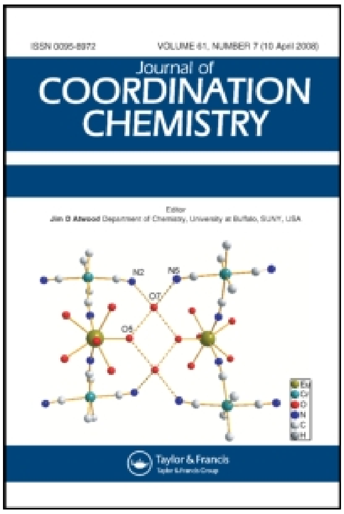

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1,3-PROPANEDIAMINE, 1,4-BUTANEDIAMINE (PUTRESCINE) AND 1,5-PENTANEDIAMINE (CADAVERINE) COMPLEXES WITH ZINC(II), CADMIUM(II) AND MERCURY(II) HALIDES AND PSEUDOHALIDES

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1,3-PROPANEDIAMINE, 1,4-BUTANEDIAMINE (PUTRESCINE) AND 1,5-PENTANEDIAMINE (CADAVERINE) COMPLEXES WITH ZINC(II), CADMIUM(II) AND MERCURY(II) HALIDES AND PSEUDOHALIDES

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Coordination compounds formed by zinc(II), cadmium(II) and mercury(II) halides and pseudohalides with 1,3-propanediamine, 1,4-butanediamine (putrescine) and 1,5-pentanediamine (cadaverine) have been prepared and characterized by molecular conductance and infrared spectral measurements down to 200 cm^{-1}. Possible structures for these complexes in the solid state are discussed.

INTRODUCTION

Ethylenediamine possesses two donor sites and may act as (i) bidentate chelating ligand forming five-membered rings resulting in monomeric structures, or (ii) bidentate bridging ligand resulting in polymeric structures and coordination compounds formed by this ligand with metal(II) salts have been the subject of several investigations. The chelating or *cis*- and bridging or *trans*- configurations of the coordinated ligand can readily be distinguished by infrared spectroscopy. The *trans*- form being more symmetrical gives rise to fewer absorptions in the infrared while multiplicity of bands indicate the less symmetrical *cis*- configuration of ethylenediamine.[1] Earlier investigations on Group II B metal complexes[2–5] have shown that MenX$_2$ (M=Zn(II), Cd(II) or Hg(II), X=Cl and en=ethylenediamine) are polymeric structures with ethylenediamine in the *trans*-configuration bridging between two metal ions. On the other hand, 1:1 mercury(II) cyanide and thiocyanate and 1:2 zinc(II) and cadmium(II) thiocyanate complexes with ethylenediamine are considered to have monomeric structures with *cis*-chelating form of ethylenediamine.[6] Furthermore, N,N-diethylethylenediamine, an unsymmetrically disubstituted ethylenediamine, is shown to form 1:1 complexes not only with mercury(II) halides and pseudohalides but with zinc(II) and cadmium(II) thiocynates as well. All the N,N-diethylethylenediamine complexes studied are considered as four-coordinated monomeric structures with chelated form of the diamine.[7] However, symmetrically disubstituted ethylenediamines are known to form monomeric as well as polymeric structures[8–13] having chelating and bridging diamine, respectively, with transition metal(II) salts. Although infrared spectral studies appear to have been made on the coordination compounds formed by 1,3-propanediamine and 1,4-butanediamine with some metal(II) salts[12–14] there is no report on the complexes of zinc(II), cadmium(II) and mercury(II) halides and pseudohalides with 1,3-propanediamine, 1,4-butanediamine and 1,5-pentanediamine. The increased number of methylene groups introduced between the two amino groups of ethylenediamine would be expected to have an effect on the nature of bonding of the ligand. Coordination of the two amino groups to different metal ions would result in polymeric structures but bonding with the same metal ion (bidentate chelating) would lead to the formation of six-, seven- and eight-membered rings with 1,3-propanediamine, 1,4-butanediamine and 1,5-pentanediamine, respectively. Five- and six-membered rings (including the metal ion) are very common.[15] Examples of the five-membered rings are provided by ethylenediamine and presence of substituents on the carbon atoms do not affect the ring stability. Increasing the number of carbon atoms between the two amino groups would result in an expansion of the ring size if the two donor sites coordinate with the same metal ion. 1,4-Butanediamine and 1,5-pentanediamine are well known by their biological names – putrescine and cadaverine, respectively. Both these compounds also called "biogenic amines" have long been known for their unpleasant odour as well as for their role in protein metabolism and are the important precursors of

