025		465		420	
K ₂ [Co ₂ Ni(VP) ₂]	1575	1590	1160	1025		460		425	
K ₂ [Ni ₂ Co(VP) ₂]	1575	1595	1160	1030		460		425	
K ₂ [Co ₂ Cu(VP) ₂]	1570	1595	1160	1030		460		425	
K ₂ [Cu ₂ Co(VP) ₂]	1565	1590	1155	1025		465		420	
K ₂ [Ni ₂ Cu(VP) ₂]	1575	1600	1165	1035		460		425	
K ₂ [Ni ₂ Cu(VP) ₂]	1465	1590	155	1025		465		425	
K ₂ [CoNiCu(VP) ₂]	575	1605	1165	1035		460		425	

Table 3- The electronic Spectral data for some of the complexes

Compound	ν_1	ν_2	ν_3	C.T	$10D_q$	β	ν_2/ν_1	CFSE	Structure
$[\text{Co}_3(\text{VPH}_4)_2(\text{NO}_3)_6]$	10560	14500	22900	32362	12440	0.347	1.37	9952	Octahedral
$[\text{Co}_2\text{Ni}(\text{VPH}_4)_2(\text{NO}_3)_6]$	10240	14200	23364	30490	13125	0.415	1.38	10510	Octahedral for Co & Ni
	11300	16060	26175	32895	11300	0.770	1.43	13560	
$[\text{Ni}_3(\text{VPH}_4)_2(\text{NO}_3)_6]$	10270	16340	27030	33220	10270	0.773	1.59	12320	Octahedral
$[\text{Co}_3(\text{VPH}_4)_2\text{Cl}_6]$	10510	14400	23530	32470	10510	0.389	1.37	9952	Octahedral
$[\text{Ni}_2\text{Co}(\text{VPH}_4)_2(\text{NO}_3)_6]$	10675	16120	24050	34250	10675	0.624	1.51	12810	Octahedral for Co&Cu
	10020	14555	23190	30770	13170	0,472	1.45	10535	
$[\text{CoNiCu}(\text{VPH}_4)_2(\text{NO}_3)_6]$	10415	---	---	31610	---	---	---	---	Octahedral for Co, Ni & Cu
	12270	17265	28040	34275	12270	0.78	1.41	14730	
	13755	---	---	30215	13755	---	---	8255	
$\text{K}_2[\text{Co}_3(\text{VP})_2]$	---	---	14625	31055	---	---	---	---	Tetrahedral
$\text{K}_2[\text{Ni}_3(\text{VP})_2]$	---	---	13830	34845	---	---	---	---	Tetrahedral
$\text{K}_2[\text{Co}_2\text{Ni}(\text{VP})_2]$	---	---	14970	32155	---	---	---	---	Tetrahedral for Co & Ni
	---	---	13180	34480	---	---	---	---	
$\text{K}_2[\text{Cu}_3(\text{VP})_2]$	19605	---	---	33100	19605	---	---	---	Sq. Planar
$\text{K}_2[\text{Ni}_2\text{Co}(\text{VP})_2]$	13250	---	---	33555	---	---	---	---	Tetrahedral For Co&Ni
	14285	---	---	31150	---	---	---	---	
$\text{K}_2[\text{Ni}_2\text{Cu}(\text{VP})_2]$	---	---	13585	35210	---	---	---	---	Ni-Tetra. Cu-Sq.Plan.
	18940	---	---	31350	---	---	---	---	

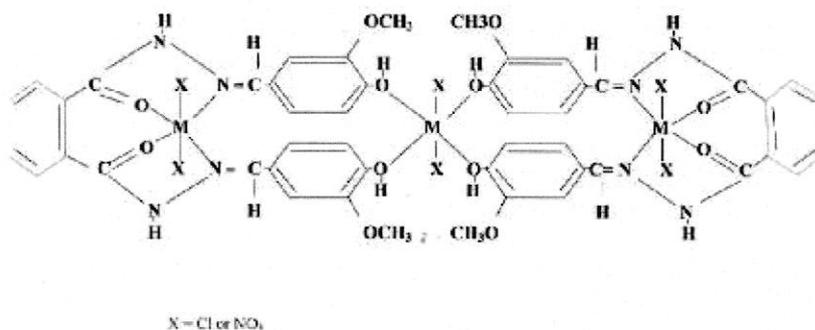


Fig. 1- Neutral type I complexes

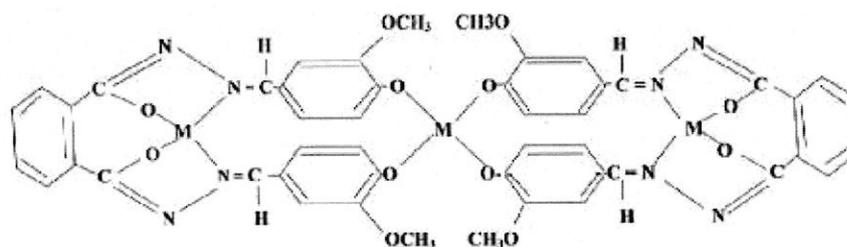


Fig. 2- Anionic type II complexes

*The reactions for the formation of the mixed metal complexes could be represented in similar equations.

