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Terpyridyl Complexes of Zinc, Cadmium, and Mercury

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2′,2″:6″,2‴-Terpyridyl complexes of mercury(II) halides, perchlorates and nitrates are reported, along with comparative observations on their zinc and cadmium analogs. Corresponding compounds of the three metals are isomorphous, so that terpyridyl brings their coordination behavior into line. The mercury halide complexes, HgX_2 . terpy, are five-coordinate like the known zinc and cadmium counterparts. In the perchlorate complexes, $[M(terpy)_2](ClO_4)_2$, the metals are six-coordinate, assuming terpyridyl again to be tridentate. In the series $M(NO_3)_2$. terpy the nitrate is covalently bound. Metal-halogen and metal-ligand infrared frequencies are given and discussed.

Introduction

Mercury commonly develops covalencies of two or four, and while there are numerous examples of higher coordination numbers the coordination polyhedra even with identical ligands are generally highly distorted through inequality of the bond lengths and bond angles.[1] In compounds where coordination numbers can be regarded as being five or six a common pattern is two short digonally directed bonds with three or four laterally placed atoms at distances 0.4-0.8 Å greater than the sum of the covalent radii. It was therefore of interest to examine the response of a mercury coordination center towards 2′,2″:6″,2‴ terpyridyl whose behavior as a rather rigid tridentate ligand can emphasize coordination preferences. With divalent halides of zinc, cadmium,[2] and other metals[3] terpyridyl produces five-coordinate complexes with all the atoms located at distances close to those expected for normal covalent bonds.[4,5] In other cases as in the *bis*-terpyridyl complexes of transition metals[2] and tin(IV) halide derivatives[5,6] it develops six coordination. We report the interaction of terpyridyl with mercury(II) halides, perchlorate, and nitrate, and include comparative observations on zinc and cadmium.

Results and Discussion

Halide Complexes. The three metals form a complete range of terpridyl complexes MX_2 . terpy (X= Cl, Br, I). The compound $HgCl_2$. terpy proved isomorphous with the known zinc and cadmium chlorides (form I of Corbridge and Cox[4]) and with the crystal structure of the zinc compound well established[4,5] there is no doubt that the mercury in this compound is thereby five-coordinate also. As obtained from the

Table I. Infrared Spectra of Terpyridyl Complexes

	ν(M—X)	ν(M—L)	Ligand and Other Bands (Possible M—L bands marked*)
Terpyridyl			302 w, 244 w, 220 w, 191 s, 150 w, 140 w, 118 m
$ZnCl_2$. terpy [a]	294 s, 271 s	180 m, 163 m	245 w,* 187 m,* 110 m
$ZnBr_2$. terpy [b]	217 s	167 m	268 w, 245 m,* 145 w, 121 w, 80 m
ZnI_2 . terpy [b]	191 s, 205 m (?)	167 m	305 w, 257 m,* 145 w, 123 m, 82 m
$CdCl_2$. terpy [a]	268 s, 251 s	158 m, 148 m	111 w, 90 w, 80 m
$CdBr_2$. terpy [b]	193 s, 182 s	158 w, 148 m	300 w, 266 w, 237 m,* 73 m
CdI_2 . terpy [b]	162 s, 151 sh	[e]	303 w, 237 m,* 185 w, 143 w, 70 m
$HgCl_2$. terpy [a]	265 s, 240 s	145 m	176 w, 119 w, 86 m
$HgBr_2$. terpy [b]	181 s, 172 m	140 ms	300 w, 260 w, 235 m,* 63 ms
HgI_2 . terpy [b]	152 s, 136 s	[e]	196 w, 232 m,* 120 w
$[Zn(terpy)_2](ClO_4)_2$ [e]		175 s	311 w, 232 w,* 86 m
$[Cd(terpy)_2](ClO_4)_2$ [c]		157 m, 135 m	300 m, 265 w, 245 w, 237 w,* 185 w, 86 m
$[Hg(terpy)_2](ClO_4)_2$ [c]		130 sh, 125 m	297 w, 248 w, 187 w
$Zn(NO_3)_2$. terpy		188 s, 180 sh, 170 m	302 w, 275 s,[f] 250 m,[f] 141 m
$Cd(NO_3)_2$. terpy [d]		158 m	308 w, 220 w, 202 w, 185 w
$Hg(NO_3)_2$. terpy [d]		150 s, 143 s, 136 sh	309 w, 250 w, 215 m, 208 m, 91 s, 75 s

