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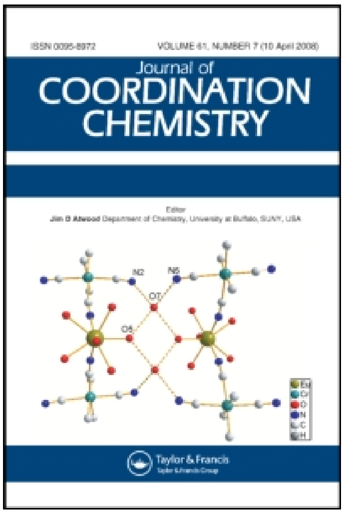

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SYNTHESIS AND CHARACTERIZATION OF AMINO ALCOHOL COMPLEXES

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Thirty-eight amino alcohol complexes were prepared and analyzed in the mole ratios 1 : 1, 1 : 2 and 2 : 3 (M : L). The IR spectra proved that coordination occurs *via* oxygen nitrogen atoms of the ligands. The nujol mull electronic absorption spectra and the room temperature magnetic moment values proved that the complexes are of O_h and T_d geometry. All complexes, except those of Zn^{II}, Cd^{II} and Hg^{II} are high spin with the existence of a Cu – Cu interaction in the copper complexes. The ESR parameters are calculated including the c-bond parameter (α^2) and the fraction of 3*d* character in the Cu^{II} 3*d*-4S ground state (f^2) of the axial compressed triethanolamine complexes.

Keywords: Amino alcohol; Ethanolamine; Transition metal salts

INTRODUCTION

Metal ethanolamine complexes were the subject of many studies in the last decade [1]. These investigations arose mainly from the importance of their technical applications in different fields: buffers [2], catalysts [3], inhibitors [4], ion exchangers [5], and additives in building materials [6], electroplating [7], and dyes [8]. In spite of extensive studies on the structural chemistry of ethanolamine complexes from our laboratory [9 – 15], the subject needs more investigation. The following paper gives spotlight on the structural

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chemistry of some prepared transition metal amino alcohol complexes by means of different spectral measurements focusing on isomerization of Co^{III} complexes.

EXPERIMENTAL

Synthesis of Ethanolamine Complexes

The solid metal-ethanolamine complexes were prepared by mixing the required molar amount of the metal salt, (Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, Cd^{II} and Hg^{II}), dissolved in minimum water with the calculated amount of the ligand saturated with ethanol. The mixture was retluxed for about 5 minutes. The complexes precipitated and were filtered, then washed several times with a mixture of EtOH-H_2O and dried in a desiccator over anhydrous $CaCl_2$. The metal ion contents were determined by complexmetric titration procedures [16]. The halogen content was determined by titration with a standard $Hg(NO_3)_2$ solution using diphenyl carbazone indicator [17]. The sulphate content was determined gravimetrically as $BaSO_4$ [17]. The analytical data, color and mp of the prepared complexes are collected in Table I.

TABLE I Analytical data, colour and m.p (°C) of metal ethanolamine complexes

			%Found (%Expected)		
Complex	*Colour*	*m.p/°C*	*M*	*Cl*	*SO_4*
$Co(MEA)C1_2 \cdot 2H_2O$	Pale violet	280	25.6 (25.9)	30.9 (31.2)	–
$Co(MEA)_2Cl_2$	Green	> 300	23.3 (23.3)	28.0 (28.1)	–
$Co(DEA)Cl_2$	Green	190	24.9 (25.0)	30.1 (30.2)	–
$Co(TEA)C1_2 \cdot H_2O$	Pale brown	285	19.8 (19.8)	23.9 (23.9)	–
$Co(TEA)_2Cl_2 \cdot 2H_2O$	Violet	265	12.6 (12.7)	15.0 (15.3)	–
$Co_2(TEA)_2C1_4$	Reddish brown	200	21.1 (21.1)	25.3 (25.4)	–
$Co_2(TEA)_3C1_4$	Dark brown	260	16.5 (16.6)	19.9 (20.0)	–
$Ni(MEA)Cl_2 \cdot 2H_2O$	Pale green	< 300	25.8 (25.9)	31.2 (31.3)	–
$Ni(MEA)_2Cl_2$	Pale green	> 300	23.4 (23.3)	28.1 (28.2)	–
$Ni(DEA)Cl_2 \cdot 2H_2O$	Pale green	> 300	21.5 (21.6)	26.0 (26.2)	–
$Ni(DEA)_2Cl_2$	Pale green	> 300	17.0 (17.2)	20.6 (20.9)	–

TABLE I (Continued)

			%Found (%Expected)		
Complex	*Colour*	*m.p/°C*	*M*	*Cl*	*SO_4*
$Ni(TEA)Cl_2 \cdot 2H_2O$	Pale green	> 300	18.5 (18.6)	22.4 (22.5)	–
$Ni(TEA)_2C1_2$	Pale green	> 300	13.5 (13.7)	16.5 (16.6)	–
$Cu(MEA)C1_2 \cdot 2H_2O$	Bluish green	159	27.3 (27.4)	30.5 (30.6)	–
$Cu(MEA)_2Cl_2$	Blue	171	24.6 (24.7)	27.5 (27.6)	–
$Cu(TEA)Cl_2 \cdot 2H_2O$	Pale green	141	19.8 (19.8)	22.2 (22.2)	–
$Cu(TEA)_2Cl_2$	Pale green	162	14.6 (14.6)	16.4 (16.4)	–
$Zn(MEA)SO_4 \cdot 2H_2O$	White	< 300	25.2 (25.3)	–	37.1 (37.1)
$Zn(MEA)_2SO_4$	White	> 300	23.0 (23.0)	–	33.8 (33.8)
$Zn(MEA)Cl_2 \cdot 2H_2O$	White	> 300	28.0 (28.0)	30.3 (30.4)	–
$Zn(MEA)_2Cl_2$	White	> 300	25.2 (25.3)	27.5 (27.4)	–
$Zn(DEA)_2C1_2$	White	> 300	18.8 (18.8)	20.4 (20.5)	–
$Zn(TEA)C1_2 \cdot 2H_2O$	White	> 300	20.3 (20.3)	22.0 (22.0)	–
$Zn(TEA)_2C1_2$	White	290	15.0 (15.0)	16.3 (16.3)	–
$Cd(MEA)SO_4$	White	> 300	41.1 (41.1)	–	35.5 (35.6)
$Cd(MEA)_2SO_4$	White	265	34.3 (34.4)	–	29.0 (29.0)
$Cd(DEA)SO_4$	White	225	35.8 (35.8)	–	30.5 (30.6)
$Cd(DEA)_2SO_4$	White	200	26.8 (26.8)	–	22.9 (22.9)
$Cd(TEA)SO_4$	White	220	31.4 (31.4)	–	26.8 (26.8)
$Cd(TEA)_2 \cdot SO_4$	White	> 300	22.1 (22.2)	–	18.9 (18.9)
$Hg(MEA)_2Cl_2$	White	290	50.9 (50.9)	18.1 (18.0)	–
$Hg(DEA)C1_2$	White	220	53.2 (53.2)	18.8 (18.8)	–
$Hg(DEA)_2C1_2$	White	200	41.6 (41.6)	14.7 (14.7)	–
$[CoL_2(H_2O)_2]Cl$	Purple	> 300	20.4 (20.3)	12.3 (12.5)	–
$[CoL(HL)(H_2O)_2]C1_2$	Red	> 300	20.2 (20.0)	21.9 (22.2)	–
$[Co(HL)_2(H_2O)_2]C1_3$	Brown	> 300	16.0 (16.1)	29.8 (29.9)	–
$[Co(HL)_2(H_2O)Cl]Cl_2$	Deep Purple	> 300	16.9 (17.0)	31.6 (31.5)	–
$[Co(HL)_2C1_2]C1_2$	Green	> 300	17.9 (18.0)	33.2 (33.3)	–