TABLE I
Analytical and conductance data

Compound	Method of prepn.*	M.P. (°C)	Analytical data Metal(%) Found	Metal(%) Calc.	Anion (%) Found	Anion (%) Calc.	Conductance data Concentration ($\times 10^{-3}$M)	Λ_M (&)	Nature of diamine bonding	Structural type
$\mathrm{Zn(DP)Cl_2}$	A	269 d	31.2	31.1	33.9	33.7	@		br	I
$\mathrm{Zn(DP)_2Br_2}$	A	214	17.7	17.5	41.9	41.8	@		ch	IV
$\mathrm{Zn(DP)_2I_2}$	A	235	14.1	13.9	54.5	54.2	1.011	212.2	ch	IV
$\mathrm{Cd(DP)_2Cl_2}$	A	185	34.3	34.1	21.7	21.5	@		ch	IV
$\mathrm{Cd(DP)_2Br_2}$	A	189	26.5	26.7	38.1	38.0	@		ch	IV
$\mathrm{Cd(DP)_2I_2}$	A	164	21.7	21.6	50.0	49.9	0.836	98.8	ch	IV
$\mathrm{Cd(DP)(NCS)_2}$	A	229	37.4	37.1	38.5	38.3	1.033	122.0	†	
$\mathrm{Hg(DP)Cl_2}$	A	193	58.0	58.0	20.6	20.5	@		br	I
$\mathrm{Hg(DP)Br_2}$	B	176	46.3	46.2	37.0	36.8	1.022	40.7	ch	II
$\mathrm{Hg(DP)(CN)_2}$	A	138	61.5	61.4	...	...	1.080	3.6	ch	II
$\mathrm{Hg(DP)(SCN)_2}$	C	108	51.5	51.3	30.0	29.7	0.975	90.1	br	I
$\mathrm{Zn(DP)(NCS)_2}$	A	206	25.8	25.6	45.4	45.4	0.988	100.6	ch	II
$\mathrm{Zn(DB)Cl_2}$	A	275	29.3	29.0	32.0	31.7	@		ch	II
$\mathrm{Zn(DB)Br_2}$	A	268	21.0	20.8	51.4	51.1	0.869	16.1	ch	II
$\mathrm{Zn(DB)_2I_2}$	A	286	12.5	12.4	48.5	48.6	@		ch	IV
$\mathrm{Zn(DB)(NCS)_2}$	A	194	24.3	24.2	43.4	43.1	0.922	42.5	ch	II
$\mathrm{Cd(DB)Cl_2}$	A	298 d	41.5	41.3	26.2	26.2	@		br	I
$\mathrm{Cd(DB)Br_2}$	A	271	31.3	31.1	44.2	44.4	@		br	I
$\mathrm{Cd(DB)I_2}$	A	228	25.0	24.8	56.0	55.8	0.973	38.8	ch	II
$\mathrm{Cd(DB)(NCS)_2}$	A	239	35.7	35.5	36.4	36.7	@		br	I
$\mathrm{Hg(DB)Cl_2}$	B	210 d	56.0	55.7	20.0	19.8	@		br	I
$\mathrm{Hg(DB)Br_2}$	B	188 d	45.8	45.6	35.5	35.7	@		ch	II
$\mathrm{Hg(DB)_{0.5}(CN)_2}$	A	171	67.8	67.6	...	...	0.987	4.0	ch	II
$\mathrm{Hg(DB)(SCN)_2}$	C	107	49.8	49.5	28.6	28.7	0.951	100.6	ch	II
$\mathrm{Zn(DAP)Cl_2}$	A	276	27.6	27.4	29.7	29.7	@		br	I
$\mathrm{Zn(DAP)Br_2}$	A	272	20.1	20.0	49.0	48.8	@		ch	II
$\mathrm{Zn(DAP)(NCS)_2}$	A	181	23.3	23.0	41.2	40.9	1.103	127.0	ch	II
$\mathrm{Cd(DAP)Cl_2}$	A	236	39.5	39.4	25.0	24.8	@		ch	II
$\mathrm{Cd(DAP)Br_2}$	A	208	30.3	30.0	43.0	42.7	@		ch	II
$\mathrm{Cd(DAP)I_2}$	A	204	24.0	23.7	55.1	54.8	0.974	40.2	ch	II
$\mathrm{Cd(DAP)(NCS)_2}$	A	191	34.0	34.0	35.3	35.1	0.945	118.4	†	
$\mathrm{Hg(DAP)Cl_2}$	B	183 d	53.9	53.7	19.1	19.0	@		ch	II
$\mathrm{Hg(DAP)Br_2}$	B	142	43.5	43.3	34.8	34.5	0.978	43.0	ch	II
$\mathrm{Hg(DAP)(CN)_2}$	A	139	56.5	56.5	...	...	1.141	3.3	ch	II

DP = 1,3-propanediamine; DB = 1,4-butanediamine; DAP = 1,5-pentanediamine.
@ = insoluble in dimethylformamide,
br = bridging; ch = chelating,
† = distinction of the structural type and the nature of diamine bonding cannot be made,
(&) = Λ_M in mho mole^{-1} cm^{-2}.

hormones as well as the components of certain biological constituents but it is only recently that some work as been carried out on their biological effects.

The present paper describes the preparation, molecular conductance and infrared spectra down to 200 cm^{-1} of the coordination compounds formed by the interaction of zinc(II), cadmium(II) and mercury(II) halides and pseudohalides with 1,3-propanediamine, 1,4-butanediamine and 1,5-pentanediamine.

EXPERIMENTAL SECTION

The following methods of preparation were used:

(A) The metal(II) salt was dissolved in ethanol and an excess of the ligand added.
(B) The metal(II) salt was dissolved in methanol and an excess of the ligand added.
(C) An excess of the ligand was added to an aqueous solution of $K_2Hg(SCN)_4$.

