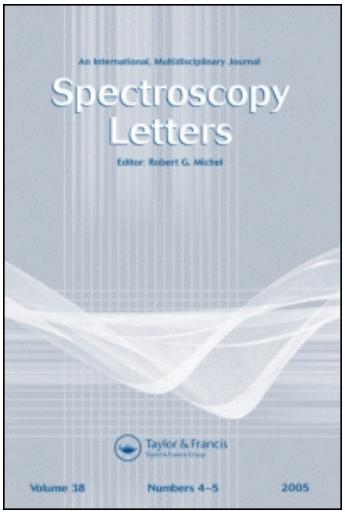

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Electron Paramagnetic Resonance and Magnetic Behaviour of Ethanolamine Complexes

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To cite this Article Masoud, Mamdouh S. , Hafez, Ahmed M. and All, Alaa E.(1998) 'Electron Paramagnetic Resonance and Magnetic Behaviour of Ethanolamine Complexes', Spectroscopy Letters, 31: 5, 901 — 911
To link to this Article: DOI: 10.1080/00387019808003270
URL: http://dx.doi.org/10.1080/00387019808003270

SPECTROSCOPY LETTERS, 31(5), 901-911 (1998)

ELECTRON PARAMAGNETIC RESONANCE AND MAGNETIC BEHAVIOUR OF ETHANOLAMINE COMPLEXES

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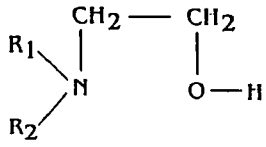
Electron paramagnetic resonance spectra of cobalt and copper complexes of ethanolamines is studied at -110 and 25 °C . The g values are determined . The magnetic susceptibilities of the cobalt , nickel and copper complexes are measured in the 4.2 - 293 °K temperature range . The Curie - Weiss constant , θ , values proved that M-M interactions appeared in the cobalt and copper complexes and didn't appear in the nickel complexes .

Introduction

Metal ethanolamine complexes were the subject of many studies in the recent decade. The origin of these invistigations arose mainly from the importance of their technical applications in different fields[1-6] . IN our laboratory, extensive studies on the structural chemistry of the ethanolamins (I) and their complexes were reported[7-18]. To give more information and deeper spot lights about the structure of the ethanolamine complexes , the ESR spectra and the magnetic behaviour at different temperatures are investigated .The ESR technique has provided detailed structural information on a variety of Paramagnetic organic and inorganic systems [19-22].



(I)

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)

Experimental

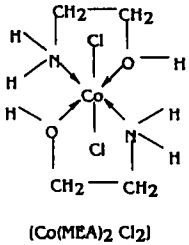
Synthesis of ethanolamine complexes:

The solid metal-ethanolamine complexes were prepared by mixing the required weight of the metal salt, (Co^{II}, Ni^{II} and Cu^{II}) dissolved in the least amount of water with the calculated amount of the ligand saturated with ethanol. The mixture was refluxed for about 5 minutes. The complexes were precipitated and filtered, then washed several times with a mixture of EtOH-H_2O solvent, then dried in a desiccator over anhydrous $CaCl_2$.The metal ion contents were determined by the usual complexmetric titration procedures[23]. The halogen content was determined titration with a standard $Hg(NO_3)_2$ solution using diphenyl carbazone as indicator[24]. The analytical data, colour and mp of the prepared complexes are collected in Table (1) .The X-band electron paramagnetic resonance spectra were recorded with a reflection spectrometer operating at 8.7 GHz in a cylindrical resonance cavity with 100 KHz modulation . The spectra of the complexes were measured in the 100-300 °K temperature range . The magnetic field was controlled with a RADIOPAN JTM-41 digital NMR-magnetometer . The g values were determined by comparison with DPPH signal . The magnetic susceptibilities of the powdered samples are measured in the 4.2-293 °K temperature range .

