CHAPTER II

MATERIAL AND METHODS

In this chapter details of preparation of ligands and their metal complexes as well as the experimental methodology are described. The ligands used are a diamine, 2-4-Diamino 5-chlorothiazole and its Schiff base obtained by condensation with salicylaldehyde. The complexes were prepared by using salts of Cu, Co, Ni, Mn, Cr, Zn and Cd. The ligand and metal complexes were characterised by chemical and instrumental and noninstrumental analytical techniques.

2.1 Synthesis of 2,4-Diamino 5-chlorothiazole [DCT]

DCT was prepared by starting with synthesis of ethyldichloroacetate, which was converted into dichloroacetamide and subsequently into the required product.

2.1.1 Synthesis of Ethyl dichloroacetate

Ethyl dichloroacetate was prepared by reported method [1]. Crystals of dichloroacetic acid (225 g) were added to 120 g (150 ml) of absolute ethanol and 36 g (20 ml) conc sulphuric acid was cautiously added to it. The mixture was refluxed for 18 hours on an oil bath. The resulting ethyl dichloroacetate was collected by distillation under normal pressure as a liquid between 156° - 159°C. The liquid was redistilled to give pure compound boiling at 158°C. The yield was 189 g and was obtained in 70 % yield on the basis of dichloroacetic acid. The literature boiling point is 158°C.

$$Cl_2CHCO.OH + C_2H_5OH \xrightarrow[\text{reflux 18 hrs}]{\text{conc } H_2SO_4} Cl_2CHCO.OC_2H_5 + H_2O$$

2.1.2 Synthesis of Dichloroacetamide

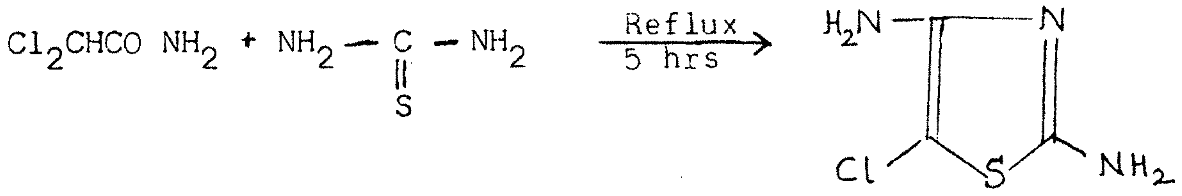
Dichloroacetamide was obtained by the reaction between ethyl dichloroacetate and liquid ammonia [2]. Ethyl dichloroacetate (250 g, 260 ml) obtained as above was mixed with (200 g, 222.3 ml) ice-cold liquior ammonia and the mixture was stirred for 15 minutes. One more portion of the same quantity of ice-cold ammonia was added and mixture was stirred vigorously. Dichloroacetamide separated as while, light-weight precipitate was filtered on a Bucknal funnel and recrystallized from ethanol. On recrystallisation, white light weight product (150 g) is obtained melting at 97°C with 86 % yield on the basis of ethyl dichloroacetate.

$$Cl_2CH\ COO\ C_2H_5 + NH_3 \longrightarrow Cl_2CH\ CONH_2 + C_2H_5OH$$

2.1.3 Synthesis of 2,4-Diamino 5-chlorothiazole [DCT]

DCT was prepared by using literature procedure [3] starting with dichloroacetamide. Dichloroacetamide (0.1 mole, 12.8 g) was dissolved in minimum quantity of absolute ethanol and thiourea (0.1 mole, 7.6 g) dissolved in hot ethanol added and heated under reflux for five hours on water bath. The resulting material was poured in an evaporating dish and evaporation was allowed at room temperature when crude DCT was obtained as brownish solid. The crude product was dissolved in boiling ethanol and was treated with activated charcoal. On filtration slow crystallisation was allowed to give light-weight, white needles (112 g). The product melts at 127°C and is obtained in 75 % yield on the basis of dichloroacetamide. The product on elemental analysis gave following results :

N = 27.9 %, C = 24.0 %, H = 2.1 %, Cl = 23.2 % and S = 21.3 % expected N = 28.09 %, C = 24.08 %, H = 2.08 %, Cl = 23.08 %, S = 21.40 %.



