Some mixed ligand complexes of cobalt (II) with bidentate Schiff bases

Rajib Lal De* & Keka Samanta (nee Bera)
Department of Chemistry, Inorganic Chemistry Section, Jadavpur University, Calcutta 700 032, India

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Cobalt(II) mixed ligand complexes, [Co(SBb)(SBb')] and [Co(SBb)(Lig)] (SBb/ SBb' = anions of bidentate Schiff bases; Lig = anion of acetylacetone, salicylaldehyde, oxime or glycine) have been isolated and characterised by elemental analyses, IR, UV-visible and mass spectral data, magnetic moment, ESR and cyclic voltammetric studies. Pseudotetrahedral arrangement of ligands around the cobalt(II) ion is suggested.

Mixed ligand complexes of transition metals involving Schiff bases have found application towards understanding of many reactions in living processes. In recent years such complexes have been studied as model complexes of biological importance. Mixed ligand complexes of cobalt(III) involving Schiff bases have been studied in some details.

We have carried out some reactions with the intention of stabilising mixed ligand complexes of cobalt(II) with bidentate Schiff bases and the results are presented here.

Experimental

Elemental analyses for C, H, N were carried out on an Elemental analyser Heraeus - Carlo Erba 1108 and cobalt was estimated spectrophotometrically. Magnetic susceptibility (uncorrected) was measured using a Gouy balance with Hg[Co(SCN)₄] as the calibrant. A Shimadzu - 2100 UV - VIS spectrophotometer was used to record the electronic spectra and the infrared spectra were recorded on a Perkin - Elmer Paragon - 1000 FT IR spectrophotometer. Mass spectra were measured on either Jeol D - 300 (EI MS) or Jeol SX - 102 (FAB MS) spectrometer. Voltammetric measurements were made using the PAR model 370 - 4 electrochemistry system under nitrogen at 298K and the data were uncorrected for junction potentials. ESR spectra were recorded on an ER - 200 spectrometer at room and at liquid nitrogen temperatures.

All solvents were dried and distilled and cobalt(II) acetate tetrahydrate was recrystallised before use. All other chemicals were either of AR, GR or Extrapure grade and were used as purchased. Tetraethylammonium perchlorate (TEAP) was prepared and acetonitrile was purified as reported elsewhere.

Preparation of the starting materials

The bidentate Schiff bases were prepared by the usual method of condensation of equimolar quantities salicylaldehyde with aniline (SANH), ortho-aminophenol (SALOPH) and ethanolamine (SALENOLH) in refluxing ethanol. The products were obtained as yellow to orange - yellow solids except SALENOLH for which the reactions were performed in situ. Solid Schiff bases were however purified by recrystallisation from ethanol. Co(SAN)₂.2H₂O was prepared by the literature method.

Preparation of the mixed ligand complexes

Method A—Co(SAN)₂.2H₂O (1.45g, 3mmol) dissolved in 25 ml of ethanol was added to equimolar quantities of SALOPH, SALENOLH, acetylacetone (acacH), salicylaldehyde (salH), oxime (oxH) and glycine (glyH) in 25ml ethanol. After stirring at room temperature for 6h, the mixture was allowed to reflux for 2h. It was filtered hot to remove the undissolved materials. The filtrates on reduction of volume to ~ 20ml and cooling to -5°C yielded [Co(SAN)(SALOP)](1);[Co(SAN)(SALENOL)],(2);[Co(SAN)(acac)],(3);[Co(SAN)(sal)],(4);[Co(SAN)(ox)](5);[Co(SAN)(gly)](6) as brown to dark brown solids in 55 - 65% yields and were collected by filtration, washed with ethanol, diethylether and finally dried in vacuo over fused CaCl₂.

Method B—Co(SAN)₂.2H₂O (1.45g, 3mmol) was mixed with equimolar quantities of the ligands in 40ml ethanol followed by addition of 0.50ml liquor ammonia and the mixture was refluxed for 2h. The above stated products, (1) - (6) were isolated after processing the reaction mixtures similarly as described in method A.

Results and discussion

Prolonged stirring of the reaction mixtures containing equimolar quantities of Co(SAN)₂.2H₂O...
and the appropriate ligands in ethanol at room temperature followed by slow increase in temperature and finally thorough reflux for 1 - 2 h provided best yields for the mixed ligand complexes of cobalt(II). Thorough reflux for ~2h in presence of a few drops of liquor ammonia also yielded the same products and in that case the addition of ammonia appeared to be an absolute necessity. Allowance of longer reaction time made the reactions to follow some different pathways and the yields of the desired products became low.

