Transition-metal Complexes of *NNN′N″N‴N‴*-Hexamethyl-3,6-diazaoctane-1,8-diamine. Part II.[1] Zinc(II), Cadmium(II), and Mercury(II) Halides

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A series of compounds of the types M(trien)X_2 and [M_2'(trien)X_4] (where trien = *NNN′N″N‴N‴*-hexamethyl-3,6-diazaoctane-1,8-diamine; M′ = Zn^{II}; X = Cl, Br, I; M = Zn^{II}; X = I; M = Cd^{II}; X = Cl, Br, I; M = Hg^{II}; X = Cl, Br; M′ = Hg^{II}; X = I) have been prepared and studied by means of i.r. and far-i.r. spectroscopy, conductivity and molecular weight measurements. Structures for these compounds are suggested.

By reaction of MX_2 salts (M = Zn, Cd, Hg; X = Cl, Br, I) with the ligand in methanol or in aqueous methanolic solution the complexes M(trien)X_2 (M = Cd; X = Cl, Br, I; M = Hg; X = Cl, Br; M = Zn; X = I) and [M_2'(trien)X_4] (M′ = Zn; X = Cl, Br, I; M′ = Hg; X = I) were obtained. The analytical data and some physical properties are reported in the Table. All the compounds are colourless, consistent with a d^{10} configuration. They are generally soluble in CH_3OH, $C_2H_5NO_2$, less soluble in H_2O, CH_3CN, CH_3NO_2 and in higher alcohols and insoluble in non-polar solvents. The low conductivity values in $C_2H_5NO_2$ or in CH_3CN show that these complexes are non-electrolytes with the exception of [Zn(trien)I]I, which is a uni-univalent electrolyte. Molecular weight data show that they are monomeric materials. A solution of the mercury(II) iodide derivative has a conductivity approaching that of a 1 : 1 electrolyte, which is probably due to partial ionisation of the Hg–I bond.

Analytical, far-i.r. spectra data and some physical properties

Compound	M.p. °C	Found %				Required %				M [a,b]	Λ_M [b,e]	Far i.r. spectra		
		C	H	N	X	C	H	N	X			ν(M–X)	ν(M–N)	Other Bands
[Zn_2(trien)Cl_4]	306 dec.	28·6	5·8	11·1	27·8	28·6	6·0	11·1	28·2	394 (503) [d]	25 [d]	339vs, 312vs	206s	490w, 460m, 449sh, 389w, 112vsbr
[Zn_2(trien)Br_4]	297 dec.	21·7	4·3	8·4	45·7	21·2	4·4	8·3	46·9	550 (680) [d]	34 [d]	251vsbr, 225vs	192s	487vw, 455m, 447sh, 429sh, 392m, 361w, 159sh
[Zn_2(trien)I_4]	324 dec.	17·3	3·2	6·5	58·3	16·6	3·5	6·4	58·4		20 [e]	240—200sbr	180s	493vw, 456m, 450sh, 428m, 392m, 345w, 300w, 140s
[Zn(trien)I]I	303	26·2	5·4	10·2	46·1	26·2	5·5	10·2	46·2	292 (549·6) [d]	135 [d]	228s	198m	493sh, 482s, 448m, 391m, 374w, 353w, 267w, 165m, 124w
[Cd(trien)Cl_2]H_2O	212	33·5	7·0	13·0	16·6	33·4	7·5	12·9	16·4	388 (431·4)	4	207vs	192sh	497vw, 465w, 448w, 397s, 377s, 355s, 264sh
[Cd(trien)Br_2]	218	28·7	6·3	11·1	31·5	28·7	6·0	11·2	31·8	487 (502·7)	2	161s	182sh	490sh, 465m, 440m, 394s, 379w, 350w, 339w, 220m
[Cd(trien)I_2]	227	24·2	5·3	9·5	42·8	24·1	5·1	9·4	42·6	597 (597·1)	7	140m	183s	494sh, 463m, 445s, 395s, 381m, 351m, 344sh, 309w, 261w, 225m, 201w, 160m
[Hg(trien)Cl_2]	135	28·7	5·9	11·2		28·7	6·0	11·2		487 (503·4)	7	195sbr	152s	485sh, 465m, 445w, 351vs, 267sh
[Hg(trien)Br_2]	115	23·8	5·0	9·3		24·4	5·1	9·5		555 (591·7)	17	143vs	143vs	347s, 337sh, 306vw, 263w, 225m, 202m, 190sh, 180m
[Hg_2(trien)I_4]	198	12·5	2·4	4·7		12·6	2·6	4·9		824 (1139·5) 888 [d]	42 86 [d]	166vs	139vs	
trien														470w, 409vw, 260vw, 236vw, 217vw

[a] Calculated value in parentheses. [b] In nitroethane unless given otherwise. [c] For solutions *ca.* 5 × 10^{-3} M; [Bu^n_4N]Br under the same conditions: $MeNO_2$, 93; $EtNO_2$, 80; MeCN, 140. [d] In MeCN. [e] In $MeNO_2$.

