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Factors Governing The Stability Of Some Metal-Thiol Complexes

by

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Factors Governing The Stability Of Some Metal-Thiol Complexes

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It is quite important for exploring the nature of the chemical bonding and for predicting unknown stability constants to find relationships between the stability constants of the complexes and the characteristic properties of their constituents. The present work is devoted for investigating the relationships of the stability of Ni (II), Pd (II), Pd (IV), Pt (II) and Pt (IV) complexes with thiophenol and p-toluenethiol and the values of ionic radii, ionization potentials and electronegativities of the central ions. The stability of the coordinate compounds of the two similar ligands with the concerned metal ions are also compared.

The stability constants of Ni (II), Pd (II), Pd (IV), Pt (II) and Pt (IV) complexes with thipohenol (A) and p-toluenethiol (B) were determined in previous works[1]. Some of the results are given in tables (1.&2).

Stability of Complexes and the Properties of the Central Ions.

The ionic radii, ionization potentials and electronegativities of nickel, palladium and platinum are shown in table (1) together with log B_1 and log B_2 values of their complexes with thiophenol (A) and p-toluenethiol (B). It is apparent that the stability constants are not inversely proportional to the ionic radii of these cations. Therefore it may be disclosed that the interaction between the above metal cations and thiols (A) and (B) is not purely electrostatic.

Table 1. Characteristic properties of nickel, palladium and platinum ions and log B_1 and log B_2 values of their complexes with thiophenol (A) and p-toluenethiol (B).

Characteristic property	Nickel	Palladium	Platinum
Ionic radii (A)			
M (II)	0.69	0.80	0.80
M (IV)	—	0.65	0.65
Ionisation potentials			
M^{2+}	18.17	19.43	18.56
Electronegativity	1.91	2.20	2.28
log B_1			
M (II) -A	5.07	5.53	5.23
M (II) -B	3.88	5.34 (at pH 11)	4.28
log B_2			
M (II) -B	9.70	10.52	9.97
M (II) -B	7.25	9.68 (at pH 11.0)	8.24

The ionisation potential can be regared as a direct measure of the electron affinity of metal ion, which contributes to the stability of the metal complex. Although this comparison is only a rough approximation owing to the change in the electronic configuration during complex formation, fairly good relationships between ionisation potentials and stability constants have been reported[2]. The values of log B_1 and log B_2 of Ni (II), Pd (II) and Pt (II) complexes with thiols (A) and (B) are plotted against the ionisatios potentials of the metal ions (Fig. 1). It is obvious that the stability constants of the metal-thiol complexes increases linearly with the increase of ionisation potential.

In a series of increasing electronegativities of the metals, the electronegativity difference between a metal atom and the donor atom of the ligand would expectedly decrease, associated with the increase of covalent character of the metal-ligand bond. This may eventually result into greater stability of the metal chelates. Relationships between the electronegativities of the metal ions and stability constants of the complexes have been established by many authers[3]. In Fig. (2) are given plots of stability constants of Ni (II), Pd (II) and Pt (II) complexes with thiols (A) and (B) against the electronegativities of the metal ions. It is obvious that the stability constants of Pd (II) and also Pt (II) complexes are greater than the corresponding stability constants of Ni (II) complexes, which may be correlated with different electronegativities of the corresponding metal ions. This also suggests significant covalent nature of the metal-ligand bond in these complexes.