HL = MEA.

Ultraviolet and visible spectra were recorded using a Perkin Elmer spectrophotometer model Lambda 4B covering the wavelength range 190 – 900 nm. The complexes were measured in Nujol mull, following the method described by Lee *et al.* [18]. The IR spectra were recorded using a Perkin Elmer spectrophotometer model 1430 covering the frequency range 200 – 4000 cm^{-1}. The molar magnetic susceptibilities, corrected for the diamagnetic component using Pascal's constants, were determined at room temperature (298°K) using Farady's method [19]. The ESR spectra were recorded at 100 KHz modulation and 10 G modulation amplitude on a varian E-9 Spectrometer. The field was calibrated with a powder sample of DPPII ($g = 2.0037$) [20].

RESULTS AND DISCUSSIONS

Table II lists the IR absorption peaks of MEA. Characteristic bands due to ν_{OH}, ν_{NH_2}, ν_{CH_2}, δ_{OH}, δ_{CH_2} ν_{CN}, τ_{CH_2} ν_{C-C} and γ_{OH} are assigned. The low intensity of the wagging vibration band of NH_2 supports the existance of an internal hydrogen bond in MEA [21]. The broadness of all vibrations of the —OH groups is mainly due to a strong intermolecular hydrogen bond. The ν_{OH} of MEA at a lower frequency, 3450 cm^{-1}, compared to the free-OH group, 3610 cm^{-1} suggests a polymeric chain structure. A similar conclusion is valid in the DEA and TEA compounds.

Structural Chemistry of Cobalt Complexes

MEA gives two Co^{II} complexes; pale violet $Co(MEA)Cl_2 \cdot 2H_2O$ and green $Co(MEA)_2Cl_2$. The IR spectra of both complexes indicated coordination through both nitrogen and oxygen sites, where MEA acts as a bidentate ligand. The nujol mull electronic spectra and room temperature magnetic moment values of the two complexes gave the following: 1. The pale violet complex gave two identified bands at 430 and 536 nm and a room temperature μ_{eff} of 4.39 BM. 2. The green complex gave bands at 431 and 647 nm and a room temperature magnetic moment value of 4.63 BM. 3. Both complexes are insoluble in water and non-conducting, *i.e.*, the chloride ions are coordinated. 4. The

TABLE II IR spectral data of ethanolamine compounds

Compound	ν_{OH}	$\nu^{as}_{CH_2}$	$\nu^{s}_{CH_2}$	δ_{OH}	δ_{NH}	δ_{CH_2}	γ_{CH_2}	σ_{NH_2}	ν_{C-OH}	$TCH_2 \cdot C-C$	$TNH_2\ OHNH$	$\rho CH_2 \cdot CH$	γ_{OH}
MEA	3450	2950	2900	1610	–	1500 1480 1450	1390	1160	1120 1080 1040	980	880	–	650
DEA	3500 3350	2980	2900	1620	1600 1570	1490 1450	1390 1300	–	1130 1075 1030	960	880	–	650
TEA	3380 3340 3200	2900	2800	1630	1600	1460 1450	1390 1280 1240 1220	–	1130 1060 1030	–	890	870	650

detected bonds are due to ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ and ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ transitions, respectively of O_h geometery [22].

Diethanolamine gave a 1 : 1 $Co(DEA)Cl_2$ complex. Its IR spectrum exhibits charactaristic band at $3471\,cm^{-1}$ corresponding to ν_{OH} overlapped with ν_{NH} vibrations, and a strong band at $1610\,cm^{-1}$ due to δ_{OH} and δ_{NH} vibrations. The two weak bands at 1484 and $1448\,cm^{-1}$ are due to δ_{OH} and δ_{NH} vibration. Those at 1120 and $1045\,cm^{-1}$ are due to ν_{C-C} and τ_{CH_2} vibrations, respectively. The two bands at 994 and $855\,cm^{-1}$ are assigned to ν_{C-N} overlapped with ρ_{CH_2} vibration. The, sharp bands at 658,593 and $510\,cm^{-1}$ are for γ_{OH} vibrations. The band at $386\,cm^{-1}$ is assigned ν_{Co-O}. Three distinctive bands due to ν_{Co-Cl} vibrations are at 343,317 and $298\,cm^{-1}$. The band at $493\,cm^{-1}$ is due to ν_{Co-N}. The observed data suggest that coordination occurs through nitrogen and oxygen.

The nujol mull electronic absorption spectra of the green $Co(DEA)C1_2$ complex gave a band at 700 nm correspondingto ${}^4A_2 \rightarrow {}^4T_{1g}(P)$, witch with its room temperature magnetic moment value of 4.17 BM, indicated T_d geometry [22].

Four cobalt-triethanolamine complexes were obtained on complexation of TEA with Co^{II}, with the formulas $Co(TEA)Cl_2 \cdot H_2O$, $Co(TEA)_2Cl_2 \cdot 2H_2O$, $Co_2(TEA)_2Cl_4$ and $Co_2(TEA)_3Cl_4$. The IR spectra of the complexes, Table III, indicated that coordination was through both nitrogen and oxygen sites, as proved by the appearance of ν_{Co-O} and ν_{Co-N} bands. The presence of ν_{Co-Cl}, $293\,cm^{-1}$ indicated that the chlorides are in the innersphere of the complex, in agreement with its insolubility and non-conducting behavior. The nujol mull electronic absorption spectra of these complexes gave two bands for each at about 432 and 647 nm, assigned to ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ and ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ transitions, respectively, indicating O_h geometry [22]. The data are supported by room temperature magnetic moment values for these complexes, Table IV, of 4.15 and 4.14 BM, respectively.

