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Mercury(II) Thiocyanate Complexes with Some Bidentate Ligands

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Coordination compounds formed by the interaction of mercury(II) thiocyanate with some bidentate ligands—ethylenediamine, N,N-diethylethylenediamine, 1,3-propanediamine, 1,4-butanediamine, morpholine, methylpyrazine, 1,4-dioxane, 2,2′-bipyridyl, 1,10-phenanthroline, 2,2′-bipyridylamine, 2,2′-bipyridyl N,N′-dioxide, 4,4′-bipyridyl and 4,4′-bipyridyl N,N′-dioxide—have been prepared. Stoichiometries of the complexes have been established by metal and thiocyanate estimations gravimetrically. The complexes isolated in the solid state have been characterized by infrared spectral measurements down to 200 cm^{-1} to elucidate the mercury(II)-ligand and mercury(II)-thiocyanate bonding modes. Tentative stereochemistries of the complexes in the solid state are discussed.

INTRODUCTION

Coordination compounds formed by mercury(II) halides with potentially bidentate ligands have been the subject of several reviews.[1-5] The present communication describes the coordination compounds formed by the interaction of mercury (II) thiocyanate with ethylenediamine, N,N-diethylethylenediamine, 1,3-propanediamine, 1,4-butanediamine, morpholine, methylpyrazine, 1,4-dioxane, 2,2′-bipyridylamine, 2,2′-bipyridyl, 1,10-phenanthroline, 2,2′-bipyridyl N,N′-dioxide, 4,4′-bipyridyl and 4,4′-bipyridyl N,N′-dioxide and 1,3-bis-(4-pyridyl) propane.

EXPERIMENTAL

Mercury (II) thiocyanate was obtained from M/s Ega Chemie, West Germany and used as such. Ethylenediamine, N,N′-diethylethylenediamine. 1,3-propanediamine, 1,4-butanediamine, 2,2′-bipyridyl, 1,10-phenanthroline, 4,4′-bipyridyl, 2,2′-bipyridylamine (all from Koch Light Laboratories, England), methylpyrazine (Wyandotte Chemicals Corporation, U.S.A.) were used as such. 2,2′-Bipyridyl N,N′-dioxide and 4,4′-bipyridyl N,N′-dioxide were prepared by oxidizing the respective bipyridyls.[6]

The mercury(II) thiocyanate complexes were synthesized by boiling a suspension of the metal (II) thiocyanate in ethanol with an excess of the respective ligand (except the first three complexes which were prepared by reacting $K_4Hg(SCN)_4$ in ethanol with the respective ligand) and the mixture was filtered hot. The complexes which crystalized out on cooling were suction-filtered, washed with ethanol and dried in an air oven at *ca.* 60°C.

Stoichiometries of the solid complexes isolated were established by metal and thiocyanate estimations gravimetrically.[7] Mercury was estimated by dissolving the complex in dilute hydrochloric acid and completing the estimation as mercury(II) sulphide. For the estimation of thiocyanate, the complexes were decomposed by boiling with sodium carbonate solution containing some caustic soda, neutralizing the filtrate with dilute nitric acid and completing the estimation as silver thiocyanate. Analytical data of the complexes are listed in Table 1.

TABLE 1

ANALYTICAL DATA OF MERCURY(II) THIOCYANATE COMPLEXES

Compound	Mercury %		Thiocyanate %	
	Found	Calcd.	Found	Calcd.
$Hg(en)(SCN)_2$	53.1	53.2	30.6	30.8
$Hg(dien)(SCN)_2$	46.4	46.2	26.6	26.8
$Hg(PAD)(SCN)_2$	51.5	51.3	30.0	29.7
$Hg(BAD)(SCN)_2$	49.8	49.5	28.6	28.7
$Hg(Morpholine)_2(SCN)_2$	41.0	40.8	23.5	23.6
$Hg(Dioxane)(SCN)_2$	49.5	49.5	28.5	28.7
$Hg(MP)(SCN)_2$	48.5	48.6	28.1	28.2
$Hg(2,2'\text{-}Bipy)(SCN)_2$	42.1	42.3	24.5	24.5
$Hg(1,10\text{-}Phen)(SCN)_2$	40.5	40.3	23.5	23.3
$Hg(2,2'\text{-}BipyA)(SCN)_2$	41.0	41.1	24.0	23.8
$Hg(2,2'\text{-}BipyO_2)(SCN)_2$	40.1	39.8	22.7	23.0
$Hg(4,4'\text{-}Bipy)(SCN)_2$	42.5	42.4	24.8	24.6
$Hg(4,4'\text{-}BipyO_2)_2(SCN)_2$	28.9	28.7	16.9	16.7
$Hg(DPP)(SCN)_2$	39.3	38.9	22.7	22.5

