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2,2'-Bipyridylamine Complexes with Some Zinc(II), Cadmium(II) and Mercury(II) Salts

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Received January 8, 1973

The complexes formed by some zinc(II), cadmium(II) and mercury(II) salts with 2,2'-bipyridylamine have been prepared and characterised by molecular conductance and infrared spectral measurements down to 200 cm^{-1}. Possible structures for these complexes in the solid state are discussed.

Introduction

Coordination of 2,2'-bipyridylamine through its pyridyl nitrogens has been established by recent X-ray structural[1-3] and infrared spectroscopic[4-20] studies. Among the Group II B metal salts complexes of zinc (II) halides have been studied by McWhinnie.[5] However, no work seems to have been reported on the complexes of cadmium(II) and mercury(II) salts with this potential bidentate chelating ligand. We now report the preparation, molecular conductance and i.r. spectral features of the coordination compounds formed by 2,2'-bipyridylamine with some zinc(II), cadmium(II) and mercury(II) salts.

Experimental Section

Table I. Analytical Data.

Compound	Method of prepn.*	Metal (%) Found	Metal (%) Calc.	Anion (%) Found	Anion (%) Calc.
$ZnLCl_2$	A	21.5	21.3	23.4	23.1
$ZnLBr_2$	A	16.3	16.5	40.5	40.3
$ZnLI_2$	A	13.5	13.3	52.0	51.8
$ZnL(NCS)_2$	A	18.3	18.5	32.7	33.0
$ZnL_{1.5}SO_4$	C	15.7	15.6	22.6	23.0
$ZnL(OAc)_2$	E	18.1	18.4	[a]	
$CdLCl_2$	A	31.9	31.7	20.1	20.0
$CdLBr_2$	A	25.1	25.4	35.9	36.1
$CdLI_2$	A	20.7	20.9	47.4	47.2
$CdL(SCN)_2$	A	27.8	28.0	28.9	29.4
$CdLSO_4$	D	30.0	29.6	25.1	25.3
$CdL_3(OAc)_2$	F	15.0	15.1	[b]	
$CdL(OAc)_2$	E	27.8	28.0	[c]	
$HgLCl_2$	A	45.6	45.3	15.9	16.0
$HgLBr_2$	A	38.1	37.7	29.8	30.1
$HgL(CN)_2$	A	47.7	47.4	[d]	
$HgL(SCN)_2$	B	41.0	41.1	24.0	23.8

L = 2,2'-Bipyridylamine
[a] Found: C=47.0%, H=4.30%, N=12.1%; Calc.: C=47.4%, H=4.23%, N=11.8%. [b] Found: C=54.0%, H=4.60%, N=17.1%; Calc.: C=54.9%, H=4.44%, N=16.9%. [c] Found: C=42.2%, H=4.00%, N=10.7%; Calc.: C=41.9% H=3.74, N=10.5%. [d] Found: C=34.5%, H=2.20%, N=16.8%; Calc.: C=34.0%, H=2.12%, N=16.5%.
* Methods of preparation: (A) An excess of 2,2'-bipyridylamine was added to a hot solution of the metal(II) salt in in ethanol. (B) A suspension of the metal(II) salt in ethanol was boiled with an excess of 2,2'-bipyridylamine. The mixture was filtered hot and the complex crystallized out on cooling. (C) An excess of the organic ligand was added to a solution of the metal(II) salt in methanol. (D) A saturated aqueous solution of the metal(II) salt was added into an excess of the ligand solution in ethanol. (E) The metal(II) salt solution in methanol was boiled with an excess of the ligand. The mixture was cooled to room temperature and then in ice. (F) The metal(II) salt was dissolved by heating with an excess of the ligand. The complex which crystallized out on cooling was filtered, washed with anhydrous ether and dried.

Details of the preparation methods are given in Table I. Conductivity measurements were made on freshly prepared ~ 1 m*M* solutions in absolute alcohol at 25°C with a Cambridge conductivity bridge Model L 370873. I.R. spectra of 2,2'-bipyridylamine and the metal complexes were recorded as Nujol mulls supported between sodium chloride plates (rock salt region) and thin polythene sheets (15 – 50 µ) on a Perkin-Elmer 621 spectrophotometer equipped with caesium iodide optics.