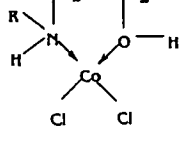
Results and discussion

ESR - spectroscopy

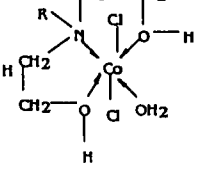
The prepared amino complexes are of tetra-and octahedral geometries [25] The structures of the cobalt complexes are given as follows :



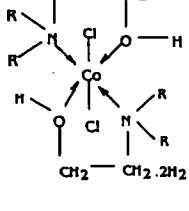
$[Co(MEA)_2Cl_2]$



$[Co(DEA)Cl_2]$



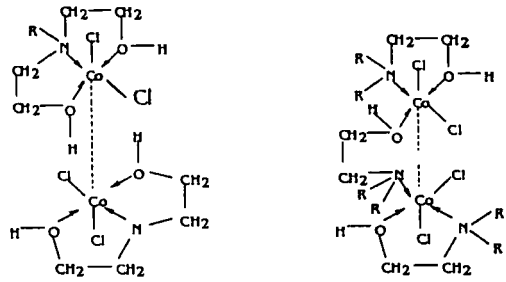
$[Co(TEA)(H_2O)Cl_2]$



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

Table (1): Analytical data, colour and m.p (°C) of metal ethanolamine complexes.

Complex	Colour	m.p/°C	% found (% expected)	
			M	Cl
$Co(MEA)_2Cl_2$	Green	> 300	23.3 (23.3)	28.0 (28.1)
$Co(DEA)Cl_2$	Green	190	24.9 (25.0)	30.1 (30.2)
$Co(TEA)Cl_2.H_2O$	Pale brown	285	19.8 (19.8)	23.9 (23.9)
$Co(TEA)_2Cl_2.2H_2O$	Violet	265	12.6 (12.7)	15.0 (15.3)
$Co_2(TEA)_2Cl_4$	Reddish brown	200	21.1 (21.1)	25.3 (25.4)
$Co_2(TEA)_3Cl_4$	Dark brown	260	16.5 (16.6)	19.9 (20.0)
$Ni(MEA)Cl_2.2H_2O$	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)
$Ni(DEA)_2Cl_2$	Pale green	> 300	17.0 (17.2)	20.6 (20.9)
$Ni(TEA)Cl_2.2H_2O$	Pale green	> 300	18.5 (18.6)	22.4 (22.5)
$Cu(MEA)Cl_2.2H_2O$	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)
$Cu(TEA)Cl_2.2H_2O$	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)

