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Five-Coordinated Complexes of Cadmium(II) and Mercury(II) with Tripod-Like Tetramines

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Some complexes of cadmium(II) and mercury(II) with the tetramines tris(2-aminoethyl)amine, tren, and tris(2-dimethylaminoethyl)amine, Me$_6$tren, are described. The anions are Cl^-, Br^-, I^-, SCN^-, NO_3^-, ClO_4^-, BPh_4^-. They were characterized by chemical analysis, electric conductivity, and vibrational spectroscopy. According to the nature of metal, amine, and anion a variety of complexes of different stoicheometries has been obtained. The cationic species are of the types $[MX(Me_6tren)]^+$ and $[MX(tren)]^+$ (X = Cl, Br, I, ClO_4, SCN) where the metal ions are five-cordinated. Metallic anionic species are $[HgCl_4]^{2-}$, $[HgBr_4]^{2-}$, and the novel ones $[Cd_2I_6]^{2-}$, $[Hg_2I_6]^{2-}$, and $[Hg_2Br_5]^{2-}$, all having tetrahedrally coordinated metal ions. The neutral complexes $CdCl_2(Me_6tren)$ and $CdBr_2(Me_6tren)$ are five-cordinated, with the amine acting as a tridentate ligand.

Introduction

The potentially quadridentate ligand tris(2-dimethylaminoethyl)amine, Me$_6$tren, has been proved to react with the bivalent ions of the first transition series from chromium to zinc to give five-coordinated trigonal bipyramidal complexes.[2] The less bulky non-methylated parent compound tris(2-aminoethyl)amine, tren, forms five-coordinated complexes with cobalt (II),[3] copper(II),[4] and zinc(II)[5] but octahedral complexes with nickel(II).[6]

It seemed interesting, therefore, to prepare the compounds of both ligands with bivalent ions of' the second and third transition series, which have higher ionic radii, with the aim of ashertaining the resulting stereochemistry.

This paper reports the preparation and properties of a series of complexes of cadmium(II) and mercury(II) with the ligands tren and Me$_6$tren.

It is noteworthy to recal that only few five-coordinated complexes are known with cadmium and mercury(II), the most usual coordination numbers being four and six with cadmium(II) and two, four and six with mercury(II).[7]

Experimental Section

Preparation of the Compounds. The amines tren and Me$_6$tren have been prepared as previously described.[2] The metal complexes have been prepared according to the following procedure. A solution of the amine (10 mmoles) in methanol (20 ml) was slowly added while stirring to a hot solution of the appropriate metal salt (10 mmoles) in methanol (40 ml). The solution was then concentrated and cooled to room temperature until the solid compound separated. With the ligand Me$_6$tren, a few ml of acetone and isopropanol were added after the addition of the amine in order to promote crystallization. The compounds were recrystallized by dissolving them in methanol and adding isopropanol to the filtered solution.

Measurements. Electric conductivity values were measured on a WTW Model LBR/B conductance bridge at 25°C. Concentrations of the solutions were approximately 10^{-3} *M*. I.r. spectra were measured on Perkin-Elmer Models 457 and 301 spectrometers. In the rock salt region they were recorded using Nujol and HCBD mulling agents between potassium bromide windows. Far i.r. spectra were recorded on polythene discs.

Results and Discussion

Table I shows the analytical data and the values of the molar conductivities of the complexes of cadmium and mercury(II) with the tetramines tren and Me$_6$tren. In Table II, the far-i.r. data of the compounds are listed. Many absorption bands are present so that a complete and unambiguous assignment of all of the bands is difficult and beyond the scope of this work. Nevertheless some of the bands are soundly attributable to metal-halogen stretching vibrations and can be used accordingly for structural purposes.