en = ethylenediamine; dien = N,N-diethylethylenediamine; PAD = 1,3-propanediamine; BAD = 1,4-butanediamine; Dioxane = 1,4-dioxane; MP = methylpyrazine; Bipy = bipyridyl; $BipyO_2$ = bipyridyl N,N'-dioxide; DPP = 1,3-bis-(4-pyridyl)propane; BipyA = 2,2'-bipyridylamine.

Infrared spectra of the uncoordinated ligands and their complexes with mercury(II) thiocyanate were recorded as nujol mulls held between sodium chloride plates (4000–650 cm^{-1}) and thin polyethylene sheets or caesium iodide plates (700–200 cm^{-1}) on a Perkin-Elmer Spectrophotometer Model 621 equipped with caesium iodide optics. The observed frequencies due to coordinated thiocyanate groups, the mode of mercury(II)-ligand bonding and the tentative stereochemistry of each complex are listed in Table 2.

TABLE 2

INFRARED SPECTRAL DATA (cm^{-1}), MODE OF Hg(II)-LIGAND BONDING AND STEREOCHEMISTRY

Compound	Coordinated SCN frequencies				Mode of Hg-Ligand Bonding	Tentative stereochemistry
	νCN	νCS	δSCN	νHg-SCN		
$Hg(en)(SCN)_2$	2100	709	428	300	Bidentate chelating	Monomeric tetrahedral
$Hg(dien)(SCN)_2$	2100	709	430	298	Bidentate chelating	Monomeric tetrahedral
$Hg(PAD)(SCN)_2$	2095	691	433	291	Bidentate bridging	Polymeric tetrahedral
$Hg(BAD)(SCN)_2$	2113	708	425 417	292	Bidentate chelating	Monomeric tetrahedral
$Hg(Morpholine)_2(SCN)_2$	2110	710	451 437	323	Terminal N-bonded monodentate	Monomeric tetrahedral
$Hg(Dioxane)(SCN)_2$	2110	720	461 430	313	Bidentate bridging	Polymeric tetrahedral
$Hg(MP)(SCN)_2$	2112	720	460 432	307	Bidentate bridging	Polymeric tetrahedral
$Hg(2,2'\text{-}Bipy)(SCN)_2$	2110	715	435 425	301	Bidentate chelating	Monomeric tetrahedral
$Hg(1,10\text{-}Phen)(SCN)_2$	2113	709	455 440	297	Bidentate chelating	Monomeric tetrahedral
$Hg(2,2'\text{-}BipyA)(SCN)_2$	2126	695	456 425	283	Bidentate chelating	Monomeric tetrahedral
$Hg(2,2'\text{-}BipyO_2)(SCN)_2$	2132	715	445 418	296	Bidentate chelating	Monomeric tetrahedral
$Hg(4,4'\text{-}Bipy)(SCN)_2$	2100	670	446 416	270	Bidentate bridging	Polymeric tetrahedral
$Hg(4,4'\text{-}BipyO_2)_2(SCN)_2$	2125 2104	717	459 453	280	Bidentate bridging	Polymeric octahedral
$Hg(DPP)(SCN)_2$	2120	705	454 422	287	Bidentate bridging	Polymeric tetrahedral

RESULTS AND DISCUSSION

The techniques of electronic absorption spectroscopy and magnetic susceptibility measurements yield unambiguous structural information of transition metal compounds. Because of the closed shell of valence electrons these could not be studied for the mercury(II) compounds. Stereochemistries of the compounds studied herein have been arrived at by comparing the mercury(II)-ligand and mercury(II)-thiocyanate bonding modes with similar modes in complexes whose structures are known through X-ray crystallography and/or magnetic suscepitibility and infrared spectral studies.