The complexes which precipitated or crystallized out by the above methods were suction-filtered, washed with ethanol/methanol and dried.

Conductivity measurements were made on freshly prepared ~1 mM solutions in purified dimethylformamide at 25°C (±0.5°C) with a Philips Conductivity measuring bridge Model PR 9500.

Infrared spectra in the rock salt region were recorded as NUJOL mulls supported between NaCl plates on a Perkin-Elmer 257 spectrophotometer. The 650 – 200 cm^{-1} i.r. spectra were recorded as NUJOL mulls supported between thin polythene sheets on a Perkin-Elmer 621 spectrophotometer equipped with CsI optics.

TABLE II
Infrared spectra of 1:1 bridged diamine complexes (4000–200 cm^{-1})

$Zn(DP)Cl_2$	$Cd(DB)Cl_2$	Zn-(DAP)Cl_2	Tentative assignments
3250 m	3283 m	3260 m	NH_2 asym. stretch
3230 m	3266 w	3240 m	NH_2 asym. stretch
3148 s	3174 w	3158 s	NH_2 sym. stretch
2950 sh	2950 sh	2955 sh	CH_2 asym. stretch
2920 m	2924 w	2930 m	CH_2 asym. stretch
2850 m	2850 m	2860 m	CH_2 asym. stretch
1600 vs	1608 s	1600 vs	NH_2 scissor
1460 s	1458 s	1462 s	CH_2 scissor
1375 s	1374 s	1380 m	CH_2 wag.
1300 ms	...	1320 m	NH_2 wag.
...	1264 ms	1260 s	CH_2 twist
1210 ms	...	1200 m	CH_2 twist
1154 vs	1124 vs	1165 vs	NH_2 wag.
1045 m	1046 s	1055 w	CN stretch
1027 w	...	1030 s	CN stretch
960 s	959 s	970 s	NH_2 twist
700 w	724 m	705 w	CH_2 rock
560 ms	541 s	560 ms	NH_2 rock
520 ms	...	540 ms	NH_2 rock
450 w	...	465 w	chain skeletal
430 m	425 w	433 w	chain skeletal
365 m	316 ms	395 ms	M – N stretch
310 m	...	305 m	M – X stretch (X = Cl)
296 m	...	...	M – X stretch
485 w	...	...	other bands
400 w	...	...	other bands
250 w	272 w	285 m	other bands

RESULTS AND DISCUSSION

The complexes obtained in the present study, their analytical and conductance data are listed in Table I. The list of complexes obtained is not likely to be the complete range of complexes as only a limited number of preparative methods were used. All the complexes studied, with the exception of mercury(II) cyanide, are insoluble in the common organic solvents like methanol, acetone, acetonitrile, nitrobenzene and nitromethane. Infrared spectral data of a few of the representative 1:1 complexes considered to have four-coordinated polymeric chain structures with the *trans-* form of the diamine bridging between the two metal ions are listed in Table II. Tables III and IV list the i.r. spectral data for 1:1 and 1:2 complexes, respectively, which are considered as monomeric, four-coordinated and six-coordinated structures with *cis-* chelating form of the diamine. Frequencies due to coordinated cynano- and thiocyanato- groups are shown in Table V. Assignments of the metal – nitrogen and metal – halogen/pseudohalogen bands are tentative. Complexes of the type MLX_2 (L = bidentate chelating ligand and X = halogen or pseudohalogen) may be postulated as four-coordinated tetrahedral structures – type I or II, with bridged or chelated form of the diamine, respectively. Similarly ML_2X_2 complexes may be formulated as types III or IV in which the halogen atoms occupy terminal positions with bridging or chelating form of

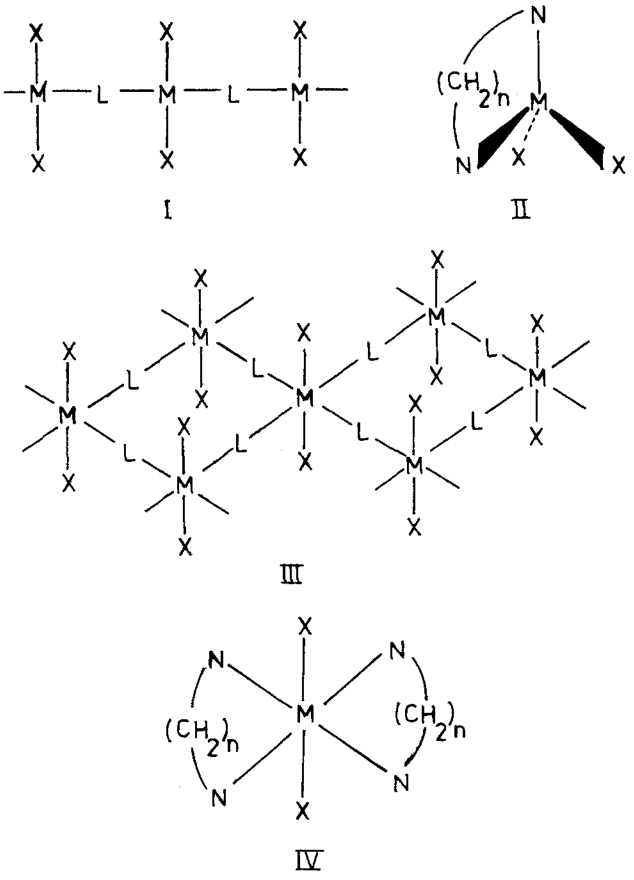
TABLE III
Infrared spectra of 1:1 chelated diamine complexes
(4000–200 cm^{-1})