[a,b,c,d] Isomorphous series of compounds. [e] M—L bands obscured by ν(M—X). [f] Possibly a ν(M—O) band.

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(1) D. Grdenic, *Quart. Revs.*, *19*, 303 (1965).
(2) G. Morgan and F. H. Burstall, *J. Chem. Soc.*, 1649, (1937).
(3) C. M. Harris, T. N. Lockyer, and N. C. Stephenson, *Aust. J. Chem.*, *19*, 1741 (1966).
(4) D. E. C. Corbridge and E. C. Cox, *J. Chem. Soc.*, 594, (1956).
(5) F. W. B. Einstein and B. R. Penfold, *Acta Cryst.* *20*, 924, (1966).
(6) J. E. Fergusson, W. R. Roper, and C. J. Wilkins, *J. Chem. Soc.*, 3716, (1965).

present preparations the bromide and iodide complexes of the three metals comprise a second isomorphous series. The entire series of halides shows regularities in the metal-halogen stretching frequencies and on the grounds discussed below it is accordingly considered that the compounds are all five-coordinate. The low conductivities of the halides in nitrobenzene show them to be essentially non-electrolytes.

The strong M–X stretching bands are a conspicuous feature of the infrared spectra (Table I). The bands, which are usually resolved into symmetric and asymmetric stretching modes, move progressively to lower frequencies with increase in the atomic number both of the metal and the halogen. These vibrational frequencies for the penta-coordinated terpridyl derivatives and some related complexes (Table II) are of interest for their potential usefulness as a diagnostic test for coordination type, particularly because clear differences between M–X frequencies associated with four- and six-coordination have been established.[7,8,9] The ν(Zn–X) frequencies of the terpyridyl complexes lie below those of the bipyridyl and *bis*pyridine complexes where the metal is four-coordinate as in the tetrahedral $ZnCl_2 . 2py$.[10] A similar relationship holds for the mercury compounds where the pyridine and bipyridyl derivatives may be considered effectively four-coordinate, as with $HgCl_2 . 2py$.[11] Here, although the structure is described as distorted octahedral two of the mercury bonds are very long (3.25 as compared with 2.34 Å).

Table II. Comparison of Metal-Halogen Infrared Stretching Frequencies.[a]

Band	MX_2 . terpy	MX_2 . bipy	MX_2 . 2py	MX_4^{2-}
ν(Zn–Cl)	294, 271	331 [b], 323 [b,c]	326, 293 [c]	281 [f], 273
ν(Zn–Br)	217	260, 252	260, 254 [c]	207 [f], 203
ν(Zn–I)	191	215, 196 (?)	210 [c]	165 [f]
ν(Cd–Cl)	268, 251	228 [d]	198	260 [g]
ν(Cd–Br)	193, 182	167, 150 [d]		183 [i]
ν(Cd–I)	162, 151	157, 149		
ν(Hg–Cl)	265, 240	270		228 [g,h]
ν(Hg–Br)	181, 172	190 [e]		
ν(Hg–I)	152, 136	162, 142 [e]		

[a] Values obtained from present work unless otherwise indicated. [b] Ref. 8. [c] Ref. 15. [d,e] Isomorphous bipyridyl complexes. [f] For NEt_4^+ salts, ref. 17. [g] For NEt_4^+ salts, ref. 18. [h] The structure of the $HgCl_4^{2-}$ ion is variable, ref. 1, p. 315; that in the NEt_4^+ salts is unknown. [i] Quoted in ref. 7.

