

Formation of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) Complexes with Benzoylacetanilides. TGA, Spectral, Conductance and Potentiometric Studies

S.M. ABU-EL-WAFA^{1*}, M. GABER², A.A. SALEH¹ AND A.A. EL-DKEN³
Chemistry Department¹, Faculty of Education, Ain Shams University, Roxy, Cairo, ²Faculty of Science, Tanta University, Tanta, ³Faculty of Science, Al-Azhar University, Nasr City, Cairo, Egypt.

(Received 18th August, 1988, revised 12th March, 1989)

Summary: The types of new Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes derived from benzoylacetanilide ligands have been prepared and characterized by elemental analysis and conductance measurements. TGA, IR and ¹HNMR spectra indicated that the bonding between the ligands and bivalent metal ions takes place through H⁺ ion displacement from the enolic OH group and co-ordinated NH group. Electronic and EPR spectra indicated octahedral geometry around the (Mn²⁺, or Ni²⁺ ions), distorted octahedral for (Co²⁺ or Cu²⁺ ions) and tetrahedral arrangement around Zn²⁺ ion. The values of the conditional stability constants calculated by potentiometric technique are found to depend on molecular structure. Deviation of the slopes of the σ* vs log K₁ plots from unity is attributed mainly to steric effect, π- electron back donation from the metal ion or structural changes in the ligand.

Introduction

The specific and selective reaction of organic reagents towards metal ions depends mainly on the presence and position of certain functional groups [1-3] capable of forming co-ordinate bonds with the metal ions. In view of this fact it seemed of interest to test the behaviour of benzoylacetanilide towards Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) ions, in which case, each anilide ligand contains different characteristic functional groups liable to form coordinate bonds with transition metal ions [4,5].

As a matter of fact, the transition metal complexes of anilide ligands have applications as catalysts in various chemical and photochemical reactions [6-8] as well as in biological systems [9]. The application of such metal chelates in a given system was found to depend to a large extent on its molecular structure [10].

The aim of the present work, is to prepare Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes with some benzoylacetanilide ligands. The prepared complexes are subjected to elemental analysis, TGA and some spectroscopic techniques viz IR, ¹HNMR, electronic, EPR spectra and conductance measurements. The composition, nature and stability of the complexes formed are also investigated by conductometric and potentiometric techniques.

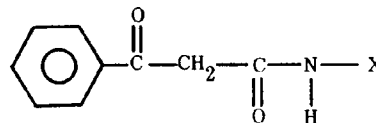
Experimental

i- Preparation of ligands:

A mixture of ethyl benzoylacetate ester (0.01 mole) and (0.01 mole) of the corresponding aniline or its derivatives were mixed in molten sodium acetate at 120°C for 1/2 hour. The mixture was poured in H₂O and the precipitate was recrystallized from H₂O/ethanol (50%); the product obtained was filtered off, washed with cold water/ethanol several times, finally with ether and then dried *in vacuo*.

The structure of the ligands was confirmed by elemental analysis, IR and ¹HNMR spectra.

The ligands used in the present investigation have the following formula:



where X = ph (L_I), py (L_{II}) and o-OCH₃ ph (L_{III}).

ii- Preparation of complexes:

A solution of the metal salt (0.01M) in bidistilled water was added to a solution of the ligand

*To whom all correspondence should be addressed.

Table-1. Analytical and EPR Data for Metal(II) - Anilide Complexes.