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Table I. Analytical and conductivity data of some cadmium(II) and mercury(II) compounds with tren and Me_6tren.

	found %			required %			
	C	H	N	C	H	N	Λ_M ^{a,b,c,d}
$[HgBr(en)]_2[Hg_2Br_6]$	8.3	2.2	6.2	8.3	2.1	6.5	106 ^{b}
$[HgI(tren)]_2[Hg_2I_6]$	6.9	1.8	5.3	6.8	1.7	5.3	156, 98 ^{b}
$[Hg(SCN)(tren)](SCN)$	20.2	4.0	17.4	20.7	3.9	18.1	73 ^{a}, 148 ^{c}
$[CdBr(tren)]Br$	17.4	4.0	13.3	17.2	4.3	13.4	61 ^{b}
$[CdI(tren)]_2[Cd_2I_6]$	8.3	2.1	6.3	8.2	2.0	6.3	112 ^{b}, 232 ^{c}
$[Cd(NO_3)(tren)](NO_3)$	18.6	4.3	21.7	18.8	4.7	21.9	102 ^{b}
$[Cd(ClO_4)(tren)](ClO_4)$	15.4	3.8	12.1	15.6	4.0	12.3	115 ^{b}
$[CdCl(tren)](BPh_4)$	59.6	6.0	9.0	58.7	6.2	9.1	45 ^{b}
$[HgCl(Me_6tren)](ClO_4)$	25.7	5.2	9.9	25.7	5.3	9.9	116
$[HgCl(Me_6tren)]_2[HgCl_4]$	22.8	4.6	8.6	22.6	4.7	8.8	140
$[HgBr(Me_6tren)]_2[HgBr_4]$	18.6	3.9	7.2	18.7	3.9	7.3	164
$[HgI(Me_6tren)]_2[Hg_2I_6]$	12.6	2.8	4.8	12.6	2.6	4.9	148
$[Hg(SCN)(Me_6tren)](BPh_4)$	54.7	6.3	9.0	55.0	6.2	8.7	76
$CdCl_2(Me_6tren)$	35.0	7.2	13.7	34.8	7.3	13.5	84
$[CdCl(Me_6tren)](BPh_4)$	63.1	7.3	8.2	62.0	7.2	8.0	60
$CdBr_2(Me_6tren)$	28.8	5.9	11.1	28.7	6.0	11.1	78
$[CdI(Me_6tren)]_2[Hg_2I_6]$	15.4	3.1	5.8	15.0	3.1	5.8	126
$[Cd(NO_3)(Me_6tren)](NO_3)$	30.8	6.8	18.0	30.9	6.5	18.0	79
$[Cd(H_2O)(Me_6tren)](ClO_4)_2$	26.8	5.8	10.2	25.7	5.8	10.1	164 ^{b}

^{a} In nitromethane. ^{b} In dimethylformamide. ^{c} In acetonitrile. ^{d} Λ_M given in units of $cm^2 . ohm^{-1} . mole^{-1}$. Reference values under the same conditions are: $[NEt_4]I$, 93, 76 ^{b}, 160 ^{c}; $[NEt_4]_2[CuBr_4]$, 175, 162 ^{b}, 300 ^{c}; $[NEt_4](BPh_4)$, 71, 53 ^{b}.

Table II. Vibrational spectra (300-100 cm^{-1}) of some cadmium(II) and mercury(II) complexes with tren and Me_6tren.