The stretching vibrational bands due to ν_{Co-N}, ν_{Co-O} and ν_{Co-Cl} were assigned at (428, 409); (389, 369) and (344, 316) cm^{-1}, respectively. The nujol mull electronic absorption spectra of the two complexes gave two bands at 539 and 898 nm for $Co_2(TEA)_2Cl_4$ and 539 and 878 nm for $Co_2(TEA)_3Cl_4$, indicating O_h geometry. The effective room temperature magnetic moment values of 1.89 and 1.85 BM, respectively, are consistent with existence of molecular association in O_h geometry [23].

TABLE III IR spectral data of cobalt complexes

Complexes	ν_{OH}	$\nu^{as}_{CH_2}$	$\nu^{s}_{CH_2}$	δ_{OH}	δ_{NH}	δ_{CH_2}	ν_{C-O}	$\tau CH_2 \cdot C-C$	$\rho CH_2 \cdot C-N$	γ_{OH}	ν_{M-N}	ν_{M-O}	ν_{M-Cl}
$Co(MEA)Cl_2 \cdot 2H_2O$	3450	2952	2900	1354	1625	1483	1047	733	1117	–	421	367	343
$Co(MEA)_2Cl_2$	3446	2951	2900	1335	1625	1482	1059	732	1117	–	411	389	340
$Co(DEA)Cl_2$	3471	2950	2900	1330	1610	1484	1048	720	994	658	493	386	343
						1448			855	593			312
										510			298
$Co(TEA)Cl_2 \cdot H_2O$	3470	2951	2900	1330	–	1491	1050	718	997	670	498	389	341
						1450			850	597	389		293
										530			
$Co(TEA)_2Cl_2 \cdot 2H_2O$	3456	2950	2900	1330	–	1490	1049	749	998	665	496	387	343
						1449			849	590			293
										529			
$Co_2(TEA)_2Cl_4$	3450	2950	2900	1330	–	1492	1040	748	995	670	428	389	344
						1450			845	590			
										530			
$Co_2(TEA)_3Cl_4$	3453	2950	2900	1330	–	1490	1050	741	991	670	409	369	316
						1451			849	590			
										530			

TABLE IV Electronic spectra (nujol) and magnetic susceptibility measurements (298°K)

Complex	*Electronic spectra/nm.*	*μ/B.M*
$Co(MEA)Cl_2 \cdot 2H_2O$	430,536	4.39
$Co(MEA)_2Cl_2$	431,647	4.63
$Co(DEA)Cl_2$	700	4.17
$Co(TEA)Cl_2 \cdot H_2O$	431,647	4.15
$Co(TEA)_2Cl_2 \cdot 2H_2O$	432,647	4.14
$Co_2(TEA)_2Cl_4$	539,898	1.89
$Co_2(TEA)_3Cl_4$	539,878	1.85
$Ni(MEA)Cl_2 \cdot 2H_2O$	430,464	2.81
$Ni(MEA)_2Cl_2$	430,646	3.27
$Ni(DEA)Cl_2 \cdot 2H_2O$	431,647	2.28
$Ni(DEA)_2Cl_2$	430,644	3.47
$Ni(TEA)Cl_2 \cdot 2H_2O$	430,664	3.34
$Ni(TEA)_2Cl_2$	430,644	3.32
$Cu(MEA)Cl_2 \cdot 2H_2O$	455,649,895	1.41
$Cu(MEA)_2Cl_2$	455,649,895	1.44
$Cu(TEA)Cl_2 \cdot 2H_2O$	454,647,893	1.43
$Cu(TEA)_2Cl_2$	455,649,893	1.44

Isomerization of Cobalt Complexes

The isomerization of cobalt-monoethanolamine complexes was tested as follows:

(i) Air was passed through a solution of 10 g MEA and 17.7 g $CoCl_2 \cdot 6H_2O$ in 120 mL H_2O in presence of 0.1 g suspended charcoal for 13 hours. The mixture was heated to dissolve the formed precipitate followed by filtration to remove the charcoal. The solution was evaporated 50 mL, where complex was precipitated as purple crystals, filtered, washed with ethanol and dried in *vacuo* at 80°C. The analytical data indicate formation of $CoL_2Cl \cdot 2H_2O$ I, where HL = MEA.

The complex gave a conductivity value of a 1:1 electrolyte ($\Lambda_\infty = 90$ S $mol^{-1}cm^2$). The nujol mull electronic absorption spectra of this complex, Table V, gave three bands at 380, 438 and 520 nm. The doublet bands of the lower energy absorption ($A_{1g} \rightarrow T_{1g}$ in O_h symmetry), suggest a *trans* configuration. The IR spectra of this complex, Table VI, indicated that coordination of MEA occurs through N- and O-sites, with the presence of well characterized bands due to ν_{Co-N} and ν_{Co-O} at 502 and 490 cm^{-1}. The bands at 800 and 541 cm^{-1} are due to rocking of coordinated water. All studies showed that the purple complex is *trans* $[CoL_2(H_2O)_2]Cl$. The

TABLE V Nujol electronic spectral data for Co^{III} isomers

Complex	*Electronic spectra* (*nm*)
$[Co(L_2)(H_2O)_2]Cl$	380,438,520
$[CoL(HL)(H_2O)_2]Cl_2$	370,434,560
$[Co(HL)_2(H_2O)_2]Cl_3$	370,435,580
$[Co(HL)_2(H_2O)Cl]Cl_2$	370,526
$[Co(HL)_2Cl_2]Cl$	370,435,588

HL = MEA.

overall oxidation process can be represented as:

$$2CoCl_2 + 4HL + 3H_2O + 1/2\ O_2 \longrightarrow 2[CoL_2(H_2O)_2]Cl + 2HCl$$

(ii) 1 g of the purple *trans*-$[CoL_2(H_2O)_2]Cl$ complex was dissolved in 50 mL 0.1 M HCl where an orange brown solution formed, that was evaporated under a stream of air giving a purple oil. The latter was dissolved in a small amount of water and precipitated as red powder on addition of ethanol.

Another method could also be used to prepare the red complex, with 0.25 g of the *trans*-$[CoL_2(H_2O)_2]Cl$ complex dissolved in 1:1 HCl (25 mL conc HCl and 25 mL H_2O). The mixture was evaporated to dryness with a stream of air where a red complex was separated rapidly, then washed with ethanol and dried in *vacuo* at 80°C.