Results and Discussion

The complexes isolated in the present study and their analytical data are summarised in Table I. Par-

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(1) H.C. Freeman,, J.F. Geldard, F. Lions, and M.R. Snow, *Proc. Chem. Soc.*, 258 (1964).
(2) H.C. Freeman and M.R. Snow, *Acta Cryst.*, *18*, 843 (1965).
(3) J.E. Johnson, T.A. Beineke, and R.A. Jacobson, *J. Chem. Soc.*, (A), 1371 (1971).
(4) W.R. McWhinnie, *J. Chem. Soc.*, 5165 (1964).
(5) W.R. McWhinnie, *J. Inorg. Nucl. Chem.*, *27* 1619 (1965).
(6) G.C. Kulasingam and W.R. McWhinnie, *J. Chem. Soc.*, 7145 (1965); *J. Less Common Metals*, *10*, 72 (1966).
(7) M. Goodgame, *J. Chem. Soc.*, (A), 63 (1966).
(8) G.C. Kulasingam, W.R. McWhinnie, and R.R. Thomas, *Spectrochim. Acta*, *22*, 1365 (1966).
(9) W.R. McWhinnie, *J. Chem. Soc.*, (A), 889 (1966).
(10) W.R. McWhinnie, R.C. Poller, and M. Thevarasa, *J. Chem. Soc.*, (A), 1671, (1967).
(11) D. St. C. Black, *Australian J. Chem.*, *20*, 2101 (1967).
(12) C.D. Burbridge and D.M.L. Goodgame, *J. Chem. Soc.*, (A), 694 (1967); 237 (1968).
(13) T.J. Hurley and M.A. Robinson, *Inorg. Chem.*, *7*, 33 (1968).
(14) R.C. Poller, J.N.R. Ruddick, M. Thevarasa, and W.R. Mc Whinnie, *J. Chem. Soc.*, (A), 2327 (1969).
(15) J.R. Hudman, M. Patel, and W.R. McWhinnie, *Inorg. Chim. Acta*, *4*, 161 (1970).
(16) G.C. Kulasingam, J.C. Lancaster, W.R. McWhinnie, and J.B. Watts, *Spectrochim. Acta*, *26 A*, 835 (1970).
(17) R.D. Dowsing, J.F. Gibson, M. Goodgame, and P.J. Hayward, *J. Chem. Soc.*, (A), 1133 (1970)
(18) R.C. Poller, J.N.R. Ruddick, and J.A. Spillman, *J. Chem. Soc.*, (D), 680 (1970).
(19) D. St. C. Black and R.C. Srivastava, *Australian J. Chem.*, *24*, 287 (1971).
(20) J.C. Lancaster, W.R. McWhinnie, and P.L. Welham, *J. Chem. Soc.*, (A), 1742 (1971).

Table II. Partial I.R. spectral data (cm^{-1}).

