Short Communication

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FORMATION OF SOME TRANSITION METAL COMPLEXES OF G-D OXIME IN SOLID STATE AND IN SOLUTION

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Preparation, isolation and characterization of some complexes derived from the interaction of Girard D-oxime with Cu(II), Zn(II), Cd(II), Zr(IV), Co(II) and Ni(II) are described. The ability of the studied metal to coordinate with the ligand in enol or keto forms was investigated by pH titration. Conductance measurements and I R spectra of the solid complexes indicate that diacetyle monoxime Girard D coordinates with Cu^{2+}, Zn^{2+} and Ni^{2+} through C=O, C=N and N-OH groups as a tridentate ligand but with CO^{2+} and Cd^{2+} coordination occurs through C=N and N-OH groups as a bidentate ligand. Formation constants of these complexes have been studied potentiometrically in aqueous medium. The formation constants increase as: Zr>Cd>Cu>Zn>Ni.

Girard's reagents and their hydrazone deravatives are well known as interesting chelating agents for most transition metal ions to form relatively stable complexes (Moussa *et al* 1970; Moussa *et al* 1973; Hafez 1974; Sigh and Sahoo 1974; Emam 1999; Emam *et al* 1999). These ligands can be used as effective metallic corrosion inhibitors (Moussa and Emam 1993; Abd El Hadi 1999). In the literature few reports on their oxime derivatives and their complexes has been published (Emam 1992). The present work is aimed to explore the formation and characterization of complexes of G-D oxime of some transition metal ions in solid state as well as in solution.

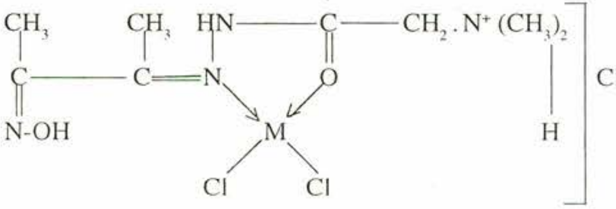
Diacetyl monoxime Girard-D(G-D) ligand was prepared according to the method reported earlier (Emam 1992). The metal chelates were prepared by refluxing equimolar of the ligand (0.1 mole) in absolute (50ml) hydrated chlorides. (0.1 mole) in 20 ml ethanol for 1-2 h. The product was filtered off, washed and dried in Vaccum desicator.

1) Isolation of pure compounds. Diacetyl monoxime Girard-D gave two types of complexes hydrated mono-ligand complexes have the stoichiometry $[MX_2(HL)]\ n\ H_2O$ for Cd, Ni and Zn $[CuX(L)]X.nH_2O$ for Cu and Zr $[(L\text{-}H).\ 3H_2O]X_3$ and di-ligand complex of the type $[MX_2(HL)_2]X_2\ nH_2O$ was obtained for Co. Where, HL=diacetyl monoxime Girard-D residue, X=halide, n=0-3, L=ligand mono basic anion and L-H ligand dibasic anion. The result of elemental analysis of the ligand and isolated complexes are shown in Table 1.

2) Conductance measurements. The molar conductance of the complexes listed in Table 1, corresponded to the number of weakly held halide group (Cotton and Wilkinson 1972).

The effect of dilution on the specific conductance of the complexes formed between diacetyl monoxime Girard-D and Cd(II), Ni(II) and Co(II) halides indicates that the ligand reacts in keto form with these cations. The ligand interacts with Zr(IV) in enol form through the liberation of highly mobile H^+ ions, since the increase in conductance of the mixture.

3) I R spectra. The I R spectrum of G-D shows a strong sharp band at 860cm^{-1} due to N-OH deformation (Ferrare 1971). A strong band was observed at 940cm^{-1} which attributed to N-O stretching frequency. A very strong band at 1700cm^{-1} and a shoulder at 1720cm^{-1} may be assigned to the stretching frequencies of free and hydrogen bonded C=O groups. In the high frequency region the ligand has a broad band (3100-3600cm^{-1}) due to OH stretching associated with inter or intramolecular hydrogen bonding. Moreover, the spectrum exhibits bands at 1640 due to n (C=N). The group that takes part in the complex formation is shifted to lower frequency by 15-25cm in the I R spectra of complexes. The interaction of the ligand in keto form by simple coordination with nickel and zinc chlorides can be represented by the structure.