2.2 Synthesis of Schiff Base

Standard literature procedure was used for preparation of the Schiff base [4].

DCT (0.1 mole, 14.9 g) and salicylaldehyde (0.2 mole, 22.4 ml) were dissolved in absolute ethanol and the mixture was heated under reflux for two hours on a water bath. The Schiff base is obtained as yellow coloured crystalline fibrous mass and on cooling it was filtered off. The crude product was dissolved in minimum quantity of hot ethanol and recrystallized product was obtained on slow cooling as long monoclinic, yellow crystals. The fibrous product was filtered off, washed with very small quantity of absolute alcohol by rapid suction and was dried under vacuum.

The pure product melted at 152° - 154°C and analysed satisfactorily to C = 52.1 %, H = 3.02 %, N = 10.5 %, Cl = 17.7 %, S = 8.0 % as against the expected analysis as C = 52.04 %, H = 3.06 %, N = 10.7 %, O = 8.16 %, Cl = 17.85 %, S = 8.16 %.

The molecular weight obtained by using Rast's method was 388 [expected 392].

2.3. Physical and Chemical Properties

DTA is a white, monoclinic crystalline material which on long standing an exposure turns to pale-buff colour and such old samples must be recrystalised from ethanol before use. DCT is insoluble in water but easily soluble in ethanol, methanol and other organic solvents. The diamine reacts with hydrochloric acid and gives dichloride of the formula

$$[C_3N\ S.Cl.(NH_2)_2.\ 2HCl]$$

The Schiff base is pale brownish material with good keeping quality. It is fairly soluble in ethanol and other organic solvents.

2.4 Purification of Solvents

Absolutely dry ethanol was prepared by using reported method [5] and it was carefully protected from hydration by keeping it in good-stoppered bottles avoiding exposer. Methanol was distilled twice before use. Wherever needed triple glass distilled pure water was used. All the chemicals were of A.R. grade from reliable sources like P.D.H., E. Merck and K.L.

2.5 Preparation of Metal Complexes of DCT

Metal complexes were prepared by reaction between the metal solution and solution of DCT.

2.5.1 Cobalt(II) Complexes

2.5.1.a Complexes Prepared from Cobalt(II) Acetate

Cobalt acetate 0.01 mol (2.49 g) was dissolved in minimum quantity of hot methanol to which methanolic solution of DCT 0.02 mole (2.98 g) and 1:4 ammonia solution were added. The mixture was refluxed on water bath for one hour. The contact with moisture was avoided by using a calcium chloride guard tube. The flux was quickly stoppered and allowed to cool in a dry box. On standing over-night a deep green coloured microcrystalline material separated which was very rapidly filtered under vacuum, washed with small quantity of dry methanol and finally with dry ether obtained by refluxing on sodium wire. The compound was then transferred to a vacuum dessicator and was completely dried. The dried material was transferred to dry glass ampoule and was sealed to protect it from hydration.

2.5.1.b Complex Prepared from Cobalt(II) Chloride

Methanolic solution of 0.01 mole (2.37 g) cobalt chloride was added to methanolic solution of 0.02 mole (2.98 g) of DCT and was refluxed on water bath for one hour. Almost half the quantity of methanol was distilled out to give very deep green coloured solution. The flask was then carefully stoppered and was allowed to cool slowly when green crystals were deposited. The crystals were quickly filtered off and washed with little methanol. The crystals were then dissolved in minimum quantity of boiling methanol and the solution was very slowly cooled in a dry box. The next day the deep green crystals were filtered, washed with methanol and dried in vacuum. The compound was either sealed in glass ampoule or kept in stoppered bottle in dessicator over P_2O_5.