The ν(M–X) frequencies for the terpyridyl complexes of zinc and cadmium (Table II) fall rather close to the values for the corresponding MX_4^{2-} anions which give lower frequencies than neutral four-coordinate, complexes. Other comparisons involving cadmium relate to six coordination, because it is known or may be inferred that cadmium halide complexes with nitrogen bases, *e.g.* $CdCl_2 . 2py$,[8] are octahedral through halogen bridging. In this and other cases, *e.g.* $CdCl_2$. bipy and $CdBr_2$.bipy, ν(Cd–X) falls below the value even for the corresponding mercury compound. This reversal of the relationship expected from mass differences must reflect the increased coordination number of the cadmium. However, ν(M–X) for CdI_2 . bipy lies close to that for HgI_2 . bipy and $CdBr_2$.bipy, which signifies a weakened bridging interaction, as has been previously recognized for iodides.[12] In this connection it is perhaps significant that CdI_2 . bipy is not isomorphous with the chloride and bromide, whereas HgI_2 . bipy and $HgBr_2$. bipy do show isomorphism.

Perchlorate Complexes. Zinc, cadmium, and mercury all form complexes of the type $[M(terpy)_2](ClO_4)_2$. X-ray powder photographs show the three compounds to be isomorphous. Their electrolytic conductivities in nitrobenzene (Λ_m = 68.7, 75.4 and 60.0 ohm^{-1} cm^2 for M = Zn, Cd, Hg respectively) are typical of 2:1 electrolytes, as with the bipyridyl complex $[Hg(bipy)_2](ClO_4)_2$ reported by Sutton.[13] Assuming terpyridyl to be tridentate it has apparently forced mercury, as well as zinc and cadmium, to a coordination number of six. Infrared spectra of the terpyridyl complexes are almost identical over the range 4000-400 cm^{-1}, with two perchlorate bands, one at 622 cm^{-1} and the second slightly split into components at 1090 and 1112 cm^{-1}. In the face of other evidence this splittings must be considered to arise from lack of symmetry in the cation field within the crystal rather than from covalency.

Nitrate Complexes. Following Morgan and Burstall[2] who reported a compound $Hg(NO_3)_2$. terpy, we find also compounds of zinc (compound I) and cadmium (compound II) of the same composition. The cadmium and mercury complexes, but not the zinc compound (I) are isomorphous. However, it did prove possible to demonstrate the existence of a second zinc compound (III) whose powder photograph show-

Table III. Infrared Spectra in the Ranges 1500-1200 and 1100-980 cm^{-1}.

	1500-1200 cm^{-1}		1100-980 cm^{-1}	
	Bands common to MCl_2.terpy	Nitrate Bands	Bands common to MCl_2.terpy	Nitrate Bands
$Zn(NO_3)_2$terpy	1455 s, 1446 s, 1369 m, 1350 w	1490-1475 sh, 1296 m, 1277 m [b]	1068 w, 1048 w, 1024 m, 1013 s	1028 sh, 1002sh
$Cd(NO_3)_2$terpy [a]	1456 s, 1448 s, 1372 m, 1360 w	1480-1470 sh, 1296 m, 1270 m [b]	1069 w, 1048 w, 1014 m, 1008 s	1029 s
$Hg(NO_3)_2$terpy [a]	1456 s, 1448 s, 1371 m, 1360 w	1480-1470 sh, 1294 m, 1280 w 1260 m [b]	1066 w, 1047 w, 1016 m, 1008 s	1028 m, 1021 m

[a] Isomorphous compounds. [b] The bands in this region merge into a broad absorption which overshadows very weak MCl_2 . terpy bands at 1304-1311, 1290-1293, and 1245 cm^{-1}.