RESULTS AND DISCUSSION

The strong bands present in the i.r. spectra for chloro-, bromo- and iodo-derivatives of general formula [Zn_2(trien)X_4] are clearly due to the Zn–X stretching vibrations, according to literature data for ν(Zn–X) vibrations in tetrahedral complexes.[2-4] The ratios ν(Zn–Br) : ν(Zn–Cl) 0·74 and ν(Zn–I) : ν(Zn–Cl) 0·65 agree very well with the data of Clark.[4] For the [Zn_2(trien)X_4] compounds we suggest a structure involving the ligand acting as a bridge between two ZnX_2 groups, with each zinc atom co-ordinated to two nitrogen atoms at each end of the ligand.

A formulation of the type [Zn(trien)X][ZnX_3] or [Zn(trien)][ZnX_4] is ruled out for steric reasons and because bands are not present due to [ZnX_4]$^{2-}$ (277 and 130 cm^{-1} for X = Cl; 209 and 199 cm^{-1} for X = Br; 167 and 122 cm^{-1} for X = I).[5] [Zn(trien)I]I could have a five-co-ordinate structure, according to ν(Zn–I),[6] conductivity, and molecular weight data (Table).

The cadmium complexes, by conductivity and molecular weight data are formulated as [Cd(trien)X_2], since they are monomeric non-electrolytes. The chloro-derivative contains a water molecule that is lost at 110 °C *in vacuo* without decomposition.

In the far-i.r. spectra of the cadmium derivatives the ν(Cd–X) are due to terminal halides.[6] The ratio

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ν(Cd–Br) : ν(Cd–Cl) 0·78 agrees with the literature data for six-co-ordinate compounds.[4] We suggest that these compounds have a six-co-ordinate structure.

As far as the mercury derivatives are concerned the chloro-, and bromo-derivatives seem to be six-co-ordinate according to far-i.r. spectra,[6] conductivity, and molecular weight data. The ratio ν(Hg–Br) : ν(Hg–Cl) 0·73 agrees well with the literature data for mercury six-co-ordinate complexes.[4] The ν(Hg–I) vibration in the [Hg_2(trien)I_4] complex appears at a similar frequency in tetrahedral complexes.[2] This compound [Hg_2(trien)I_4] is therefore assigned the same structure as the zinc compound [Zn_2(trien)I_4]. Alternative formulations such as [Hg(trien)I][HgI_3] or [Hg(trien)][HgI_4] do not agree with the band frequencies of the (Hg–I) vibration (HgI_4^{2-} 126, 41, 35 cm^{-1};[7] HgI_3^- 150, 133, 90 cm^{-1} [8]).

EXPERIMENTAL

Preparation of M(trien)X_2 *and* M_2(trien)X_4 *Compounds.*—To a hot solution of MX_2 (15 mmol) in CH_3OH or in methanolic aqueous solution were added trien [9] (17 mmol) in the same solvent and the mixture was heated for 5 min. The complexes were separated out with addition of isopropyl alcohol or acetone after cooling the solution.

Preparation of [Zn(trien)I]I.—Trien (16 mmol) was added to a hot methanolic aqueous solution of $ZnCl_2$ (15 mmol). To the resulting solution was added KI (30 mmol) dissolved in aqueous methanol. After the solution was concentrated and cooled the white complex separated out and was recrystallized from methanol.

Infrared Spectra.—All compounds were studied in the region 4000—100 cm^{-1} with Perkin-Elmer 457, 225 and FIS 3 Spectrometers. Atmospheric water was removed from the spectrophotometer housing with a stream of dry nitrogen. The i.r. spectra in the rock salt region were recorded on Nujol mulls supported between KBr plates and in the regions 2820—2760 and 1500—1300 cm^{-1} on hexachlorobutadiene mulls. The far-i.r. spectra were measured on Nujol mulls between thin polyethylene sheets.

Conductivity Measurements.—Molar conductivities were measured in dehydrated solvents at 25 ± 0·1 °C using a W.T.W. model LBR/B conductance bridge. The concentration of the solutions was *ca.* 5×10^{-3}M in CH_3NO_2, $C_2H_5NO_2$ or in CH_3CN, but no substantial differences in the conductivity values were observed in the concentration range 5×10^{-2}—5×10^{-3}M.

Molecular Weight Determinations.—Molecular weight data were performed by a Hitachi–Perkin-Elmer 115 Osmometer. The calibration was carried out with 5×10^{-3}—10^{-2}M solutions of benzil in $C_2H_5NO_2$ or in CH_3CN. The concentration of the solutions of the complexes was *ca.* 5×10^{-3}M.

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