2.5.1.c Complex Prepared from Cobalt(II) Bromide

The complex from cobalt bromide was obtained as a microcrystalline green material. In this case addition of ammonia was not necessary. The procedure of first and subsequent crystallization was carried out by using the procedure given above.

2.5.1.d Complex Prepared from Cobalt Nitrate

Same method as 2.5.1.b gave a parrot green complex of cobalt nitrate. It was also recrystallized and stored over P_2O_5.

2.5.2 Nickel(II) complexes

Ni(II) complexes were obtained by using $NiCl_2$, $NiBr_2$ and $Ni(NO_3)_2$. All the three complexes are ochre-yellow in colour and there is slight greenish brown tinge in them. The addition of ammonia was not necessary.

2.5.3 Chromium Complex

By starting with chromium acetate and DCT and by adding ammonia before refluxing a slate gray coloured complex was slowly formed as the reaction continued. On cooling the complex was filtered, washed with methanol and ether and dried in vacuum dessicator.

2.5.4 Zinc(II) Complex

DCT complex from zinc(II) acetate was obtained as pale yellow micro-crystalline product on refluxing zinc acetate with DCT. The product was filtered, washed with ethanol and dry ether and finally vacuum dried and stored in vacuum dessicator.

2.5.5 Cadmium(II) Complex

By using the above procedure without addition of ammonia a yellow coloured crystalline product was obtained from cadmium acetate.

2.5.6 Copper(II) Complexes

2.5.6.a Complex Prepared from Copper(II) Acetate

Copper(II) acetate was dehydrated under vacuum over P_2O_5, 0.01 mole anhydrous copper acetate was dissolved in 20 ml of dry methanol and 0.02 mole (2.98 g) of DCT, dissolved in dry methanol, was added to it. The mixture was shaken and refluxed in a flask fitted with condenser provided with calcium chloride guard tube. Crystals were separated, quickly washed with methanol, followed by a quickwash with dry ether, dried under vacuum over P_2O_5 and stored in stoppered bottle.

2.5.6.b Complex Prepared from Copper(II) Chloride

Copper(II) chloride dihydrate was dehydrated under vacuum over P_2O_5 and 0.01 mole (1.344 g) of it was dissolved in 20 ml dry methanol and was mixed with 0.02 mole (2.98 g) of DCT dissolved in dry methanol and refluxed for one hour.

On cooling crystals of the complex were deposited, which were filtered and washed with methanol, finally washed with ether and stored in a stoppered bottle.

2.6 Hydrated Cobalt Complexes of DCT

The blue coloured Co(II) complexes prepared as described in 2.5.1.b change to pale pink colour when they react with water. The solubility behaviour vary and although titration with water may give pink solids generally somewhat more water is to be added for total disappearance of blue form. The resulting complex is then present as pale pink solution or a pink solid dispersion in faint pink solution after filtration. The pink solid can be used for further study. If the pink filtrate is evaporated merely by exposing to sun deep blue crystals of the original complex results. It is only in case of complex obtained from cobalt nitrate that stable deep purple pink material is obtained when the deep blue complex is exposed to moisture. In contact with water this purple material which is probably a mixture of blue component on slow evaporation pink crystals are formed at bottom and can be collected by decanting the mother liquor followed by a quick wash with water. Excess water is blotted out by using whatman No.1 filter paper.

2.7 Complexes of Schiff bases

Schiff base complexes of metals were prepared by using following three routes :

In first method, the Schiff base was prepared as reported earlier (6) and the reaction was carried out in ethanolic medium with the DCT complexes, reported above were treated with appropriate quantity of salicylaldehyde in ethanol solution.

In the second method, solution of metal salicylaldehyde complex [6] was treated with solution of DCT.

In the third method, solutions of metal salts, DCT and sal were taken in appropriate proportions and refluxed. The same product was obtained by all the three methods.

