

Metal chelates of salicyl-4-aminoantipyrine

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Abstract. The formation constants of salicyl-4-amino-2,3-dimethyl-1-phenyl-3-pyrazoline-5-one (SAAP) complexes with 3d transition metal ions [Cu(II), Ni(II), Co(II), Zn(II) and Mn(II)] have been determined in 60% ethanol-water medium of $\mu = 0.1\text{M}$ (NaCl) at 25°C. It is observed that the formation constants for chelates with 3d transition metals follow the order Mn(II) < Co(II) < Ni(II) < Zn(II) < Cu(II). The effects of metal ions, ionic radii, electronegativities and ionization potentials on chelate formation constants are discussed.

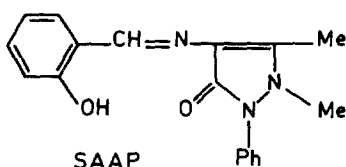
Complexes of UO₂(II) and Pd(II) have been synthesized and characterised by elemental analysis, electrolytic conductance, IR spectra and magnetic measurements. The ligand forms the complexes PdLCl and UO₂L₂·2H₂O, where L is a uninegatively charged tridentate ligand (ONO donor sets).

Keywords. Salicyl-4-aminoantipyrine; transition metal complexes; antipyrine derivatives; potentiometric studies; IR spectra.

1. Introduction

Diverse pharmaceutical activity is associated with antipyrine and its derivatives. Among these are antipyretic, analgesic and histaminic activities. A variety of antipyrine derivatives are now marketed for more than one medical purpose. However, little work has been done on the behaviour of these compounds towards transition metal ions which commonly exist in biological fluids. In continuation of our study of the metal complexes of biologically active ligands (Rabenstein *et al* 1982, 1985; Shoukry *et al* 1982, 1986, 1987; Shoukry 1985), we have synthesized an antipyrine derivative which was expected to have interesting biological activity. We now report measurements of the solution stabilities of copper(II), nickel(II), cobalt(II), zinc(II) and manganese(II) complexes of salicyl-4-amino-2, 3-dimethyl-1-phenyl-3-pyrazolin-5-one. The solid uranyl and palladium chelates have also been synthesized and characterized.

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2. Experimental

2.1 Materials

Solutions of Cu(II), Ni(II), Co(II), Zn(II) and Mn(II) were prepared from analytical grade copper chloride, nickel chloride, cobalt chloride, zinc sulphate and manganese chloride, respectively, in double distilled water. All solution concentrations were determined using standard procedures (Pribil 1982). Uranyl nitrate and potassium tetrachloropalladate were of analytical grade.

2.2 Preparation of the ligand and metal complexes

Salicyl-4-amino-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one was prepared by reacting 4-aminoantipyrine with salicylaldehyde according to the experimental conditions described by Radhakrishnan *et al* (1976). The complexes were prepared by mixing 0.5 m mol of metal salt and the ligand (0.5 m mol and 1 m mol for Pd(II) and UO(II) complexes, respectively) in ethanol. The pH was raised to ≈ 6 using dilute sodium hydroxide. The complexes were precipitated, filtered and washed thoroughly with ethanol–water (1:1) mixture and dried in vacuum.

2.3 Apparatus

A Schott 801 pH meter was used for pH measurements. The pH meter readings (B) recorded in ethanol–water solutions were converted to hydrogen ion concentrations $[H^+]$ by means of the relation (Van Uitert and Hass 1953):

$$-\log [H^+] = B + \log U_H$$

where $\log U_H$ is the correction factor for the solvent composition and ionic strength for which B is read. For this purpose, readings were taken for a series of solutions containing known amounts of HCl and NaCl such that μ was 0.1 M. The value of $\log U_H$ in 60% ethanol–water solutions and ionic strength 0.1 M at 25°C was found to be -0.25 .

Conductivity measurements were carried out with a WTW LBR B conductivity bridge at 25°C on 0.001 M solution in N,N-dimethylformamide (DMF).

IR spectra were recorded (KBr) with a Pye Unicam SP 1100 spectrophotometer. Magnetic susceptibility measurements were carried out using a Galileo–Sartorius air-damped analytical balance and the magnetic field was obtained by using an electromagnet.