Zn(DP) (NCS)$_2$	Zn(DB) (NCS)$_2$	Zn(DAP) (NCS)$_2$	Tentative assignments
3306 w	3283 ms	3296 m	NH$_2$ asym. stretch
3280 w	3254 m	3262 m	NH$_2$ asym. stretch
3250 ms	...	...	NH$_2$ asym. stretch
3200 m	3217 s	3220 vs	NH$_2$ sym. stretch
3120 m	3133 w	3135 m	NH$_2$ sym. stretch
...	...	3108 w	NH$_2$ sym. stretch
2950 sh	2960 sh	2960 sh	CH$_2$ asym. stretch
2920 m	2920 ms	2920 m	CH$_2$ asym. stretch
2850 m	2850 ms	2860 m	CH$_2$ sym. stretch
1585 m	1580 w	1580 m	NH$_2$ scissor
1572 m	1566 ms	1563 s	NH$_2$ scissor
1560 w	1556 sh	...	NH$_2$ scissor
1460 s	1458 s	1462 s	CH$_2$ scissor
1395 m	1394 ms	1400 w	CH$_2$ wag.
1375 s	1370 ms	1380 s	CH$_2$ wag.
1360 m	1350 vw	1375 sh	CH$_2$ wag.
1310 m	1313 vw	1330 m	NH$_2$ wag.
1300 w	1308 m	1310 w	NH$_2$ wag.
1280 m	1287 m	1270 m	CH$_2$ twist
1237 w	1266 ms	1256 m	CH$_2$ twist
1194 s	1204 s	1200 s	CH$_2$ twist
1148 s	1162 s	1150 vs	NH$_2$ wag.
1100 s	1096 s	1100 s	Ring mode
1065 m	1042 ms	1050 m	CN stretch
1030 w	1025 s	1030 s	CN stretch
1020 w	...	...	CN stretch
995 vs	1000 ms	...	NH$_2$ twist
980 w	964 w	975 m	NH$_2$ twist
960 w	937 s	955 ms	NH$_2$ twist
904 s	904 w	...	CH$_2$ rock
715 w	733 m	728 m	NH$_2$ rock
...	600 m	...	NH$_2$ rock
...	541 m	550 ms	NH$_2$ rock
435 m	433 mw	425 ms	Ring mode
380 m	366 m	385 ms	M – N stretch
...	400 m	...	other bands
330 w	278 w	330 w	other bands
240 w	...	305 w	other bands

the diamine. Infrared spectra of some of the representative compounds showing the bridging and chelating forms of the ligands used are shown in Figures 1–3.

Although the techniques of electronic absorption spectroscopy and magnetic susceptibility measurements yield unambiguous structural information of the transition metal compounds these could not be studied for the zinc(II), cadmium(II) and mercury(II) complexes as these metal ions have closed shells of valence electrons. However, stereochemistry of the compounds studied in the present investigation has been postulated from a comparison of the metal–ligand modes and the vibrations due to coordinated anionic groups with similar modes in complexes whose structures are known from X-ray crystallography and/or magnetic susceptibility and infrared spectral studies.

Infrared spectra of the diamines used in the present study exhibit only a small number of absorption bands in the uncoordinated state. In spite of the increased number of methylene groups in between the two amino groups the i.r. spectra of these diamines show close resemblance to the i.r. spectrum of ethylenediamine. The vibrational spectra of



