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Zn^{II}, Cd^{II}, Hg^{II} Complexes with Diethylenetriamine Synthesis and Properties

G. Cova, D. Galizzioli, D. Giusto, and F. Morazzoni

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By reaction of MX_2 (M = Zn, Cd, Hg; X = NO_3^-, ClO_4^-, SCN^-, Cl^-, Br^-, I^-, CN^-) with Dien (Diethylenetriamine) two series of compounds, $MDienX_2$ and $[MDien_2]X_2$ have been isolated. From I.R. spectroscopic data and conductivity measurements $MDienX_2$ appear to be pentacoordinated and $[MDien_2]X_2$ hexacoordinated, with diethylenetriamine acting as a tridentate ligand. Onsager's plots are reported and drawn using conductivity measurement data.

Introduction

Transition metal complexes with polydentate nitrogen ligands, mainly polyamines, have been studied for some time either because of their structural properties[1,2,3] or, in some cases, because they are able to exchange molecular oxygen.[4]

We are interested in both problems and it seemed a good starting point to study complexes of metal cations with an electronic structure such that the characteristic of the polyamine ligand could be very little affected.

In this work we prepare some complexes of Zn^{II}, Cd^{II}, and Hg^{II} with diethylenetriamine, which were already known to exist in aqueous solution, although they were never isolated in the solid state.

Results and Discussion

Two series of compounds have been prepared corresponding to $MDienX_2$ and $MDien_2X_2$ respectively (with M = Zn, Cd, Hg; Dien = diethylenetriamine $NH{-}(CH_2{-}CH_2{-}NH_2)_2$; X = Cl^-, Br^-, I^-, CN^-, NO_3^-, ClO_4^-, SCN^-); the former are pentacoordinated neutral complexes and the latter hexacoordinated cationic complexes, namely $[MDien_2]X_2$. Both these series have been observed in aqueous solution by Ciampolini *et al.*[5] M being all the transition metals from Mn^{II} through Zn^{II}.

Complexes with ligands similar to diethylenetriamine have been prepared by other authors.[2,3]

Structural analysis of these complexes were difficult because they are soluble only in very polar solvents, in which they are partially dissociated thus rendering electronic spectra completely useless. Therefore, only vibrational spectra and conductivity measurements allow inferences to their structures.

$MDienX_2$ type compounds (M = Zn, Cd, Hg; X = Cn^-, Cl^-, Br^-, I^-). All the experimental data related to the $MDienX_2$ complexes are reported on Tables I, II, III, IV.

According to the stoichiometry $MDienX_2$, a molecule could show the following structures:

$[MDienX]X$ (1), $[MDien_2]MX_4$ (2) and $MDienX_2$ (3)

The infrared spectra of a molecule with the structure (1) should have two bands, in the CN stretching frequencies region, (one due to the covalent CN and the other one to the ionic CN) and only one band in the metal-halogen stretching frequencies region. As shown on Table III, the I.R. spectra of our compounds have one band in the CN stretching frequencies region and two bands in the cadmium-halogen stretching frequencies region. According with the structures (2) the infrared spectra of the cyanoderivatives should have the bands due to $[Zn(CN)_4]^{2-}$, $[Cd(CN)_4]^{2-}$, and $[Hg(CN)_4]^{2-}$ at 2149, 2140, and 2143 cm^{-1} respectively.[6] Furthermore the infrared spectra of complexes with such a structure as (2) should have the same pattern of those of $[MDien_2]X_2$ complexes. But in our case, the spectra appear completely different either in solution or in the solid state. Therefore we suggest that these complexes have a pentacoordinated, covalent structure in the solid sate. The bands which appear at 2048 cm^{-1} in the spectra of the dimethylsulphoxide solution of the cyano derivatives indicate some dissociation in solution. This suggestion is in agreement with the data obtained by conducibility measurements. In fact the values of Λ_M reported on Table II show some dissociation and, moreover, they increase on dilution although it is not possible to draw any Onsager's plot with such data. Therefore we can suggest that

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[2] Z. Dori, R. Eisemberg, H.B. Gray, *Inorg. Chem.*, 6 (1967) 483

[3] F.S. Stephens, *J. Chem. Soc.* (A), (1969) 2233

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[5] M. Ciampolini, P. Paoletti, L. Sacconi, *J. Chem. Soc.*, (1961) 2994.