2.4 Procedure

The following mixtures (A–C) were prepared for the determination of the acid dissociation constant of the ligand and formation constants of the metal complexes.

- (A) 5 ml of 0.0092 M HCl + 5 ml of 1 M NaCl.
(B) Mixture (A) + 20 ml of 0.005 M ligand solution.
(C) Mixture (B) + 5 ml of 0.004 M metal ion solution.

The final volume was made up to 50 ml in each case. The mixtures were in 60% ethanolic aqueous solution and the ionic strength was 0.1 M. Each mixture was separately titrated with a carbonate-free 0.048 M sodium hydroxide solution. Titrations were carried out in a special vessel described earlier (Shoukry *et al* 1986) at 25°C in a purified N₂ atmosphere. The ratio of the ligand to metal salt was maintained at 5:1 in all titrations in order to satisfy the maximum coordination possibility of the metal ions. The values of \bar{n}_A , \bar{n} and pL were calculated as previously reported (Shoukry 1984b).

The magnetic susceptibility of the solid complexes was measured using the Gouy powder technique (Earnshaw 1968).

3. Results and discussion

The formation, composition and stabilities of some chelates of bivalent metal ions (Cu(II), Ni(II), Co(II), Zn(II) and Mn(II)) with antipyrine derivatives have been investigated potentiometrically using the Bjerrum–Calvin titration technique (Calving and Wilson 1945) as modified by Irving and Rossotti (1953).

3.1 Proton-ligand stability constant

The protonation constant of the ligand was calculated from the potentiometric titration curves for hydrochloric acid in the presence and the absence of ligand. The formation curve for the proton–ligand system, depicted in figure 1, is extended

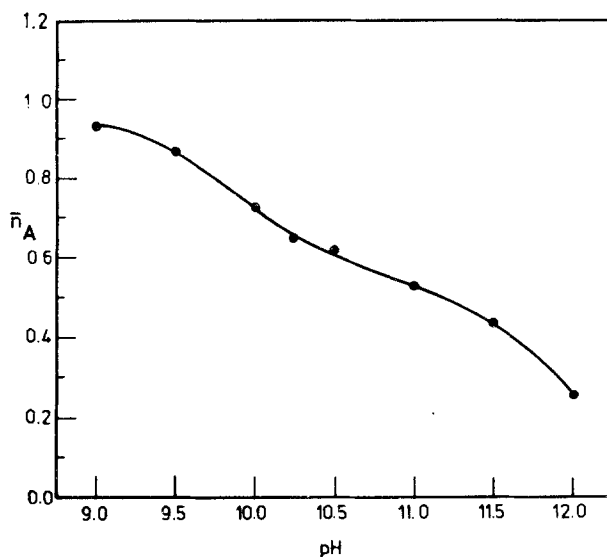


Figure 1. Formation curve for proton–ligand complexes of SAAP.

between 0 and 1 in the \bar{n}_A scale and $\log K_1^H$ was obtained directly from its formation curve. Also $\log K_1^H$ was calculated by the average value method (Nayan and Dey 1972). The value of $\log K_1^H$ is 10.95. This protonation constant is assumed to be for the hydroxyl group.

3.2 Metal-ligand system

Titration curves were carried out in the presence of both ligand and metal ion. A displacement was noticed in the metal titration curves with respect to the ligand titration curve indicating the release of hydrogen ion due to complex formation. The values of \bar{n} obtained were above 1.5 for all the metal ions. The oxidation of Co(II) to give a complex of the type CoL_3 by the release of three protons seems unlikely in view of the similar nature of all formation curves. Therefore, it may be concluded that the only pure complexes formed in solution are of the type ML^+ and ML_2 . The values of $\log K_1$ and $\log K_2$ for all the complexes were directly read from the formation curves (figure 2) and were also calculated by other methods