Compound	Metal-halogen Mode	Ligand Modes							
L		637	621	592	526	413	408	352	324
ZnLCl$_2$	327,305	645	608	581	515	412		351	
ZnLBr$_2$	233,224	645	606	578	520	424		349	
ZnLI$_2$		645	606	559	517	419		350	344
ZnL(NCS)$_2$		655	615	565	516	416		352	
		νCN 2080, νCS 863, δNCS 476, νZn-NCS 286,260							
ZnL$_{1.5}$SO$_4$		630		595	525	411		345	
	SO$_4$ Modes:	ν$_1$ 990, ν$_2$ 470, ν$_3$ 1100, ν$_4$ 610							
ZnL(OAc)$_2$		651	625	614	536	420	415	352	
	CH$_3$COO Modes:	ν$_{asym}$CO 1550, ν$_{sym}$CO 1430, δOCO 660, νZn-O 280							
CdLCl$_2$	222,212	645	605		525	510	414		329
CdLBr$_2$		635	603		523	515	411		335
CdLI$_2$ •		642	608	565	515	414	410	345	332
CdL(SCN)$_2$		640	600	580	520	413		355	330
		νCN 2110,2100, νCS 685, δSCN 460,450, νCd-SCN 244							
CdLSO$_4$		645		575	520		406		337
	SO$_4$ Modes:	ν$_1$ 990, ν$_2$ 470, ν$_3$ 1110, ν$_4$ 612							
CdL$_3$(OAc)$_2$		635	608	580	517	413			340
	CH$_3$COO Modes:	ν$_{asym}$CO 1560, ν$_{sym}$CO 1415, δOCO 665							
CdL(OAc)$_2$		635	605	570	525	410	400	337	325
	CH$_3$COO Modes:	ν$_{asym}$CO 1550, ν$_{sym}$CO 1430, δOCO 660, νCd-O 250							
HgLCl$_2$	285	640	602		520	411	405		335
HgLBr$_2$	210	640	603		520	410	404		332
HgL(CN)$_2$		638	600		525	410		355	335
		νCN 2178, νHg-C 400, δHgCN 300,273							
HgL(SCN)$_2$		637	601	531	523	410	406	339	330
		νCN 2126,2120, νCS 695, δSCN 456,432,425, νHg-SCN 283							

tial i.r.- spectral data are listed in Table II. Absorption bands in the range 650 − 200 cm^{-1} due to the coördinated 2,2'-bipyridylamine in the complexes, which occur at almost the same frequencies as the free ligand, are also listed in Table II. Residual features were assigned to the coordinated anionic groups.

Except for the 1:3 cadmium(II) acetate-2,2'-bipyridylamine complex all the other complexes studied here are either insoluble or have low values of the molecular conductance in absolute alcohol indicating that they are non-electrolytes. Zinc(II), cadmium(II) and mercury(II) being d^{10} ions do not show d → d transitions and, therefore, stereochemistry of their complexes cannot be derived from their u.v. and visible reflectance spectra. Information on the structure of complexes in the present studies has been derived from their infrared spectral measurements.

Rock salt region as well as the low frequency i.r. spectra of the complexes studied here indicate that the 2,2'-bipyridylamine is bonded through the two pyridyl nitrogens to the same metal ion (chelating ligand) resulting in the formation of 6-membered rings. I.R. spectra also show clearly that the anionic groups are coordinated in these complexes. 2,2'-Bipyridylamine in which two pyridyl groups are joined together at the α– or 2-position on each ring through a –NH– group possesses three potential donor sites — two pyridyl nitrogens and a secondary amino group. However, this molecule acts only as a bidentate chelating ligand leading to the formation of six-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. Infrared spectra of zinc(II), cadmium(II) and mercury(II) complexes with 2,2'-bipyridylamine show close resemblance with the spectrum of the free ligand. This is in accord with the previous observations on metal-pyridine and metal-2,2'-bipyridine complexes[21,22] in that 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 the complexes are characteristic of coordination through pyridyl nitrogen atoms.[21,22]

Metal(II) Halide Complexes. All the metal(II) halide-2,2'-bipyridylamine complexes isolated in the present study are of the stoichiometry MLX$_2$, where L = 2,2'-bipyridylamine and X = Cl, Br or I. The frequencies of metal-halogen stretching modes in coordination compounds have proved very useful in distinguishing between monomeric pseudotetrahedral species from those having halogen-bridged polymeric octahedral structures.[23] The frequency of metal-halogen stretching modes (Table II) strongly suggest pseudotetrahedral environment of ligands around the metal atoms in 1:1 zinc(II) chloride, bromide and iodide, mercury(II) chloride and bromide and cadmium(II) chloride–2,2'–bipyridylamine complexes. In spite of the higher mass of mercury (than cadmium) the frequency of νM – Cl in the mercury(II) complex (285 cm^{-1}) occurs at higher wave numbers compared to the cadmium(II) chloride complex (222, 212 cm^{-1}). This

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(21) N.S. Gill, R.H. Nuttall, D.E. Scaife, and D.W.A. Sharp, *J. Inorg. Nucl. Chem.*, *18*, 79 (1961); M. Goldstein, E.F. Mooney, A. Anderson, and H.A. Gebbie, *Spectrochim. Acta*, *21*, 105 (1965).