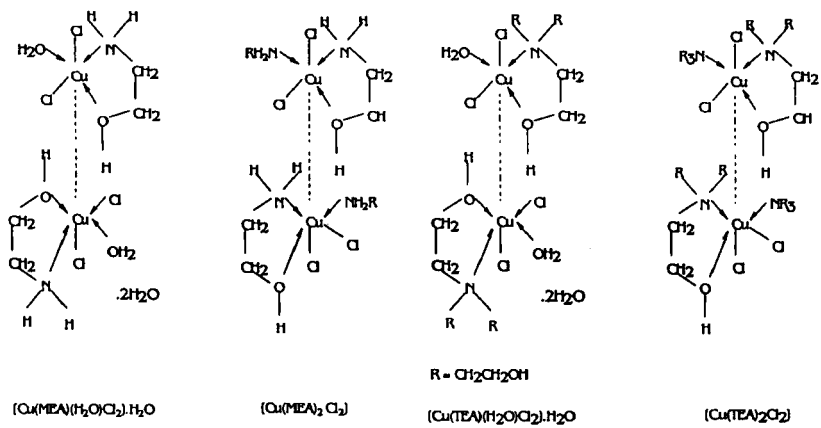


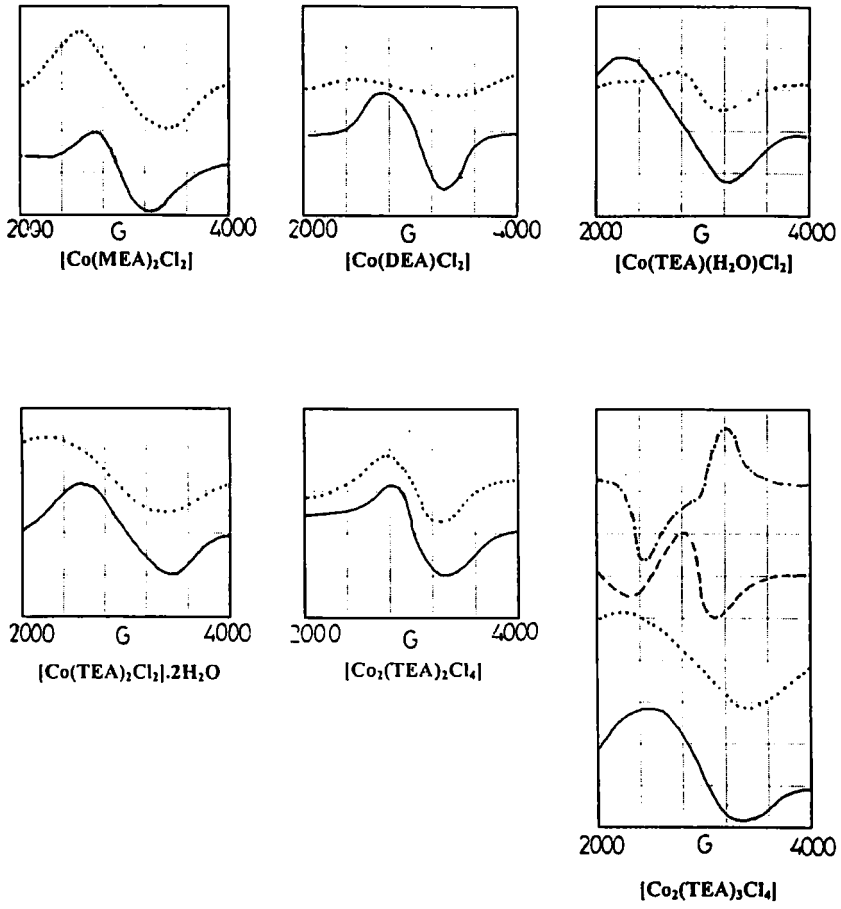
It seems that all the cobalt complexes are of octahedral geometry except the $[Co(DEA)Cl_2]$ complex , which is tetrahedral[25] .

The ground state for Oh high spin Co^{II} complexes is ^4T_1g (f) with extensive spin - spin coupling . In case of the $[Co(MEA)_2Cl_2]$, $[Co(TEA)Cl_2.H_2O]$ and $[Co(TEA)_2Cl_2).2H_2O$ Complexes , Figure (1) , with S = 3/2 and 3 orbital components in T , a total of 12 low-lying spin states result [26] . At low temperature due to spin relaxation problems , only the low-lying doublet is populated giving a singlet peak from an effective S=1/2 [26] . The ESR spectrum of $[Co_2(TEA)_2Cl_4]$ complex , Figure (1) , is of an isotropic nature at room temperature and of an anisotropic behaviour at - 110°C . This is in harmony with that the crystal field resonates at the three directions at room temperature giving the isotropic nature [26] . In the case of the $[Co_2(TEA)_3Cl_4]$ complex , the ESR spectra were studied at 240 , 140 , 25 and -110 °C , Figure (1) . The behaviour in all is of isotropic trend except that at 140 °C . Which is an isotropic . This can be explained in terms of thermal behaviour where at 140°C , the two chlorides of the complex begin to dissociate with the appearance of an anisotropic nature .

The difficulty to detect the room temperature ESR spectral pattern of the Td$[Co(DEA)Cl_2]$ complex , Figure (1) , is probably due to relaxation time problems [26]

However , the ESR spectra of this complex at -110 °C , Figure (1) , with g_e=2.2239 , indicated its isotropic nature . The ESR parameters for the cobalt complexes are collected in table (2) . However . all the prepared copper-complexes are of octahedral geometry with possible Cu-Cu. interaction as follows [25] :





.....) 25° C ——) 110 ° C ----) 140 ° C —.—) 240 ° C

Figure (1) : ESR spectra of the cobalt - ethanölámine complexes .

Table (2): ESR spectral data of cobalt- and copper- ethanolamine complexes.

Complex	T/°C	g_s	$g_\perp$	g_{11}	G	g_1	g_2	g_3	<g>
$Co(MEA)_2Cl_2$	25	2.5197	-	-	-	-	-	-	-
	-110	2.1794	-	-	-	-	-	-	-
$Co(DEA)Cl_2$	25	-	-	-	-	-	-	-	-
	-110	2.2239	-	-	-	-	-	-	-
$Co(TEA)Cl_2.H_2O$	25	2.1742	-	-	-	-	-	-	-
	-110	2.2922	-	-	-	-	-	-	-
$Co(TEA)_2Cl_2.2H_2O$	25	2.2973	-	-	-	-	-	-	-
	-110	2.2849	-	-	-	-	-	-	-
$Co_2(TEA)_2Cl_4$	25	2.2185	-	-	-	-	-	-	-
	-110	-	-	-	-	2.2255	2.0386	1.9270	2.o637
$Co_2(TEA)_3Cl_4$	240	2.1335	-	-	-	-	-	-	-
	140	-	2.5518	2.1457	0.2640	-	-	-	2.4164
	25	2.2542	-	-	-	-	-	-	-
	-110	2.3058	-	-	-	-	-	-	-
$Cu(MEA)Cl_2.2H_2O$	25	2.1250	-	-	-	-	-	-	-
	-130	2.1062	-	-	-	-	-	-	-
$Cu(MEA)_2Cl_2$	25	2.1174	-	-	-	-	-	-	-
	-130	2.0864	-	-	-	-	-	-	-
$Cu(TEA)Cl_2.2H_2O$	25	-	-	-	-	2.2200	2.1881	2.1129	2.1737
	-130	-	-	-	-	2.2394	2.1875	2.0017	2.1429
$Cu(TEA)_2Cl_2$	25	-	-	-	-	2.2206	2.1875	2.0108	2.1396
	-130	-	-	-	-	2.2376	2.1848	1.9975	2.1400