[6] D.M. Adams, Metal Ligand and related vibrations - E. Arnold Ltd. London, p. 164.

Table I..

Compound	% Calc. C	% Calc. N	% Calc. H	% Found C	% Found N	% Found H	M.P.
ZnDien(CN)$_2$	32.70	31.60	5.90	32.61	31.53	6.05	179
ZnDienCl$_2$	20.04	17.60	5.43	20.40	17.46	5.56	228
ZnDienBr$_2$	14.62	12.80	3.96	15.06	12.92	3.70	218
ZnDienI$_2$	11.38	9.95	3.08	10.10	8.70	2.90	—
CdDien(CN)$_2$	27.00	26.20	4.70	27.03	25.86	5.00	205
CdDienCl$_2$	16.75	14.70	4.55	16.95	14.40	4.31	247
CdDienBr$_2$	12.80	11.20	3.46	12.38	11.53	3.71	250
CdDienI$_2$	10.20	8.99	2.76	10.39	9.02	2.88	253
HgDien(CN)$_2$	20.20	19.70	3.68	20.32	19.42	3.56	168
HgDienCl$_2$	12.80	11.20	3.48	12.84	11.15	3.68	155
HgDienBr$_2$	10.35	9.10	2.81	10.19	8.86	2.64	177
HgDienI$_2$	8.60	7.55	2.35	8.56	7.45	2.34	138

Table II.

Compound	Λ_M [a]
ZnDien(CN)$_2$	22
ZnDienCl$_2$	28
ZnDienBr$_2$	36
ZnDienI$_2$	—
CdDien(CN)$_2$	16
CdDienCl$_2$	20
CdDienBr$_2$	25
CdDienI$_2$	32
HgDien(CN)$_2$	5
HgDienCl$_2$	18
HgDienBr$_2$	17
HgDienI$_2$	17
$[(C_2H_5)_4N]Br$	45
$[Ni(o\text{-}fen)_3]Cl_2$	57

[a] Λ_M = molar conductance (ohm^{-1}. cm^2. mole^{-1}) of 10^{-3} *M* dimethylsulphoxide solutions at room temperature.

Table III.

Compound [a]	$\nu(C\equiv N)cm^{-1}$	$\nu(Me\text{-}X)cm^{-1}$
ZnDien(CN)$_2$	2151 (s)	
CdDien(CN)$_2$	2160 (s)	
HgDien(CN)$_2$	2164 (s)	
CdDienCl$_2$		256 (s) - 230 (s)
CdDienBr$_2$		177 (s) - 145 (s)
CdDienI$_2$		144 (s) - 120 (sh)

[a] All the spectra recorded in nujol mull (s) = strong; (sh) = shoulder.

Table IV.

Compound [a]	$\nu(C\equiv N)$ cm^{-1}
ZnDien(CN)$_2$	2136(s) - 2048(m)
CdDien(CN)$_2$	2126(s) - 2048(m)
HgDien(CN)$_2$	2160(s) - 2048(m)
KCN	2048(s)

[a] All the spectra recorded in dimethylsulphoxide solution. (s) = strong; (m) = medium.

the following equilibrium:

$$MDienX_2 \rightleftharpoons [MDienX]X$$

takes place in a dimethylsulphoxide solution. Unfortunately, we were not able to obtain reproducible results for conductivity measurements in aqueous solution.

The infrared spectra of the cyano derivatives in the solid state show only one band in the CN stretching region, leading us to consider a possible trans configuration of the cyano groups. However the infrared spectra of the halogeno derivatives of cadmium, show two bands in the cadmium halogen stretching frequency suggesting a cis configuration of the halogen atoms. A covalent pentacoordinated structure could bave, in the solid state, two different geometries namely a trigonal bipyramidal or tetragonal pyramidal configuration; however, in this case, as in many other analogous examples[2,7,8] an intermediate geometry seems to be the most favored. Only a X-ray analysis, now in progress, will give more detailed information in order to ascertain the geometry of these complexes.