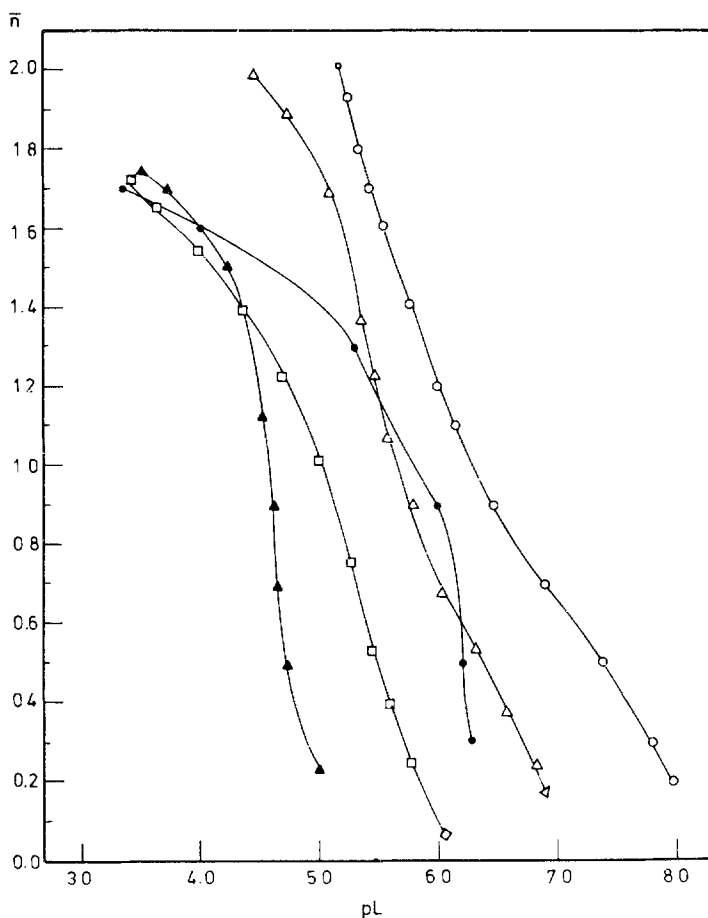


Figure 2. Formation curves for metal complexes of SAAP [○-Cu(II); △-Ni(II); ●-Zn(II); □-Co(II); ▲-Mn(II)].

Table 1. Formation constants of some bivalent metal ion chelates formed with the antipyrine derivative (Temperature = 25°C, $\mu = 0.1$ M NaCl).

Metal ion	Computational method	$\log K_1$	$\log K_2$	$\log \beta_2$
H ⁺	Half value	11.00	–	11.00
	Average value	10.90	–	10.90
	Mean	10.95	–	10.95
Cu(II)	Half value	7.40	5.66	13.06
	Successive approximation	7.26	5.72	12.98
	Correction term	7.29	5.73	13.02
	Mean	7.32	5.70	13.02
Ni(II)	Half value	6.30	5.26	11.56
	Successive approximation	6.18	5.37	11.55
	Correction term	6.21	5.37	11.58
	Mean	6.23	5.33	11.56
Co(II)	Half value	5.50	4.10	9.60
	Successive approximation	5.44	4.20	9.64
	Correction term	5.42	4.16	9.58
	Mean	5.45	4.15	9.60
Zn(II)	Half value	6.20	4.60	10.80
	Successive approximation	6.30	4.60	10.90
	Correction term	6.27	4.65	10.92
	Mean	6.26	4.62	10.88
Mn(II)	Half value	4.70	4.20	8.90
	Successive approximation	4.51	4.44	8.95
	Correction term	4.56	4.35	8.91
	Mean	4.59	4.33	8.92

(Beck 1970), viz. successive approximation and correction term methods. The values are given in table 1.

As the tendency of metal ions to take up ligands is proportional to the number of vacant sites, the ratio between consecutive constants is, to a certain extent, statistically determined (Bjerrum 1941). For an anionic ligand, the coulombic attraction is greater for M^{2+} than for ML^+ , and $(\log K_1 - \log K_2)$ is usually positive (Sillen and Martell 1971, 1974). Table 1 shows that for all systems studied here, $\log K_1 - \log K_2$ is positive and the values lie within the range 0.26 to 1.62 log K units.

Here, we shall discuss the relationship between the properties of metal ions and the stability constants of the complexes.

3.3 The electronic configuration of the metal ion

The complex-forming abilities of the transitional metal ions are frequently characterized by stability orders. It can be seen that the $\log K_1$ and $\log \beta_2$ ($\log K_1 K_2$) order $Cu > Zn > Ni > Co > Mn$, is in accordance with that reported by Irving and Williams (1953) for divalent metals of the 3d series.