2.7.1 Cobalt(II) Schiff Base Complex

Anhydrous cobalt chloride 0.01 mole (1.29 g) was dissolved in ethanol and to it 0.01 mole of Schiff base [DCT $(Sal)_2$ H_2] in minimum ethanol was added. The flask was fitted with a bent tube and the solution was boiled to distil off almost half the quantity of ethanol. The water from hydrated cobalt chloride distilled off as water alcohol azeotrope and the colour of the solution gradually became intense blue. The bent tube was replaced by a condenser with guard tube containing calcium chloride and the mixture was refluxed for about two hours. The condenser was again replaced by the bent tube and almost all the solvent was distilled off. The resulting deep blue coloured powder was further dissolved in hot, dry methanol and was refluxed for further one hour. On cooling the solution and keeping it overnight, deep blue-green micro-crystalline compound was obtained, which was filtered, washed with small volume of dry methanol and finally with dry ether and dried under vacuum.

2.7.2 Copper(II) Schiff Base Complex

Anhydrous copper chloride was obtained by vacuum dehydration over P_2O_5. 0.01 mole (1.34 g) of it was dissolved in dry ethanol and methanolic solution of Schiff base [DCT $(Sal)_2$ H_2] (0.01 mole, 3.92 g) was added to it and was reduced to half by distilling off the solvent. It was refluxed for 10 min and the solution was further heated on water bath to distil off all the solvent giving dirty gray coloured residue. The residue was triturated with methanol and was transferred to a small flask and immediately fitted with reflux condenser with $CaCl_2$ guard tube. Addition of small quantity of methanol was necessary for complete dissolution. The solution was cooled and kept overnight when dirty greenish gray coloured copper complex separated out. It was filtered, washed with little methanol and finally with dry ether.

2.7.3 Nickel(II) Schiff Base Complex

Nickel chloride (0.01 mole, 2.37 g) and Schiff base [DCT $(Sal)_2$ H_2] (0.01 mole, 3.92 g) were used to prepare the Ni(II) complex by following method given in 2.7.1 where ochre yellow powder of Ni(II) complex was obtained.

2.7.4 Chromium(II) Schiff Base Complex

Methanolic solution of 0.01 mole of chromium chloride (2.66 g) was mixed with ethanolic solution of 0.01 mole (3.92 g) of Schiff base [DCT $(Sal)_2$ H_2] and on following the procedure 2.7.1 a pale gray coloured powder was obtained. On further refluxion with methanol and subsequent slow crystallization yielded pale buff powder along with shining steel gray platelets.

2.7.5 Manganese(II) Schiff Base Complex

By following procedure 2.7.1 and by using 0.01 mole (1.97 g) of manganese(II) chloride $MnCl_2.2H_2O$ and 0.01 mole (3.92 g) of [DCT $(Sal)_2$ H_2] buff coloured crystals of the complex were obtained.

2.7.6 Zinc(II) Schiff Base Complex

Zinc(II) complex was obtained by using method 2.7.1 yielding cream yellow coloured complex.

2.8 Aduct Complexes of Nickel

$Ni(DCT)_2$ X_2 and $Ni(DCT(Sal)_2)X_2$ complexes can be converte into adducts of reaction with pyridine, ethylene diamine and 2,2'-bipyridyl, α-, β or r-picolin and 1-10-phenonthroline [7, — 10].

Yellow complex (1 g) was dissolved in minimum amount of acetone by boiling to this solution 10 ml of pyridine was added. The yellow colour was changed to pale green in case of complexes obtained from chloride and nitrate. The complex $Ni(DCT)_2Br_2$

gave deep orange solution. The solution was cooled and much of the acetone was removed by distillation finally pyridine was distilled out when brick red material started appearing at bottom. The flask was allowed to cool when brick red precipitate was deposited it was filtered off, washed with little acetone and after drying kept in dessicator and finally stored.

In case of $NiCl_2$ and $Ni(NO_3)_2$ complexes, the pale green solution was subjected to heating to remove first acetone and much of pyridine. On cooling pale green waxy crystals appear. These were filtered, washed with acetone, dried over vacuum and stored.