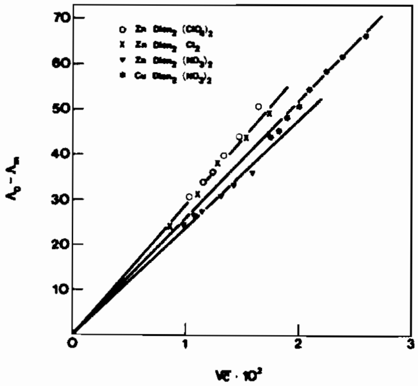

Figure 1.

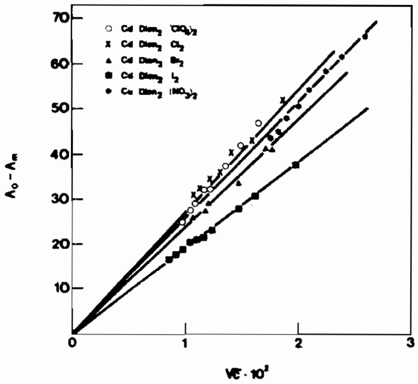

Figure 2.

Table V.

Complex	% Found C	% Found N	% Found H	% Calcd. C	% Calcd. N	% Calcd. H	M.P.
ZnDien$_2$(ClO$_4$)$_2$	20.85	18.20	5.65	21.20	17.81	5.25	272
ZnDien$_2$(NO$_3$)$_2$	24.26	28.55	6.57	24.44	28.43	7.22	239
ZnDien$_2$Cl$_2$	28.00	24.50	7.60	28.19	23.89	8.24	251
ZnDien$_2$Br$_2$	22.30	19.50	6.04	22.60	19.25	6.20	259
ZnDien$_2$I$_2$	18.25	15.97	4.95	18.09	16.07	5.08	228
CdDien$_2$(ClO$_4$)$_2$	18.50	16.20	5.00	18.33	15.92	5.14	266
CdDien$_2$Cl$_2$	24.60	21.60	6.85	24.53	21.30	7.07	219
CdDien$_2$Br$_2$	20.00	17.55	5.44	20.09	17.60	5.61	238
CdDien$_2$I$_2$	16.80	17.40	4.55	16.75	14.61	4.56	240
HgDien$_2$(ClO$_4$)$_2$	15.85	13.85	4.30	15.89	13.83	4.43	203
HgDien$_2$(SCN)$_2$	23.00	21.00	4.97	23.50	21.26	5.14	138

Table VI.

Complex	Λ_M[a]	Λ_o[b]
ZnDien$_2$(ClO$_4$)$_2$	67	128
ZnDien(NO$_3$)$_2$	82	116
ZnDien$_2$Cl$_2$	59	128
ZnDien$_2$Br$_2$	79	—
ZnDien$_2$I$_2$	70	—
CdDien$_2$(ClO$_4$)$_2$	73	125
CdDien$_2$Cl$_2$	57	110
CdDien$_2$Br$_2$	54	100
CdDien$_2$I$_2$	66	102
HgDien$_2$(ClO$_4$)$_2$	72	99
HgDien$_2$(SCN)$_2$	78	100
CuDien$_2$(NO$_3$)$_2$	83	135

[a] Λ_M = molar conductance (ohm^{-1}. cm^2. mole^{-1}) for a ca 10^{-3} M dimethylsulphoxide solutions at room temperature. [b] Λ_o values are obtained by extrapolation on Onsager's plot.

The Onsager's plots, reported on Figures 1, 2, 3, show these complexes to be uni-bivalent electrolytes, as can be seen by comparison with the slope of the plot of CuDien$_2$(NO$_3$)$_2$ which is well known[8] to be hexacoordinated ionic with the nitric groups out of the coordination sphere.

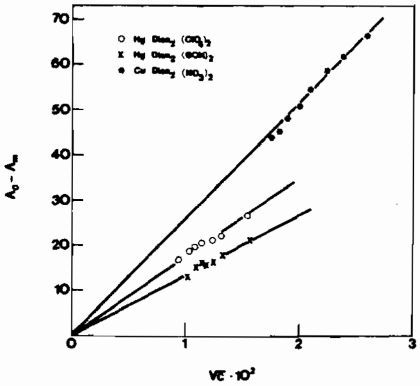

Figure 3.