References

1. J. W. Lu, Y. H. Huang, S. I. Lo and H. H. Wei, *Inorg. Chem. Commun.*, 10, 1210 (2007).
2. L. Lecren, W. Wernsdorfer, Y. T. Li, A. Vindingni and R. Clerac, *J. Am. Chem. Soc.*, 129, 5045 (2007).
3. S. D. Bella, *Chem. Sci. Rev.*, 30, 355 (2001).
4. M. Reta, M. Tavaholi, F. Faridbod, S. Rahi and M. Nassari, *Int. J. Electrochem. Sci.*, 3, 1559 (2008).
5. L. A. Saghatforash, S. Ershad, G. Karem and R. kahiri, *Polish J. Chem.*, 81, 2069 (2007).
6. P. G. Cozzi, L. S. Dolci, A. Garelli, M. Montalti and L. Prodi, *New J. Chem.*, 27, 692 (2003).
7. K. E. Splan, A. M. Massar, G. A. Morris and J. T. Hupp, *Eur. J. Inorg. Chem.*, 234 (2003).
8. N. C. Gianneschi, S. H. Cho, S. T. Nguyen and C. A. Mirkin, *Angew. Chem.*, 43, 5503 (2004).
9. L. Z. Flores-Lopes, A. L. Iglesias, A. Gama, G. Aguirre and R. Sonanathan, *J. Mex. Chem. Soc.*, 51, 175 (2007).
10. S. Ershad, L. Ali, G. Karem and S. Kangari, *Int. J. Electroche. Sci.*, 4, 846 (2009).
11. M. Shamsipur, M. Yousefi, G. M. Reza and M. Faal, *Sensors Chemicals*, 82, 105 (2002).
12. S. Chandra, D. Jaria, A. Kumar and P. Sharma, *Molecules*, 14, 174 (2009).
13. F. J. Ferrer, S. Gutierrez, F. Bedioui and A. Alatorre, *Electroanal.*, 15, 70 (2003).
14. Z. Chen, H. Morimoto, S. Matsunaga and M. Shibasaki, *J. Am. Chem. Soc.*, 130, 2170 (2008).
15. I. Yoon, M. Narita, T. Shimizu and M. Asakawa, *J. Am. Chem. Soc.*, 126, 16740 (2004).
16. Li. Chen, Fu. Mei and G. Li, *React. Kinet. Catal. Lett.*, 98, 99 (2009).
17. Z. Chen, M. Furutachi, Y. Kato, S. Matsunaga and M. Shibasaki, *Angew Chem.*, 121, 2252 (2009).
18. H. Adams and B. A. Najera, *J. Coord. Chem.*, 56, 1215 (2003).
19. T. Trollund, P. Ardiles, M. J. Aguirre and R. C. Rocha, *Polyhedron*, 19, 2303 (2000).
20. T. Hasobe, H. Imahori, K. Ohkubo, H. Yamada, T. Sate and S. Fukusumi, *J. Porphyrins and Phthalocyanines*, 7, 296 (2003).
21. J. Losado, I. Peso and L. Beyer, *Inorg. Chim. Acta*, 321, 107 (2001).
22. K. C. Gupta and A. K. Sutar, *J. Macromolecular Science, A*, 44, 1171 (2007).
23. Ya. Li Sang, Xue. Song Lin, *J. Coord. Chem.*, 63, 315 (2010).
24. D. Qin, F. Han, Y. Yao and Qi. Shen, *J. Chem. Soc., Dalton Trancs*, 28, 5535 (2009).
25. O. P. Molls, T. L. Borgne, T. Thuery and M. Ephritikhine, *Acta Cryst.*, C57, 392 (2001).
26. S. Gakias, C. Rix, A. Fowless and A. Hobday, *Inorg. Chim. Acta*, 359 (2006).
27. F. A. Abdlseed and M. M. El-ajaily, *Int. J. Pharm. Tech.*, 1, 1097 (2009).
28. T. S. Basu, S. Vos and S. Kangari, *Int. J. Electrochem. Sci.*, 4, 846 (2009).
29. R. Wany, N. He, P. Song, Yu. Feng and Z. Lei, *Pure Appl. Chem.*, 81, 2397 (2009).
30. S. L. Ma, Xu-Xia Sun, S. Gao, C. Qi, H. Huang and W. X. Zhu, *Eur. J. Inorg. Chem.*, 846 (2009).
31. W. Baker, C. N. Hasker and J. F. W. McOmire, *J. Chem. Soc.*, 170 (1950).
32. I. J. Sallomi and A. J. Shaheen, *Polyhedron*, 17, 1429 (1998).
33. A. E. Harvey and D. L. Manning, *J. Am. Chem. Soc.*, 72, 4488 (1952).
34. G. S. Girolami, T. B. Rauchuss and R. J. Angelici, "Synthesis and Techniques in Inorganic Chemistry", 3rd ed., University Science Book, Sausalito, p.254 (1999).
35. B. Chiswell, J. B. crowford and E. J. Oreilly, *Inorg. Chim. Acta*, 49, 223 (1980).
36. W. H. Hegazy, *Monatsh. Chem.* 132, 639 (2001).
37. R. M. Silverstein and F. X. Webster "Spectroscopic Identification of Organic Compounds", 6th ed., Wiley, New York (1998).
38. K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds", A, 6th ed., Wiley, New Jersey (2009).
39. I. J. Sallomi and A. J. Shaheen, *Transition Met. Chem.*, 19, 275 (1994).
40. I. J. Sallomi, A. A. Rahman and T. H. Mahmood, *Mu'atah, Jordan*, 18, 95 (2003).
41. S. Padhye and G. Kuffman, *Coord. Chem. Rev.*, 63, 127 (1985).
42. I. L. Dorokhte, I. I. Scifullina and S. V. Zubkov, *Russ. J. Coord. Chem.*, 29, 714 (2003).
43. H. A. and E. Teller, 161, 220 (1937).
44. J. Terceno, C. R. Bas, J. Mahia and A. Maestro, *Inorg. Chem.*, 41, 5383 (2002).
45. G. Wilkinson "Comprehensive Coordination Chemistry", Vol. 2, Pergamon Press, London (1997).