Similar series of complexes showing the same colour changes were prepared from α-, β- and γ- picolin.

In in above cases instead of pyridine, ethylenediamine is used, we get blue green crystalline complexes in all cases.

When in the above preparation ethanolic solution of 2,2'-bipyridil and 1-10 phenonthroline was used and refluxed with acetone solution of the complexes a deep pink red solution results in all cases. The solution on evaporation a reduction of volume gives deep pink coloured crystals of 2,2'-bipyridil and 1-10 phenonthroline adduct.

Attempts were done to obtain adducts of amino acid but the original crystals of $Ni\ L_2X_2$ complexes reverse back.

2.9 Physical and Chemical Properties

All the Schiff base complexes are micro-crystalline or powdery solids and are sparingly soluble in ethanol, methanol and the solubility is moderate in boiling solvents. The metal complexes are insoluble in water. The complexes start decomposing before melting.

2.10 Elemental Analysis

The metal complexes were analysed for their metal content by wet ashing with perchloric acid as well as by ashing of metal complexes in silica crucible and dissolving resulting oxide residue in nitric or perchloric acid. The resulting solutions were made upto the mark in volumetric flask and were subjected to appropriate colorimetric methods.

ion	Colorimetric method
Cu^{++}	Bicyclohexanone-oxalyldihydrazone
Ni^{++}	DMG after the oxidation with Bromine
Co^{++}	Nitroso-R-salt
Cr^{+++}	1,5-diphenylcarbazide
Mn^{++}	Oxidation to MnO_4
Zn^{++}	Dithizone
Cd^{++}	Dithizone

Nitrogen was estimated by using Kjeldahl method [ ]. Sulphur [11] content was determined by Schoniger flask method.

Molecular [11] weights were determined by using Rast's method by using sublimed pure camphor melting at 175 - 76°C [12].

2.11 Electronic Absorption Spectra

Electronic absorption in refluctance mode were recorded on Hitachi ratio recording double beam fully computerised UV-Vis-NIR absorption spectrophotometer model 330.

Total internal refluctance attachment model working upto 1500 nm in refluctance mode was used. The complex was finely powdered in agali mortar and pested and was filled in hoiders specifically fabricated by us for powdered samples. Wherever necessary the samples were diluted by grinding with pure $BaSO_4$. Inner surface of reflection sphere was given fresh coating of MgO by using burning Mg ribbon.

Solution spectra were recorded on Shimdzudouble beam UV-spectrophotometer model 240 using 10 mm matched pairs of silica cuvettes. The visual appearance of complexes gave a clue regarding asymmetry. The spectral data obtained as above was subjected to the band fitting programme given by Konig [13] and the band positions were properly adjusted, extremely weak or long wavelength band missing in recorded spectra were calculated and reported (As given in details in chapter III). The ligand field parameters and inter electronic repulsion parameters were calculated [14].

2.12 Vibrational Spectra

Vibrational spectra in KBr pallets of the complexes were recorded on Perkin Elemer ratio recording double beam dispersive optics infrared absorption spectrophotometer model 783 over the range 4000 to 200 cm^{-1}. The band positions were accurately determined by referring to a standard reference line of the polystyrene film (1601.4 cm^{-1}).

2.13 Magnetic Susceptibility Measurement

The paramagnetic susceptibility values of the transition metal complexes were determined by using a magnetic susceptibility unit built in your laboratory. It consisted of an Alcomax UK make permanent alnico magnet of 7000 gauss strength at one inch gap. Soft iron pole-pieces of conical shape were used to reduce the pole gap to 10 mm. An Achme screw system was used for raising or lowering the magnet. Thin uniform bore glass tubes with silver stirrups were used for filling the complex. The tube was suspended by thin platinum wire to a hook below a pan of a chainomatic analytic balance mounted above. The magnetic measurements were done at room temperature. The instrument was calibrated by using standard calibrants, mercury tetracyanocobaltate, tris-ethylenediamine nickel thiosulphate and copper sulphate. Diamagnetic corrections were applied using Pascal's constants [15].