The infrared spectra of these complexes show the bands respectively due to the coordinated ligand the ionic perchlorate (1090 cm^{-1}), ionic nitrate (1400-1340 cm^{-1}) and SCN$^-$ (2040 cm^{-1}). However no bands in the M-halogen stretching frequencies region appear. We thus can conclude that these complexes are hexacoordinated and octahedral with the diethylenetriamine acting as a tridentate ligand.

As in the case of the analogous complexes of Co^{3+}, geometric and optical isomers could exist,[9] but unfortunately we were not able to separate them. These attempts were carried out under the same experimental conditions as the cobalt derivatives. In order to confirm the absolute configurations of these complexes X-ray analysis are now in progress.

Experimental Section

Apparatus. Infrared spectra are recorded on a Perkin-Elmer mod. 621 grating spectrometer (4000-400 cm^{-1}) and on Hitachi - P.E. FIS3 (400-50 cm^{-1}).

Materials. Diethylenetriamine (Fluka A.G.) and all the metallic salts (C. Erba R.P.) were used without further purification.

Monodiethylenetriaminedicyanozinc(II). 5.42 ml of diethylenetriamine (0.05 moles) in 50 ml of ethanol were added to an ethanolic solution containing 5.85 g of Zn(CN)$_2$ (0.05 moles) in 50 ml of ethanol on stirring. A white crystalline precipitate is formed, which is soluble in water, methanol, dimethylsulphoxide; insoluble in ethanol, acetone, chloroform.

Monodiethylenetriaminedichlorozinc(II). 1.08 ml of diethylenetriamine (0.01 moles) in 10 ml of ether, were added to an ethereal solution containing 1.36 g of ZnCl$_2$ (0.01 moles) on stirring. A white precipitate is formed which, after decantation, is washed with ethanol on stirring and then filtered. It is soluble in methanol, dimethylsulphoxide, water; insoluble in ethanol, acetone, chloroform.

Monodiethylenetriaminedibromozinc(II). 1.08 ml of diethylenetriamine (0.01 moles) in 10 ml of ether were added to an ethereal solution containing g 2.25 of ZnBr$_2$ (0.01 moles) on stirring; a white precipitate is formed which, after decantation is washed with ethanol on stirring and then filtered. It is soluble in water, methanol, dimethylsulphoxide; insoluble in ethanol, acetone, chloroform.

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(7) B.J. Hathway, M.J. Bew, D.E. Billing, R.J. Dudley, P. Nicholls, *J. Chem. Soc.* (A) (1969) 2312

(8) B.J. Hathaway, M.J. Bew, D.E. Billing, *J. Chem. Soc.* (A), (1970) 1090

(9) F.R. Keene, G.H. Searle, Y. Yoshikawa, A. Imai, K. Yamasaki, *Chem. Comm.*, (1970(784

Monodiethylenetriaminedichlorocadmium(II). 1.08 ml of diethylenetriamine (0.01 moles) in 10 ml of ethanol were added to an acqueous solution containing g 1.83 of $CdCl_2$ (0.01 moles) on stirring. A white precipitate is formed which is recrystallized from water. Soluble in water and dimethylsulphoxide; insoluble in methanol, ethanol, acetone, chloroform.

Monodiethylenetriaminedibromocadmium(II) - monodiethylenetriaminediiodocadmium(II) and monodiethylenetriaminedicyanocadmium(II). Were prepared likewise the previous dichloro derivative.

Except the dicyano compound, which is soluble in methanol, ethanol and acetone, they show the same solubilities.

Monodiethylenetriaminedichloromercury(II). 1.08 ml of diethylenetriamine (0.01 moles) were added to 20 ml of ethanol containing 3.74 g of $HgCl_2$ (0.01 moles) on stirring. A white crystalline precipitate is formed. It is soluble in water and dimethylsulphoxide; insoluble in methanol, ethanol, acetone, chloroform.