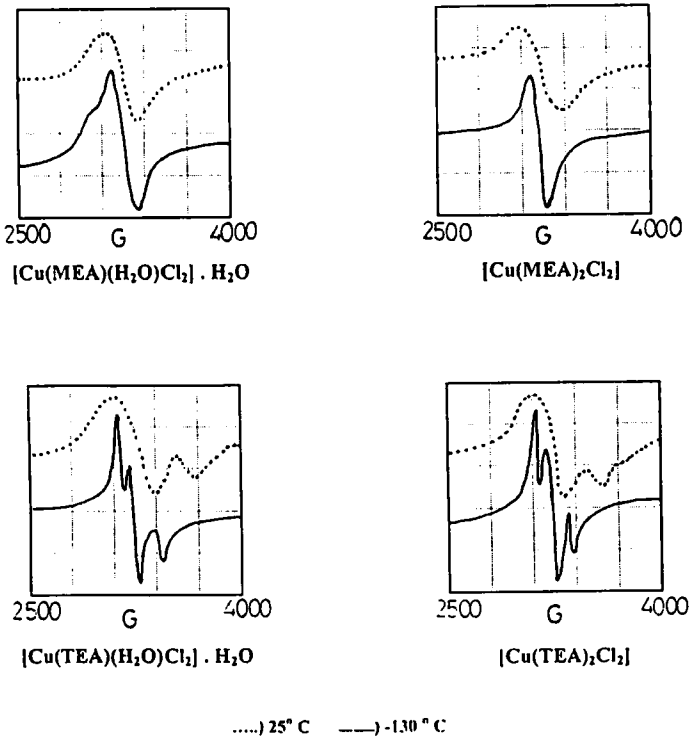


Figure (2) : ESR spectra of the copper - ethanolamine complexes .

In Octahedral field , the Cu^{II} ion has ^2Eg ground state . A large Jahn-Taller effect is expected makining observation of the ESR spectrum at room temperature is possible [26] . At both room temperature and -130 °C , the spectra of both the $(Cu(MEA)(H_2O)Cl_2) . H_2O$ and $(Cu(MEA)_2Cl_2)$ complexes , Figure (2) , are of isotropic nature . However , the spectra of the $(Cu(TEA)(H_2O)Cl_2) . H_2O$ and $(Cu(TEA)_2Cl_2)$ complexes , Figure (2) , are of an anisotropic behaviour . The difference may be due to the steric effect of the TEA molecules with the existance of a strong Cu-Cu interaction in the copper TEA complexes [25] .

Generally , the broadening of the ESR signals may occur due to spin lattice relaxation results from the interaction of the paramagnetic ions with the thermal vibrations of the lattice . Also , the spin-spin interaction results from the magnetic field that originate in the neighbouring paramagnetic ions resulted in slightly changing in the total field at each ion and the energy levels might be shifted .The distribution of the energies results , can produce broadening of the signal [26] .