Complex	Colour	Results of Microanalysis					log K ₁	log K ₂	g _{eff} ^b
		% Ca	% H ^a	% N ^a	% M ^a				
[Mn(L _I) ₂ (H ₂ O) ₂]	yellow-brown	63.00 (63.44)	4.50(4.94)	4.60(4.94)	9.20(9.70)	5.26	4.92	2.0011	
[Mn(L _{II}) ₂ (H ₂ O) ₂]	""	58.90(59.05)	4.40(4.57)	9.60 (9.84)	9.30(9.67)	5.59	4.30	1.9982	
[Mn(L _{III}) ₂ (H ₂ O) ₂]	""	60.70(61.05)	5.30(5.41)	4.30(4.45)	8.30(8.74)	4.46	4.29	-	
[Co(L _I) ₂ (H ₂ O) ₂]	pink	62.70(63.05)	4.60(4.90)	4.70(4.90)	9.70(10.33)	5.23	5.07	2.0023	
[Co(L _{II}) ₂ (H ₂ O) ₂]	""	58.30(58.64)	4.10(4.53)	.60(9.77)	9.90(10.29)	4.59	4.33	-	
[Co(L _{III}) ₂ (H ₂ O) ₂]	""	60.40(60.66)	5.20(5.37)	4.10(4.42)	9.00(9.32)	4.26	4.17	-	
[Ni(L _I) ₂ (H ₂ O) ₂]	blue	62.80 (63.16)	4.50(4.91)	4.60(4.91)	9.80(10.18)	5.33	5.07	-	
[Ni(L _{II}) ₂ (H ₂ O) ₂]	""	58.60(58.74)	4.10 (4.55)	9.40(9.79)	9.70 (10.14)	4.96	4.83	-	
[Ni(L _{III}) ₂ (H ₂ O) ₂]	""	60.30(60.76)	5.10(5.38)	4.20(4.43)	8.90(9.18)	4.59	4.33	-	
[Cu(L _I) ₂].2H ₂ O	green	62.30(62.55)	4.50(4.86)	4.50(4.86)	10.80(11.03)	6.30	6.23	2.0462	
[Cu(L _{II}) ₂ (H ₂ O) ₂]	""	57.90(58.18)	4.30(4.50)	9.50(9.69)	10.30(10.99)	5.79	5.53	2.0352	
[Cu(L _{III}) ₂].2H ₂ O	""	61.70(61.99)	4.90(5.16)	4.40(4.52)	9.80(10.25)	5.10	4.86	2.0327	
[Zn(L _I) ₂].H ₂ O	yellow-brown	64.10 (64.40)	4.30(4.65)	4.70(5.01)	11.20(11.63)	5.17	5.10	-	
[Zn(L _{II}) ₂].2H ₂ O	""	57.70(58.03)	4.20 (4.49)	9.30(9.67)	10.70(11.23)	4.89	4.69	-	
[Zn(L _{III}) ₂].H ₂ O	""	61.30(61.84)	4.80(5.15)	4.30(4.15)	9.90(10.47)	4.96	4.86	-	

a % Found (% Calculated); b EPR g_{eff} value at 298K.

(0.002M) in the least amount of pure ethanol. The mixture was stirred for one hour during which the solid complexes were separated and then filtered off, washed several times with bidistilled water to remove any traces of metal ions finally washed by diethylether and then dried *in vacuo*.

iii- Physical Measurements:

The IR spectra were recorded on a Perkin-Elmer 598 infrared spectrophotometer and the ^1H NMR spectra were obtained with the aid of a Perkin-Elmer R 34,220 MHz spectrometer. Visible spectra were recorded on a Cary 14 spectrophotometer. TGA curves were obtained in nitrogen atmosphere at a rate of $10\text{C}^\circ/\text{min}^{-1}$ using Du Pont apparatus. EPR spectra were recorded on a Varian E-9 x-band spectrometer equipped with an E 101 microwave. The magnetic field was calibrated using DPPH as standard. Other apparatus and physical measurements as those described previously [11].

Results and Discussion

A- Complexes in the Solid State:

All the prepared complexes were subjected to elemental microanalysis are listed in Table (1). From these results it is found that the composition of the solid complexes, produced from the ligands (L_I , L_{II} and L_{III}) with the metal ions Cu(II) , Co(II) , Ni(II) , Mn(II) and Zn(II) have the 1:2 (metal ion: ligand) ratios. The result also indicates that complex formation takes place through proton displacement from the ligands and the ligands would behave as monobasic bidentate towards bivalent metal ions.