(22) A.A. Schilt and R.C. Taylor, *J. Inorg. Nucl. Chem.*, *9*, 211 (1959); R.G. Inskeep, *ibid.*, *24*, 763 (1962); C. Postmus, J.R. Ferraro, and W. Wozniak, *Inorg. Chem.*, *6*, 2030 (1967).

(23) G.E. Coates and D. Ridley, *J. Chem. Soc.*, 166 (1964); R.J.H. Clark in «Halogen Chemistry» Vol. III, Edited by V. Gutmann, Academic Press, New York, 1967; G.B. Deacon and J.H.S. Green *Chem. Comm.*, 629 (1966); G.B. Deacon, J.H.S. Green, and D.J. Harrison, *Spectrochim. Acta*, *24 A*, 1921 (1968).

is probably because of the greater covalent character of Hg – Cl bond relative to the Cd – Cl bond. The effect of mass on νM – Cl in the complexes of cadmium(II) and mercury(II) chlorides thus appears to be compensated by the reverse effect of the covalent character of metal – halogen bond. Both tetrahedral and octahedral (monomeric and polymeric) νCd – Br and νCd – I modes in the 1:1 cadmium(II) bromide and iodide-2,2'-bipyridylamine complexes are expected to absorb below 200 cm^{-1}, the lower frequency limit of the infrared spectrophotometer used in the present studies. Hence there is no positive evidence as to the coordination arrangement in 1:1 cadmium(II) bromide/iodide-2,2'-bipyridylamine complexes reported here.

Metal(II) Thiocyanate Complexes. Zinc(II) thiocyanate complex: In addition to the ligand vibration modes modified slightly on account of coordination, new absorption bands were observed at 2080, 863, 476, 286 and 260 cm^{-1} in the i.r. spectrum of 1:1 zinc(II) thiocyanate-2,2'-bipyridylamine complex. Such bands were not observed in the i.r. spectra of 1:1 zinc(II) chloride, bromide and iodide complexes with 2 2'-bipyridylamine. These new bands are, therefore, identified as νCN (2080 cm^{-1}), νCS (863 cm^{-1}), δ NCS (476 cm^{-1}) and ν Zn-NCS (286, 260 cm^{-1}) modes, respectively, due to coordinated thiocyanate groups. The frequencies of the fundamental modes due to coordinated thiocyanate groups in this complex are in good agreement with similar modes in $ZnL_2(NCS)_2$ complexes,[24-26] where L = pyridine or a ring substituted alkyl– or dialkyl– pyridine, which are considered to have terminal N–bonded thiocyanate groups. It is, therefore, suggested that the metal atoms in this complex have a four-coordinated tetrahedral environment of two N–bonded thiocyanate groups and two nitrogens of the bidentate chelating 2,2'-bipyridylamine molecule. The observed frequencies due to coordinated thiocyanate groups rule out the possibility of thiocyanato-bridged polymeric octahedral structure for the complex.

Cadmium(II) and mercury(II) thiocyanate complexes: I.R. spectra of 1:1 cadmium(II) and mercury(II) thiocyanate-2,2'bipyridylamine complexes show absorption bands at ~ 2100, ~ 700, ~ 460, ~ 430 and ~ 250 cm^{-1} but not in the corresponding metal(II) halide complexes studied here. These bands are assigned as ν CN (~2100 cm^{-1}), ν CS (~700 cm^{-1}), δ SCN (~460, ~430 cm^{-1}) and ν M–S (~250 cm^{-1}), modes (M = Cd or Hg), respectively, due to coordinated thiocyanate groups. The frequencies of these modes are in good agreement with similar fundamental frequencies normally associated with terminal S–bonded thiocyanate groups.[26,27] It is, therefore, suggested that the metal atoms in these complexes have a monomeric four-coordinated tetrahedral environment of two S–bonded thiocyanate groups and two nitrogens of the bidentate chelating 2,2'-bipyridylamine molecule.