4) In solution. A series of pH- titrations of the G-D oxime in aqueous solution at different temperatures (25-45°C) and ionic strength (0.1-0.5 mol dm^{-3} KCl) were carried out. The average number of proton associated with G-D oxime was calculated according to Irving-Rosstti (1954). The values of dissociation constant of the ligand. pk_a values of the ligand are reported in Table 2.

It is clear that the pk_a values decrease with increase of temperature in accordance with the weak acid nature of the ligand. On the other hand pk_a values are directly proportional to ionic strength of the medium which means that the degree of the dissociation increases with the increase of interfering ions concentration.

Potentiomertic curves of the interaction of Zr^{4+}, Cu^{2+}, Cd^{2+}, Ni^{2+} and Co^{2+} with G-D oxime in molar ratio 1:2 at 25°C and ionic strength 0.1M KCl were recorded. Analysis of these

Table 1
Elemental analysis of G-D oxime and its solid complexes

Compound	% Calculated					% Found						Molar conductance M obs.
	C	H	N	Cl	M	C	H	N	Cl	M	Charge	
$C_8H_{16}N_4O_2Cl$	40.76	6.79	23.78	15.07	-	40.12	6.43	23.28	14.95	-	-	-
[Cu Cl ($C_8H_{15}N_4O_2$) $2H_2O$] Cl	25.90	5.12	15.11	19.16	17.13	25.63	4.97	14.90	18.88	16.92	+1	112
[Cd Cl_2 ($C_8H_{16}N_4O_2$)] Cl H_2O	21.97	4.12	12.82	24.14	12.86	21.75	3.95	12.40	23.81	12.70	+1	105
[Zn Cl_2 ($C_8H_{16}N_4O_2$)] Cl $3H_2O$	22.54	5.16	13.15	24.77	15.36	22.10	4.89	12.90	24.29	15.11	+1	135
[Ni Cl_2 ($C_8H_{16}N_4O_2$)] Cl $2H_2O$	23.91	4.98	13.95	26.28	14.67	23.35	4.52	13.45	26.00	14.45	+1	156
[Co Cl_2 $(C_8H_{16}N_4O_2)_2$] 2Cl $5H_2O$	27.78	6.08	16.21	20.55	8.53	27.18	5.93	16.00	20.15	8.15	+2	218
[Zn Br_2 ($C_8H_{16}N_4O_2$)] $3ClH_2O$	18.68	4.28	10.89	6.91	12.73	18.27	4.12	10.70	6.67	12.51	+1	107
[Zr ($C_8H_{14}N_4O_2$) $3H_2O$] 3Cl	21.23	4.87	12.39	23.35	20.19	20.95	4.66	12.12	23.15	20.15	+3	319
[Co Br_2 $(C_8H_{16}N_4O_2)_2$] 2Cl $2H_2O$	26.45	4.95	15.43	9.78	8.11	26.21	4.55	15.16	9.57	8.00	+2	220
[Cd Br_2 ($C_8H_{16}N_4O_2$)] Cl $2H_2O$	17.65	3.67	10.29	6.53	20.66	17.19	3.45	10.11	6.40	20.16	+1	115

Table 2
Influence of ionic strength and temperature on ionization constants of the ligand (G-D oxime)

I, mol dm^{-3} $temp^{-1}$	Tc 25	Tc 35	Tc 45
0.1	9.75	9.64	9.51
0.2	9.83	9.69	9.57
0.4	9.89	9.74	9.61
0.8	9.94	9.80	9.66
1.0	10.00	9.85	9.71

Table 3
Over all stability constants of the G-D oxime complexes

Compound	Log β
Zr complex	12.89
Cd Br_2 complex	11.57
Cd Cl_2 complex	11.11
Cu Cl_2 complex	10.62
Co Br_2 complex	10.12
Co Cl_2 complex	9.58
Zn Br_2 complex	9.74
Zn Cl_2 complex	9.37
Ni Cl_2 complex	8.57

curves which gives the values of the formation constants of these complexes (Irving and Rosstti 1954). The values of over all stability of these complexes are gives in Table 3. The formation constants of these complexes increase in the following order: $Zr^{4+} > Cd^{2+} > Cu^{2+} > Co^{2+} > Zn^{2+} > Ni^{2+}$.

This difference in the stability of the given complexes may be due to the variation in the effective electric charge (Z) and radius (r) of the metal ion i.e. the effective ionic potential (Z^2/r) of the metal ion, which increases with increasing of stability of the complexes in the same direction (Emsley 1989).

Key words: Transation metal, G-D oxime complexes.

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