Thermogravimetric analysis (TGA), Table (2) of some solid complexes indicated the following:-

- i- Lattice water molecules associated with complex formation are removed within the $45\text{--}120\text{C}^\circ$ range, whereas co-ordinated water molecules are only volatilized between $130\text{--}160\text{C}^\circ$.
- ii- The anhydrous or nonsolvated complexes show thermal stability up to $210\text{--}445\text{C}^\circ$.
- iii- $\text{Zn (L}_{III})_2 \cdot \text{H}_2\text{O}$ complex has higher thermal stability than the other complexes under in-

vestigation. The order of stability is $\text{L}_{III} > \text{L}_I > \text{L}_{II}$, this means that the substitution of pyridyl group instead of phenyl group increases the volatility of complexes whereas the substitution of OCH_3 group to the phenyl group decreases the volatility of Zn^{2+} complexes.

- iv- The decomposition of complexes to the metal oxides starts at $450\text{--}625\text{C}^\circ$ depending on the metal (II) ion used.

On examining the IR spectra of the (1:2) M:L complexes, Table (3), in comparison to those of the free ligands the following can be pointed out:

- a- The spectra of most complexes exhibit a broad band around $3640\text{--}3400\text{cm}^{-1}$ which could be assigned to ν_{OH} of water molecules associated with complex formation. The presence of water molecules in the metal complexes is also supported from TGA measurements.
- b- In the spectra of all metal chelates, the NH band is shifted to lower frequency by $100\text{--}300\text{cm}^{-1}$ ($3360\text{--}3280\text{cm}^{-1}$) whereas the band located at $1710\text{--}1680\text{cm}^{-1}$ due to ν_{CO} , in the spectra of the free ligands, still lies at the same position.
- c- The participation of enolic OH group in chelate formation through proton displacement is gathered from the disappearance of ν_{OH} and $\nu_{\text{C-OH}}$ present in the spectra of the free ligands at $1510\text{--}1520$ and $1130\text{--}1140\text{cm}^{-1}$ respectively, for all 1:2 (M:L) complexes.
- d- The new bands observed at $445\text{--}490$ and $380\text{--}360\text{cm}^{-1}$ for all 1:2 (M:L) complexes, not observed in the spectra of free ligands and similar to the bands observed previously [12,13] on O-M and N-M coordination respectively, could be assigned to $\nu_{\text{M-O}}$ and $\nu_{\text{M-N}}$.

On comparing the ^1H NMR spectra of Zn(II) complexes with those of free ligands in DMSO (d^6) using TMS as internal standard, Table (4), the following can be pointed out:

- i- The enolic OH signals, observed at $6.2\text{--}6.5$ ppm in the spectra of all benzoylacetonilide

- ligands, disappeared on complex formation, confirming that the bonding of metal (II) ion to the ligands takes place through a proton displacement from the enolic OH group. This idea is supported by disappearance of CH₂ signals from the spectra of the Zn(II) chelates, which appeared at 4.3- 4.4 ppm in the spectra of free ligands.
- ii- The signals due to the aromatic protons, NH and CH aliphatic groups which are observed within the 7.3-8.2, 8.2-8.5 and 3.6-4.4 ppm ranges respectively in the spectra of free ligands, show some shifts of varied magnitude on complex formation by 0.2-0.6, 0.2-0.4 and 0.3-5.0 ppm towards down field. The shift of the signals down field is due to the deshielding effect of the metal ion on the ligand as a result of its co- ordination with the lone pair of the nitrogen atom of the NH group.
- iii- The new signals observed in the spectra of Zn(II) complexes at 3.3-3.6 ppm, which is not present in the spectra of free ligands, can be assigned to H₂O molecules associated with complex formation.
- The data obtained from ¹H NMR of the benzoylacetanilide Zn(II) complexes are in accordance with the results obtained from IR spectra, thus supporting the mode of bonding between the metal ion and the benzoyl-acetanilide ligand.

Table II: TGA Data of some Metal (II) Benzoylanilides Complexes.

