



Revista de la Sociedad Química del Perú

ISSN: 1810-634X

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Sociedad Química del Perú
Perú

Zamorano, Sergio; Camus, Juan; Meghea, A.
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Revista de la Sociedad Química del Perú, vol. 74, núm. 3, julio-septiembre, 2008, pp. 182-
189
Sociedad Química del Perú
Lima, Perú

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SYNTHESIS AND EPR CHARACTERIZATION OF COPPER AND VANADYL COMPLEXES DERIVED FROM PYRAZOLONE

Sergio Zamorano*, Juan Camus and A. Meghea**

ABSTRACT

The synthesis of complexes from copper (II) and vanadyl (VO^{2+}) with pyrazolone ligands Pir-C₆, Pir-C₈ and Pir-C₁₂ are described. The EPR spectra of this compounds are interpreted and the physical and spectroscopic measurements were made.

Key words: Synthesis of complexes, pyrazolone ligands, EPR spectra

SÍNTESIS Y CARACTERIZACIÓN POR EPR DE COMPLEJOS DE COBRE Y VANADIO DERIVADOS DE LA PIRAZOLONA

RESUMEN

En este trabajo se describe la síntesis de complejos a partir de cobre (II) y vanadilo (VO^{2+}) con ligandos de pirazolona Pir-C₆, Pir-C₈ y Pir-C₁₂. Se interpretan los espectros EPR de estos compuestos y se dan las medidas físicas y espectroscópicas.

INTRODUCTION

Compounds of the transition metals ions with unpaired electrons are paramagnetics and EPR has been used extensively to investigate, the electronic structure of transition metals ion and the nature of the chemical bond M-L; in this sense, there are many excellent textbooks and review articles^{1,2} deal with this subject in detail.

Low temperatures are frequently required to detect EPR spectra; however, at room temperature, the presence of ligands eliminate the effects of spin-spin interaction which produce line broadening and the signal obtained gives detailed information about the ground state electronic structure of the paramagnetic ion “diluted” into diamagnetic host crystal: - the specific oxidation state, the symmetry of the crystalline electric field about the ion, - the nature of the ground state d orbital and its relation to structure, - the extent of covalence of the metal ligand bond and – the presence of the Jahn-Teller effect. The EPR spectra also is used to study the distortion in the macrocyclic ring of copper (II) chlorophylls³. The covalence parameters obtained from EPR spectra, are high indicating an appreciable ionic character of the metal-ligand bond in the copper complexes of quinoxalinic ligands⁴

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EXPERIMENTAL

Materials and methods

Analytical reagent grade chemicals were used for the synthesis of the compounds. Fourier Transform Infrared (FTIR) spectra of the ligands and its metal complexes as KBr pellets were recorded in the spectral range $4000\text{--}400\text{ cm}^{-1}$ with a Bruker FTIR Vector 22. ESR spectra were recorded on a Bruker ECS 106 spectrometer operating in the X-band (9,78 GHz). Traces of Mn^{2+} were used as the g marker ($g_3=2,03584$; $g_4=1,98040$ with $H_3=3179,5$ and $H_4=3268,5$). The C, H, N, and S content was analysed on a Microanalyser Fisons EA-1108 CHNS-O.

Synthesis of ligands

Pir-C₆: 4-Dithiocarboxilate of hexil-phenyl-3-metil-5-pyrazolone⁵. Phenylpyrazolone (12,5 mmol) 2,175 g, were dissolved in 50 ml of ethanol, in hot alcoholic solution of KOH (0,700 g in 50 ml of EtOH) by refluxing one hour. The original solution is transparent and yellow. After cooling to room temperature was added 1 ml of CS_2 , then the colour of the solution changed to orange. The resultant solution was stirred by 8 hours at room temperature and 1 hour by refluxing.

After cooling was added 3,5 ml of 1-bromohexane and refluxing during 24 hours. The resultant solution was distilled for to concentrate and then was recrystallized at cool temperature for one week.

The solid was filtered off, washed with water, EtOH and ether and dried under reduced pressure at room temperature (yield 21,77%). The melting point of the product is $117,2^\circ\text{C}$. The planar structure of the ligand L_1 is shown in figure 1.