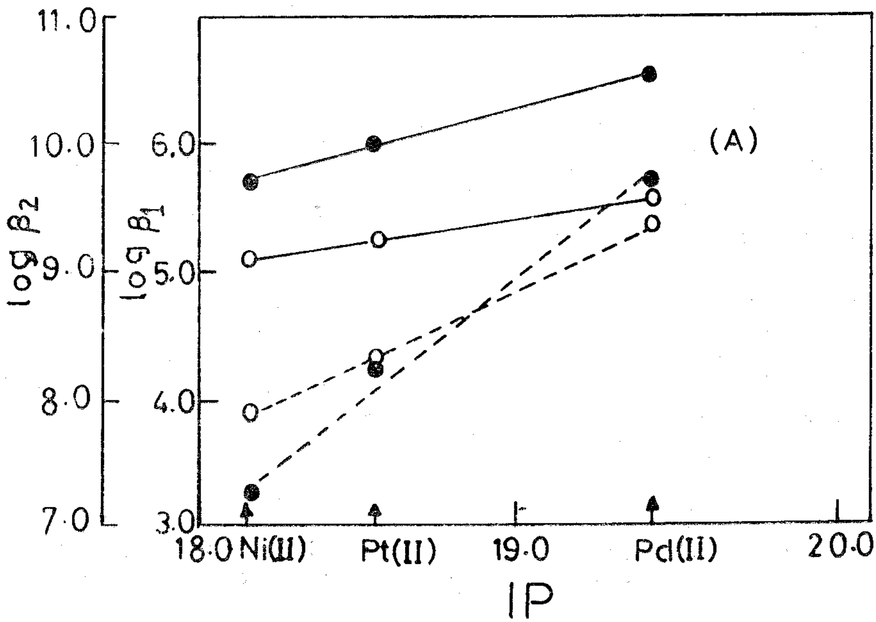

Fig. 1: Stability constants of Ni (II), Pd (II) and Pt (II) complexes with thiophenol (A), — and p-toluenethiol (B), - - - as a function of the ionisation potential (IP) of the central ion (o log B_1 values ● log B_2 values).

The complex-forming abilities of transition metal ions are frequently characterised by stability orders. The stability order established by Irving and Williams [4,5] is valid for most nitrogen and oxygen donor ligands, irrespective of the nature of the ligand. According to the crystal field theory, the general validity of the Irving-Williams order is a consequence of crystal field stabilization. The above considerations are valid for high spin complexes only[6]. It is already established[7] that thiols frequently form low spin complexes with Ni (II). Fig. 3 comprises plots of log B_1 and log B_2 values of thiol complexes of Ni (II), Pd (II) and Pt (II), against the atomic numbers of the metals. It is seen from the plots that the straight line relationship is not valid.

Comparison of Stability Constants of the Complexes of Two Similar Ligands With a Number of Metal Ions.

Irving and Rossotti[8] pointed out that the logarithms of the stability constants of complexes of a certain ligand with a number of metals