3.4 The ionic radius

Assuming that the interaction of the metal ion and the ligand is electrostatic, the stability constants of metal ion complexes of the same charge should be inversely

proportional to metal ion radii. For ions of similar electronic configuration this relationship may be approximately valid. A linear relationship is obtained between $\log K_1$ values and reciprocal ionic radii (Cotton and Wilkinson 1967).

3.5 The electronegativity

With respect to the increasing electronegativities of the metals, the electronegativity difference between the metal atom and the donor atom of the ligand will decrease. Hence, the metal–ligand bond would have more covalent character which may result in greater stability of the metal chelate. A plot of $\log K_1$ values against electronegativities (Cotton and Wilkinson 1967) of the metal atoms gives a more or less straight line.

3.6 The ionization potential

A linear correlation has been obtained between $\log K_1$ and second ionization potentials (El Ezaby and El-Eziri 1976) of the bivalent metal ions studied as shown in figure 3. This confirms the validity of the Van Panthaleon–Van Eck equation

$$\log K_1 = P(I - q),$$

where I is the ionization for the reaction ($M \rightleftharpoons M^{m+} + me$) in the gaseous phase, and P and q are constants depending on the ligand and the experimental conditions but independent of the metal ion. P depends on the number of donor groups and the polarizability of the ligand, while q is a characteristic of the donor groups and m is the number of electrons involved.

It is observed from table 1 that the stability constant of the Cu(II) complex is considerably larger as compared to other metals of the 3d series. Under the influence of the ligand field Cu(II) ($3d^9$) receives some extra stabilization due to tetragonal distortion of the octahedral symmetry in its complex. Subject to the Jahn–Teller effect, the Cu(II) complex is further stabilized (Orgel 1966).

The analytical data given in table 2 show that the ligand forms a 1:1 complex with Pd(II) and a 1:2 complex with UO₂(II). The molar conductance values of these

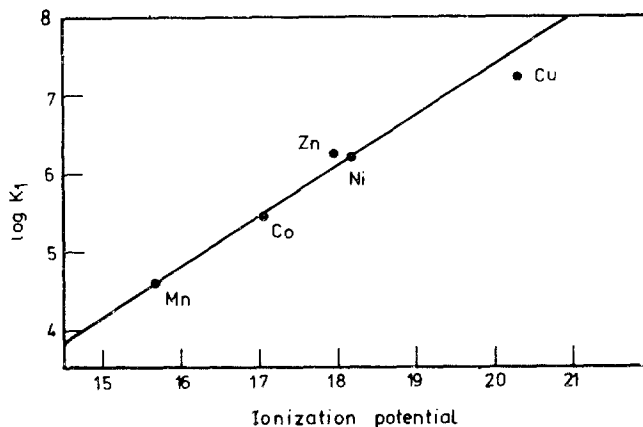


Figure 3. Correlation of $\log K_1$ of some bivalent metal ion complexes of SAAP with their ionization potentials.

Table 2. Analytical data for the ligand and its complexes.

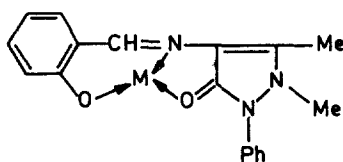
Compound	Colour	Yield (%)	Decomposition point (°C)	Elemental analysis* (%)					
				C	H	N	ν OH	ν C=O	ν C=N
SAAP (I)	White	85	204	70.4 (70.36)	5.8 (5.54)	13.7 (13.68)	3070	1655	1595
Pd(SAAP)Cl**	Brown	70	300	47.7 (48.23)	4.0 (3.57)	9.2 (9.38)	—	1600	1575
UO ₂ (SAAP) ₂ ·2H ₂ O	Yellow	80	300	46.8 (47.06)	4.1 (3.92)	8.9 (9.15)	3400	1605	1565

* Calculated values in parentheses; ** Cl % 8.2 (7.92).

metal chelates in N,N-dimethylformamide (DMF) were found to be quite low ($\Lambda_M = 5-8 \text{ ohm}^{-1} \text{ cm}^2$). This is in accordance with the non-electrolytic nature of the complex (Shoukry *et al* 1979). The magnetic investigations show that the Pd(II) and UO₂(II) complexes are diamagnetic as usual.