Complex	Temp. (C°)	% loss actual (Calc.)	Assignment
	thermal step		
[Mn(L _I) ₂ (H ₂ O) ₂]	130-145	3.00(3.15)	loss of coord. H ₂ O
	150-210	6.20(6.30)	loss of coord. H ₂ O
	215-295	48.00(48.33)	loss of L _I
	300-430		decomposition
	450-470	89.80(90.36)	formation of oxides
[Zn(L _I) ₂].H ₂ O	110-120	3.10(3.22)	loss of lattice H ₂ O
	120-425		thermal stability
	425-620	45.40(45.79)	loss of L _I
	520-600		decomposition
	600-625	88.00(88.37)	formation of ZnO
[Zn(L _{II}) ₂].2H ₂ O	45-120	6.10(6.19)	loss of lattice H ₂ O
	120-320		thermal stability
	320-345	47.10(47.50)	loss of L _{II}
[Zn(L _{III}) ₂].H ₂ O	445-625		decomposition
		89.00(88.88)	formation of ZnO
	80-120	3.00(2.91)	loss of lattice H ₂ O
	120-445		thermal stability
	445-470	46.70 (46.20)	loss of L _{III}
	470-625 d		decomposition
		88.80(89.49)	formation of ZnO

Table-III: IR and Electronic Spectral Data of Metal(II) - Benzoylacetonilide Complexes.

Complex	IR (cm ⁻¹)			UV, Visible			$\epsilon_{\max} \times 10^4$ ^b
	$\nu_{\text{OH}_{\text{water}}}$	$\nu_{\text{N-Ha}}$	$\nu_{\text{C=O}}$	$\nu_{\text{M-N}}$	$\nu_{\text{M-O}}$	λ_{\max} (nm)	
[Mn(L _I) ₂ (H ₂ O)]	3460 - 3580	3320	1700	370	485	263, 283, 325, 490	1.7, 1.55, 2.87, 0.10
[Mn(L _{II}) ₂ (H ₂ O) ₂]	3520 - 3460	3150	1680	380	445	255, 265, 290, 365, 510	0.68, 0.84, 0.76, 1.32, 0.09
[Mn(L _{III}) ₂ (H ₂ O) ₂]	3500 - 3400	3220	1710	360	490	235, 267, 280, 350, 460	0.50, 0.75, 0.80, 0.93, 0.11
[Co(L _I) ₂ (H ₂ O) ₂]	3520 - 3400	3260	1680	375	480	235, 265, 280, 365, 530	0.90, 1.5, 0.72, 0.50, 0.15
[Co(L _{II}) ₂ (H ₂ O) ₂]	3500 - 3400	3140	1690	380	460	260, 280, 285, 350, 550	0.80, 1.22, 0.62, 0.46, 0.18
[Co(L _{III}) ₂ (H ₂ O) ₂]	3620 - 3580	3230	1700	365	490	240, 260, 290, 340, 540	0.22, 0.32, 0.26, 0.22, 0.09
[Ni(L _I) ₂ (H ₂ O) ₂]	3560 - 3460	3320	1690	370	445	255, 265, 290, 340, 650	0.68, 1.11, 0.52, 0.23, 0.13
[Ni(L _{II}) ₂ (H ₂ O) ₂]	3450 - 3400	3150	1680	380	470	240, 267, 285, 355, 600	0.84, 0.68, 0.51, 0.36, 0.09
[Ni(L _{III}) ₂ (H ₂ O) ₂]	3500 - 3440	3230	1700	370	480	265, 280, 290, 600	2.0, 1.88, 1.76, 0.16
[Cu(L _I) ₂ .2H ₂ O]	3560 - 3400	3280	1680	380	490	255, 265, 290, 365, 590	2.1, 0.30, 0.86, 0.74, 0.33
[Cu(L _{II}) ₂ (H ₂ O) ₂]	3400 - 3500	3160	1690	360	470	245, 265, 290, 360, 750	0.98, 0.75, 0.65, 0.32, 0.25
[Cu(L _{III}) ₂ .2H ₂ O]	3500 - 3400	3310	1710	370	490	255, 267, 295, 325, 620	0.70, 1.03, 0.83, 0.34, 0.18
[Zn(L _I) ₂ .H ₂ O]	3450 - 3400	3300	1700	380	480	255, 263, 280, 310	0.46, 0.68, 0.46, 1.19
[Zn(L _{II}) ₂ .2H ₂ O]	3560 - 3450	3160	1710	370	490	265, 285, 320	0.13, 0.15, 0.14
[Zn(L _{III}) ₂ .H ₂ O]	3500 - 3400	3225	1690	380	460	260, 280, 315	1.50, 1.88, 1.05