Thiocyanates of Group II B metals offer interesting examples of the mode of metal-thiocyanate bonding. Zinc(II) and mercury(II) form M-NCS and M-SCN bonded complexes, respectively. Thiocyanato-bridged complexes of mercury(II) are also known.[8, 9] Cadmium(II) is intermediate in character as both Cd-NCS and Cd-SCN bonded species have been observed[10]. The mode of metal-thiocyanate bonding can be distinguished from the frequency ranges in the infrared spectrum for the three fundamental vibrational modes of the thiocyanate group,[8,9] viz., νCN, νCS and the doubly degenerate δNCS.

Diamine Complexes

Infrared spectra of the 1 : 1 mercury(II)thiocyanate complexes with ethylenediamine, N,N′-diethylethylenediamine, 1,3-propanediamine and 1,4-butanediamine show clearly that the diamines are coordinated via both the nitrogen atoms of the amino groups. The formation of coordinate bond between the diamines and the mercury(II) 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 *ca.* 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 mercury(II) thiocyanate complexes studied. The CN asymmetric and symmetric stretching vibrations in these uncoordinated diamines occur at *ca.* 1090 and *ca.* 1070 cm^{-1}, respectively. The shift of NH and CN stretching modes to lower frequencies in the mercury(II) thiocyanate complexes can be explained as resulting from the election drainage from the nitrogen atom on account of its coordination to the metal(II) ion. In general, infrared spectra of the complexes with diamines bridging between two metal ions exhibit 9–10 absorption bands in this region 1600–650 cm^{-1} while 20–22 bands are observed in complexes with chelated form of the diamines.[11-14]

Infrared spectra of 1 : 1 mercury(II) thiocyanatc complexes with ethylenediamine, N,N-diethylethylenediamine and 1,4-butanediamine show significant differences from the infrared spectra of metal(II) chloride and bromide complexes with these ligands which have been shown by infrared, Raman and/or X-ray structural studies to have trans configuration of the diamine acting as a bridge between two metal atoms.[11] On the other hand, infrared spectra of the mercury(II) thiocyanate complexes with the diamines studied (except 1,3-propanediamine) exhibit multiplicity of bands and closely resemble those of the metal(II) ethylenediamine complexes in which the chelating form of ethylenediamine has been established.[14-17] It is thus clear that ethylenediamine, N,N-diethylethylenediamine and 1,4-butanediamine act as bidentate chelating ligands in their complexes with mercury(II) thiocyanate and lead to the formation of 5-membered rings in the case of first two ligands and 7-membered ring with the third ligand.

Infrared spectrum of the 1 : 1 mercury(II) thiocyanate complex with 1,3-propanediamine shows remarkable similarities with 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 polymeric chain structures with the diamine in its trans configuration acting as a bridge between two metal ions.[11]

In addition to absorption bands due to coordinated diamines, infrared spectra of these complexes show bands at *ca.* 2100, 700 and 430 cm^{-1} (Table 2) which are assigned as νCN, νCS and δNCS modes, respectively, due to coordinated thiocyanato groups. The frequencies of these modes are consistent with similar fundamental frequencies normally associated with terminally S-bonded SCN groups.[8,9] With bidentate chelating nature of ethylenediamine, N,N-diethylethylenediamine and 1,4-butanediamine and the terminally S-bonded SCN groups, the 1 : 1 mercury(II) thiocyanate complexes with these ligands are considered as monomeric four-coordinated structures with a tetrahedral environment of two nitrogen atoms from the diamines and two sulphur atoms from SCN groups around mercury(II) in the solid state. The 1 : 1 mercury(II) thiocyanate complex with 1,3-propanediamine is postulated to have four-co-ordinated tetrahedral polymeric structure with trans form of the diamine bridging between the metal ions (vide supra) and terminally S-bonded SCN groups.