The IR spectrum of the ligand exhibits bands at 3070, 1655 and 1595 cm^{-1} . These bands are due to stretching of the hydroxyl, ring carbonyl and imido groups, respectively. The IR spectra of the Pd(II) and UO₂(II) complexes show the disappearance of the hydroxyl group indicating that the hydrogen ion of the OH group is replaced by the metal ion in the complex. The IR spectrum of the uranyl complex shows a broad and more intense band centred at 3400 cm^{-1} . This may be attributed to the stretching vibrations of the hydroxyl groups of water molecules masked in the complex sphere; the existence of these is confirmed by elemental analysis. The IR spectra of both complexes show shifting of the ring carbonyl and imido bands to lower wave numbers. This can be taken as evidence for participation of ring carbonyl oxygen and imido nitrogen in coordination to form stable five- and six-membered rings. The presence of the uranium-oxygen covalent bond in the complex was established. The uranium complex exhibits a very strong band at 930 cm^{-1} characteristic of asymmetric stretching of the uranyl ion in accordance with the earlier (Manchanda and Subramanian 1982; Shoukry 1984a) observation in many uranyl complexes (900–950 cm^{-1}).

The observations suggest that the ligand might be expected to be uninegatively charged tridentate by coordinating UO₂(II) and Pd(II) through the phenolic oxygen (O), imido nitrogen (N) and carbonyl oxygen (O) atoms as shown below:



References

- Beck M T 1970 *Chemistry of complex equilibria* (Budapest: Akademiai Kiado)
- Bjerrum J 1941 *Metal amine formation in aqueous solution* (Copenhagen: Hasse)
- Calving M and Wilson K W 1945 *J. Am. Chem. Soc.* **67** 2003
- Cotton F A and Wilkinson C W 1967 *Advanced inorganic chemistry* (New York: Interscience)
- Earnshaw A 1968 *Introduction to magnetochemistry* (New York: Academic Press)
- El Ezaby M S and El-Eziri F R 1976 *J. Inorg. Nucl. Chem.* **38** 1901
- Irving H and Rossotti H J 1953 *J. Chem. Soc.* 3397
- Irving H and Williams R J P 1948 *Nature (London)* **162** 746
- Manchanda V K and Subramanian M S 1982 *Acta Chim. Acad. Sci. Hung.* **111** 69
- Nayan R and Dey A K 1972 *Indian J. Chem.* **10** 109
- Orgel L E 1966 *An introduction to transition metal chemistry ligand field theory* (London: Methuen)
- Pribil R 1982 *Applied complexometry* (London: Pergamon Press)
- Rabenstein D L, Isab A A and Shoukry M M 1982 *Inorg. Chem.* **21** 3234
- Rabenstein D L, Daignault S A, Isab A A, Arnold A P and Shoukry M M 1985 *J. Am. Chem. Soc.* **107** 6345
- Radhakrishnan T, Joseph P T and Prabhakaran 1976 *J. Inorg. Nucl. Chem.* **38** 2217
- Shoukry M M 1984a *Indian J. Chem.* **A23** 537
- Shoukry M M 1984b *Rev. Roum. Chim.* **29** 283
- Shoukry M M 1985 *Egypt. J. Chem.* **28** 433
- Shoukry M M, Darwish N A and Hosny W M 1986a *J. Chin. Chem. Soc. (Taipei)* **33** 179
- Shoukry M M, Elmoghayar M R H and Elghandour A H 1987a *Synth. React. Inorg. Met.-Org. Chem.* **17** 1
- Shoukry M M, Elnagdi M H and Mahgoub A E 1979 *Ann. Chim. (Rome)* **69** 211
- Shoukry M M, Ghoneim A Kh, Shoukry E M and Elnagdi M H 1982 *Synth. React. Inorg. Met.-Org. Chem.* **12** 815
- Shoukry M M, Khater M M and Shoukry E M 1986b *Indian J. Chem.* **A25** 488
- Shoukry M M, Mahgoub A E and Hosny W M 1987b *Transition Met. Chem.* **12** 77
- Sillen L G and Martell A E 1971 Supplement No. 1, Spec. Publ. No. 25 (London: Chemical Society)
- Sillen L G and Martell A E 1974 *Stability constants of metal-ion complexes*, Special Publ. No. 17 (London: Chemical Society)
- Van Uitert L G and Hass C G 1953 *J. Am. Chem. Soc.* **75** 451