Compound	ν(M-X), cm^{-1}	other bands, cm^{-1}
$[CdI(tren)]_2[Cd_2I_6]$	184s, 173s, 169sh, 146sh, 123m, 105vw	273vw, 251m, 155m
$[CdI(Me_6tren)]_2[Cd_2I_6]$	177vs, 140m, 124m. 106w	211vw
$[HgBr(tren)]_2[Hg_2Br_6]$	179vs. 167m, 149-141m, 108mbr	251m br, 130vw
$[HgI(tren)]_2[Hg_2I_6]$	177s, 140sh, 133vs, 116w	245m
$[HgI(Me_6tren)]_2[Hg_2I_6]$	165vs, 140sh, 133vs, 116w	217sh, 212m, 154vs
$[CdCl(tren)](BPh_4)$	284vs	259vs, 252vs, 208w, 204w, 187m, 136m, 120w
$[CdCl(Me_6tren)](BPh_4)$	276vs	253sh, 222w, 212sh, 204sh, 178m, 133w, 120vw
$[HgCl(Me_6tren)](ClO_4)$	264vs	249s, 220w, 149w, 130vw
$[HgCl(Me_6tren)]_2[HgCl_4]$	267s, 232s, 103m br	275sh, 218s, 156vw, 146vw, 132sh
$[HgBr(Me_6tren)]_2[HgBr_4]$	192vs, br, 154vs br	215w, 146vs
$[CdBr(tren)]Br$	178s	271m, 228w, 212w, 190sh, 150w, 113vw
$CdCl_2(Me_6tren)$	262vs, 234vs	202sh, 174w, 118sh
$CdBr_2(Me_6tren)$	192s br, 170s br	150sh, 112w
$[Cd(NO_3)(tren)](NO_3)$	176s br(Cd-O)	295m, 193sh, 140vw, 100w
$[Cd(NO_3)(Me_6tren)](NO_3)$	220vs br(Cd-O)	150w, 130m
$[Cd(ClO_4)(tren)](ClO_4)$	226s br(Cd-O)	293m, 189sh, 150m br, 134w
$[Cd(H_2O)(Me_6tren)](ClO_4)_2$	193vs(Cd-O)	221m, 150w, 131w
$[Hg(SCN)(tren)](SCN)$	266m(Hg-S)	204m, 185m, 153w, 133sh
$[Hg(SCN)(Me_6tren)](BPh_4)$	231s(Hg-S)	280m, 263m, 250sh, 195s, 168w, 138w

The present complexes are best grouped into six classes, which are examined in the following.

A) *Compounds $M_2(Me_6tren)I_4$, $M_2(tren)I_4$ (M = Cd, Hg) and $Hg_2(tren)Br_4$.* A complete X-ray analysis showed that the compound $Cd_2(Me_6tren)I_4$ is made up by five-coordinated cations $[CdI(Me_6tren)]^+$ and dinuclear anions $[Cd_2I_6]^{2-}$.[8] The cation is a slightly distorted trigonal bipyramid whereas the anion is formed by pairs of tetrahedra CdI_4 sharing an edge. The complex is thus to be formulated as $[CdI(Me_6tren)]_2[Cd_2I_6]$.

The i.r. band at 177 cm^{-1} in the spectrum of the above compound is assigned to the Cd–I stretching vibration of the cation $[CdI(Me_6tren)]^+$ on account of its prominent relative intensity. This frequency is only slightly higher than those (162 and 151 cm^{-1}) of the Cd–I stretching vibrations in the five-coordinated $[CdI_2(terpy)]$ complex.[9] Three bands at 140, 124, and 106 cm^{-1} are assigned to Cd–I stretching vibrations of the $[Cd_2I_6]^{2-}$ anion and compare well with the frequencies reported for the compound $[Bu_4{}^nN]CdI_3$, i.e. 174, 170 (both masked in our case by the more intense Cd–I vibration of the cation), 142, 119, 108 cm^{-1}[10] This agreement confirms unambiguously the occurrence of the dimeric anion $[Cd_2I_6]^{2-}$ previously postulated for the tetrabutylammonium triiodocadmate.[10]

All of the compounds in this class exhibit far-i.r. spectra consistent with their formulations as $[MXL]_2$-$[M_2X_6]$. The metal-halogen stretching frequencies of the cations fall at 184 cm^{-1} for $[CdI(tren)]^+$, 165 cm^{-1} for $[HgI(Me_6tren)]^+$, 177 cm^{-1} for $[HgI(tren)]^+$

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and 179 cm^{-1} for $[\mathrm{HgBr(tren)}]^+$. The values of the Hg–I stretching frequencies are, as in the case of the above mentioned Cd–I vibrations, slightly higher than those reported for the five coordinated $[\mathrm{HgI_2(terpy)}]$, i.e. 152 and 136 cm^{-1}.[9] Surprisingly, the value of the Hg–Br stretching frequency appears to be rather low, being almost equal to the value of ν(Hg–I) and the values exhibited by $[\mathrm{HgBr_2(terpy}]$, i.e. 181 and 172 cm^{-1}.[9]