Structural Types

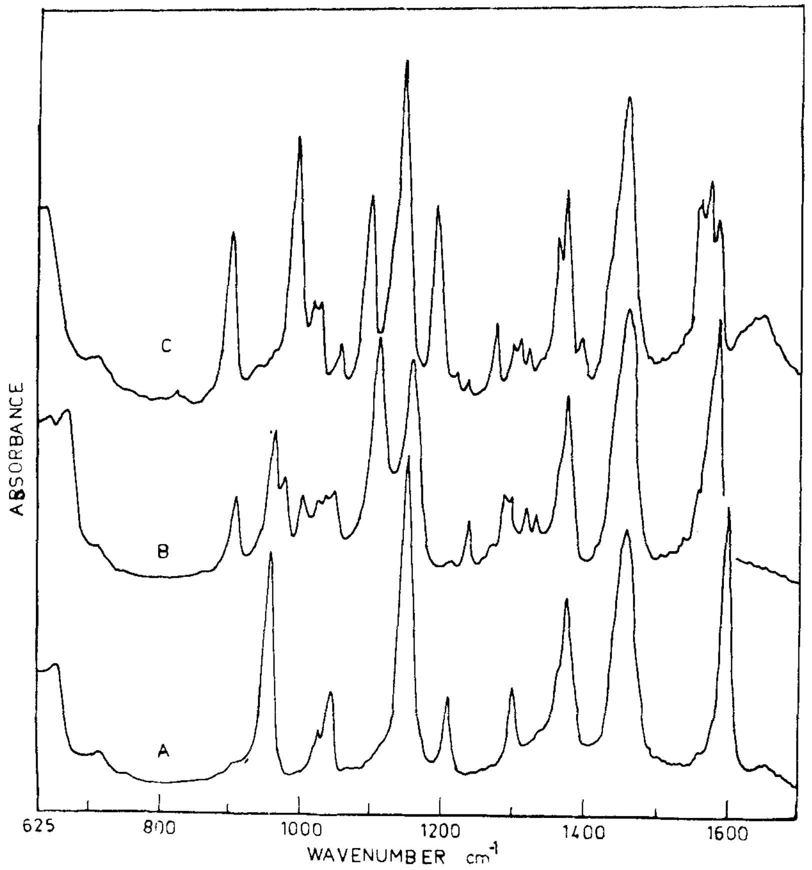


FIGURE 1 1,3-Propanediamine complexes A – $Zn(DP)Cl_2$; B – $Zn(DP)_2Br_2$; C – $Zn(DP)(NCS)_2$

1,3-propanediamine, 1,4-butanediamine and 1,5-pentanediamine, their hydrochlorides[16–18] and their metal complexes[12–14,19] have received some attention. Infrared spectra of the compounds studied here show clearly that the diamines used are coordinated via both the nitrogen atoms of the amino groups. The formation of coordinate bond between the diamines and the metal(II) salts is immediately apparent in the NH and CN stretching regions. The NH stretching frequency region (3400–3100 cm^{-1}) generally shows three or four distinct sharp peaks in all these compounds. Only two bands would be expected for the NH asymmetric and symmetric stretching modes. However, appearance of more than two bands may possibly be due to Fermi interactions.

The NH deformation mode at ~1600 cm^{-1} in the free diamines appear as medium to strong sharp peaks usually with a shoulder in the region 1610–1550 cm^{-1} in the complexes studied here. This shift in the NH deformation mode has also proved useful in distinguishing the chelating and bridging forms of the diamines.[20,21] The CN asymmetric and symmetric stretching vibrations in the uncomplexed diamines occur at ~1090 cm^{-1} and ~1070 cm^{-1}, respectively. On coordination these bands suffer negative shifts and occur at ~1050 cm^{-1} and ~1030 cm^{-1}, respectively. The shift of NH and CN stretching modes to lower frequencies in the complexes can be explained as resulting from the electron drainage from the nitrogen atom on account of its coordination to the metal ion. In general infrared spectra of the complexes with the diamines bridging between two metal ions exhibit 9–10 absorption bands in the region 1600 – 650 cm^{-1} while 20 – 22 bands are observed in complexes with chelated form of the diamine. Splitting of bands in the spectra of chelated diamines generally occurs in two regions (i) 1320–1250 cm^{-1}, and (ii) 1070–1000 cm^{-1} Usually one sharp band is observed for bridging diamines at ~1040 cm^{-1} which splits up into 2–3 bands in the range 1070–1000 cm^{-1}, while the band at ~1250 cm^{-1} splits up into 2–3 bands in the