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(7) R. J. H. Clark, *Spectrochim. Acta, 21,* 955 (1965).
(8) G. E. Coates and D. Ridley, *J. Chem. Soc.*, 166 (1964).
(9) R. J. H. Clark and C. S. Williams, *Inorg. Chem., 4,* 350 (1965).
(10) M. A. Porai-Koshits, L. O. Atovmyan, and G. N. Tishchenko, *Zh. Strukt. Khim., 1,* 337, (1960).
(11) D. Grdenic and I. Krstanovic, *Arkiv Kem., 27,* 143 (1955).
(12) N. S. Gill, R. S. Nyholm, G. A. Barclay, T. I. Christie, and P. J. Pauling, *J. Inorg. Nucl. Chem., 18,* 88 (1961).
(13) G. J. Sutton, *Aust. J. Chem., 12,* 637 (1959).

ed it to be isomorphous with the cadmium and mercury analogs, but is was obtained only in association with considerable non-crystalline material of higher ligand content. A second cadmium product (IV) with a distinct powder photograph was also of composition close to $Cd(NO_3)_2$. terpy. It was obtained on only one occasion despite efforts at repetition. We confine structural discussion to the analytically pure products (I) and (II).

Information from conductivity measurements was limited by solubility difficulties. It was shown, however, that the zinc compound (I) is non-ionic in nitrobenzene ($\Lambda_m = 0.5$). The mercury compound, insoluble in other conductivity solvents, behaved as a 1:1 electrolyte in ethanol. Its infrared spectrum, however, showed it to be covalent in the crystalline state.

Comparison of the rather similar spectra of the nitrate and chloride complexes enabled identification of the additional nitrate bands within the ranges 1500-1250 and 1050-990 cm^{-1} (Table III). The bands near 1480 and at 1300-1260 cm^{-1} are characteristic of covalent nitrate.[14] Correspondingly there was no evidence of an additional band in the region 1400-1340 cm^{-1} as would be typical of ionic nitrate; the regions 1420-1385 and 1355-1320 cm^{-1} showed no alteration. It is therefore concluded that in these compounds both nitrate groups are covalently linked to the metal. The nitrate bands at 1030-1000 cm^{-1} afford corroborative evidence of covalent bonding since the symmetric stretching vibration in this region becomes infrared active only upon reduction of the D_{3h} symmetry of the ion. But since the evidence does not serve to distinguish between monodentate and bidentate nitrate the coordination number of the metal can be established only as being not less than five. Despite this uncertainty over coordination numbers the three metals must, at least in the isomorphous series, be developing the same coordination environment.

In combination with monodentate ligands cadmium can show a higher coordination number than zinc, but mercury often reverts to lower coordination numbers or develops less symmetrical coordination polyhedra. Yet the present results on the three classes of terpyridyl derivatives with their coordination numbers of five or six illustrate the influence of this rather rigid polydentate ligand in bringing the coordination behavior of the three metals into line.

The Metal-Terpyridyl Frequency. Few metal-terpyridyl assignments have been reported. The vibrations occur at low frequencies but may still be complicated by ligand bands even below 200 cm^{-1}. There are two distinct metal-nitrogen bonds, each within a ring system, thus giving greater probability of combination modes. However, in the perchlorate complexes the spectra below 300 cm^{-1} are dominated by one or more strong to medium bands which move from 175 to 125 cm^{-1} on passing from the zinc to mercury compounds (Table I). We suggest these bands represent primarily a metal-ligand stretching mode. In examining the spectra of the zinc halide complexes Postmus, Ferraro, and Wozniak[15] have assigned these bands to a δ(M–N) mode with ν(M–N) at 243-245 cm^{-1}. Bands which are stronger than the ligand absorption at 244 cm^{-1} do appear throughout the halide series and move towards 230 cm^{-1} on passing to mercury; but they are less easily identifiable in the perchlorates and nitrates. It remains a possibility, however, that both sets of bands are essentially ν(M–N) modes, those above 200 cm^{-1} associated with the nitrogen atom of the middle ring and those at lower frequency attributable to vibration of the more weakly bonded nitrogren atoms of the terminal rings. In the zinc chloride complex these latter nitrogen atoms are further from the metal and are displaced from the «trigonal» axis.[4,5]