The metal-halogen stretching frequencies of the $[\mathrm{M_2X_6}]^{2-}$ anion, fall probably at 173,169, 146, 123 and 105 cm^{-1} with $[\mathrm{CdI(tren)}]_2[\mathrm{Cd_2I_6}]$, at 140, 133 and 116 cm^{-1} with both compounds $[\mathrm{HgI(Me_6(tren)}]_2[\mathrm{Hg_2I_6}]$ and $[\mathrm{HgI(tren)}]_2[\mathrm{Hg_2I_6}]$ and at 167, 149-141 and 108 cm^{-1} with $[\mathrm{HgBr(tren)}]_2[\mathrm{Hg_2Br_6}]$.

All of the compounds in this series have electric conductivity values analogous to that of the $[\mathrm{CdI(Me_6tren)}]_2[\mathrm{Cd_2I_6}]$ complex and in agreement with those expected for 2:1 electrolytes. This fact may be taken as suggestive of the occurrence of the above $[\mathrm{M_2X_6}]^{2-}$ species also in solution.

B) *Compounds* $[\mathrm{CdCl(Me_6tren)}](\mathrm{BPh_4})$, $[\mathrm{CdCl(tren)}](\mathrm{BPh_4})$ *and* $[\mathrm{HgCl(Me_6tren)}]\mathrm{ClO_4}$. These complexes behave as typical 1:1 electrolytes. Their far-i.r. spectra are suggestive of a coordinated chlorine atom since they show a very strong band attributable to the M–Cl stretching vibration of the five-coordinated cation. The frequency values for ν(M–Cl) are: $[\mathrm{CdCl(Me_6tren)}]\mathrm{BPh_4}$, 276 cm^{-1}; $[\mathrm{CdCl(tren)}]\mathrm{BPh_4}$, 284 cm^{-1}; $[\mathrm{HgCl(Me_6(tren)}]\mathrm{ClO_4}$, 264 cm^{-1}. These values compare fairly well with those reported for the five-coordinated complexes $[\mathrm{MCl_2(terpy)}]$, which are 268, 251 cm^{-1} with ν(Cd–Cl) and 265, 240 cm^{-1} with ν(Hg–Cl).[9]

C) *Compounds* $\mathrm{Hg_3(Me_6tren)_2X_6}$, *with* $X = Cl, Br$. X-ray powder photographs show that these compounds are mutually isomorphous. Even though several structural hypotheses are conceivable for these complexes, nevertheless their most probable formulation appears ot be $[\mathrm{HgX(Me_6tren)}]_2[\mathrm{HgX_4}]$. Actually, their conductivity values are typical of 1:2 electrolytes. Furthermore, the chloro- and bromo-derivatives show i.r. bands at 267 and 192 cm^{-1}, respectively, which must be attributed to the five-coordinated cation $[\mathrm{HgX(Me_6tren)}]^+$ on account with their strict similarity with the frequency values found for $[\mathrm{HgCl(Me_6tren)}]\mathrm{ClO_4}$, 264 cm^{-1}, and for $[\mathrm{HgBr(tren)}]_2[\mathrm{Hg_2Br_6}]$, 179 cm^{-1}.

The bands at 232 and 103 cm^{-1}, for the chloro-complex, and at 154 cm^{-1}, for the bromo-complex, are attributed to the Hg–X vibrations of the anions $[\mathrm{HgCl_4}]^{2-}$ and $[\mathrm{HgBr_4}]^{2-}$, in accord with literature values of 229, 110 and 154 cm^{-1}, respectively.[11]

