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Cobalt(II) Complexes of *Schiff* Bases Derived From o-Anisidine

By

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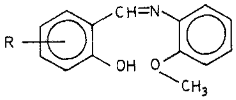
A few complexes of cobalt(II) with monovalent tridentate *Schiff* bases have been prepared and characterised by elemental analysis. The magnetic, electronic and infrared spectral data show that cobalt(II) has coordination number six in these complexes.

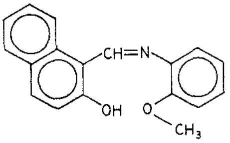
Introduction

A large number of papers has been published on the *Schiff* bases and their metal complexes[1–3]. Of these, the tridentate ligands containing N,N,N-sequences are shown to form complexes of 1 : 2 stoichiometry in which the ligand molecules occupy the equatorial planes in an octahedral array around the metal ion. The bifunctional tridentates containing either O,N,O- or O,N,S- or S,N,S-sequences form 1 : 1 com-



R

1 : H
2 : 3-*Me*
3 : 4-*Me*
4 : 5-*Me*
5 : 5-Cl



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plexes with the bivalent transition metals which exist in the dimeric form[4]. However, these bases with tetravalent metal ions form complexes of coordination number six with the two ligand molecules arranged spatially in equatorial planes of an octahedron[5, 6]. The information gathered up to date depicts that the amount of attention concentrated on the monofunctional tridentates is meagre. By blocking one of the active centres it is possible to change the geometry of the complexes which otherwise yield tetracoordinated dimeric complexes.

In this paper a few *Schiff* bases, **1–6**, and their Co(II) complexes are reported.

Experimental

The chemicals used for preparing the substituted aldehydes were of reagent grade; o-anisidine and salicylaldehyde were of BDH make. The substituted salicylaldehyde and 2-hydroxy-1-naphthaldehyde were prepared by the *Duff* method[7].

The *Schiff* bases **1–6** were prepared by refluxing 1 : 1 (molar) quantities of aldehydes and o-anisidine in an alcoholic medium for about half an hour. The products were recrystallized from alcohol.

Preparation of the Complexes

Co(II) acetate tetrahydrate was obtained from Albright Wilson Ltd., England, and was used as such for complexation.

Cobalt(II) acetate in minimum quantity of water was added to an alcoholic solution of *Schiff* base maintaining 1 : 2 metal to ligand ratio. The reaction mixture was refluxed for about 5 to 6 hours. The crystalline complex was filtered, washed several times with aqueous alcohol and dried in vacuum over fused $CaCl_2$.

Elemental Analyses

Co in the complexes (VII–XII) was determined gravimetrically as $Co(oxine)_2 \cdot 2\,H_2O$[8] and N by *Kjeldahl's* method.

Physical Measurements

Conductance measurements in nitrobenzene were determined on an ELICO conductivity bridge with a cell of cell constant 0.829 cm^{-1}.

The molecular weights were determined in nitrobenzene by the freezing point method. The magnetic susceptibilities at room temp. were measured on a *Gouy* balance with a glass tube calibrated for the diamagnetism; $Hg[Co(NCS)_4]$ was used as a calibrant. The obtained molar susceptibility values were corrected for diamagnetism of the constituents of the complexes using *Pascal's* constants.

The visible spectra of the complexes were recorded on a Beckman DB-2 recording spectrophotometer using 1 cm matched glass cells in *DMF*. In certain cases the spectra were taken in Nujol mull too. The infrared spectra of the ligands and the complexes in Nujol mull were recorded on a Perkin-Elmer Infracord 137-B in the region 4,000–650 cm^{-1}. For a few complexes the spectra were obtained in the region 4,000–200 cm^{-1} on a Perkin-Elmer 621 spectrophotometer.