Mercury(II) cyanide complex: Mercury(II) cyanide gave 1:1 complex with 2,2'-bipyridylamine. Zinc(II) and cadmium(II) cyanides did not react with 2,2'-bipyridylamine. Infrared spectrum of the mercury(II) cyanide complex showed absorption bands at 2178, 400, 300 and 273 cm^{-1} but not in the spectra of mercury(II) chloride and bromide complexes (vide supra). Mercury(II) cyanide has a linear cyanide-bridged polymeric chain structure in the solid state[28] and absorbs at 2193, 442 and 341 cm^{-1} due to νCN, νHg–C and δHgCN modes,[29] respectively. The frequency of νCN suffers a significant negative shift when the cyano bridges break down and mercury(II) complexes with terminal cyano groups absorb at lower frequencies[30-32] than pure mercury(II) cyanide. Furthermore, νHg–C shifts to higher frequencies in complexes containing bridging cyano groups and this positive shift may be attributed to coupling of νHg–C with νCN in the HgCN part of the molecule. Since terminal cyano groups absorb at lower frequencies than pure mercury(II) cyanide, the terminal νHg–C and δHgCN modes would also be expected to absorb at lower energies. The observed frequencies of νCN (2178 cm^{-1}), νHg–C (400 cm^{-1}) and δHgCN (300, 273 cm^{-1}) modes strongly suggest the presence of terminal cyano groups and the 1:1 mercury(II) cyanide-2 2'-bipyridylamine complex may thus be assigned a four-coordinate tetrahedral structure with two terminal CN groups and two nitrogens of the bidentate chelating 2,2'-bipyridylamine molecule around the mercury atoms.

Zinc(II) and cadmium(II) sulphate complexes: Zinc (II) and cadmium(II) sulphates formed 1:1.5 and 1:1 complexes, respectively, with 2,2'-bipyridylamine. Insolubility of these compounds in suitable organic solvents precluded molecular weight and conductivity measurements. Infrared spectra of both these complexes show strong broad absorption bands at ~ 1100 cm^{-1}, masking the medium intensity ligand bands in this region, and medium intensity bands at ~ 610 cm^{-1}. These bands are identified as ν_3 and ν_4 modes, respectively, of the sulphate groups with T_d symmetry.[33] Moreover, a weak band is also observed at ~ 990 cm^{-1} owing to ν_1 vibration of the sulphate group. Although i.r. forbidden in the sulphate spectrum with T_d symmetry, ν_1 appears as a weak band at ~ 980 cm^{-1} in the i.r. spectra of ionic solid sulphates owing to site-symmetry effects,[33,34] but is absent in the spectra of sulphates in aqueous solutions[35] Besides ν_1, ν_3, and ν_4 of the sulphate group with T_d symmetry, ν_2 appears as a weak band at ~ 460 cm^{-1} in the spectra of the complexes studied

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(24) S.M. Nelson and T. Shepherd, *J. Inorg. Nucl. Chem.*, *27*, 2123 (1965).

(25) R.J.H. Clark and C.S. Williams, *Spectrochim. Acta*, *22*, 1081 (1966).

(26) I.S. Ahuja and A .Garg, *J. Inorg. Nucl. Chem.*, *34*, 1929 (1972).

(27) A.R. Davis, C.J. Murphy, and R.A. Plane, *Inorg. Chem.*, *9*, 423 (1970).

(28) J. Hvoslef, *Acta Chem. Scand.*, *12*, 1568 (1958).

(29) L.H. Jones, *J. Chem. Phys.*, *27*, 665 (1957).

(30) S.C. Jain and R. Rivest, *Can. J. Chem.*, *47*, 2209 (1969).

(31) S.C. Jain and R. Rivest, *Inorg. Chim. Acta*, *4*, 291 (1970).