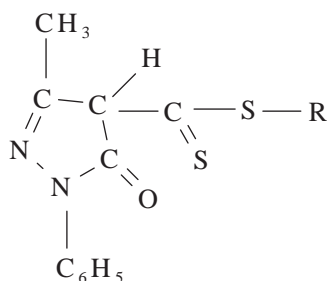


Figure 1. Structure of ligands

In the ligand L_1 ; R is $-\text{CH}_2-(\text{CH}_2)_4-\text{CH}_3$

In the ligand L_2 ; R is $-\text{CH}_2-(\text{CH}_2)_6-\text{CH}_3$

In the ligand L_3 ; R is $-\text{CH}_2-(\text{CH}_2)_{10}-\text{CH}_3$

Pir-C₈ : 4-Dithiocarboxilate of octil- phenyl-3-metil-5-pirazolone⁵. Phenylpyrazolone (12,5 mmol) 2,175 g, were dissolved in 50 ml of ethanol, in hot alcoholic solution of KOH (0.700 g in 50 ml of EtOH) by refluxing one hour. The original solution is transparent and yellow. After cooling to room temperature was added 1 ml of CS₂; then the colour of the solution changed to orange. The resultant solution was stirred by 8 hours at room temperature and 1 hour by refluxing.

After cooling was added 3,0 ml of 1-bromooctane and refluxing during 24 hours. The resultant solution was distilled for to concentrate and then was recrystallized at cool temperature for one week.

The yellow solid was filtered off, washed with water, EtOH and ether and dried under reduced pressure at room temperature (yield 21,65%). The melting point of the product is 68,9°C. The planar structure of the ligand L₂ is shown in figure 1.

Pir-C₁₂ : 4-Ditiocarboxilato de dodecil- fenil-3-metil-5-pirazolona⁶. Phenylpyrazolone (12,5 mmol) 2,175 g, were dissolved in 50 ml of ethanol, in hot alcoholic solution of KOH (0,700 g in 50 ml of EtOH) by refluxing one hour. The original solution is transparent and yellow. After cooling to room temperature was added 1 ml of CS₂, then the colour of the solution changed to orange. The resultant solution was stirred by 8 hours at room temperature and 1 hour by refluxing.

After cooling was added 3,5 ml of 1-bromodecane and refluxing during 24 hours. The resultant solution was distilled for to concentrate and then was recrystallized at cool temperature for one week.

The yellow solid was filtered off, washed with water, EtOH and ether and dried under reduced pressure at room temperature (yield 23,15%). The melting point of the product is 117,2°C. The planar structure of the ligand L₃ is shown in figure 1.

Synthesis of complexes

Pir-C₆ + Cu (II). 4-Dithiocarboxilate of hexyl- phenyl-3-metil-5-pirazolone (10 mg) was dissolved in 50 ml of EtOH obtaining the yellow solution. To this solution was added 109,5 mg of the copper(II) acetate dissolved in 20 ml of EtOH obtaining the maroon solution. The solution was refluxed for 1 h. Then was filtered off, washed with water, EtOH and ether and dried under reduced pressure at 20°C. The obtained solid is deep green (yield 46,03%).

Pir-C₆ + VO²⁺. 4-Dithiocarboxilate of hexyl- phenyl-3-metil-5-pirazolone (50 mg) was dissolved in 50 ml of EtOH obtaining the yellow solution. To this solution was added 13.55 mg of vanadyl sulphate dissolved in 12,6 mg of sodium bicarbonate dissolving in 1 ml of water and 3 ml of EtOH solution. The yellow-oranged solution obtained was refluxed for 1 h. Then was filtered off, washed with water, EtOH and ether and dried at room temperature. The obtained solid is yellow-green (yield 40,91%).

Pir-C₈ + Cu (II). 4-Dithiocarboxilate of octyl- phenyl-3-metil-5-pirazolone (50 mg) was dissolved in 50 ml of EtOH obtaining the yellow solution. To this solution was added 13,78 mg of copper(II) acetate dissolved in 20 ml of EtOH obtaining the maroon

solution . The solution was refluxed for 1 h. Then was filtered off, washed with water, EtOH and ether and dried at room temperature . The obtained solid is deep green (yield 88,50%).

Pir-C₈ + VO²⁺. 4-Dithiocarboxilate of octyl- phenyl-3-methyl-5-pirazolone (100 mg) was dissolved in 25 ml of EtOH obtaining the yellow solution. To this solution was added 24,99 mg of vanadyl sulphate dissolved in 1ml of water and 3 ml of EtOH The green solution was refluxed for 1 h. Then was filtered off, washed with water, EtOH and ether and dried at room temperature . The obtained solid is green (yield 53,97%)

Pir-C₁₂ + Cu (II). 4-Dithiocarboxilate of dodecyl-1- phenyl-3-methyl-5-pirazolone (100 mg) was dissolved in 50 ml of EtOH obtaining the yellow solution. To this solution was added 107,6 mg of the cooper(II) acetate dissolved in 20 ml of EtOH obtaining the red- green solution . The solution was refluxed for 1 h. Then was filtered off, washed with water, EtOH and ether and dried at 20°C . The obtained solid is dark green (yield 79,09%)