Experimental Section

Mercury Halide-Terpyridyl Complexes. Following the general procedure the components were brought together in ethanol solution, using stoichiometric proportions. The adducts, which precipitated immediately, were washed with solvent and pumped dry. The compounds often had an off-white to pinkinsh cast. Conductivities, Λ_m, in nitrobenzene are: $HgCl_2$. terpy, 0.7; $HgBr_2$. terpy, 1.0; HgI_2 . terpy, 1.7 cm^2 mol^{-1} ohm^{-1}

Anal. Calcd. for $HgCl_2$. terpy: C, 35.7; H, 2.2; N, 8.3. Found: C, 36.0; H, 2.3; N, 7.9%. Calcd. for $HgBr_2$. terpy: C, 30.4; H, 1.8. Found: C, 30.5; H, 2.0%. Calcd. for HgI_2 . terpy: C, 37.9; H, 2.7. Found: C, 37.3; H, 2.9%.

Of the bipyridyl and pyridine complexes, MX_2 . bipy and MX_2 . 2py, which were obtained similarly all but CdI_2 . bipy and HgI_2 . bipy have previously been characterized.

Anal. Calcd. for CdI_2 . bipy: C, 23.0; H, 1.5. Found: C, 23.3; H. 1.7%. Calcd. for HgI_2 . bipy: C, 19.7; H, 1.3. Found: C, 19.6; H, 1.5%.

Perchlorate Complexes. The zinc and cadmium compounds were precipitated from warm ethanol and the mercury complex from acetone using ethyl orthoformate as dehydrating agent.[16] Complexes of composition $[M(terpy)_2](ClO_4)_2$ were obtained even using the components in equimolar proportions.

Anal. Calcd. for $[Zn(terpy)_2](ClO_4)_2$: C, 49.3; H, 3.0. Found: C, 49.2; H. 3.2. Calcd. for $[Cd(terpy)_2](ClO_4)_2$: C, 46.3; H, 2.9. Found: C, 46.3; H, 3.3%. Calcd. for $[Hg(terpy)_2](ClO_4)_2$: C, 41.6; H, 2.6. Found: C, 41.7; H, 2.9%.

Nitrate Complexes. In order to obtain analytically pure complexes of 1:1 composition it was necessary to add slowly a warm solution of terpyridyl to that of the metal salt. Ethanol and acetone, containing ethyl orthoformate were satisfactory solvents. The white crystalline precipitates were sometimes slow to form.

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[14] B. M. Catehouse, S. E. Livingstone, and R. S. Nyholm, *J. Chem. Soc.*, 4222, (1957); C. C. Addison and B. M. Gatehouse, *J. Chem. Soc.*, 613 (1960).

[15] C. Postmus, J. R. Ferraro, and W. Wozniak, *Inorg. Chem.*, 6, 2030, (1967).

[16] P. W. N. M. van Leeuwen and W. L. Groeneveld, *Inorg. Nuclear Chem. Letters*, 3, 145 (1967).

Anal. Calcd. for $Zn(NO_3)_2$. terpy: C, 42.6; H, 2.6. Found (product I): C, 42.9; H, 3.05%. Calcd. for $Cd(NO_3)_2$. terpy: C, 38.3; H, 2.4. Found (product II): C, 38.6; H, 2.2%. Calcd. for $Hg(NO_3)_2$. terpy: C, 32.3; H, 2.0. Found: C, 31.9; H, 2.4%

Spectra. Infrared spectra were recorded on a Perkin Elmer 337 spectrophotometer and additionally in the case of the nitrates on a P.E. 421 over the ranges 1500-1200 and 1100-950 cm^{-1} where higher resolution was required. An R.I.I.C. FS-720 interferometer was used below 400 cm^{-1}. The spectra confirmed the absence of water or coordinated solvent in all cases.

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(17) R. J. H. Clark and T. M. Dunn, *J .Chem. Soc.*, 1198, (1963).

(18) D. M. Adams, J. Chatt, J. M. Davidson, and J. Gerratt, *J. Chem. Soc.*, 2189, (1963).