(32) I.S. Ahuja and A. Garg, *J. Inorg. Nucl. Chem.*, *33*, 1515 (1971); *34*, 2074 (1972).

33) K. Nakamoto, J. Fujita, S. Tanaka, and M. Kobayashi, *J. Amer. Chem. Soc.*, *79*, 4904 (1957).

(34) M. Haas and G.B.B.M. Sutherland, *Proc. Roy. Soc.*, 236 *A*, 427 (1956).

(35) S.D. Ross, *Spectrochim. Acta*, *18*, 1575 (1962).

here. From a consideration of the i.r. frequencies due to the coordinated sulphate groups in the zinc(II) and cadmium(II) sulphate-2,2'-bipyridylamine complexes, it appears that a regular coordination by all the oxygens of the sulphate group occurs. It is thus suggested that the sulphate groups retain an essentially T_d symmetry and that the complexes are highly polymeric structures. It is not possible to postulate the probable coordination numbers of zinc(II) and cadmium(II) in these complexes.

Zinc(II) and cadmium(II) acetate complexes: Zinc (II) and cadmium(II) acetates gave 1:1 complexes with 2,2'-bipyridylamine. In addition to 1:1 complex, cadmium(II) acetate also formed 1:3 complex with 2,2'-bipyridylamine. The 1:3 cadmium(II) acetate-2,2'-bipyridylamine complex behaves as a 1:2 electrolyte in absolute ethanol[36] (experimental value of Λ_m for 0.958 m mole^{-1} solution at 25°C = 91.11 mho mole^{-1} cm^2), thereby indicating that the acetate groups are outside the coordination sphere. I.R. spectrum of this complex is also in agreement with ionic acetate groups.[33] It is thus suggested that the metal ion in this complex has an octahedral environment of six nitrogens of the three 2,2'-bipyridylamine molecules. The 1:1 zinc(II) and cadmium(II) acetate-2,2'-bipyridylamine complexes are non-electrolytes and i.r. spectra of these complexes indicate the presence of coordinated 2,2'-bipyridylamine and acetate groups. In addition to the ligand vibration modes modified slightly on account of coordination, strong absorption bands were observed in the regions ~ 1550, ~ 1430 and ~ 670 cm^{-1} in the rock salt region i.r. spectra of 1:1 zinc(II) and cadmium(II) acetate-2,2'-bipyridylamine complexes. Such bands were neither observed in the i.r. spectra of free 2,2'-bipyridylamine nor in the zinc(II) and cadmium(II) chloride, bromide or iodide complexes (vide supra). These new bands are, therefore, assigned as CO asymmetric (~1550 cm^{-1}), CO symmetric (~1430 cm^{-1}) stretching and OCO bending (~670 cm^{-1}) modes, respectively, due to coordinated acetate groups. The observed carboxy frequencies with a separation of ~120 cm^{-1} in these complexes are in good agreement with similar modes (1550 and 1430 cm^{-1}; separation 120 cm^{-1}) in bisacetatobisaquozinc(II),[37] $Zn(OAc)_2 \cdot 2H_2O$, which has been shown by X-ray crystallography to have a pseudo-octahedral structure with both the acetate groups acting as symmetrical chelates.[38] From a consideration of the i.r. frequencies due to coordinated acetate groups it is suggested that the 1:1 zinc(II) and cadmium(II) acetate-2,2'-bipyridylamine complexes are pseudo-octahedral structures with bidentate symmetrically chelated acetate groups.[37,38]

Acknowledgements: We thank Professor G. B. Singh, Head of the Chemistry Department, B.H.U., for providing facilities, and C.S.I.R. for financial assistance (R.S.).

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(36) W.J. Geary, *Coord. Chem. Revs.*, 7, 81 (1971).

(37) N.F. Curtis, *J. Chem. Soc.*, (A), 1579 (1968).

(38) J.N. van Niekerk, F.R.L. Schoening, and J.H. Talbot, *Acta Cryst.*, 6, 720 (1953).