D) *Compounds* $\mathrm{CdX_2(Me_6tren)}$ ($X = Cl, Br$) *and* $\mathrm{CdBr_2(tren)}$. These Me$_6$tren compounds have some non-coordinated $-\mathrm{N(CH_3)_2}$ in contrast to all of the remainders of the present compounds. Indeed, just these $\mathrm{CdX_2(Me_6tren)}$ complexes exhibit strong bands, in the 2820-2760 cm^{-1} region, which are taken to be characteristic[12] of the C–H stretching vibrations of non-bonded methylamino groups. The far-i.r. spectra of both compounds show two strong bands at 262, 234 cm^{-1} for the chloro-derivative, and at 192, 170 cm^{-1}, for the bromo-derivative, which are attributable to ν(Cd–X) stretching vibrations. The occurrence of two bands indicates that both halogen atoms are coordinated to cadmium atom. The frequency values agree with those found with the five-coordinated $\mathrm{CdX_2(terpy)}$ complexes, having the chromophore $\mathrm{CdX_2N_3}$, which are 268, 251 cm^{-1} for ν(Cd–Cl) and 193, 182 cm^{-1} for ν(Cd–Br).[9] The Cd–Cl frequencies also agree with the values of 276 cm^{-1} exhibited by $[\mathrm{CdCl(Me_6tren)}]\mathrm{BPh_4}$.

These $[\mathrm{CdX_2(Me_6tren)}]$ complexes, therefore, are assigned in the solid state a five-coordinated structure, where the tetramine acts as a tridentate ligand with a non-bonded $-\mathrm{N(CH_3)_2}$ group. It is interesting to note that a complete X-ray characterization of the complex $[\mathrm{ZnBr(Me_6tren)}]\mathrm{Br}$ showed the tetramine Me$_6$tren to act as a quadridentate ligand.[13]

In nitromethane solution, the electric conductivity values are only slightly lower than that typical of 1:1 electrolytes, indicating extensive ionisation of coordinated halides, possibly followed by rearrangment or solvation of the complexes.

The near-i.r. spectra of $\mathrm{CdBr_2(tren)}$, as well as of all of the present tren complexes, showed that all of the three $-\mathrm{NH_2}$ groups are coordinated to cadmium.[14] Its far-i.r. spectrum exhibits a very strong band at 178 cm^{-1} and a shoulder at 190 cm^{-1}. A band at 190 cm^{-1} is also present in all of the Cd-tren complexes and is, therefore, to be attributed to Cd-N stretching vibration. This complex, therefore, is attributed the formula $[\mathrm{CdBr(tren)}]\mathrm{Br}$. In dimethylformamide solution the molar conductance of this complex is slightly lower than the typical of 1:1 electrolytes, possibly indicating the formation of a small proportion of coordinated dibromo complex.

E) *Compounds* $\mathrm{CdX_2L\,.\,nH_2O}$ ($X = NO_3, ClO_4$; $L = tren, Me_6tren$; $n = 0, 1$). The near-i.r. spectra of the nitrate compounds are indicative of both ionic and unidentate nitrate groups.[14] The frequency values are listed in Table III.

The values of the molar conductivity fall in the range of typical 1:1 electrolytes. Accordingly, these compounds are assigned five-coordinated structures $[\mathrm{Cd(NO_3)L}]\mathrm{NO_3}$, both in solution and solid state.

The complex $\mathrm{Cd(ClO_4)_2(Me_6tren)\,.\,H_2O}$ exhibits i.r. bands indicative of sole ionic perchlorate groups (Table III).[15] The occurrence of a band at 193 cm^{-1}, assigned as Cd-O stretching vibration, suggests that the water molecule is coordinated to the cadmium ion, the complex being thus formulated as $[\mathrm{Cd(H_2O)\,.\,(Me_6tren)}]\mathrm{ClO_4}$. Accordingly, it behaves as a typical 1:2 electrolyte.

The complex $\mathrm{Cd(ClO_4)_2(tren)}$, on the contrary, exhibits i.r. bands indicative of both ionic and unidentate perchlorate groups (Table III).[15]

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Table III. I.r. data for some cadmium complexes.