The electronic absorption spectra of the complexes in DMF solution are studied in UV and visible regions, Table (3). The spectra in UV region exhibit four absorption bands with λ_{\max} situated at 235-260, 260-267, 280-290 and 285-365 nm. The first two bands can be assigned to the ($1L_a$ $1A$) and ($11b$ $1A$) $\pi-\pi^*$ transition within the benzene ring respectively, whereas the last two bands can be assigned to $\pi-\pi^*$ transition of CO group and charge transfer band respectively. The electronic spectra in the visible region are characterized by a weak broad band located at λ_{\max} 460-510 nm for Mn(II) (${}^6A_{1g}$ ${}^4T_{1g}$ (G)), 530-550 nm for Co(II) (${}^4T_{1g}$ ${}^4A_{2g}$ (F)) 600-650nm for Ni(II) (${}^3A_{2g}$ 1E_g (D)) and 590-750 nm for Cu^{2+} (2E_g ${}^2T_{2g}$) transitions. The spectral patterns are relevant to octahedral geometry for

Mn(II) and Ni(II) ions, distorted octahedral for Co^{2+} and Cu^{2+} ions due to Jahn-Teller effect [14,15] and a tetrahedral arrangement of the ligands around the central Zn(II) ion.

x-band EPR spectra of Cu(II), Co(II) or Mn(II) complexes at room temperature Fig (1), show generally three or two strong signals for Cu(II) complexes, a sharp signal (for Co(II) complexes) or an isotropic signal consisting of a pattern of six doublets, for Mn(II) complexes. The shape of the line observed and the pattern of the g_{eff} values, Table (1), may indicate the pattern of the geometry around Mn(II) ion [16], distorted octahedral for Co(II) ion [17] and a tetragonally distorted geometry around Cu(II) ion (octahedral elongation