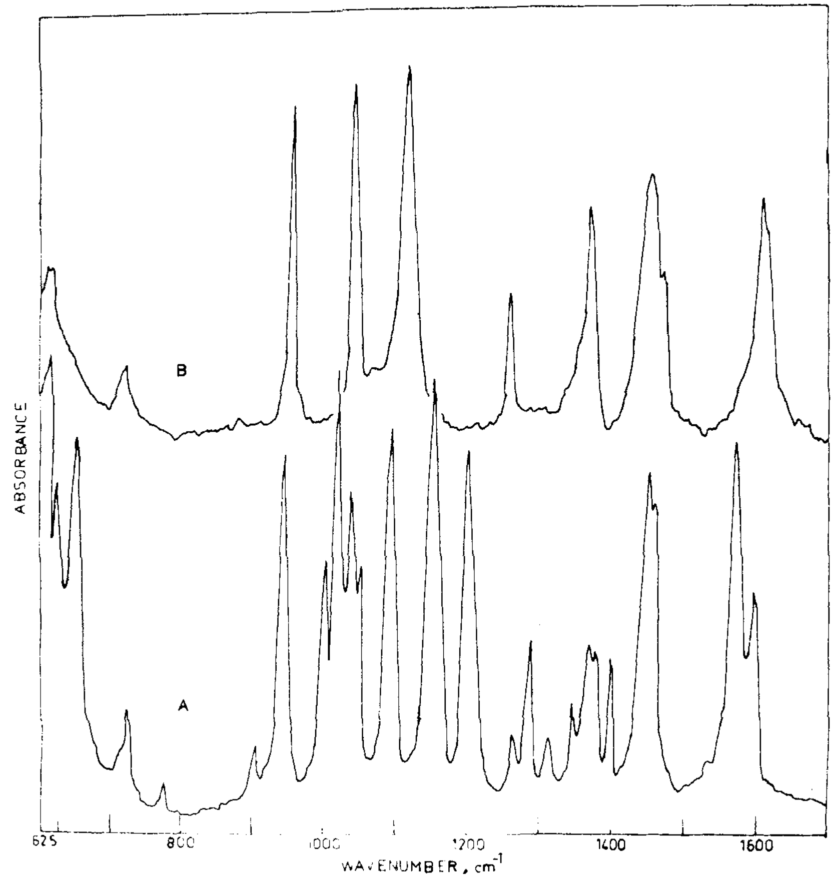


FIGURE 2 1,4-Butanediamine complexes A – Zn(DB)Cl_2; B – Cd(DB)Cl_2

range 1325–1250 cm^{-1} in the chelated diamine complexes. In addition to these the NH deformation mode suffers a significant negative shift (vide supra) and shows multiplicity of bands when the two nitrogen atoms of the diamine coordinate to the same metal ion.

Infrared spectra of the complexes reported here have many features in common to those of the ethylenediamine complexes. Spectra of the compounds marked type I (Table I) show remarkable similarities with those of the 1:1 complexes of zinc(II), cadmium(II) and mercury(II) chlorides with ethylenediamine which have been shown by infrared, Raman and/or X-ray structural investigations to have linear polymeric chain structures with the diamine in its *trans*- configuration acting as a bridge between two metal atoms.[1–5,22,23] On the other hand, i.r. spectra of the complexes considered to have chelated form of the diamines (Types II and IV) exhibit multiplicity of bands and resemble closely with those of the metal(II)–ethylenediamine complexes in which the *cis*- chelating form of ethylenediamine has been established.[1,20,21,24,25] Thus 1,3-propanediamine, 1,4-butanediamine and 1,5-pentanediamine may act as bidentate bridging or chelating ligands; when chelating they lead to the formation of six-, seven- and eight-membered rings, respectively. Several complexes of metal salts are known with six-, seven- or eight-membered rings which are quite stable.[15] The present studies indicate that among the mercury(II) complexes of the same stoichiometry (metal:ligand ratio) with a given diamine the tendency towards chelation increases in going from chloro- to bromo- derivatives. Further the tendency for chelation also appears to increase as the number of methylene groups increases between the two amino groups.

Metal(II) Halide Complexes

From a consideration of the metal–halogen stretching modes[26] the 1:1 zinc(II) and mercury(II)

TABLE IV
Infrared spectra of 1:2 chelated diamine complexes (4000–200 cm^{-1})

$Zn(DP)_2Br_2$	$Zn(DP)_2I_2$	$Cd(DP)_2Cl_2$	$Cd(DP)_2Br_2$	$Zn(DB)_2I_2$	Tentative assignments
3280 m	3266 m	3308 m	3285 w	3238 ms	NH_2 asym. stretch
3242 m	3180 ms	3250 m	3235 s	3183 ms	NH_2 asym. stretch
3180 ms	3100 m	3160 s	3136 ms	3117 m	NH_2 sym. stretch
3100 m	...	...	...	...	NH_2 sym. stretch
2950 sh	2950 sh	2960 sh	2940 sh	2950 sh	CH_2 asym. stretch
2920 m	2924 m	2930 w	2920 m	2917 m	CH_2 asym. stretch
2850 ms	2852 ms	2880 mw	2855 m	2850 ms	CH_2 sym. stretch
1583 vs	1575 sh	1600 sh	1582 s	1575 sh	NH_2 scissor
1575 w	1560 s	1583 ms	1575 sh	1562 ms	NH_2 scissor
...	1554 sh	...	1554 sh	1554 sh	NH_2 scissor
1460 s	1458 s	1470 s	1460 s	1458 m	CH_2 scissor
...	1437 sh	1440 sh	1435 sh	1450 m	CH_2 scissor
1375 s	1374 s	1384 ms	1372 s	1370 s	CH_2 wag.
1365 sh	...	1370 m	1365 vw	...	CH_2 wag.
1335 m	1333 m	1310 w	1300 vw	1325 w	NH_2 wag.
1320 m	1316 m	...	...	...	CH_2 wag.
1290 mw	1295 ms	1280 m	1265 m	1287 w	CH_2 twist
1240 m	1233 s	1255 m	1245 w	1270 m	CH_2 twist
1215 vw	1208 w	...	...	1200 vw	CH_2 twist
1157 s	1158 s	1150 sh	1166 vw	1170 s	NH_2 wag.
...	...	...	1140 sh	1141 s	NH_2 wag.
1110 s	1108 w	1120 ms	1110 m	1108 w	Ring mode
...	...	1100 ms	1090 m	1083 m	Ring mode
1055 m	1050 ms	1060 s	1074 w	1041 sh	CN stretch
1030 w	1033 m	1035 m	1050 s	1033 ms	CN stretch
1007 m	1016 w	1010 s	1000 s	...	NH_2 twist
980 m	1000 s	970 s	960 s	987 w	NH_2 twist
965 s	975 s	...	...	962 s	NH_2 twist
910 m	914 s	890 s	880 s	933 s	CH_2 rock
...	858 w	...	...	900 w	CH_2 rock
715 w	717 w	763 m 720 w	752 w 715 w	783 w 717 w	CH_2 rock
670 ms	654 s	...	...	675 ms	NH_2 rock
600 w	612 ms	600 s	591 s	617 ms	NH_2 rock
565 m	562 ms	562 m	560 m	583 w	NH_2 rock
535 ms	520 ms	505 ms	505 ms	525 ms	NH_2 rock
430 ms	425 ms	465 s	460 s	435 m	Ring mode
365 ms	338 ms	355 m	338 m	300 ms	M – N stretch
485 m 330 w 305 m 230 ms	474 s 292 m	260 ms 228 w	320 w 260 m	450 ms 417 ms	other bands