Analytical data of the red complex indicated formation of $CoL(HL)Cl_2 \cdot 2H_2O$ II. This complex had a conductivity value for a 1:2 electrolyte in aqueous solution ($\Lambda_\infty = 226\,S\,mol^{-1}\,cm^2$). The nujol mull electronic absorption spectrum of this complex, Table V, gave three bands at 370, 434 and 560 cm^{-1} indicating *trans* O_h geometry. The IR spectra of $CoL(HL)Cl_2 \cdot 2H_2O$, Table VI, indicated that MEA is bidentate through N- and O-sites. The ν_{Co-N}, ν_{Co-O} and rocking vibrations of coordinated water were assigned. The equation which represents the previous transformation can be written as:

$$[CoL_2(H_2O)_2]Cl + HCl(0.1M) \longrightarrow [CoL(HL)(H_2O)_2]Cl_2$$

(iii) 0.25 g of either $[CoL_2(H_2O)_2]Cl$ or $[CoL(HL)(H_2O)_2]Cl_2$ was dissolved in 25 mL conc HCl. The acidic solution was slowly evaporated with a stream of air to give brown crystals. Which were washed with acetone and dried in *vacuo*. The analytical data implicated the formula $Co(HL)_2Cl_3 \cdot 2H_2O$; III.

TABLE VI IR spectral data of the isomeric cobalt (III) complexes, HL = MEA

Complex	ν_{OH}	$\nu^{as}_{CH_2}$	$\nu^{s}_{CH_2}$	δ_{OH}	δ_{NH}	δ_{CH_2}	$\rho_{r(H_2O)}$	$\rho_{w(H_2O)}$	ν_{C-O}	$\tau CH_2 \cdot C-C$	$\rho CH_2 \cdot C-H$	ν_{M-N}	ν_{M-O}	ν_{M-Cl}
trans($CoL_2(H_2O)_2$)Cl	3400	2951	2900	1354	1625	1480	800	541	1040	733	1116	502	490	–
trans($CoL(HL)(H_2O)_2$)Cl_2	3550 3400	2950	2900	1339	1623	1482	810	540	1046	731	1102	500	490	–
trans($Co(HL)_2(H_2O)_2$)Cl_3	3560 3400	2950	2900	1340	1622	1484	802	535	1050	730	1110	500	490	–
cis($Co(HL)_2(H_2O)Cl$)Cl_2	3554 3400	2950	2900	1342	1623	1488	805	539	1050	722	998	500	490	274
trans($Co(HL)_2Cl_2$)Cl	3550	2952	2900	1343	1626	1490	–	–	1052	718	992	504	490	335

The complex gave a conductivity value for a 1:3 electrolyte ($\Lambda_\infty = 362$ S mol^{-1} cm). The nujol mull electronic absorption spectrum, Table V, gave three bands at 370, 435 and 580 nm, indicating O_h geometry. Its IR spectrum, Table VI, indicated the bidentate nature of MEA and the presence of coordinated water. The mechanism of formation of the brown complex, III, is:

$$[CoL_2(H_2O)_2]Cl + 2HCl \longrightarrow [Co(HL)_2(H_2O)_2]Cl_3$$
$$[CoL(HL)(H_2O)]Cl_2 + HCl \longrightarrow [Co(HL)_2(H_2O)_2]Cl_3$$

(iv) 1.25 g of *trans*[$CoL_2(H_2O)_2$]Cl was dissolved in 25 mL conc HCl. The acidic solution was refluxed for 5 hours at 90°C. On addition of 100 mL ethanol and 25 mL acetone, deep purple crystals of formula $Co(HL)_2Cl_3$, IV precipitated. This complex gave the conductivity value of a 1:2 electrolyte ($\Lambda\infty = 202$ S mol^{-1} cm^2). The nujol null electronic absorption spectra of the formed complex, Table V, gave two bands at 370 and 526 nm, corresponding to O_h geometry. The non-splitting in the low absorption band typified the *cis*-cofiguration. The IR spectrum (Tab. VI) indicated that coordination of MEA to Co^{III} occurs through O- and N-sites with the presence of one water molecule and one chloride ion in the inner sphere. The ν_{Co-Cl} vibration band is at 274 cm^{-1}.

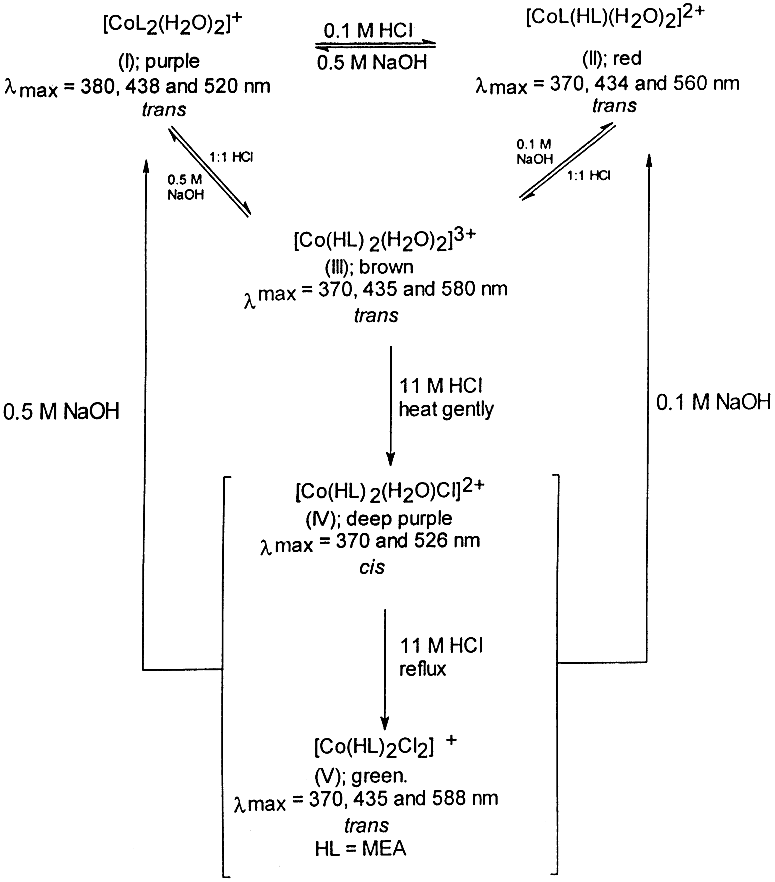
The stereochemical change of *trans*[$CoL_2(H_2O)_2$]Cl to *cis*-[$Co(HL)_2$ $(H_2O)Cl]Cl_2$ can be represented by the following equation:

$$\underset{trans}{[CoL_2(H_2O)_2]Cl} + \text{conc HCl} \xrightarrow{reflux} \underset{cis}{[Co(HL)_2(H_2O)Cl]Cl_2} + H_2O$$

(v) An acetone solution of *cis*[$Co(HL)_2(H_2O)Cl]Cl_2$ (1 g in 50 mL) was filtered. The filtrate was refluxed for 30 minutes after the addition of a mixed solvent of 1:1 ethanol–acetone (25 mL of each), and a green $Co(HL)_2Cl_3$, complex V, separated. This complex had a conductivity value for a 1:1 electrolyte ($\Lambda_\infty = 86$ S mol^{-1} cm^2) and three visible electronic absorption spectral bands at 370, 435 and 588 nm indicating *trans* O_h configuration. The IR spectrum of this complex (Tab. VI) indicated the bidentate nature of MEA with the presence of ν_{Co-Cl} at 335 cm^{-1}. The following equation represents the mode of formation of this complex:

$$cis[Co(HL)_2(H_2O)Cl]Cl_2 \xrightarrow{reflux/conc.HCl} trans[Co(HL)_2Cl_2]Cl + H_2O$$

All the complexes are in equilibria to each other depending on the acidity of the medium. The following scheme provides a summary.