1,4-Dioxane Complex

Except for some intensity changes and the slightly lower frequencies of some absorption bands (particularly the asymmetric C-O-C and symmetric stretching vibrations at 1125 and 880 cm^{-1}, respectively, in the complex which provides good evidence for the absence of uncoordinated ligand) infrared spectrum of the 1 : 1 mercury(II) thiocyanate complex with 1,4-dioxane is almost superimposable on the spectra of its constituent molecules. This close similarity in the infrared spectra of the complex and the free constituent molecules was earlier observed[18] for Hg(1,4-dioxane)Cl_2. X-ray structural studies[19] on Hg(1,4-dioxane)Cl_2 have shown the mercury(II) chloride and dioxane molecules to be linked together by weak O-Hg-O bonds to make a planar chain and that the two constituent molecules retain essentially similar configurations to those in their free molecules.[18] This close similarity in the infrared spectra of the 1 : 1 mercury(II) thiocyanate complex with 1,4-dioxane to that of its constituent molecules strongly suggests that the interaction between dioxane and the mercury(II) thiocyanate molecules is almost of the same order as in Hg(1,4-dioxane)Cl_2. However, if the coordinated dioxane molecules had a boat rather than a chair configuration in its complex with mercury(II) thiocyanate, the infrared spectrum would be expected to have a multiplicity of absorption bands owing to the increased number of infrared active fundamentals. It has been pointed out[20] that for 1,4-dioxane 17 infrared active fundamentals in the region 1500–750 cm^{-1} are permitted for the boat structure while only 7 are allowed for the chair form. Since the fundamental frequencies due to coordinated thiocyanate groups in this complex do not suffer any significant shift it is suggested that the planar chain arrangement of the two oxygens and the two chlorines (two S-bonded SCN groups in the thiocyanate complex) surrounding mercury(II) in the Hg(1,4-dioxane)Cl_2 is retained in the 1 : 1 mercury(II) thiocyanate complex as well.

Morpholine Complex

Infrared spectrum of the 1 : 2 mercury(II) thiocyanate complex with this ligand shows that the NH stretching mode of the uncoordinated morpholine at 3440 cm^{-1} occurs at 3230 cm^{-1} in this compound. The observed lowering in the NH stretching frequency is of the same magnitude as has been previously reported for the morpholine complexes with metal(II) salts.[21,22] The weakening of the NH bond can be explained as resulting from the electron drainage from the nitrogen atom on account of its coordination to the metal ion. The νC-O-C at 1091 cm^{-1} in uncoordinated morpholine does not suffer any shift at all. The morpholine thus acts as N-bonded monodentate ligand[21–23] in this complex. The observed bands due to coordinated thiocyanato groups—νCN 2110 cm^{-1}, νCS 710 cm^{-1} and δSCN 451, 437 cm^{-1} are consistent with terminally S-bonded SCN groups. With unidentate terminal N-bonded morpholine molecules and S-bonded SCN groups the 1 : 2 mercury(II) thiocyanate complex with morpholine is suggested to have a four-coordinated monomeric tetrahedral structure in the solid state.

Methylprazine and 4,4′-bipyridyl complexes

Pyrazine and 4,4′-bipyridyl may be considered as pyridine derivatives, replacement of one of the CH groups para to the nitrogen by another nitrogen results in pyrazine and that of a proton in the para position by a pyridyl group resulting in 4,4′-bipyridyl. Whereas pyrazine is known to act as a monodentate ligand as well as bidentate bridging ligand, 4,4′-bipyridyl acts predominantly as a bidentate bridging ligand and metal complexes exhibiting the monodentate behaviour of 4,4′-bipyridyl are relatively few.[24, 25] Geometries of both these ligands, however, rule out their bidentate chelating behaviour.

Except for slight shifting and/or splitting of some absorption bands and the appearance of bands at 990 and 1250 cm^{-1} (which indicate that the ligand is bonded through both the ring nitrogens and that the complex has a short chain length polymeric structure[26–28] infrared spectrum of the 1 : 1 mercury(II) thiocyanate complex with methylpyrazine studied herein is almost superimposable on the spectra of the constituent molecules and may be compared with the bidentate bridging nature of 1,4-dioxine[18] in the Hg(1,4-dioxane)Cl_2 complex. It is thus concluded that the interaction between methylpyrazine and mercury(II) thiocyanate is of the same order as in Hg(1,4-dioxane)Cl_2. Moreover, the fundamental frequencies due to thiocyanato groups (Table 2) do not suffer any significant shift/splitting in this complex. Thus the complex has a planar chain arrangement of two nitrogen atoms (bridging methylpyrazine molecules) and two sulphur atoms of S-bonded SCN groups around mercury(II) in the solid state.