Monodiethylenetriaminedibromomercury(II). To a solution containing 4.32 g of HgO in 10 ml of water and 15 ml of concentrated HBr (47%), diethylenetriamine is added until no further precipitation is obtained. The white compound is recrystallized from water. It is soluble in water, acetone and dimethylsulphoxide; insoluble in methanol, ethanol, chloroform.

Monodiethylenetriaminediodomercury(II). To a solution containing 4.54 g of HgI_2 (0.01 moles) in 150 ml of water and 6 ml of concentred HI (57%), 3.24 ml of diethylenetriamine (0.03 moles) were added on stirring. A yellow precipitate is formed which is recrystallized from ethanol. It is soluble in ethanol, methanol, dimethylsulphoxide, acetone; insoluble in water and chloroform.

Monodiethylenetriaminedicyanomercury(II). It is prepared likewise the previous dichloro derivative. It is also soluble in water.

Bisdiethylenetriaminezinc(II) chloride, Bisdiethylenetriaminezinc(II) iodide, Bisdiethylenetriaminezinc(II) bromide, Bisdiethylenetriaminezinc(II) nitrate and Bisdiethylenetriaminezinc(II) perchlorate. A solution of 0.1 moles of diethylenetriamine in 50 ml of ethanol was added, on stirring, to a solution containing 0.05 moles of zinc salt in 200 ml of ethanol. A white precipitate is formed, which is recrystallized from methanol. It is soluble in water, ethanol, dimethylsulphoxide; insoluble in methanol, acetone, chloroform.

Bisdiethylenetriaminecadmium(II) chloride. An acqueous solution containing 1.83 g $CdCl_2$ (0.01 moles) was added dropwise on stirring to 4.32 ml of diethylenetriamine (0.04 moles). Acetone is then added until two layers were formed. The heavier phase is then added to an equal amount of ethanol. A white precipitate is obtained by adding ether. It is recrystallized from ethanol and ether. It is soluble in water, methanol, ethanol, dimethylsulphoxide; insoluble in acetone, chloroform.

Bisdiethylenetriaminecadmium(II) bromide. A solution of 2.2 ml of diethylenetriamine (0.02 moles) in 20 ml of ethanol was added to a saturated acqueous solution containing 2.72 g of $CdBr_2$ (0.01 moles) on stirring. A white precipitate formed and then quickly dissolved. A white crystalline compound is obtained on addition of ethanol. It is recrystallized from water and ethanol. Soluble in water dimethylsulphoxide; insoluble in ethanol chloroform and acetone.

Bisdiethylenetriaminecadmium(II) iodide. As acqueous solution containing 3.66 g of CdI_2 (0.01 moles) was added dropwise, on stirring, to 4.32 ml of diethylenetriamine (0.04 moles). A white crystalline precipitate is formed, which is recrystallized from water and dimethylsulphoxide; insoluble in methanol, ethanol, acetone, chloroform.

Bisdiethylenetriaminecadmium(II) perchlorate. To an acqueous solution containing 1.72 g of $CdCO_3$ (0.01 moles) and 4 ml of $HClO_4$ (70%), 2,16 ml of diethylenetriamine (0.02 moles) were added dropwise on stirring. A white precipitate is formed, which is soluble in water and dimethylsulphoxide; insoluble in methanol, ethanol, acetone, chloroform.

Bisdiethylenetriaminemercury(II) thiocyanate. A suspension containing 3.166 g of $Hg(SCN)_2$ (0.01 moles) in hot ethanol was added dropwise on stirring to 4.32 ml of diethylenetriamine (0.04 moles). A precipitate is formed, which is recrystallized from ethanol as a white crystalline compound. It is soluble in water, ethanol, methanol and dimethylsulphoxide; insoluble in acetone and chloroform.

Bisdiethylenetriaminemercury(II) perchlorate. To an acqueous solution containing 4.7 g of HgO (0.022 moles) and 8 ml of $HClO_4$ (70%), 7.5 ml of diethylenetriamine were added dropwise on stirring. A white precipitate is obtained which is washed with water and then with ethanol. It is recrystallized from water.. Soluble in water, acetone and dimethylsulphoxide; insoluble in methanol, ethanol, chloroform.