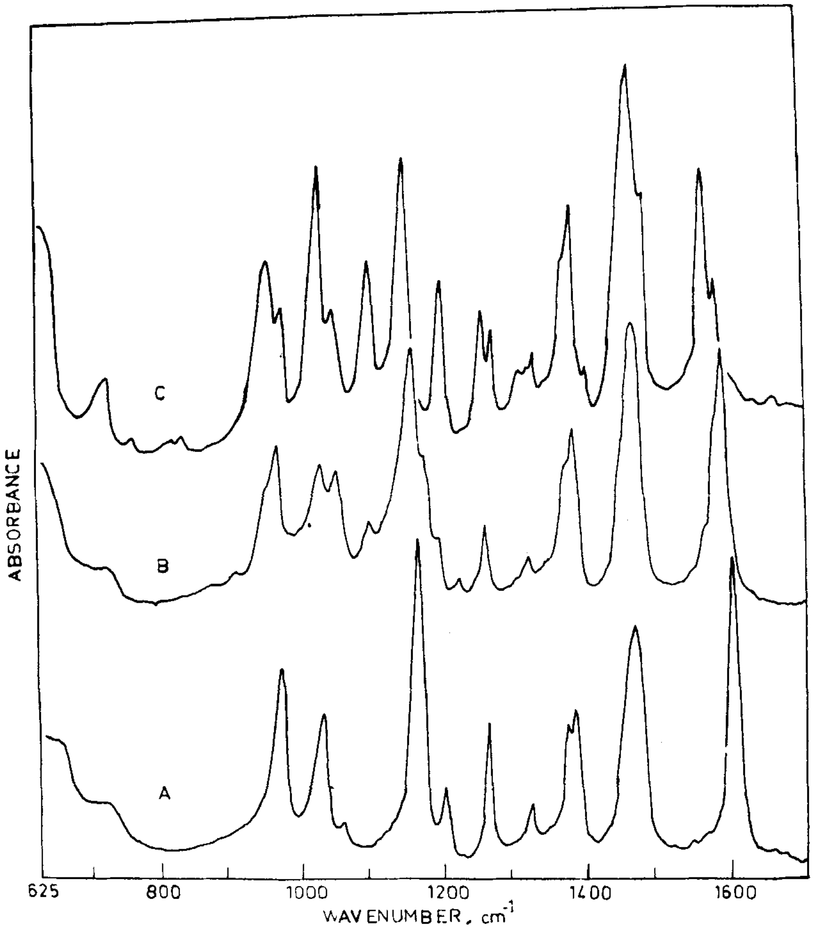


FIGURE 3 1,5-Pentanediamine complexes A – Zn(DAP)Cl$_2$; B – Zn(DAP)Br$_2$; C – Zn(DAP)(NCS)$_2$

halide complexes in the present studies shown to have chelating diamines (Table III) may be considered as monomeric four-coordinated structures (type II). On the other hand, 1:1 compounds with bridging diamines (Table II) are considered as four-coordinated polymeric structures with only terminal halogens (type I). The 1:2 complexes ML_2X_2 are postulated to have an octahedral environment of the ligand atoms around the metal ions. The two halogens in the 1:2 complexes may be in *cis-* or *trans-* positions to each other. The *cis-* and *trans-* isomers in bisethylenediamine metal complexes can easily be recognized from their infrared spectra. Consistent variations in the *cis-* and *trans-* isomers in bisethylenediamine complexes have been observed in the regions (A) 1630 – 1520 cm^{-1} (B) 1150 – 1120 cm^{-1} and (C) 900 – 850 cm^{-1} and several complexes have thus been characterized.[27–29] Infrared spectra of the 1:2 complexes studied here indicate clearly that the two anionic groups are in *trans-* positions to each other as the unsymmetrical *cis-* disposition of these groups will give rise to greater number of absorption bands in the regions cited above.[27–29] Cadmium(II) halides gave 1:2 complexes with 1,3-propanediamine but 1:1 with 1,4-butanediamine and 1,5-pentanediamine. Rock salt region i.r. spectra show bidentate chelating nature of the diamines in all the cadmium(II) halide complexes except the 1:1 cadmium(II) chloride and bromide complexes with 1,4-butanediamine. The bidentate chelating nature of 1,3-propanediamine (vide supra) combined with the non-electrolytic nature, the 1:2 cadmium(II) halide complexes with this ligand are considered as six-coordinated structures with the two halogens in the *trans-* positions. The metal–halogen stretching modes in octahedral cadmium(II) halide complexes and the Cd–Br and Cd–I stretching modes in four-coordinated complexes are expected to occur[30] below 200 cm^{-1} the