معقدات الكوبلت والنيكل والنحاس مع ليكاند بس (فانيليدين) فثالوليل هيدرازيد

عصام جرجيس سلومي ، وجدان عبدالقهي الزيدان

قسم الكيمياء ، كلية التربية ، جامعة الموصل ، الموصل ، العراق

المخلص

يتضمن هذا البحث تحضير ودراسة عدد من معقدات الكوبلت والنيكل والنحاس ثلاثية النواة مع الليكاند من نوع قاعدة شيف، بس (فانيليدين) فثالوليل هيدرازيد. حُضرت المعقدات في المحيطين المتعادل والقاعدي ونتج عن ذلك نوعين من المركبات: النوع الأول عبارة عن معقدات متعادلة، والنوع الثاني، المعقدات الأيونية السالبة. وتم تشخيص الليكاند ومعقداته بالطرق الكيموفيزيائية والطيفية والمغناطيسية التي بينت عمل الليكاند بشكل سداسي السن متعادل في الوسط المتعادل وسداسي السن رباعي القاعدة في الوسط القاعدي. اقترحت بنية ثماني السطوح للمعقدات المتعادلة من النوع الأول ذات التناسق السداسي وبنيتي رباعي السطوح والمربع المستوي للمعقدات رباعية التناسق من النوع الثاني. وأشارت نتائج التحليل الدقيق للعناصر والنسب التكوينية للمعقدات الى امتلاك مركبات النوع الأول للصيغ العامة:



أما معقدات النوع الثاني فلها الصيغ العامة:



حيث تمثل M^{**} ، M^* ، M كل من أيونات الكوبلت والنيكل والنحاس الثلاثية الموجبة، و VPH_4 و VP الصورتين المتعادلة والأيونية السالبة لليكاند، و NO_3 ، $Cl = X$.

استخدمت طريقة جوب لدراسة طبيعة هذه المعقدات في المحلول واتضح بأن للمعقدات المدروسة النسب التكوينية 1:1 فلز الى ليكاند، على خلاف الحالة الصلبة التي تكون فيها النسبة 2:3 فلز الى ليكاند. أما ثوابت الاستقرار فإنها متقاربة للمعقدات المدروسة مما يشير الى تشابه الظروف المؤثرة على النوعيات المتكونة في المحلول.