Table 1. *Elemental Analysis, Molecular Weight, Magnetic Data and Electronic Spectra in Nujol Mull of Cobalt(II) Complexes (VII–XII) with Schiff Bases* (**1**–**6**)

No.*	Complexes	Empirical formula	% Co found (calc.)	% N found (calc.)	Mol. Wt.	μ_{eff}, μ_B	Band maxima in nm $4\,T_{1g} \rightarrow 4\,T_{1g}\,(P)$	Band maxima in nm $4\,T_{1g} \rightarrow 4\,T_{2g}$
1	VII	$(C_{14}H_{12}NO_2)_2Co$	11.50 (11.54)	5.35 (5.48)	500.89 (510.94)	4.13	475	1233
2	VIII	$(C_{15}H_{14}NO_2)_2Co$	10.82 (10.95)	5.33 (5.20)	537.48 (542.94)	4.30	475	1175
3	IX	$(C_{15}H_{14}NO_2)_2Co$	10.75 (10.95)	5.10 (5.20)	540.00 (542.94)	4.40	480	1200
4	X	$(C_{15}H_{14}NO_2)_2Co$	11.00 (10.95)	5.09 (5.20)	530.50 (542.94)	4.18	465	1160
5	XI	$(C_{14}H_{11}ClNO_2)_2Co$	10.15 (10.17)	4.71 (4.72)	—	4.78	470	1200
6	XII	$(C_{18}H_{14}NO_2)_2Co$	9.60 (9.65)	4.62 (4.58)	—	4.98	475	1150

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* Of *Schiff* base.

Note: The values in the parenthesis are the calculated values.

Results and Discussion

The results of the elemental analyses listed in (Table 1) agree well with the empirical formula of 1 : 2 stoichiometry. The molecular weight determinations (in nitrobenzene) show that the complexes are monomers and agree well with the empirical formula CoL_2 where LH is the ligand. The *Van't Hoff* factor i reveals the existence of the complexes as single species in nitrobenzene. The complexes are highly coloured microcrystalline substances soluble in common organic solvents.

The molar conductances values in nitrobenzene are too low to account for any dissociation of the complexes in the solvent. Hence the complexes may be regarded as non-electrolytes.

Magnetic Data

The room temperature measurements of magnetic susceptibilities for all these complexes are listed in Table 1. All these complexes show magnetic moments in the range of 4.13 to 4.98 μ_B. It is theoritically predicted[9] that the magnetic properties of high spin octahedral Co(II) complexes are under the direct influence of the orbitally degenerate $4\,T_{1g}$ ground state which provides a high magnetic orbital contribution to the magnetic moments. This is why the room temperature magnetic values fall in the range of 4.72 to 5.2 μ_B. The observed values of these Co(II) complexes are in the range of values reported for octahedral Co(II) complexes.

Electronic Spectra

Electronic spectra of the complexes VII–XII have been studied with a view to procure an additional evidences for the conclusions adduced with the help of magnetic data. The band maxima observed for these complexes have been listed in Table 1. High spin Co(II) complexes have the ground term $4\,T_{1g}$ arising from the configuration $t_{2g}5_{eg}2$ and one can expect three spin allowed d–d transitions from $4\,T_{1g}$ ground state to various states viz. $4\,T_{2g}$, $4\,A_{2g}$ and $4\,T_{1g}$ (P) states[9]. Though *Liehr*[10] has presented the complete calculations. The electronic spectral interpretation of hexacoordinate Co(II) complexes remains as a matter of debate. The previous reports predict a wide range from 450–1,600 nm for the various transitions[9, 11–13]. Of these the band appearing in the near infrared region is assigned to the $4\,T_{1g} \rightarrow 4\,T_{2g}$ transition and one in the visible region is assigned to the $4\,T_{1g} \rightarrow 4\,T_{1g}$ (P) transition. The $4\,T_{1g} \rightarrow 4\,A_{2g}$ transition is frequently not observed. The $4\,T_{1g} \rightarrow 4\,T_{1g}$ (P) band around 500 nm has a shoulder on the high frequency side. This is the consequence of spin orbit coupling in the $4\,T_{1g}$ (P) state. Taking into account these