TABLE V
Infrared spectral data (cm^{-1}) of metal(II) pseudohalide complexes

Compound	νCN	νCS	δNCS	νM-NCS/SCN	νM-C	δMCN
$Zn(DP)(NCS)_2$	2100 sh 2080 s	825 w	480 w 470 m	285 m 260 m	...	...
$Zn(DB)(NCS)_2$	2100 w 2083 s	816 m 792 m	483 m 466 m	280 m 250 m	...	...
$Zn(DAP)(NCS)_2$	2116 m 2090 m	765 m	470 s 465 sh	290 m 260 m	...	...
$Cd(DP)(NCS)_2$	2090 vs	770 m	465 w	215 w	...	...
$Cd(DB)(NCS)_2$	2108 vs	770 m	458 ms	...	...	...
$Cd(DAP)(NCS)_2$	2085 vs	760 ms	470 sh 462 s	220 mw	...	...
$Hg(DP)(SCN)_2$	2095 vs	691 m	433 m	291 w 266 w	...	...
$Hg(DB)(SCN)_2$	2113 vs 2066 w	708 m	425 m 417 sh	292 w 274 m	...	...
$Hg(DP)(CN)_2$	2158 s	...	...	...	385 s	320 m 305 w
$Hg(DB)_{0.5}(CN)_2$	2175 s	...	...	...	374 m	316 m
$Hg(DAP)(CN)_2$	2152 ms	...	...	...	365 s	290 m

lower frequency limit of the far infrared spectrophotometer used in these studies.

Metal(II) Pseudohalide Complexes

Zinc(II), cadmium(II) and mercury(II) thiocyanates gave 1:1 complexes with the diamines studied except that mercury(II) thiocyanate did not react with 1,5-pentanediamine. Rock salt region i.r. spectra indicate the bidentate chelating nature of the diamines in these compounds except the 1:1 mercury(II) thiocyanate–1,3-propanediamine and 1:1 cadmium(II) thiocyanate–1,4-butanediamine complexes which show bridging diamines. Fundamental vibrations associated with the coordinated thiocyanate groups (Table V) are consistent with terminal N-bonded SCN groups in the 1:1 zinc(II) and cadmium(II) thiocyanate complexes and terminal S-bonded in the case of mercury(II) thiocyanate complexes.[31] The 1:1 mercury(II) thiocyanate–1,3-propanediamine and 1:1 cadmium(II) thiocyanate–1,4-butanediamine complexes are postulated to have four-coordinated polymeric chain structures (type I) with the *trans*-form of the diamine bridging between the metal ions while other 1:1 zinc(II) and mercury(II) thiocyanate complexes are considered as monomeric four-coordinated tetrahedral structures with *cis*- chelating configuration of the diamines (type II). The monomeric tetrahedral structures exhibit two bands in the νCN, δSCN and νM–NCS/SCN regions consistent with the symmetry group of the compounds.[32] In the cadmium(II) thiocyanate complexes (except that with 1,4-butanediamine) the bridging or chelating nature of the diamines used cannot be distinguished clearly from their i.r. spectra. These compounds exhibit less splitting of bands and the total number of bands in the range 1600–650 cm^{-1} is slightly more than the bridged diamines complexes but much fewer when compared with chelated complexes. Hence no definite information can be derived from the i.r. spectra of these complexes.

Mercury(II) Cyanide Complexes

Mercury(II) cyanide gave 1:1 complexes with 1,3-propanediamine and 1,5-pentanediamine, but a 2:1 compound with 1,4-butanediamine. Zinc(II) and cadmium(II) cyanides did not react with the diamines studied. Infrared spectra indicate clearly the presence of bidentate chelating nature of these diamines. The observed frequencies associated with νCN, νHg – C and δHg C N modes are consistent with terminal cyano groups.[7,33,34] With bidentate chelating diamines and terminal cyano groups the 1:1 complexes may be considered to have a four-coordinated environment about the metal ions.

Metal – Nitrogen Stretching Modes

The two terminal amino groups in ethylenediamine which are separated by two methylene groups are considered to have an inductive effect and thus perturb the molecular vibrations. However, in the uncoordinated 1,3-propanediamine, 1,4-butanediamine and 1,5-pentanediamine there is no interaction between the two terminal amino groups because of complete free rotation and this fact can easily be recognized from their almost identical values of dipole moments.[35] The basicity of these diamines show an increase from ethylenediamine to cadaverine.[36] Furthermore, from a consideration of the ability of the NH_2 groups to donate electron density to metal ions one may postulate the relative strength of the metal – ligand bonding in metal – diamine complexes as

ethylenediamine < 1,3-propanediamine <
1,4-butanediamine < 1,5-pentanediamine.

In the present studies these diamines appear to form weaker complexes as indicated by the lower metal – nitrogen stretching frequencies (Tables II–IV) than in the case of ethylenediamine complexes. This is easily understandable by considering the flexibility of the ring size which increases from ethylenediamine to cadaverine. As a result the ring skeletal frequencies would be expected to absorb at lower energies, in fact, much closer to the expected range of metal – nitrogen stretching frequencies, Tables II–IV

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