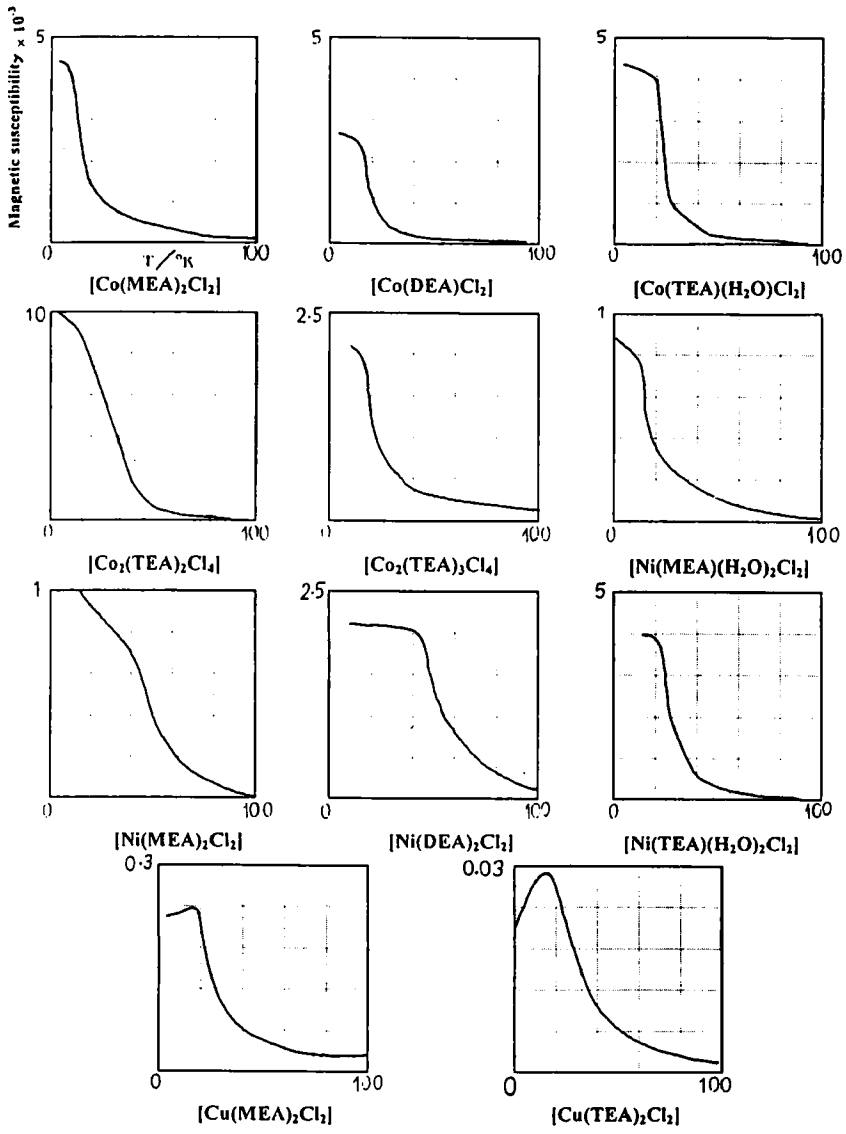


Figure (3) : Magnetic susceptibilities -T relations of the ethanolamine complexes .