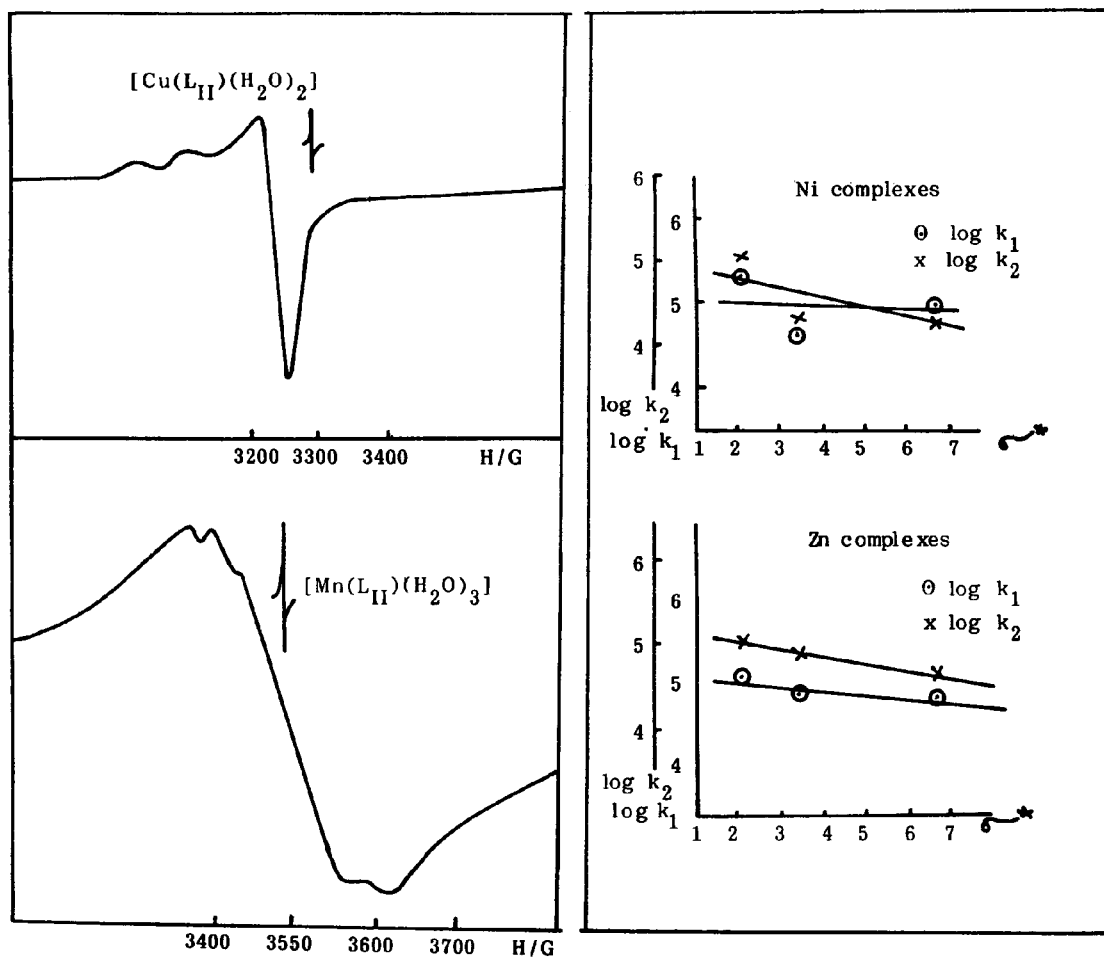


Fig.1: X-band EPR spectra of Cu(II) and Mn(II) complexes at room temperature.

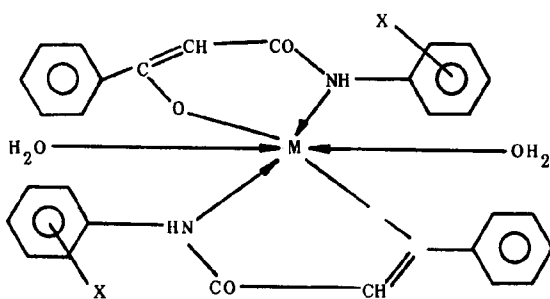
Fig.2: Effect of stability constants of metal(II) anilide complexes on molecular structure.

Table-IV: $^1\text{H-NMR}$ spectral data for Zn(II)-Benzoyl acetanilides complexes

Compound	OH	CH ₂	NH	CH _{arom.}	CH arom. ali Ph.	H ₂ O
L _I	6.20	4.30	8.50	7.3-7.6	3.60	-
L _{II}	6.50	4.40	8.20	7.4-8.20	4.40	-
L _{III}	6.30	4.35	8.40	7.6-8.10	3.90	-
[Zn(L _I) ₂].H ₂ O	-	-	8.20	7.10-7.40	3.30	3.30
[Zn(L _{II}) ₂].2H ₂ O	-	-	8.10	7.00-7.60	3.90	3.40
[n(L _{III})].H ₂ O	-	-	8.00	7.10-7.9	3.40	3.60

leading to square planar constitution in the extreme state). Axial ligands are bonded at a large distance [18].

Based on the above results gained from TGA, IR, NMR, electronic and EPR spectra, the bonding between bivalent metal ion and benzoylacetanilide ligands can be represented as follows:-



where
 $M = \text{Mn}^{2+}, \text{Co}^{2+}, \text{Ni}^{2+} \text{ or } \text{Cu}^{2+}$
 Cu^{2+} (square planar, H_2O molecules are absent)
 Zn^{2+} (tetrahedral).

(B) Complexes in solution:

i) Conductometric titrations:

Conductometric titrations can be applied for testing complex formation in solution by titrating a known volume of the metal ion in solution having a definite concentration with the chelating agent.

The results obtained indicate that the H^+ ions are displaced from the ligand on complex formation so that complex formation should take place through a covalent bond between the metal ion and the ligand groups.

ii) Potentiometric Method:

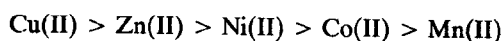
The pH titration curves of the Mn(II), Co(II), Ni(II), Cu(II) or Zn(II) chelates under investigation are S-shaped, the volume of alkali consumed in the titration corresponds to the liberation of one H^+ ion per metal ion on complex formation. The titration curves of Mn(II), Co(II), Ni(II), Cu(II) or Zn(II) chelates exhibit some inflections within the 8.5-10.5 pH range which can be ascribed to formation of complexes, of hydroxo type [19,20].