Structural Chemistry of Nickel Complexes

The bidentate MEA compound gave two nickel(II) complexes: Ni(MEA)$Cl_2 \cdot 2H_2O$ and Ni$(MEA)_2Cl_2$ where the coordination occurs through nitrogen and oxygen sites. The positions of the IR bands of these two complexes, Table VII, are very close to each other especially those absorptions due to ν_{CH_2}, δ_{NH}, δ_{OH}, δ_{CH_2}, ν_{CN}, τ_{CH_2}, ν_{C-C}, ν_{Ni-N}, ν_{Ni-O} and ν_{Ni-Cl}.

The nujol mull electronic absorption spectra of Ni(MEA)$Cl_2 \cdot 2H_2O$ and Ni$(MEA)_2C1_2$ complexes gave two bands at 430 and 646 nm, respectively, indicating the O_h geometry [24] $^3A_{2g} \rightarrow ^3T_{1g}(P)$ and $^3A_{2g} \rightarrow ^3T_{1g}(F)$ transitions, respectively. Further support of the conclusion obtained from the room temperature magnetic moment values of 2.81 and 3.27 BM, respectively, to assign the O_h configuration with two unpaired electrons.

TABLE VII IR spectral data of nickel complexes

Complex	ν_{OH}	$\nu^{as}_{CH_2}$	$\nu^{s}_{CH_2}$	δ_{OH}	δ_{NH}	δ_{CH_2}	ν_{C-O}	$\tau CH_2 \cdot C-C$	$\rho CH_2 \cdot C-N$	γ_{OH}	ν_{M-N}	ν_{M-O}	ν_{M-Cl}
Ni(MEA)$Cl_2 \cdot 2H_2O$	3450	2950	2900	1355	1630	1480	1056	741	1115	661	458	385	295
Ni$(MEA)_2Cl_2$	3450	2950	2900	1340	1632	1481	1055	743	1115	650	464	389	299
Ni(DEA)$Cl_2 \cdot 2H_2O$	3500	2950	2900	1340	1605	1483	1073	742	1111	654	460	389	291
						1450			997				
Ni$(DEA)_2Cl_2$	3500	2950	2900	1340	1610	1481	1072	739	1109	661	460	389	296
						1449			1001				
Ni(TEA)$Cl_2 \cdot 2H_2O$	3500	2950	2900	1350	–	1491	1044	731	1114	666	459	388	296
						1445			991				
Ni$(TEA)_2Cl_2$	3500	2950	2900	1340	–	1487	1045	742	1116	653	460	383	297
						1451			995				

Two diethanolamine complexes were prepared, $Ni(DEA)Cl_2 \cdot 2H_2O$ and $Ni(DEA)_2Cl_2$. The IR bands due to ν_{NH}, ν_{OH}, ν_{CH_2}, ν_{CN}, ν_{CO}, τ_{CH_2}, γ_{OH}, ν_{Ni-N}, ν_{Ni-O} and ν_{Ni-Cl} are assigned, Table VII. The nujol mull electronic absorption spectra of the complexes gave two bands at 431 and 647 nm for $Ni(DEA)Cl_2 \cdot 2H_2O$ and 430 and 644 nm for $Ni(DEA)_2C1_2$, indicating O_h geometry [24], confirmed by room temperature effective magnetic moment values of 3.28 and 3.47 BM, respectively.

Two nickel triethanolamine complexes were prepared $Ni(TEA)Cl_2 \cdot 2H_2O$ and $Ni(TEA)_2Cl_2$. The fundamental IR bands, Table VII, are assigned. The nujol mull electronic absorption spectra of the two complexes gave two bands at 430 and 664 nm for $Ni(TEA)Cl_2 \cdot 2H_2O$ and 430 and 644 nm for $Ni(TEA)_2Cl_2$, to assign the O_h geometry, with room temperature μ_{eff} values of 3.34 and 3.32 BM, respectively, to indicate the presence of two unpaired electrons (Tab. IV).

In general, N^{II} in an octhedral field has the non-degenerate $^3A_{2g}$, $(t_{2g})^6(e_g)^2$, as the ground state, so no appreciable spin-orbit contribution occurred. The values above spin only may arise from slight mixing of the multiplet excited states in which the spin-orbit coupling is appreciable, due to the second Zeeman effect.

Structural Chemistry of Copper Complexes

The IR spectra of $Cu(MEA)Cl_2 \cdot 2H_2O$ and $Cu(MEA)_2Cl_2$ (Tab. VIII) proved that oxygen and nitrogen atoms are coordinated and the ν_{Cu-O} and ν_{Cu-N} bands are assigned. The appearance of ν_{Cu-Cl} bands indicated that chlorides are in the inner sphere. The nujol mull electronic absorption spectra of these complexes exhibit three bands at 455, 649 and 895 nm, due to $^2B_{1g} \rightarrow {}^2A_{1g}$, $^2B_{1g} \rightarrow {}^2B_{2g}$ and $^2B_{1g} \rightarrow {}^2E_g$ transitions, respectively, of weakly distorted O_h geometry [25]. The room temperature magnetic moment values of both complexes were 1.41 and 1.44 BM, respectively, due to the weak antiferromagnetic coupling between neighboring Cu^{II} ions, [26] through polynuclear molecules and electron pairing by a super exchange phenomenon (Tab. IV).

However, Cu^{II} gives two TEA complexes: $Cu(TEA)Cl_2 \cdot 2H_2O$ and $Cu(TEA)_2Cl_2$. The similarity between both the IR and electronic spectral data of these complexes to that of the MEA complexes indicates similar bonding and stereochemical structures. The magnetic moment values support such views.