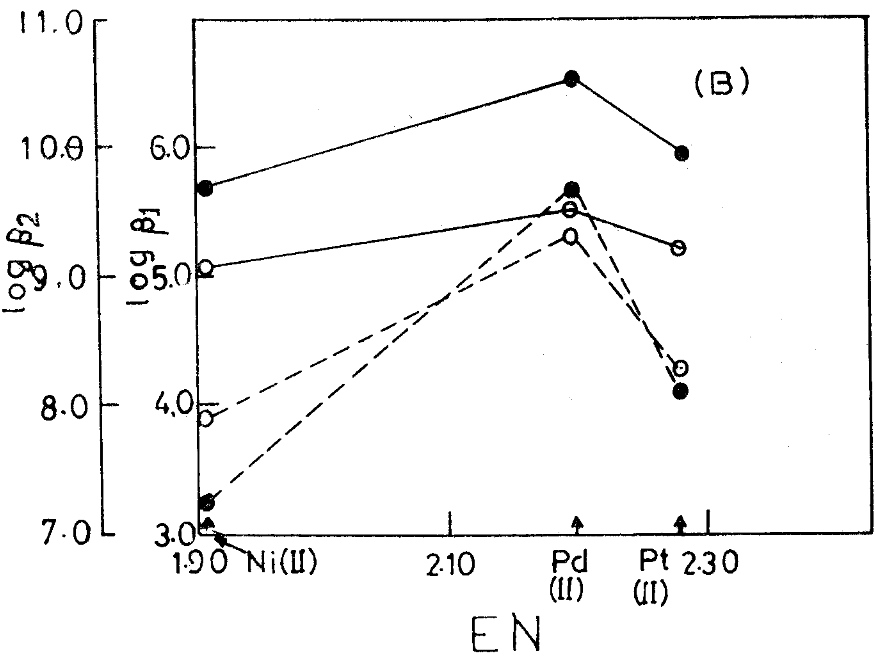

Fig. 2: Stability constants of Ni (II), Pd (II) and Pt (II) complexes with thiophenol (A), — and p- toluenethiol (B), - - as a function of electronegativity (EN) of the metal ion. (o log B_1 values ● log B_2 values).

plotted as function of log B_n of the corresponding metal complexes formed with another but anologus ligand gives a straight line. From table (2), it is apparent that the stabilities of M-thiophenol (A) complexes are consistently greater than those of the M-p-toluenethiol (B) complexes. A plot of log B_n of M-(A) complexes against the corresponding log B_n values of M-(B) complexes is shown in Fig (4). A good linear relationship is obtained for log B_1 values but for log B_2 values this relationship holds roughly.

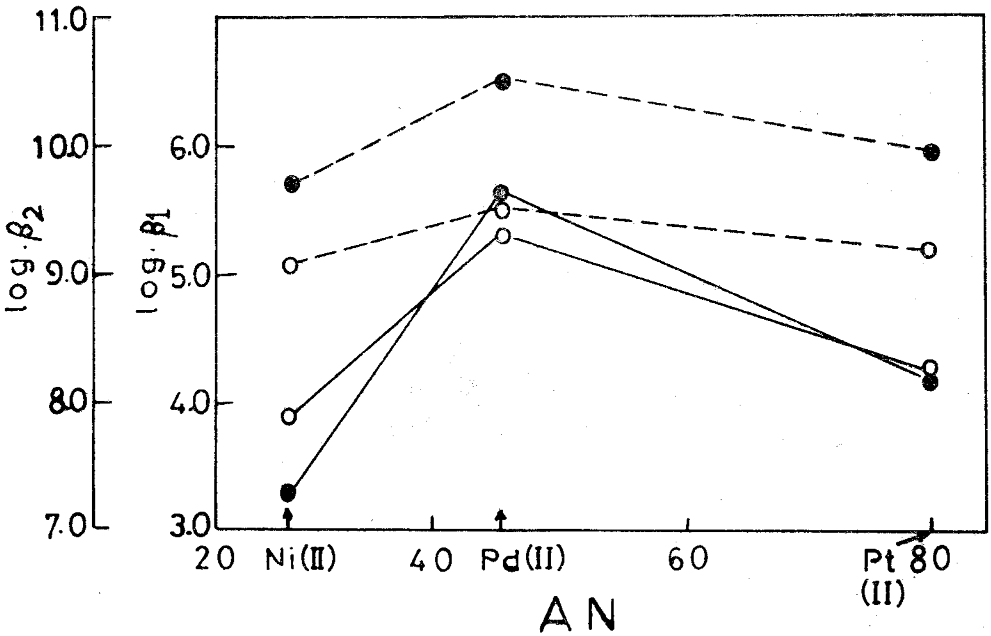

Fig. 3: Log B_n of Ni (II), Pd (II) and Pt (II) complexes with thiophenol, (A), — and p-toluenetenethiol, (B), - - as a function of atomic number (AN) of metals. (o log B_1 values ● log B_2 values).

Table 2. Log B_1 and log B_2 for Ni (II), Pd (II & IV) and Pt (II & IV) complexes with thiophenol (A) and p-toluenethiol (B).