Pir-C₁₂ + VO²⁺. 4-Dithiocarboxilate of dodecyl-1-phenyl-3-methyl-5-pirazolone (50 mg) was dissolved in 50 ml of EtOH obtaining the yellow solution. To this solution was added 10,82 mg of vanadyl sulphate and 10,08 mg of sodium bicarbonate dissolved in 1ml of water and 3 ml of EtOH obtaining the orange-red solution . The solution was refluxed for 1 h. Then was filtered off, washed with water, EtOH and ether and dried at room temperature. The obtained solid is green (yield 59,44%)

RESULTS AND DISCUSSIONS

All the copper (II) and vanadyl(II) complexes: Cu(PirC₆)₂, Cu(PirC₈)₂ and Cu(PirC₁₂)₂, VO(PirC₆)₂, VO(PirC₈)₂ and VO(PirC₁₂)₂ are green. They are stable solids, soluble in DMSO, DMF and CHCl₃, and insoluble in alcohol and water. The elemental analysis agree well with a 1:2 metal:ligand stoichiometry for all the complexes (table 1). The conductivity values measured en DMSO at room temperature fall in the range expected for these electrolytes.

Table 1. Analytical data of the ligand and its metal complexes.

Compounds	Found (Calculated),%			
	% C	% H	% N	% S
Pir-C₆	61,20 (61,07)	6,66 (6,59)	8,38 (8,38)	18,43 (19,16)
[Cu(Pir-C₆)₂]	54,61 (55,93)	5,78 (5,76)	7,39 (7,68)	17,62 (17,55)
[VO(Pir-C₆)₂]	54,12 (55,67)	5,69 (5,73)	7,29 (7,64)	17,16 (17,46)
Pir-C₈	63,02 (62,98)	8,12 (7,18)	7,85 (7,73)	16,56 (17,68)
[Cu(Pir-C₈)₂]	58,27 (58,05)	6,08 (6,36)	7,38 (7,13)	17,42 (16,29)
[VO(Pir-C₈)₂]	59,86 (57,80)	6,84 (6,33)	7,44 (7,09)	11,44 (16,22)
Pir-C₁₂	66,02 (66,02)	8,13 (8,13)	6,84 (6,70)	14,48 (15,31)
[Cu(Pir-C₁₂)₂]	61,53 (61,50)	7,46 (7,35)	6,93 (6,24)	14,58 (14,26)
[VO(Pir-C₁₂)₂]	59,91 (61,27)	7,32 (7,32)	6,80 (6,22)	14,67 (14,21)

IR spectra

In the ligand Pir-C₆ the (C=S) vibrations appear as a low band at 1058 cm⁻¹. The same band appear at 1063 and 1065 cm⁻¹ in the copper and vanadyl complex, respectively, is suggestive of the chelating character of the ligand in the case of the metal complexes. In the case of the ligand Pir-C₈ the (C=S) vibrations appear as a low band at 1060 cm⁻¹. The same band appear at 1064 cm⁻¹ in the copper and vanadyl complex, respectively. And in the ligand Pir-C₁₂ the (C=S) vibrations appear as a low band at 1058 cm⁻¹. The same band appear at 1062 cm⁻¹ in the copper and vanadyl complex, respectively. (table 2).

Table 2. Characteristic IR peaks (cm⁻¹) of the ligand and its metal complexes

	Methyl Group	Pirazol ring	Bencenic ring	C=S	V=O
Pir-C₆	2928	1525 1457	756 688	1058	
[Cu(Pir-C₆)₂]	2928	1552 1455	755 690	1063	
[VO(Pir-C₆)₂]	2927	1536 1442	756 690	1065	1001
Pir-C₈	2923	1558 1458	751 688	1060	
[Cu(Pir-C₈)₂]	2925	1551 1457	755 689	1064	
[VO(Pir-C₈)₂]	2925	1548 1446	755 688	1064	
Pir-C₁₂	2921	1562 1459	751 688	1058	
[Cu(Pir-C₁₂)₂]	2923	1561 1468	754 690	1062	
[VO(Pir-C₁₂)₂]	2923	1550 1449	753 688	1062	1012

EPR spectra

The EPR spectra of the copper complexes shows that all three spectra are very intensive indicating the presence of Cu(II) ion, mainly into an axially elongated geometry. This is most evident in Cu (PirC₁₂)₂ compound, having parameters $g_{\parallel} > g_{\perp}$. For compounds Cu(PirC₈)₂ and Cu(PirC₆)₂ an increasing third component is noted, corresponding to a compression, the resulted spectra being characteristic for a rhombic distorted surroundings. Such a geometry may be assessed to a five- or six- coordination round Cu²⁺ ion (possibly with one or two water molecules). Therefore, for Cu (PirC₁₂)₂ having most bulk ligand, a four-coordination is adopted, and the axially elongated pattern of EPR spectra as well as its electronic spectra are arguments for a square planar geometry.

