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Synthesis and Characterisation of Schiff Base Complexes of Copper(II), Nickel(II), Vanadium(IV) and Uranium(VI)†

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Two organic Schiff base ligands derived from phenylbutazone or oxyphenebutazone and *o*-aminophenol have been synthesised. Their eight metal complexes of Cu^{2+}, Ni^{2+}, VO^{2+} and UO_2^{2+} have been prepared. The isolated ligands and metal complexes are characterised by elemental analysis, magnetic measurements, X-ray diffraction, reflectance and IR spectral studies. The Schiff base ligands and their metal complexes were tested for their antibacterial behaviour using *E. Coli* as a test organism. Uranium and vanadium complexes are found to be excellent antibacterial agents.

INTRODUCTION

Much interest has been evinced in the last few years in the study of Schiff base metal complexes, which have occupied an important position in modern inorganic chemistry.[1–4] The interest in these compounds arises from their various applications in the field of bio-inorganic chemistry.[5] A number of Schiff base complexes are reported to be of great utility in pharmacological and biological aspects.[6, 7] They are also reported to possess good luminescence and pigmentation properties.[8, 9]

This has led us to synthesise some novel tailored molecules possessing good biological properties. A successful attempt has been made in the present work to synthesise Schiff bases of phenylbutazone or oxyphenebutazone and *o*-aminophenol and their eight metal complexes of Cu^{2+}, Ni^{2+}, VO^{2+} and UO_2^{2+} have been prepared.

EXPERIMENTAL

All chemicals were of AR grade. The compounds phenylbutazone (Sigma) and oxyphenebutazone (Sigma) were used as such without further purification.

Preparation of ligands: Schiff base ligands (1a) and (1b) were synthesised by refluxing DMF solution of phenylbutazone or oxyphenbutazone and *o*-aminophenol in 1 : 1 molar ratio for 2 h. The mixture was cooled, filtered and recrystallised from DMF.

Preparation of complexes: A solution of metal salts *viz.* vanadyl sulphate monohydrate, uranyl nitrate, aceeate and nickel acetate in 95% ethanol (20 mmol) was mixed with the Schiff base ligand in 95% ethanol (40 mmol) in 1 : 2 (M : L)

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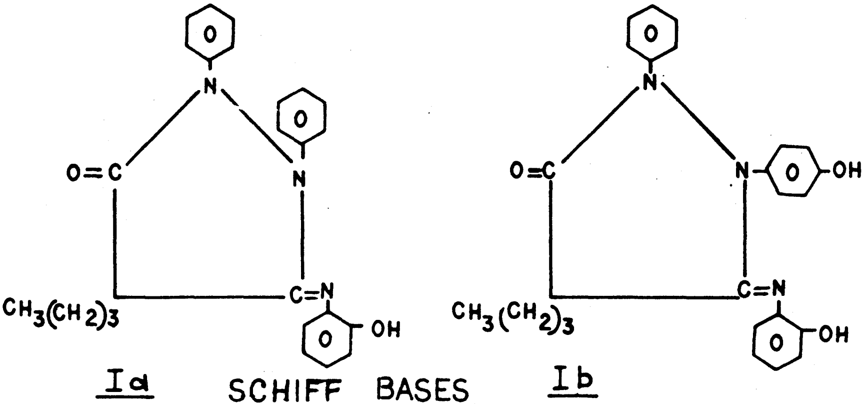
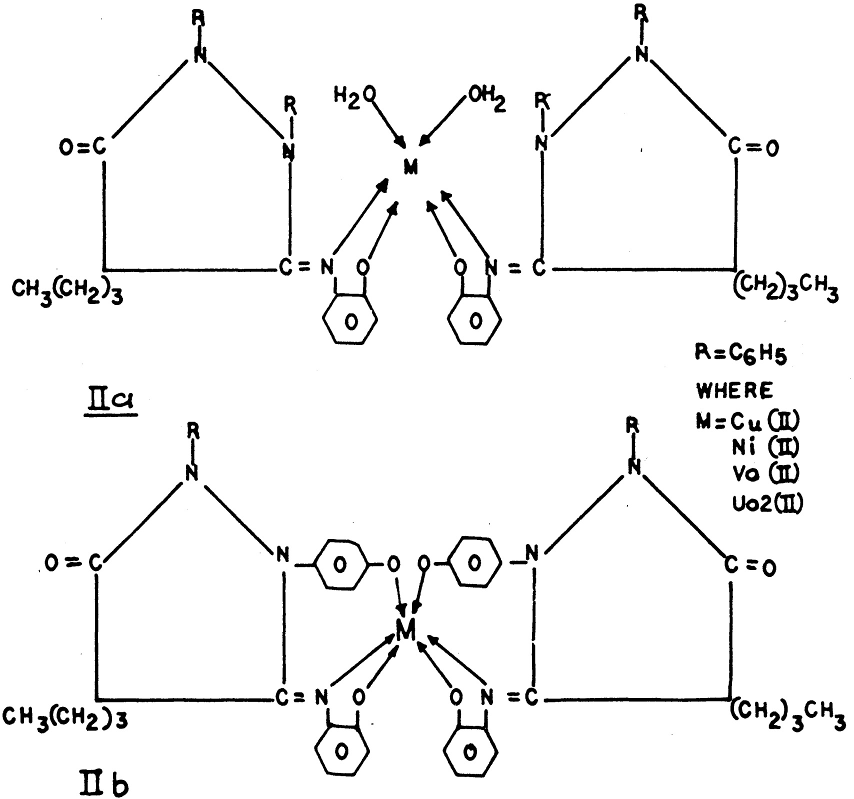