Cation	Log B_1		Log B_2	
	Ligand A	Ligand B	Ligand A	Ligand B
Ni (II)	5.07	3.88	9.70	7.25
Pd (II)				
at pH 6.0	5.52	5.25	10.15	9.37
at pH 11.0	5.53	5.34	10.52	9.66
Pt (II)	5.23	4.28	9.97	8.24
Pd (IV)				
at pH 6.0	5.42	5.09	10.26	9.76
at pH 11.0	5.45	5.14	10.60	9.52
Pt (IV)	5.38	4.42	10.12	8.42

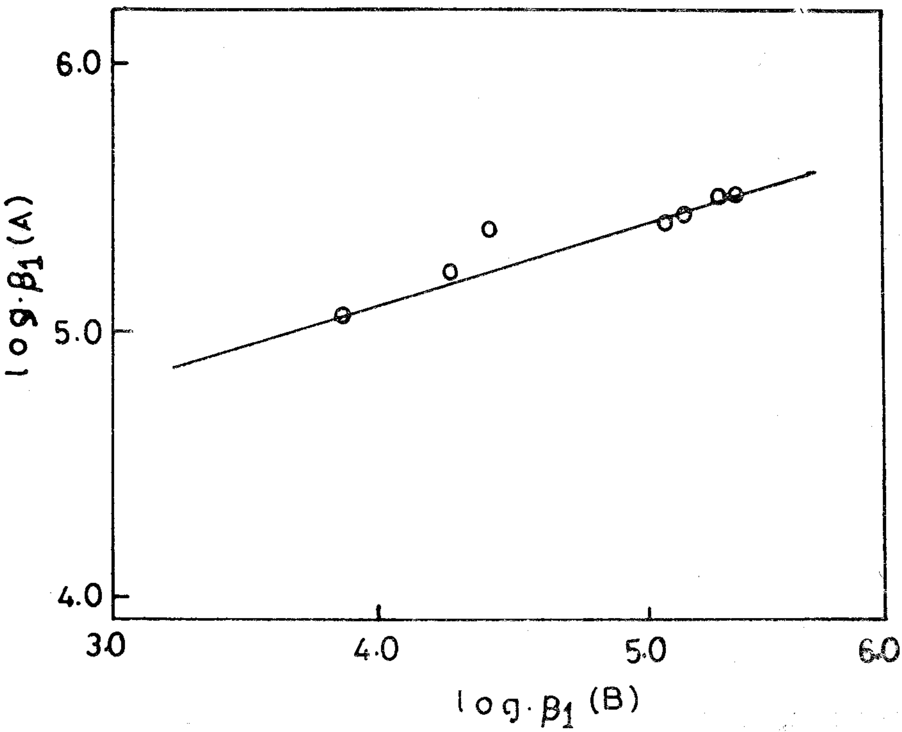

Fig. 4: Log B_1 of Ni (II), Pd (II & IV) and Pt (II & IV) complexes of thiophenol (A) as a function of the logarithms of the stability constants of the corresponding complexes of p-toluenethiol (B).

REFERENCES

1. a) **Khairy, E.M., Shoukry, A.F. and Ahmad,** J., Ind. J. Chem., 20, A, 421, 1981.
   b) **Ibid.,** Egypt. J. Chem., 25, No 6, 1982.
   c) **Ibid,** Microchem. J., 28, 180, 1983.
   d) **Ibid.,** Anales De Quimica, in press, B 64/83.
2. **Mellor, D.P. and Maley, L.E.,** Nature, 159, 370, 1947; 161, 436, 1948.
3. **Swinarski, A. and Iodzinska, A.,** Proc. 7th Intern. Conf. Coord. Chem., Stockholm, 320, 1962.
4. **Irving, H. and Williams, R.J.P., Nature,** 162, 746, 1948.
5. **Ibid.,** J. Chem. Soc., 3192, 1953.
6. **Beck, M.T.,** "Chemistry of Complex Equilibria", Akademiai Kaido, Budapest, 1970, p. 251.
7. **Livingstone, S.E.,** J. Chem. Soc., (a) 1042, 1956, (b) 437, 1956, (c) 1989, 1956.
8. **Irving, H.M. and Rossotti, H.S.,** Acta Chem. Scand., 10, 72, 1956.