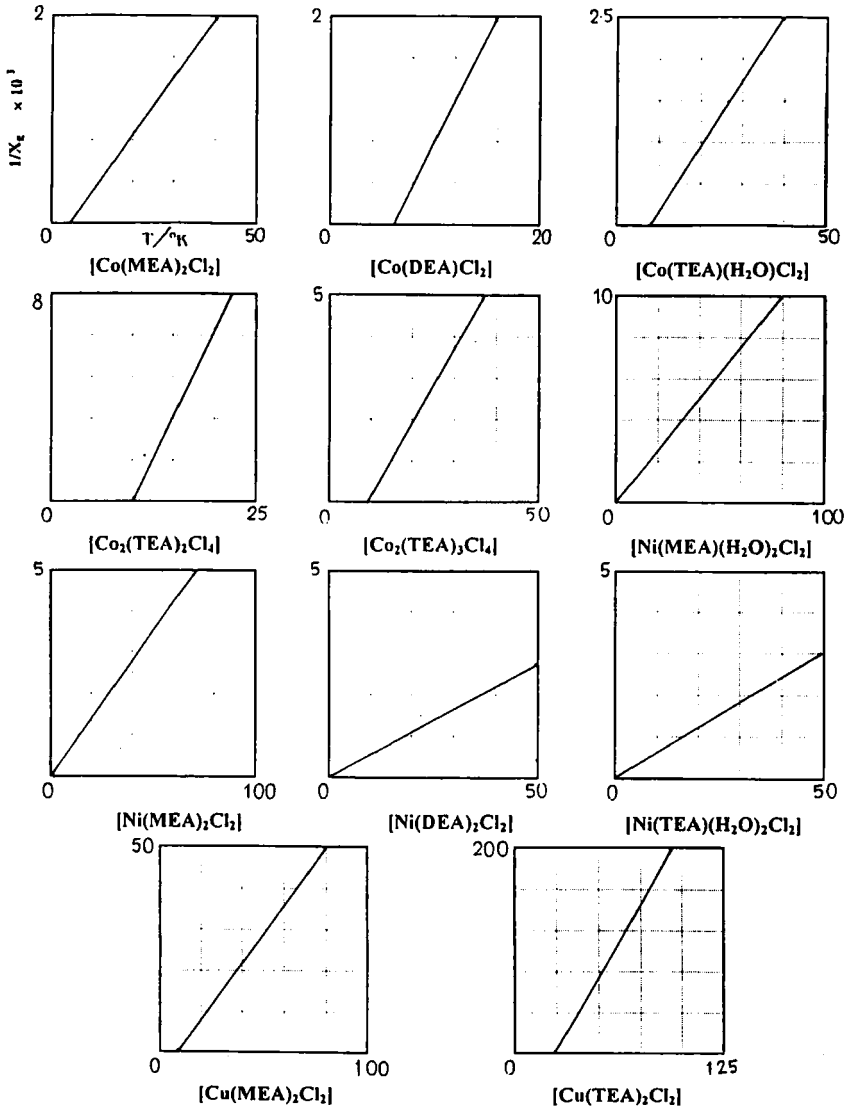


Figure (4) : $1/X_g$ -T relations of the ethanolamine complexes .

Magnetic behaviour at different temperatures

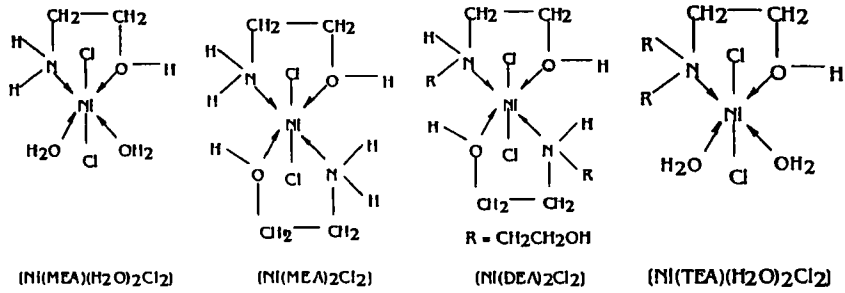
System with very weak interactions between the magnetic centers are paramagnetically diluted . Such trend is based on Curie-Weiss law [27] .

$$\overline{X}_M = \frac{C}{T-\theta}$$

Where C and θ are the Curie-Weiss constants , T is the absolute temperature and $\overline{X}_M$ is the corrected molar magnetic susceptibility . For magnetically diluted compounds , very small θ values are expected indicating the monomeric structure . If the magnetic interaction between the magnetic center is of high appreciable magnitude , high θ values are obtained and the compounds are magnetically concentrated due to metal-metal interaction between the two adjacent monomers . In general , the non-zero value of θ may indicate an intermolecular interaction operative in the solid complexes .

The magnetic susceptibility values of the cobalt complexes decrease with increasing temperature , Figure (3) , probably due the retardation of the magnetic moment arrangement . The $\frac{1}{x_g} - T$ relations gave straight lines . The θ values of the $(Co(MEA)_2Cl_2)$, $(Co(DEA)Cl_2)$ and $(Co(TEA)Cl_2.(H_2O))$ complexes are 5 , 8 and 8 °K respectively , to assign the existance of Co-Co interaction in these complexes .However both the $(Co_2(TEA)_2Cl_4)$ and $(Co_2(TEA)_3Cl_2)$ complexes are with the same θ value , 10 °K , to reflect the dimeric nature of these complexes [26] , Figure (4) .

In the case of the nickel complexes the $\frac{1}{X_g} - T$ relations gave straight lines with θ = zero indicating the monomeric nature of these complexes . The structure of these complexes were given as follows [25] :



$(Ni(MEA)(H_2O)_2Cl_2)$ $(Ni(MEA)_2Cl_2)$ $(Ni(DEA)_2Cl_2)$ $(Ni(TEA)(H_2O)_2Cl_2)$

However , the θ values of the copper complexes are found to be 13°K for $(Cu(MEA)_2Cl_2)$ and 25 °K for $(Cu(TEA)_2Cl_2)$. The high values of θ indicated strong Cu-Cu inter action in harmony with the ESR data . The high θ value of the TEA complex compared to that of the MEA complex may be due to the steric effect of the TEA molecule , This is in turn weakens the bonds between copper and TEA itself resulting in a strong Cu-Cu interaction , Figure (4) .

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Date Received: May 22, 1997
Date Accepted: April 1, 1998