TABLE VIII IR spectral data of copper complexes

Complex	ν_{OH}	$\nu^{as}_{CH_2}$	$\nu^{s}_{CH_2}$	δ_{OH}	δ_{NH}	δ_{CH_2}	ν_{C-O}	$\tau CH_2 \cdot C-C$	$\rho CH_2 \cdot C-N$	γ_{OH}	ν_{M-N}	ν_{M-O}	ν_{M-Cl}
$Cu(MEA)Cl_2 \cdot 2H_2O$	3450	2950	2900	1347	1576	1448	1021	718	1121	645	496	292	336
$Cu(MEA)Cl_2$	3450	2950	2900	1352	1589	1485	1009	722	1118	651	490	290	333
$Cu(TEA)Cl_2 \cdot 2H_2O$	3450	2950	2900	1347	–	1485	1021	719	1121	650	496	292	329
$Cu(TEA)_2Cl_2$	3450	2950	2900	1326	–	1485	1031	715	1195	649	425	292	325

Structural Chemistry of Zinc Complexs

MEA gives four zinc complexes: $Zn(MEA)SO_4 \cdot 2H_2O$, $Zn(MEA)_2SO_4$, $Zn(MEA)Cl_2 \cdot 2H_2O$ and $Zn(MEA)_2Cl_2$. The free sulfate ion is T_d only ν_3 and ν_4 are infrared active [27]. If the ion is coordinated to a metal, the symmetry is lowered and splitting of the degenerate modes occurs, together with the appearance of new bands in the infrared spectrum ccrresponding to Raman active bands in the free ion [27]. The lowering of symmetry caused by coordination is different for unidentate and bidentate complexes. Since both bidentate chelating and bridging sulfate groups are C_{2v}, it is possible to distinguish them from the number of S–O stretching bands.

It should be rioted that the S–O stretching frequencies of bidentate complexes [28] are higher (1211, 1176, 1075 and 993 cm^{-1}) than those of bridging complexes (995, 462, 1170 and 610 cm^{-1}).

The IR spectra of the sulfato complexes of $Zn(MEA)SO_4 \cdot 2H_2O$ and $Zn(MEA)_2SO_4$, Table IX suggest that the sulfate group is bidentate with distinctive sulfate bands at 1210, 1125, 1068 and 961 cm^{-1} assigned. In addition, the fundamental IR bands indicated that coordination with MEA occurred through both nitrogen and oxygen sites. No barids are seen for rocking vibrations of the water molecules at 650–880 cm^{-1} in case $Zn(MEA)SO_4 \cdot 2H_2O$ indicating that the water molecules are in the outer sphere. The structure of $Zn(MEA)SO_4 \cdot 2H_2O$ is suggested as T_d and that of $Zn(MEA)_2SO_4$ as O_h.

The IR spectra of $Zn(MEA)Cl \cdot 2H_2O$ and $Zn(MEA)_2Cl_2$ (Tab. IX) give bands due to stretching vibrations of Zn–N, Zn–O and Zn–Cl at 461, 388 and (344, 292) cm^{-1} in case of the $Zn(MEA)C1_22H_2O$ and 411, 318 and 294 cm^{-1} in case of $Zn(MEA)_2C1_2$, respectively. The splitting of the a Zn–Cl stretching vibration in the former complex favors a *cis*- O_h structure rather than *trans*-O_h predicted to be the structure of the latter complex. The bands at 655 and 830 cm^{-1} in $Zn(MEA)Cl_2 \cdot 2H_2O$ are due to the rocking vibrations of the water molecules suggesting that the water molecules are innersphere.

DEA gives $Zn(DEA)_2Cl_2$; its IR spectra, Table IX have split bands at 3559, 3492 and 3448 cm^{-1} corresponding to ν_{OH} and ν_{NH} stretching vibrations. Distinctive bands due to ν_{Zn-N}, ν_{Zn-O} and ν_{Zn-Cl} are assigned at 461, 388 and 344 cm^{-1}, respectively. Consequently, *trans* O_h geometry is proposed.

TEA gives two zinc complexes of formulae $Zn(TEA)Cl_2 \cdot H_2O$ and $Zn(TEA)_2Cl_2$ with characteristic IR bands at 3494 and 3447 cm^{-1}, respecively, assigned to ν_{OH} vibrations. The δ_{OH} of the free ligand is shifted to lower frequency on complexation due to Zn–O interaction.

TABLE IX IR spectral data of zinc complexes

Complex	ν_{OH}	$\nu^{as}_{CH_2}$	$\nu^{s}_{CH_2}$	δ_{OH}	δ_{NH}	δ_{CH_2}	ν_{C-O}	$\tau CH_2 \cdot C-C$	$\rho CH_2 \cdot C-N$	γ_{OH}	ν_{M-N}	ν_{M-O}	ν_{M-Cl}
Zn(MEA)$SO_4 \cdot 2H_2O$	3400	2950	2900	1551	1625	1482	1033	717	1124	630	465	381	–
Zn$(MEA)_2SO_4$	3405	2950	2900	1554	1629	1468	997	723	1125	634	420	330	–
Zn(MEA)$Cl_2 \cdot 2H_2O$	3400	2950	2900	1552	1607	1482	991	726	1112	631	461	388	344 292
Zn$(MEA)_2Cl_2$	3400	2950	2900	1552	1625	1482	990	718	1088	639	411	318	294
Zn$(DEA)_2Cl_2$	3559 3492 3448	2950	2900	1551	1615	1483	999	718	1110	639	461	388	344
Zn(TEA)$Cl_2 \cdot 2H_2O$	3494	2950	2900	1535	–	1482	1001	724	1123	635	463	425	386 290
Zn$(TEA)_2Cl_2$	3447	2950	2900	1534	–	1482	992	723	1098	629	462	432	387 286

Meanwhile the C–N bands of TEA are shifted to lower frequencies indicating a Zn–N interaction. The stretching vibrations corresponding to Zn–N and Zn–O are observed at 463 and 425 cm^{-1} for $Zn(TEA)Cl_2 \cdot H_2O$ and at 462, and 432 cm^{-1} for $Zn(TEA)_2Cl_2$. The vibrations due to ν_{Zn-Cl} are assigned at 386, 290 and 387, 286 cm^{-1} in the two complexes, respectively. No bands are shown for rocking vibrations of coordinated water molecules at 650–880 cm^{-1} for $Zn(TEA)Cl_2 \cdot 2H_2O$ indicating that the water molecules are outersphere.

Structural Chemistry of Cadmium Complexes

Two series of cadmium amino alcohol complexes: $CdLSO_4$ amid CdL_2SO_4 L = MEA, DEA or TEA are prepared. The IR spectral data of these complexes, Table X, showed that the sulfate group is bidentate and both oxygen and nitrogen sites of the organic ligand are active sites for complexation. Thus, T_d and O_h structures are suggested for $CdLSO_4$ and CdL_2SO_4, respectively.

Structural Chemistry of Mercury Complexes

Monoethanolamine gave $Hg(MEA)_2C1_2$ and its IR spectrum, Table XI gave the characteristic fundamental bands for bidentate behavior *via* nitrogen and oxygen atoms.