Ia SCHIFF BASES Ib



IIa

IIb

METAL COMPLEXES

ratio and contents were refluxed for 2–3 h. The refluxed solution was then poured into ice-cold water when a coloured solid separated out which was isolated by filtration and washed with ether and *vacuum*-dried at room temperature.

The complexes were analysed for metal contents. Carbon, hydrogen and nitrogen were determined by microanalysis at Chemistry Department, Faculty of Science, M.S. University of Baroda. The reflectance spectra were recorded on a Shimadzu-240 spectrophotometer. The IR spectra were recorded in KBr on a Perkin-Elmer 577 spectrophotometer. The magnetic susceptibility measurements were carried out using the Gouy's balance at room temperature with $Hg[Co(CNS)_4]$ as calibrant. The X-ray diffraction studies were carried out on X-ray diffractometer of Rigaku (Japan). Analytical and physical data of Schiff bases and their complexes are reported in Table-1.

TABLE-1
ANALYTICAL DATA OF SCHIFF BASES AND THEIR METAL COMPLEXES

Ligand/Complexes	Found/(Calcd.) %				μ_{eff} (B.M.)
	M	C	H	N	
$L^1 = C_{25}H_{24}N_3O_2$	—	74.17 (75.37)	5.98 (6.03)	9.95 (10.55)	—
$CuL'_2(H_2O)_2$	7.35 (7.09)	68.03 (67.00)	5.73 (5.80)	10.32 (9.38)	1.60
$NiL'_2(H_2O)_2$	6.93 (6.59)	67.03 (67.41)	6.02 (5.84)	9.81 (9.43)	3.25
$VOL'_2(H_2O)_2$	5.48 (5.66)	65.83 (66.66)	6.13 (6.00)	9.72 (9.33)	1.69
$UO_2L'_2(H_2O)_2$	22.03 (21.64)	55.20 (54.41)	5.15 (4.89)	7.89 (7.61)	—
$L'' = C_{25}H_{25}N_3O_3$	— —	73.06 (72.28)	6.15 (6.02)	10.51 (10.12)	
$CuL''_2(H_2O)_2$	6.98 (7.33)	65.23 (64.55)	5.53 (5.37)	9.13 (9.03)	1.90
$NiL''_2(H_2O)_2$	6.56 (6.32)	65.31 (64.89)	5.43 (5.40)	9.10 (9.08)	3.15
$VOL''_2(H_2O)_2$	5.62 (5.46)	65.52 (64.30)	5.75 (5.78)	9.89 (9.00)	
$UO_2L''_2(H_2O)_2$	21.15 (20.99)	53.12 (52.78)	4.83 (4.75)	7.21 (7.38)	—

The Schiff bases and their metal complexes were tested for their antibacterial behaviour using *E. coli* as a test organism.

RESULTS AND DISCUSSION

The analytical data (Table-1) shows that the composition of the complexex is $ML_2(H_2O)_2$ where M = Cu(II), Ni(II), VO(II) and UO_2(II) and L = Schiff bases.

The reflectance spectra of Cu(II) complexes show recognisable spectral bands at *ca* 16200 cm^{-1} and *ca* 26000^{-1}. The broad band (unsymmetrical) at *ca.* 16200 cm^{-1} may be due to $^3E_g \rightarrow {}^3T_{2g}$ transitions in octahedral geometry and the band at 26000 cm^{-1} may be due to ligand metal charge transfer.[10] The magnetic measurements for Cu(II) complexes is 1.6–1.9 B.M. which suggests an octahedral geometry[11] for Cu(II) complexes. The approximate demarcation given by Figgis is that μ_{eff} values above 1.9 B.M. for a square-planar or octahedral geometry. However, normally the range for the octahedral copper complexes is 1.5 to 2.5 B.M.[12]

The reflectance spectra of Ni(II) complexes show an octahedral geometry with electronic transitions at 9300 cm^{-1}, 14000 cm^{-1} and 23300 cm^{-1} which may be assigned to $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)\ (\nu_1)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)\ (\nu_2)$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)\ (\nu_3)$ transitions respectively. The ratio ν_2/ν_1 falls in the range required for octahedral configuration.[13, 14]

Reflectance spectra of vanadium(IV) show three bands at 12050 cm^{-1}, 15380 cm^{-1} and 17860 cm^{-1} which can be assigned to the following d-d transitions: $d_{xy} \rightarrow d_{xz}, d_{yz} \rightarrow d_{xy} \rightarrow d_{x^2-y^2}$ and $d_{xy} \rightarrow d_{z^2}$ while the band appearing at *ca* 25580 cm^{-1} is assigned to metal-ligand charge transfer transition.[15]

The magnetic susceptibility measurements indicate that the complexes of oxovanadium(IV) are paramagnetic in the range of 1.69 B.M. to 1.89 B.M. at room temperature corresponding to octahedral nature of the complexes.[16, 17] The VO(II) bonds can be regarded as multiple with component arising from electron density $O(p_\pi) \rightarrow V(d_\pi)$.