Except for some minor changes due to coordination, infrared spectrum due to coordinated 4,4′-bipyridyl in the 1 : 1 mercury(II) thiocyanate complex shows close similarities with the spectrum of uncoordinated ligand and is in agreement with the previous observations on the metal-pyridine complexes.[29] Steric position of the nitrogen atoms in 4,4′-bipyridyl precludes chelation but favours coordination to two different metal ions. Infrared bands due to thiocyanato groups are consistent with terminally S-bonded groups (Table 2) and the complex is considered as a polymeric chain structure with a tetrahedral environment of two nitrogen atoms of the bidentate bridging 4,4′-bipyridyl molecules and two sulphur atoms of the thiocyanato groups around mercury(II) in the solid state.

2,2′-Bipyridylamine complex

Rock salt region as well as low frequency infrared spectrum of the 1 : 1 mercury(II) thiocyanate complex with this ligand indicate that 2,2′-bipyridylamine is bonded through the two pyridyl nitrogens to the same metal ion (bidentate chelating ligand) resulting in the formation of 6-membered rings. 2,2′-Bipyridylamine in which the two pyridyl groups are joined together at the α- or 2-position on each ring through a –NH– group possesses three potential donour sites—two pyridyl nitrogens and a secondary amino group. However, this molecule acts only as bidentate chelating ligand leading to the formation of 6-membered rings. It seems that the secondary amino group is devoid of donor properties probably because of steric effects and delocalization of the lone pair of electrons onto the two pyridyl groups. With the exception of relatively minor shifts and splitting of some absorption bands the fundamental frequencies of the free base are altered little on coordination to metal ions. The slight shift of some of the 2,2′-bipyridylamine bands in this complex are characteristic of coordination through pyridyl ring nitrogen atoms.[29] With terminally S-bonded thiocyanato groups (Table 2) the complex is postulated to have a monomeric four-coordinated tetrahedral environment of two S-bonded thiocyanato groups and two nitrogens of the bidentate chelating 2,2′-bipyridylamine molecule.

2,2'-Bipyridyl and 1,10-phenanthroline complexes

Infrared spectra of the 1 : 1 mercury(II) thiocyanate complexes with both these ligands have several absorption bands characteristic of CC, CN and CH groups of the organic ligands and are in accord with the previous observations on their complexes with metal salts.[32, 33] With the exception of relatively minor shifts and splitting of some bands the fundamental frequencies of the uncoordinated ligands are altered little on coordination to metal ions. Rock salt as well as low frequency infrared spectra indicate clearly that both the donor sites are bonded to the same metal ion (chelating ligands) resulting in the formation of 5-membered rings.[30, 31] The fundamental frequencies due to coordinated thiocyanato groups (Table 2) are consistent with terminally S-bonded SCN groups. From considerations of bidentate chelating nature of 2,2′-bipyridyl and 1,10-phenanthroline and S-bonded SCN groups both these compounds are assigned monomeric four-coordinated structures with a tetrahedral environment of two nitrogen and two sulphur atoms around mercury(II) in the solid state.

1,3-Bis-(4-pyridyl) propane complex

This ligand consists of two pyridyl groups both bonded in γ-position to the two terminal carbon atoms of propane. Molecular models show considerable free rotation about the carbon-carbon bonds of propane. In one of the possible configurations the two pyridyl rings may be parallel to each other (C_s symmetry) and the two nitrogens may coordinate to the same metal ion. The chelate ring thus formed would be a 12-membered one. In the other possible geometry of this molecule the two pyridyl rings may be far away from each other (C_{2v} symmetry with the pyridyl rings in one and the same plane or C_s when the two rings are non-planar). Such configurations would not permit chelation as the nitrogen atoms, being far apart from each other, would not be able to coordinate to the same metal ion. Coordination of the two pyridyl nitrogens to different metal ions would thus be favoured resulting in polymeric chain structures.