Compound		
$[Cd(NO_3)(tren)]NO_3$	Ionic NO_3	1350vs br(ν_3); 174w($\nu_1+\nu_4$); 2380w($\nu_1+\nu_3$); 829m(ν_2)
	Unidentate NO_3	1400s, 1310s(ν_3); 1735w, 1770w($\nu_1+\nu_4$); 2340sh-2490sh ($\nu_1+\nu_3$); 817m(ν_2)
$[Cd(NO_3)(Me_6tren)]NO_3$	Ionic NO_3	1370vs br(ν_3); 1770m($\nu_1+\nu_4$); 2360m($\nu_1+\nu_3$); 830s(ν_2)
	Unidentate NO_3	1770m, 1740($\nu_1+\nu_4$); 2480w, 2300w ($\nu_1+\nu_3$); 820s(ν_2)
$[Cd(ClO_4)(tren)]ClO_4$	Ionic ClO_4	1090vs br(ν_3), 932m(ν_1), 625s(ν_4)
	Unidentate ClO_4	995s, 977m(ν_3), 695s, 519s(ν_4)
$[Cd(H_2O)(Me_6tren)](ClO_4)_2$	Ionic ClO_4	1100vs br(ν_3), 930vs(ν_1), 625vs(ν_4)

This complex is thus formulated as $[Cd(ClO_4)(tren)]ClO_4$. In dimethylformamide solution, the conductivity value is indicative of extensive displacement of the bound perchlorato by a solvent molecule.

The different coordinative behaviour of perchlorato groups in the above compounds may perhaps be explained by considering the greatest bulkiness of Me_6tren, with rispect to tren, which prevents the close approach of the perchlorate ions but not of the water molecule.

F) *Compounds $Hg(SCN)(BPh_4)(Me_6tren)$ and $Hg(SCN)_2(tren)$.* The compound $Hg(SCN)_2(tren)$ shows i.r. bands at 2105, 2030 (C-N stretching), 750, 710 (C-S stretching), and 465, 432 (N-C-S bending) which are indicative of both ionic and S-bonded thiocianate groups.[16] This is also confirmed by the occurrence of just one i.r. band at 266 cm^{-1} attributed to Hg-S stretching vibration. The electric conductivity value is also in agreement with the formula $[Hg(SCN)(tren)]SCN$. In the compound $[Hg(SCN)(Me_6tren)]BPh_4$, the thiocyanate group is S-bonded as shown by the i.r. bands at 2145, 725 and 45 cm^{-1} as well as by the Hg-S stretching frequency, falling at 231 cm^{-1}. This compound behaves as a 1:1 electrolyte wiht ionic tetraphenylborate.

Conclusions

Cadmium(II) and mercury(II) form with tren and Me_6tren only five-coordinate species: no octahedral species are found even with the less bulky tren. Hence as far as the coordination number is concerned, both these elements behave as zinc(II) does. The differences in stoichiometric ratios occurring among these complexes of zinc, cadmium and mercury appear not to be attributable to the direct interaction between metal and amine, since five-coordinated species are formed in any case. Such a different behaviour, therefore, should indicate the increasing stabilities of the anionic four-coordinated species $[M_2X_6]^{2-}$ and $[MX_4]^{2-}$ on going from zinc to cadmium and mercury. Furthermore, the different structures of $[ZnBr(Me_6tren)]Br$ and $CdBr_2(Me_6tren)$ should probably be due to the relative strengthening of the M-Br bond with respect to the M-N bond on passing from the harder zinc(II) to the softer cadmium(II) ion.[17]

Finally, the occurrence of the novel dinuclear species $[Cd_2I_6]^{2-}$, $[Hg_2I_6]^{2-}$ and $[Hg_2Br_6]^{2-}$ has been proved in the solid state. They probably persist even in solution. It is interesting to recall that the species $[CdX_3^-]_\infty$ and $[HgX_3^-]_\infty$ have been longknown but they present octahedrally coordinated metal atoms.[18]

Note Added in Proofs. Recently, a X-ray diffraction study has proved the occurrence of the $[Hg_2I_6]^{2-}$ anion in 3,5-bis(N,N-diethylimonium)-1,2,4-trithiolane-tetraiododi-μ-iododimercurate(II). *Cf.* P.T. Beurskens, W.P.J.H. Bosman and J.A. Cras, *J. Cryst. Mol. Struct.*, *2*, 183 (1972).

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