Two diethanolamine mercury complexes $Hg(DEA)C1_2$ and $Hg(DEA)_2Cl_2$ were prepared; their IR spectra, Table XI, suggested the bidentate behaviour of DEA and the presence of chloride in the innersphere.

Electron Spin Resonance of Copper Complexes

It is possible to meassure the c-bond parameter α^2, where α is the coefficient of the ground state d_{x2-y2} orbital, from the approximate expression [29–31]:

$$\alpha^2 = \frac{A_{\|}}{0.036} + (g_{\|} - 2.0023) + \frac{3}{7}(g_{\perp} - 2.0023) + 0.04$$

where, $A_{\|}$ is the parallel coupling constant expressed in cm^{-1}. The α^2 value for Cu^{II} complexes with tetragonal distortion lie in the range 0.63–0.84 for nitrogen donor ligands [32] and 0.84–0.94 for oxygen donor ligands [33].

Axial ligands cause changes in the equatorial band length and hence in g and A values [34]. Bonding between apical ligands and Cu^{II} occurs through interaction of the metal 4s and 4p orbitals with ligand orbitals. The presence of apical ligands introduces 4s-character in the ground state which decreases

TABLE X IR spectral data of cadmium complexes

Complex	ν_{OH}	$\nu_{CH_2}^{as}$	$\nu_{CH_2}^{s}$	δ_{OH}	δ_{NH}	δ_{CH_2}	ν_{C-O}	$\tau CH_2 \cdot C-C$	$\rho CH_2 \cdot C-N$	γ_{OH}	ν_{M-N}	ν_{M-O}
Cd(MEA)SO_4	3400	2950	2900	1551	1625	1482	1078	716	1109	639	429	366
Cd$(MEA)_2SO_4$	3450	2950	2900	1549	1629	1484	1063	715	1119	643	432	366
Cd(DEA)SO_4	3450	2950	2900	1548	1622	1480	1039	725	1112	649	437	363
Cd$(DEA)_2SO_4$	3450	2950	2900	1551	1620	1483	1038	720	1112	653	438	365
Cd(TEA)SO_4	3450	2950	2900	1549	–	1481	1047	723	1114	650	431	363
Cd$(TEA)_2SO_4$	3450	2950	2900	1546	–	1484	1044	725	1116	651	431	365

TABLE XI IR spectral data of mercury complexes

Complex	ν_{OH}	$\nu^{as}_{CH_2}$	$\nu^{s}_{CH_2}$	δ_{OH}	δ_{NH}	δ_{CH_2}	ν_{C-O}	$\tau CH_2 \cdot C-C$	$\rho CH_2 \cdot C-N$	γ_{OH}	ν_{M-N}	ν_{M-O}	ν_{M-Cl}
$Hg(MEA)_2Cl_2$	3400	2950	2900	1552	1626	1483	1047	715	1129	640	446	368	329
$Hg(DEA)Cl_2$	3400	2950	2900	1534	1625	1486	1045	715	1125	641	411	369	330
$Hg(DEA)_2Cl_2$	3400	2950	2900	1533	1626	1483	1062	715	1115	642	436	369	333

TABLE XII Room temperature ESR spectral parameters of copper-amino alcohol complexes

Complex	g_s	$g_{\vert}$	$g_{\Vert}$	$\langle g \rangle$	$10^4 A$	$10^4 A_{\vert}$	$10^4 A_{\Vert}$	$104\langle A \rangle$	G	f^2	α^2
$[Cu(MEA)(H_2O)Cl_2] \cdot H_2O$	2.15	–	–	–	100	–	–	–	–	–	–
$[Cu(MEA)_2Cl_2]$	2.13	–	–	–	125	–	–	–	–	–	–
$[Cu(TEA)(H_2O)Cl_2] \cdot H_2O$	–	2.2542	2.0262	2.178	–	22.5	225	90	0.10300	0.794	0.73
$[Cu(TEA)_2Cl_2]$	–	2.2636	2.0262	2.185	–	25.0	250	100	0.00997	0.810	0.80

the contact hyperfine interaction. Therefore, if the 4s character in the ground state is known, it is possible to know the axial field strength. In the presence of a small percentage of 4s character in the ground state, the fraction of the 3*d* character in the Cu^{II} 3*d*-4s ground state, f^2, can be determined from the following equation [30]:

$$\alpha^2 f^2 = \frac{7}{4}\left[-\frac{A_{\|}}{0.036} - \frac{A}{0.036} + \frac{2}{3}g_{\|} - \frac{5}{21}g_{\perp} - \frac{6}{7}\right]$$

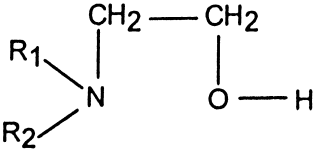
The room temperature polycrystalline X-band ESR spectral pattern of both $[Cu(MEA)(H_2O)Cl_2]\cdot H_2O$ and $[Cu(MEA)_2Cl_2]$ complexes, Table XII, gave a similar pattern. Both are isotropic with g_s values of 2.15 and 2.13 and A values of 100 and 125, respectively. The presence of ESR signals at $g = 4$ may be assigned to the spin-spin interaction between Cu atoms, suggesting the dimeric nature of both complexes. The room temperature polycrystalline X-band ESR spectral pattern of $[Cu(TEA)(H_2O)Cl_2]\cdot H_2O$ and $[Cu(TEA)_2Cl_2]$, Table XII, are axially compressed. The spectral analysis of these complexes gave two g values. $g_{\|} = 2.0262$ and 2.0263, respectively, and $g_{|} = 2.254$ and 2.263, respectively. The calculated $\langle g\rangle$ values; $\langle g\rangle = (g_{\|} + 2g_{|})/3$, are 2.178 and 2.185, respectively.

The lowest *g* value was found to be more than 2.00, consequently, the tetragonal distorted symmetry associated with a d_{x2-y2} ground state rather than a dz^2 ground state is suggested [35]. The G values for the $[Cu(TEA)Cl_2(H_2O)]\cdot H_2O$ and $[Cu(TEA)_2Cl_2]$ complexes, Table XII, are 0.103 amid 0.099 respectively, *i.e.*, very much less than 4 indicating the presence of very strong interaction between copper atoms in the solid state. The spectra have $A_{\|}$ values more than 100, Table XII, preventing the *pseudo* T_d structure around copper [29]. The calculated values of o^2 and f^2 are collected in Table XII where the metal ligand o-bond in $[Cu(TEA)Cl_2(H_2O)]\cdot H_2O$ is slightly less covalent than that of $[Cu(TEA)_2Cl_2]$. Because the copper-O bonds are less covalent than copper-N bonds. The $[Cu(TEA)_2Cl_2]$ complex has two copper-N bonds while $[Cu(TEA)(H_2O)_2C1_2]$ has only one.

