

Abstract

Four Schiff-bases were prepared, two of them derived from acetylacetone and trifluoroacetylacetone with ethylenediamine, (AA.EN) and (TFAA.EN) respectively, while the others derived from salicylaldehyde with ethylenediamine and ortho-phenylenediamine, (SAL.EN) and (SAL.PN) respectively.

Some metal complexes of copper (II) and vanadium (IV) were prepared from Schiff-bases above, namely, Cu(AA.EN), Cu(TFAA.EN), Cu(SAL.EN), Cu(SAL.PN), VO(SA.EN) and VO(SAL.PN).

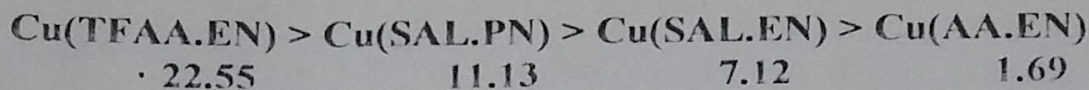
The prepared compounds were identified by ultraviolet and visible spectra, infrared spectra and melting points. The ultraviolet spectra of AA.EN and TFAA.EN were showed double bands between 300-335 nm, which attributed to $\pi \rightarrow \pi^*$ transitions. SAL.EN and SAL.PN were showed bands at 223, 259 and 320 nm for the first compound, 220, 260 and 327 nm and shoulder at 370 nm for the second, attributed to $\pi \rightarrow \pi^*$ transitions. Metal complexes Cu(AA.EN) and Cu(TFAA.EN) were showed two bands at 251 and 308 nm for the first complex, two bands at 239 and 302 nm for the second. While, Cu(SAL.EN) and Cu(SAL.PN) were showed some bands at 240, 275 and 358 nm for the first complex, 241, 307 and 417 nm with shoulders for the second. VO(SAL.EN) and VO(SAL.PN) were showed bands at 241, 284 and 362 nm for the first complex, 243, 317 and 400 nm with shoulder for the second. All metal complexes above were displayed weak absorption bands ($\epsilon < 100$) between 540-600 nm which attributed to d-d transitions. The infrared spectra of the prepared compounds were characterized by strong absorption bands between 1580-1638 cm^{-1} which attributed to azomethane stretching band.

Lewis acid-base interactions have been studied for the prepared metal complexes as acceptors with nitrogen, oxygen and sulfur donors in benzene. Molar ratios of donor-metal complex interactions have been calculated, and all reactions have been showed 1:1 interactions. Equilibrium constants of these interactions have been determined, these values less than 150 l.mole^{-1} .

Thermodynamic functions ΔH , ΔG and ΔS were determined, heat of reaction values were between - 8.62 to -22.30 kJ.mole^{-1} , free energy values were between +0.92 to - 11.63 kJ.mole^{-1} , while, entropy values were between - 25.65 to - 42.47 $\text{J.mole}^{-1}\text{K}^{-1}$.

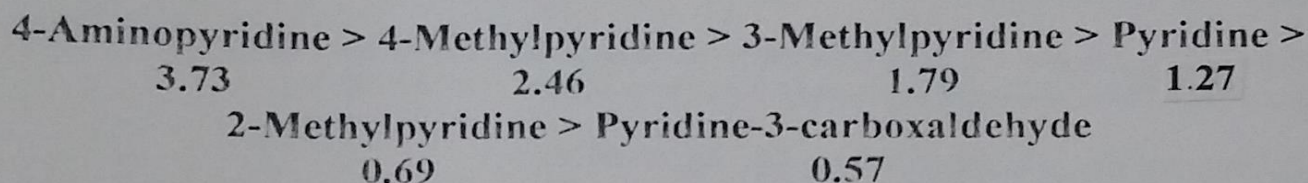
Metal ion effect on Lewis acid-base interactions have been studied, and showed that equilibrium constants of vanadium complexes interactions (71.90 l.mole^{-1} at 30°C) were greater than copper complexes interactions (7.12 l.mole^{-1} at 30°C) with the same electron donor. This may be attributed to strong interaction of vanadium complexes with the donor as a result of the greater positive charge on vanadium ion in comparison with copper ion.

Ligand effect of copper complexes on Lewis acid-base interactions with the same electron donor have been studied, and showed that the equilibrium constants increase in direction:



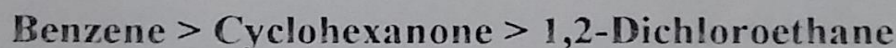
The difference in the values of the equilibrium constants were attributed to the difference of the electron density on the metal ion as a sequence of the donating or withdrawing effects of the ligand. For it is found that the strongest interaction with the same donor being with the complex that constitutes on electron withdrawing ligand (TFAA.EN) as compared with an electron donating ligand (AA.EN).

The donating and withdrawing effects of substituted groups of pyridine on the interaction with Cu(SAL.EN) acceptor have been studied, and it was showed that the equilibrium constants values of these interactions increase as following:



This situation was interpreted as a result of different electron donating strength of these donors, which affect by substitution position and steric effects.

Solvent effect on interaction of Cu(SAL.EN) with n-propylamine showed that the equilibrium constants are increasing in the direction:



Benzene was preferable for this study, because it has the least effect on Lewis acid-base interaction comparison with the other solvents.

Further more, reaction constants ρ of interactions of pyridine substituted in 3 or 4 positions and copper (II) or vanadium (IV) complexes of Schiff-bases SAL.EN and SAL.PN, have been determined. It was found that the reaction constants values of copper complexes ($\rho=+0.824$ and $+0.859$) are greater than reaction constants values of vanadium complexes ($\rho=+0.405$ and $+0.344$). This indicates that the copper ion is more sensitive to the electron density of the donors than the vanadium ion. The positive values of reaction constants indicate that this reaction is preferable when the electron density on the metal ion is smaller.