The formation curves obtained, for the different complexes investigated are expanded over the range 0.5 and 0.3 \bar{n} showing distinct breaks indicating the stoichiometric ratios 1:1 and 1:2 (M:L).

The conditional stability constant of the two types of chelates $\log K_1$ and $\log K_2$ were then determined by the method of Bjerrum [21] and Albert [21] applying the least square method and the graphical representation method (\bar{n} vs pL). The data obtained, Table (1), indicate that the values of the conditional stability constant depend on both the nature of the ligand as well as the metal ion. Generally, the $\log K$ values for the complexes increase as the donor property of the substituent (X)

increases. The plot of $\log K_1$ or $\log K_2$ for the same metal ion as a function of the σ^* (Taft-constant) is a linear relation, Fig(2). The negative values of the slope indicate that metal complexation is favoured by high electron densities at the co-ordination sites, a factor which favours increased co-valent nature of the metal-ligand bond. Deviation from a slope of unity is attributed mainly to steric effect, π -electron back donation from the metal ion, or structural changes in ligand which alter the strength of the donor atom within the ligands [22].

For the same ligand, the stability of the chelates increase in the order.



This runs parallel to the decreased tendency of the metal ions for hydrolysis in solution as a result of the decreased e/r ratio.

References

1. S. Dill and E. Patsalides, *Aust. J. Chem.*, **34**, 1579 (1981).
2. R.P. Scaringe and D.J. Hodgson, *Inorg. Chem.*, **15**, 1193 (1976).
3. L.F. Lindoy, W.E. Moody and D. Taylori, *Inorg. Chem.*, **16**, 1962 (1977).
4. A-El-Toukhy, A.F.M. Hafny, L. El-Sayed and M.F. Iskender, *Monatshefte fuer Chemie*, **113**, 171 (1982).
5. J.R. Dilwoith, *Coord. Chem. Rev.*, **21**, 29 (1976).
6. M.D. Cohen and S. Flavian, *J. Chem. Soc. (B)* 317 (1967).
7. L. Sacconi, *J. Am. Chem. Soc.*, **74**, 4503 (1972).
8. A. Syamal, S. Ahmed and M.A. Bariniazi, *J. Ind. Chem. Soc.*, **60**, 493 (1983).
9. T. Takeuchi, *J. Antibot (Tokyo)* **10**, 1818 (1957).
10. M. Inoue and M. Kubo, *Coord. Chem. Rev.*, **21**, 1 (1976).
11. S.M. Abu-El-Wafa, F.M. El-Wafa, F.M. El-Zawawi and R.M. Issa, *Bull. Soc. Chim. Belg.*, **92**, 77 (1983).
12. K. Nakamoto "Infrared Spectra of Inorganic and Coordination Compounds" John Willy, N.Y. (1977).
13. S.M. Abu-El-Wafa, R.M. Issa and C.A. McAuliffe, *Inorg. Chim. Acta.*, **99**, 103 (1985).
14. A. Saavedra and D. Reinen, *Z. Anorg. Allg. Chem.*, **435**, 91 (1977).
15. M.A. El-Ries, S.M. Abu-El-Wafa, F.A. Aly and M.A. El- Behairy, *Analy. Lett.*, **18**, 1905 (1985).
16. C.A. McAuliffe, R.V. Paris, S.M. Abu-El-Wafa and R.M. Issa, *Inorg. Chim. Acta.*, **115**, 91 (1986).
17. S.M. Abu-El-Wafa, M.A. El-Ries and F.H. Ahmed, *Inorg. Chim. Acta.*, **136**, 127 (1987).
18. H. Yokoi and T. Isote, *Bull. Chem. Soc. Jap.* **42**, 7187 (1969), **41**, 2835 (1968).
19. A.L. Ansary, S.M. Abu-El-Wafa, and Y.M. Issa, *Indian J. Chem.*, **24A**, 803 (1985).
20. Bjerrum "Metal Amine Formation in Aqueous Solution" P. Haas & Son, Copenhagen (1941).
21. A. Albert, *Biochem. J.* **47**, 531 (1950), **54**, 646 (1953).
22. Irving and Rossotti, *Acta. Chem. Scand.*, **10**, 72 (1956).