Table 2. *Infrared Frequencies (in* cm^{-1}*) of Cobalt(II) Complexes (VII–XII) with Salicylidene o-Anisidene and its Derivatives* (**1–7**)

Assignments	VII	VIII	IX	X	XI	XII
Intramolecular H-bonded —OH stretching vibration	—	—	—	—	—	—
C=N stretching vibration	1609 v.s.	1610 s	1620 s	1618 s	1610 s	1620 m
Phenolic C—O stretching vibration	1330 s	1350 m	1330 m	1325 s	1320 s	1320 m
	1300 m	1290 w	1310 m	1300 s	1305 m	—
Assymetric C—O—C deformation vibration	1250 m	1250 s	1250 s	1255 s	1240 s	1260 m
ν (*M*—N) vibrations	540 m			545 m	540 m	
ν (*M*—O) vibrations	450 s			440 m	450 w	
ν (*M* ← O) vibration	485 m			485 m	490 m	

Note: s = strong; m = medium; w = weak; br = broad.

evidence, the band around 475 nm is assigned to the $4\ T_{1g} \rightarrow 4\ T_{1g}$ (P) transition. The tetrahedral Co(II) complexes also produce such bands in the 400–700 nm region. The probability of these complexes being tetrahedral is excluded on the basis of the intensity of the bands. The bands observed for these complexes are weak ones whereas the tetrahedral Co(II) complexes exhibit high intensity bands. The band appearing in the region 1,100–1,300 nm is assigned to the $4\ T_{1g} \rightarrow 4\ T_{2g}$ transition. These spectral observations also favour the octahedral configuration in these complexes.

Infrared Spectra

The important infrared frequencies are listed in Table 2 along with the assignments. The broad weak band appearing in the region 2,740–2,680 cm^{-1} attributable to the intramolecular hydrogen bonded OH[14, 15] is not observed in the complexes suggesting that the hydroxy group of the *Schiff* base has been utilized in the bond formation. Another support for this conclusion is the shifting of the phenolic C—O appearing in the region to the higher frequency[16] viz. 1,350–1,300 cm^{-1}.

A strong band in the region 1,630–1,610 cm^{-1} is assigned to the C=N of the *Schiff* bases in view of previous assignments[17]. In the complexes this band is observed in the 1,620–1,605 cm^{-1}. The low frequency shift observed in these complexes suggests that the coordination has taken place through the azomethine nitrogen. As a result of this the bond order of the carbon to nitrogen link is decreased.

The medium intensity band is observed in the region 1,240–1,220 cm^{-1} attributable to the assymetric out of plane deformation vibration of C—O—C[18] is observed in the region 1,260–1,240 cm^{-1} showing that the o-methoxy group is coordinatively linked to the cobalt ion through oxygen.

The metal nitrogen frequencies are reported to occur in the range of 600–500 cm^{-1} for the *Schiff* base complexes[19]. The band found in the region 540–510 cm^{-1} is assigned to the CO—N stretching vibration in view of previous assignments[20]. The metal oxygen bands are found in the region between 500–400 cm^{-1} for the transition metal complexes[19, 21]. There is also report about the ν (M—O) bands below 400 cm^{-1} [22]. Taking into consideration these assignments we have assigned a band of medium to high intensity in the region 450–440 cm^{-1} to the ν (M—O) vibration. The 485 ± 5 cm^{-1} medium to high intensity band is assigned to the ν ($M \leftarrow$ O) vibration.

The analytical data and the spectral observation along with the magnetic data envisage that the cobalt exhibits coordination number six in these complexes. Hence it may be concluded that the ligands under present investigation behave as monovalent tridentates. *Kogan* and coworkers have arrived at a similar conclusion in the case of zinc complexes[6a].

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