Infrared spectrum of the 1 : 1 mercury(II) thiocyanate complex with this ligand shows the bidentate bridging nature of the organic ligand. The steric position of the nitrogen atoms in this ligand precludes chelation but favours coordination to different metal ions. Coordination through only one of the pyridyl ring nitrogen atoms (monodentate ligand) would have given a rather complex infrared spectrum particularly in the regions which suffer splitting or shifting upon coordination. Futhermore, infrared spectrum due to coordinated ligand in this complex shows fewer absorption bands as compared with the uncoordinated ligand spectrum. This is attributed to the fact that the two pyridyl groups which are non-planar in the uncoordinated ligand become coplanar upon coordination and that the coordinated ligand achieves a higher symmetry. The observed fundamental frequencies due to νCN, νCS and δSCN modes (Table 2) suggest the exclusive presence of terminally S-bonded SCN groups and a four-coordinated polymeric tetrahedral environment of two nitrogens (from bridging organic ligand molecules) and two sulphur atoms (of the terminally S-bonded SCN groups) is suggested about the metal atoms in the 1 : 1 mercury(II) thiocyanatc complex with 1,3-bis-(4-pyridyl) propane.

2,2′-Bipyridyl N,N′-dioxane and 4,4′-bipyridyl N,N′-dioxide complexes

Infrared spectrum of the 1 : 1 mercury(II) thiocyanate complex with 2,2′-bipyridyl N,N′-dioxide shows clearly that both the oxygen atoms of this ligand are coordinated to a single metal ion resulting in the formation of 7-membered rings.[34, 35] On the other hand, steric positioning of the two oxygen atoms in 4,4′-bipyridyl N,N′-dioxide precludes chelation but they can coordinate to different mercury ions thus forming a bridge between two mercury ions leading to polymeric chain structures.[37] Normal modes of both these ligands that are likely to be affected the most on coordination are the νNO and δNO modes.[34–37] The νNO which appears as a doublet (1262 and 1255 cm^{-1} in the former and 1249 and 1234 cm^{-1} in the latter) in the solid state (nujol mull) suffers a significant negative shift in the mercury(II) thiocyanate complexes with both these ligands studied here. The lowering of νNO modes is attributed to a decrease in π-bond character of the NO bond as a result of oxygen-to-metal coordination and is of the magnitude expected for complexes in which the N-oxide and negatively charged ligands (halides, NO_3^-, SO_4^{2-} etc.) constitute the first coordination sphere of the metal ion. The δNO oppearing as strong absorptions (at 852 and 840 cm^{-1} in the former and 840 and 834 cm^{-1} in the latter) is observed with almost similar intensity but shifted slightly to lower frequencies in the infrared spectra of the mercury(II) complexes. Since the oxygen of the NO group is involved in coordination a noticeable negative shift would be expected for the δNO mode in going from the uncoordinated ligand to metal complexes. The small shift observed may in fact be due to two opposing effects: (i) the effect of coordination on the NO group which would cause a vibrational shift to higher frequencies, and (ii) the decrease in the NO double bond character which would tend to lower the frequency. If both these effects were roughly equal a very small or negligible shift of the δNO would result. These observations are in good agreement with the earlier observations on metal(II)-2,2'-bipyridyl N,N′-dioxide complexes. With terminally S-bonded thiocyanato groups (Table 2) the metal atoms in 1 : 1 mercury(II) thiocyanate-2,2′-bipyridyl N,N′-dioxide complex are suggested to have monomeric, four-coordinated tetrahedral environments of two terminal S-bonded thiocyanato groups and two oxygens the bidentate chelating 2,2′-bipyridyl N,N′-dioxide molecules and a polymeric chain structure with an octahedral environment of four oxygen atoms from two bidentate bridging 4,4′-bipyridyl N,N′-dioxide molecules and two sulphur atoms of the terminally S-bonded SCN groups is assigned to the 1 : 2 mercury(II) thiocyanate complex with 4,4′-bipyridyl N,N′-dioxide complex.

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