The EPR spectra of the vanadyl complexes show that the VO(PirC₆)₂ and VO(PirC₁₂)₂ spectra are intensive with a good hyperfine structure. The eight hyperfine lines are observed exhibiting a variation in linewidth of which is typical^{7,8}. Hyperfine couplings are large, but a large nuclear moment and spin cause a large line width which tends to obscure the hyperfine structure however, in this case, we can determine the g and A parameters. The higher A value is associated with greater localisation of the electron on the metal because of the increased electrophilic nature of the ligands and consequent, reduced covalence of the V-O (chelate) bonds. These complexes probably has the square pyramidal structure. The spectra of the VO(PirC₈)₂ complex, presents only one broad band and a bad resolution of the hyperfine

structure, that allow to determine only the parameter $g=1,9930$ and $A=39,13$ for the square pyramid structure. A lower A value is possible due to the presence of solvent⁹⁻¹², (because of the greater delocalization of the unpaired electron), and the system are very sensitive to solvation and coordination.

The EPR data of the copper and vanadyl complexes is shown in the table 3.

The EPR spectra of the two complexes are shown in figure 2 and 3.

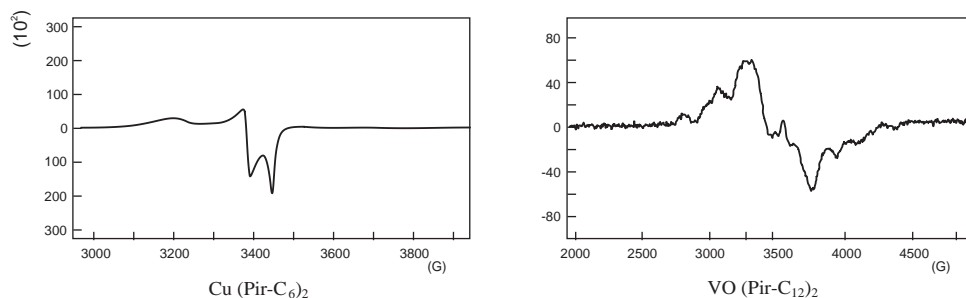


Figure 2. EPR spectra of the copper complex. **Figure 3.** EPR spectra of the vanadyl complex

Table 3. EPR data for copper complexes as crystalline powders at room temperature

Compound	g_1	g_2 / g_{\perp}	g_3 / g_{\parallel}
$\text{Cu}(\text{PirC}_6)_2$	2,0277	2,0633	2,1781
$\text{Cu}(\text{PirC}_8)_2$	2,0273	2,0647	2,1792
$\text{Cu}(\text{PirC}_{12})_2$	-----	2,0467	2,1459

Compound	g_{\parallel}	g_{\perp}	A_{\parallel}	A_{\perp}
$\text{VO}(\text{Pir-C}_6)_2$	1,8494	1,8220	223,68	78,95
$\text{VO}(\text{Pir-C}_{12})_2$	1,9677	1,8254	211,84	78,94

Compound	g	A_T
$\text{VO}(\text{Pir-C}_8)_2$	1,9930	39,13

Electronic spectra

The brown colour of the $\text{Cu}(\text{PirC}_{12})_2$ complex points out that the charge transfer transition M-L in 400 nm region is dominant, while absorption in 600-700 nm domain specific for d-d transition is rather diminished. The absence of an absorption band after 750 nm rules out a tetrahedral geometry.

Far from this behaviour, electronic spectra of $\text{Cu}(\text{PirC}_8)_2$ complex have a prominent band at 640 nm and the greenish colour as well as shape of EPR spectra indicate a rhombic distortion; for instance, a distorted pyramid.

This rhombic distortion is enhanced in $\text{Cu}(\text{PirC}_8)_2$ complex, which having the smallest ligand, allow for one or two water molecules to be accommodated into a distorted pyramidal or octahedral surroundings.

Structure of complexes

The pyrazolone ligands are two donor atoms for coordinating to the metal, the sulphur and the oxygen. Supposing that two oxygen and two sulphur atoms of the ligand are coordinated to the metal, as seems likely from an inspection of molecular model, it follows that the complexes would be four coordinate with respect to the bidentate ligand as shown in figure 4.

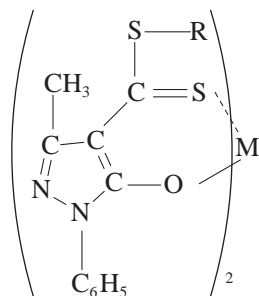


Figure 4. Suggested structure for the metal complexes ($M = \text{Cu(II)}$ and VO (II))

ACKNOWLEDGEMENTS

The authors express their sincere thanks to Dirección General de Investigación of the Universidad de Playa Ancha for financial support, as well as to Applied Spectroscopy Laboratory. Faculty of Industrial Chemistry. Politechnical University of Bucharest for carrying out the EPR measurements.

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