Magnetic moments and electronic spectra

The magnetic moment values for the mixed ligand complexes involving two different schiff bases (1) and (2) which range between 2.90 and 3.30 BM, and the appearence of a weak band in the region 530 - 560nm suggest a highly distorted tetrahedral arrangement of ligands around cobalt(II) ion\textsuperscript{12}. On the other hand, the magnetic moment values of 2.66 - 2.82 BM along with the presence of a shoulder in the region 590 - 620 nm for the mixed ligand complexes involving a bidentate schiff base and other bidentate ligands support a low - spin near square planar environment around the cobalt(II) ion\textsuperscript{12,13}. The composition of the complexes is supported by satisfactory elemental analyses of C, H, N and Co (Table 1).

ESR spectra

The ESR spectra of the complexes were recorded in DMSO solution. The microwave frequency of each ESR spectrum was calculated from the line of a point standard of powdered DPPH fixed on the bottom side of the cavity. The field set and scan range were 3200 and 2000 respectively at LNT. For the complex (1) several \textit{"g"} values were obtained in the range 2.03 - 2.26, e.g., 2.26, 2.16, 2.11, 2.10, 2.08, 2.06 and 2.03 whereas the \textit{"g"} values obtained for the complex (3)
range between 1.91 and 2.28, e.g., 2.28, 2.13, 2.06, 2.03, 1.97 and 1.91.

Mass and IR spectra
The mass spectral investigation was performed on representative complexes. Molecular ion peaks along with some assignable peaks were observed for them (Table 2) which convincingly support the composition of the complexes. Although the IR spectra of the complexes are complicated due to the overlap of the bands of different ligands, assignments of important bands furnish structural information indicating coordination modes of the ligands (Table 2). The IR spectra of the compounds (1) and (2) showed the presence of medium but broad bands in the region 3450 - 3350 cm⁻¹ assignable to ν(OH)¹⁴ of the non bonded -OH groups of the Schiff base anions SALOP - and SALENOL-. For all the compounds (1) - (6), the weak bands at 3030 - 3000 cm⁻¹ are due to aromatic ν(C-H) whereas aliphatic ν(C-H) (symmetric and asymmetric) due to -CH₂, -CH₃ groups appear distinctly at 2930 - 2850 cm⁻¹ (ref. 15). The presence of coordinated >C=N- groups is indicated by the appearance of ν(C=N) at 1645 - 1620 cm⁻¹ (ref. 16). ν(C-O) of the medium but sharp bands observed at 760 - 750 cm⁻¹ are the - C - H deformation vibration bands.¹⁶,¹⁷ The bands at ~540 and ~470 cm⁻¹ are due to ν(C-N) and ν(C-O) absorptions respectively.¹⁸,¹⁹ The presence of oxygen bonded acetylacetone is inferred from the appearance of ν(C=O) at 1580 - 1578 cm⁻¹ while ν(C=O) is usually observed at 1540 - 1520 cm⁻¹在他和 and the carbon bonded ν(C=O) appears at 1650cm⁻¹.²²

Cyclic voltammetry
The electrochemical studies by cyclic voltammetry were carried out to explore the redox properties of the complexes. The complexes (1) and (2) exhibited reversible cyclic voltammogram assignable to Co(II) / Co(III) redox couple with $E^{\theta}_{1/2}$ = 0.99 V, ΔE = 70 mV and $E^{\theta}_{1/2}$ = 1.34 V, ΔE = 80 mV respectively. The complex (3), on the other hand, showed an irreversible voltammogram assignable to Co(II) / Co(III) redox couple with $E_{pa}$ = 1.16 V, ΔE = 280 mV.

The increase in $E^{\theta}_{1/2}$ ( or $E_{pa}$ ) values in the order [Co(SAN)(SALENOL)] < [Co(SAN)(acac)] < [Co(SAN)(SALENOL)] may be attributed to the decrease in electron withdrawing property of the ligands in the reverse order namely [Co(SAN)(SALENOL)] > [Co(SAN)(acac)] > [Co(SAN)(SALENOL)] and that the reduction occurred at the lowest and highest potential for (1) and (2) respectively.

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References
1 Williams D R (Ed), An introduction to bio-inorganic chemistry. (Thomas Springfield), (1975).
7 Dey K & De R L, Z anorg allg Chem, 402 (1973) 120.
16 Gruber S J, Harris C M & Sinn E, J inorg nucl Chem, 30 (1968) 1805.
23 Solvent, acetonitrile; supporting electrolyte. TEAP (0.1 M); working electrode, platinum; reference electrode, SCE; solution concentration ~10⁻³ M; $E^{\theta}_{1/2}$ = 0.5 ($E_{pa}$ + $E_{pc}$) where $E_{pa}$ and $E_{pc}$ are anodic and cathodic peak potentials respectively, ΔE = $E_{pa}$ - $E_{pc}$; scan rate, 50 mVs⁻¹.