2.14 Thermal Analysis

Thermal analysis was carried out by using TGA equipment fabricated in our laboratory. Since most of the metal complexes gave the structural information below 400°C our study hardly surpassed the temperature of 500°C. In most cases the resultant solid was simple metal oxide. This was confirmed by separately heating the weighed quantity of the complex in silica crucible to 700°C and by further analysis of metal oxide residue by using atomic absorption spectrometry after disolution of residue in perchloric acid. Since our home made TGA unit required large quantity of sample DTA was not taken. The balance consisted of a long cylindrical manifold of borosilicate glass on which a canthol wire furnace was wound. The upper part was furnished with several hooks of silica fiber of 0.5 mm diameter and a double hook silica fiber spring to which a platinum bucket was hung by using suitable lengths of silica hooks. Chromel-allumel thermocouple was fixed in side the chamber and it was connected through a voltage amplifier to a 4$\frac{1}{2}$ digit multimeter of Aplab make. Amplification factor was so selected and set so as to read directly the temperature of the furnace with an accuracy of ± 1°C. Extension of the spring was measured by using research grade Osaw make cathetometer with least count of 0.001 mm. The uniformity of extension of spring was tested by hanging in several 5 mg platinum wire riders at room temperature. The glass manifold has inlet and outlet for gas, the other junction of thermocouple dipped in ice bath. Thermocouple was connected with compensating leads. To minimise spurious e.m.f. by minimum number of metal junctions were involved and wherever possible such junctions were kept away from radiant heat. The instrument was often checked by using standard substance like crystalline $CuSO_4$ and the profile of the thermogram was compared with the standard profile [16].

2.15 Electrical Conductivity

Specific conductivities of the solutions of complexes were measured by using Toshniwal make digital conductivity meter model specially using Philips conductivity cell with cell constant. The complexes were dissolved in pure acetone and conductivity measured at room temperature. The concentration of solution were measured by weighing residual complex obtained by evaporation of solvent and weighing. Specific and molecular conductivities were calculated using standard method [17].

References

1. A.I. Vogel. Practical Organic Chemistry,
Third Edition, p. 383 (1951).
2. A.I. Vogel. Practical Organic Chemistry,
Third Edition, p. 403 (1951).
3. W.E. Eilbeck, F. Holmes and A.E. Underhill,
J. Chem. Soc. (A) 1977, 757-61.
4. A.I. Vogel. Practical Organic Chemistry,
Third Edition, p. 653 (1951).
5. A.I. Vogel. Practical Organic Chemistry,
Third Edition, p. 163 (1951).
6. L.E. Marclu. Inorganic Synthesis, vol. II, p. 10.
McGraw-Hill book Co., New York (1946).
7. J. Charalambous and M.J. Kensett.
Inorganica Chimica Acta, 16 (1976) 213- 7.
8. J. Charalambous, P. Maple, N.A. Nasset and F.B. Taylor.
Inorganica Chimica Acta, 26 (1978) 107
9. S. Kitagawa, T. Murakami and M. Hatana.
Inorganic Chemistry, vol. 14 (1975) 2347.
10. L. Menabue, G. Pellacani and M. Saladini.
Inorganic Chemica Acta, 32 (1979) 149
11. F.G. Mann and B.C. Sauders.
Practical Organic Chemistry (Longman) (1970).
12. A.I. Vogel. Practical Organic Chemistry,
Third Edition, p. 1037 (1951).
13. E. Konig. Structure and bonding. 9. 175 (1971).

14. A.E.P. Lever. Inorganic Electronic Spectroscopy (Elsevier). volume 33 (1984).

15. G. Marr and B.W. Rockett. Practical Inorganic Chemistry, p. 367 (1972).

16. Duval (Clement). Inorganic Thermogravimetric Analysis, Edition-2 (1963).

17. T.J.V. Findlay and G.H. Aylward. Chemical data book, Edition 2 (1968).