The low value of f^2 in $[Cu(TEA)(H_2O)Cl_2]\cdot H_2O$ indicates a stronger axial field than in $[Cu(TEA)_2Cl_2]$.

In conclusion, the difference in the ESR spectral pattern of Cu-MEA complexes and that of Cu-TEA complexes can be attributed to steric hinderance of the TEA molecules. Steric effects weaken the bonds between the Cu^{II} non and the TEA molecules resulting in a compressed tetragonal O_h structure in the Cu-TEA complexes.

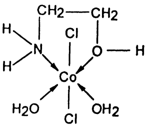
Summarized structures are given for the prepared complexes through this manuscript:



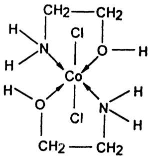
R_1=H : R_2=H : Monoethanolamine, MEA

R_1=H : R_2=CH_2CH_2OH : Diethanolamine, DEA

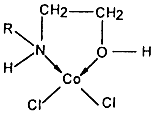
R_1=CH_2CH_2OH : R_2=CH_2CH_2OH : Triethanolamine, TEA



$[Co(MEA)(H_2O)_2Cl_2]$

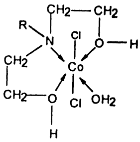


$[Co(MEA)_2 Cl_2]$

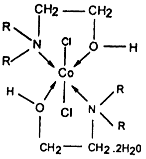


R=CH_2CH_2OH

$[Co(DEA)Cl_2]$

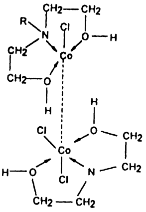


$[Co(TEA)(H_2O)Cl_2]$



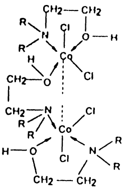
$[Co(TEA)_2Cl_2].2H_2O$

R = CH_2CH_2OH



$[Co_2(TEA)_2Cl_4]$

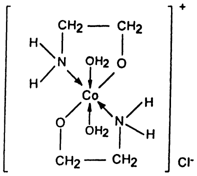
Reddish brown



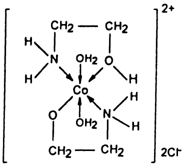
R = CH_2CH_2OH

$[Co_2(TEA)_3Cl_4]$

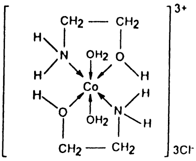
Dark brown



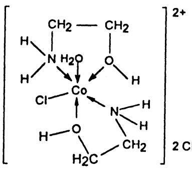
trans-$[CoL_2(H_2O)_2]Cl$, (I); HL = MEA



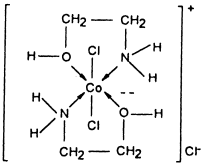
trans-$[CoL(HL)(H_2O)_2]Cl_2$, (II); HL = MEA



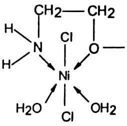
trans-$[Co(HL)_2(H_2O)_2]Cl_3$, (III); HL = MEA



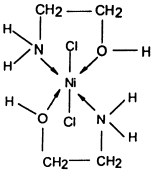
cis-$[Co(HL)_2(H_2O)Cl]Cl_2$, (IV); HL = MEA



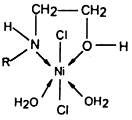
trans-$[Co(HL)_2Cl_2]Cl$, (V); HL = MEA



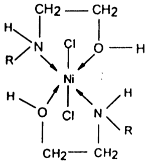
$[Ni(MEA)(H_2O)_2Cl_2]$



$[Ni(MEA)_2Cl_2]$

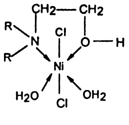


$[Ni(DEA)(H_2O)_2Cl_2]$

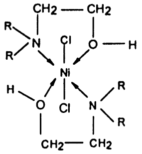


R = CH_2CH_2OH

$[Ni(DEA)_2Cl_2]$

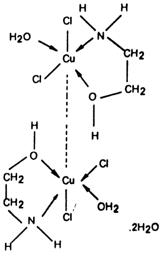


$[Ni(TEA)(H_2O)_2Cl_2]$



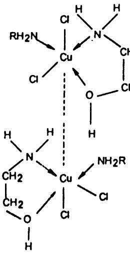
R = CH_2CH_2OH

$[Ni(TEA)_2Cl_2]$

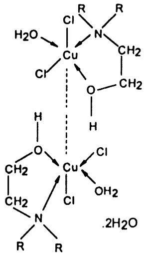


R = CH_2CH_2OH

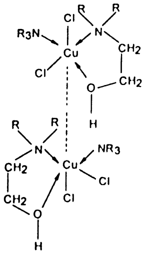
$Cu(MEA)(H_2O)Cl_2]H_2O$



$[Cu(MEA)_2Cl_2]$

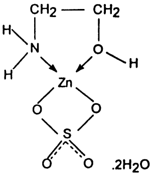


$[Cu(TEA)(H_2O)Cl_2]H_2O$

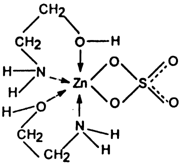


R = CH_2CH_2OH

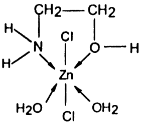
$[Cu(TEA)_2Cl_2]$



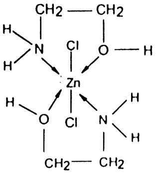
$[Zn(MEA)SO_4]H_2O$



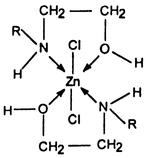
$[Zn(MEA)_2SO_4]$



$[Zn(MEA)(H_2O)_2Cl_2]$

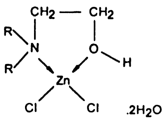


$[Zn(MEA)_2Cl_2]$

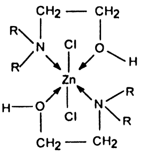


R = CH_2CH_2OH

$[Zn(DEA)_2Cl_2]$

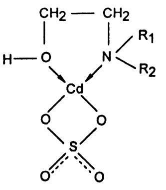


$[Zn(TEA)Cl_2]2H_2O$

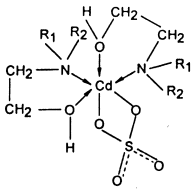


R = CH_2CH_2OH

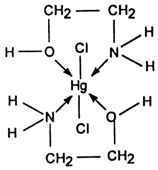
$[Zn(TEA)_2Cl_2]$



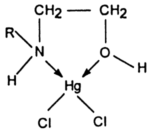
$[Cd(L)SO_4]$



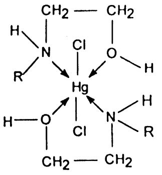
$[Cd(L)_2SO_4]$



$[Hg(MEA)_2Cl_2]$



$[Hg(DEA)Cl_2]$



$R = CH_2CH_2OH$

$[Hg(DEA)_2Cl_2]$

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