The uranium complexes are found to be diamagnetic in nature[18, 19]. Their magnetic susceptibilities are independent of field strength and temperature[20]. The ground state of dioxouranium complexes contained no unpaired electrons. The compounds are therefore expected to be weakly diamagnetic as observed.[19, 21]

The IR spectra of the free Schiff base ligands exhibit a strong band in the region 1610–1600 cm^{-1} assigned to $\nu(C{=}N)$. This band is shifted to lower energy by 10–15 cm^{-1} indicating co-ordination of nitrogen of azomethine group.[22, 23] In the IR spectra of the ligands, the medium band at 2900 cm^{-1} disappears in the metal complexes showing the deprotonation of the phenolic OH group on co-ordination. Water molecules present in the complexes are reported to be co-ordinated water. The broad band in the region 3400–3300 cm^{-1} is due to stretching mode and a band at 780 cm^{-1} due to rocking mode of the co-ordinated water in the complexes.

The IR spectra of vanadium complexes showed a strong band in the region 1000–950 cm^{-1} due to (V=O) group.[24] In the oxovanadium(IV) complexes two bands located at *ca.* 640 cm^{-1} and 545 cm^{-1} can be assigned to ν(V—N) and ν(V—O) respectively.

The infrared spectrum of dioxouranium(VI) complexes shows an intense band at *ca.* 937 cm^{-1} which is attributed to the $\nu_{asym}(UO_2)$ mode whereas band at 810 cm^{-1} is attributed to the $\nu_{sym}(UO_2)$ mode. The far IR bands at *ca.* 580 cm^{-1} and 460 cm^{-1} are assigned to ν(U—N) and ν(U—O) vibrations respectively.[25]

Using X-ray diffraction data the unit cell parameters have been calculated by trial and error method.[26] All main peaks have been indexed and their $\sin^2\theta$ values compared with the calculated ones. A comparison of the values reveals that there is good agreement between the calculated and observed values of $\sin^2\theta$. The observed values fit well in tetragonal system for ligands and their complexes. Also the calculated values of the density are in good agreement with the observations. The number of units per cell (n-values) are found to be 6 and 5 for ligands and metal complexes respectively.

Antibacterial study: In this work the ligand and their metal complexes were tested for their antibacterial activity by cup-plate method,[27] in DMF solvent against *Escherichia coli* (gram-negative bacteria) as test organism (Table-2).

TABLE-2
ANTIBACTERIAL ACTIVITY OF SCHIFF BASES AND THEIR METAL COMPLEXES

S. No.	Compounds	Conc. 10 mg/mL DMF activity against *E. coli*
1.	L' = APPB	+
2.	$CuL'_2(H_2O)_2$	++
3.	$NiL'_2(H_2O)_2$	++
4.	$VOL'_2(H_2O)_2$	+++
5.	$UO_2L'_2(H_2O)_2$	++++
6.	L'' = APOPB	++
7.	CuL''_2	+++
8.	NiL''_2	+++
9.	VOL''_2	+++
10.	$CO_2L''_2$	++++

L' = APPB—Aminophenol phenylbutazone
L'' = APOPB—Aminophenol oxyphenebutazone
Activities: (++++) = Excellent, (+++) = High
(++) = Moderate (+) = Slight

The compounds were used at concentrations of 10 mg/mL in DMF.

From the data reported in this work, it is observed that ligands and their complexes possess good antibacterial activity. It is also observed that oxyphenebutazone has better activity than phenylbutazone. This may be due to extra phenolic group present in oxyphenebutazone. It is also clear from bacterial screening data (Table-2) that the metal complexes are much more toxic in comparison to their parent ligand itself. The toxicity decreases in the following order.

Uranium > Vanadium > Nickel > Copper.

The increased toxicity of metal complexes may be due to the effect of metal ion configuration and charge, on the normal cell. A possible mode of toxicity may be specified in the light of chelation theory.[28]

Chelation reduces considerably the polarity of the metal ion mainly because of partial sharing of its π electrons and delocalisation over the whole chelate ring. Such chelation increases the lipophilic character of the metal chelate which probably leads to break down the permeability barrier of cells resulting in interference with normal cell process.[29, 30] Finally it is concluded that uranium and vanadium oxyphenebutazone complexes are excellent bactericides.

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