

Complexes of Quinoline and Isoquinoline with Some Zinc(II), Cadmium(II) and Mercury(II) Salt

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

Introduction

Coordination compounds formed by the interaction of zinc(II), cadmium(II), and mercury(II) halides and pseudohalides with pyridine and its ring substituted methyl and dimethyl derivatives have received considerable attention. Structures of some of these compounds have been established by X-ray crystallography.^{1,4} Metal-ligand modes have been identified in the low frequency i.r. spectra and correlated with the stereochemistry of the complexes.⁵⁻¹³ In contrast to the extensively studied pyridine complexes few investigations appear to have been made^{11,12} on the donor ability of quinoline and isoquinoline—first members in the condensed ring N-heterocyclic compounds—with these metal ions. The annelation of a benzene ring on to pyridine ($\text{pK}_a = 5.2$) is known to cause only a small change in the basic strength.¹⁴ This may rise a little as in isoquinoline ($\text{pK}_a = 5.40$) or fall as in quinoline ($\text{pK}_a = 4.94$). Probably the electron-attracting effect of the far benzene ring is much greater in the α - than in the β -position and this is perhaps the main reason why quinoline is $\sim 0.50\text{ pK}_a$ unit lower than isoquinoline. We now report the preparation, molecular conductance and i.r. spectral features of the coordination compounds formed by zinc(II), cadmium(II), and mercury(II) salts with these ligands.

Experimental Section

The details of the preparations are given in Table I. Conductivity measurements were made on freshly prepared $\sim 1\text{ mM}$ solutions in absolute alcohol at 25°C with a Phillips magic eye conductivity bridge type PR 9500. I.R. spectra were recorded in the rock salt region using a Perkin-Elmer 621 spectrophotometer. Spectra were obtained as Nujol mulls in the case of solid compounds and as liquid films for the free ligands. The mulls were supported between sodium chloride plates. The far i.r. spectra ($15\text{--}20\ \mu$) were recorded as Nujol mulls held between thin polythene or CsI plates on Beckman IR-12 and Perkin-Elmer 225 spectrophotometers equipped with caesium iodide optics.

Results and Discussion

The complexes isolated in the present study, their methods of preparation and analytical data are summarised in Tables I and II. Partial i.r. spectral data are listed in Tables III and IV. Some of the complexes prepared contain non-integral ratios of the ligand molecules to the metal atoms. These compounds were obtained reproducibly by varying the ratios of the reactants and must, therefore, be regarded as definite chemical entities. Absorption bands in the range $650\text{--}200\text{ cm}^{-1}$ due to the coordinated quinoline and isoquinoline in the complexes, which occur at almost the same frequencies as the free ligands, are also listed in Tables III and IV.

Low values of the molecular conductances (Λ_m range $< 20\text{ mho}$) of the complexes in ethanol show that they are non-electrolytes. Zinc(II), cadmium(II) and mercury(II) being d^{10} ions do not show $d \rightarrow d$ transitions and, therefore, stereochemistry of their complexes cannot be derived from u.v. and visible reflectance spectra. Information on the structure of complexes in the present studies has been derived from their infrared spectral measurements.

The i.r. spectra of quinoline and isoquinoline have

- (1) M.A. Porai-Koshits, L.O. Atovmyan and G.N. Tishchenko, *Zh. Strukt. Khim.*, **1**, 337 (1960); Yu. A. Sokolova, L. O. Atovmyan, and M. A. Porai-Koshits, *ibid.*, **7**, 855 (1966).
- (2) D. Grdenic and I. Kristanovic, *Arhiv. Kemi.*, **27**, 143 (1955).
- (3) A.V. Ablov and T.I. Malinovskii, *Dokl Akad. Nauk.*, S.S.S.R., **123**, 677 (1958); T. I. Malinovskii and Y. A. Simonov, *ibid.*, **147**, 96 (1962).
- (4) A.B.P. Lever, *Inorg. Chem.*, **4**, 1042 (1965).
- (5) G.E. Coates and D. Ridley, *J. Chem. Soc.*, 166 (1964).
- (6) R.J.H. Clark and C.S. Williams, *Chem. and Industry*, (London) **1317** (1964); *Inorg. Chem.*, **4**, 350 (1965).
- (7) J.R. Allan, D.H. Brown, R.H. Nuttall and D.W.A. Sharp, *J. Chem. Soc.*, **A**, 1051 (1966).
- (8) C. Postmus, J.R. Ferraro, and W. Wozniak, *Inorg. Chem.*, **6**, 2050 (1967).
- (9) I.S. Ahuja and P. Rastogi, *J. Chem. Soc.*, **A**, 2161 (1970).
- (10) S.M. Nelson and T.M. Shepherd, *J. Inorg. Nucl. Chem.*, **27**, 2125 (1965).
- (11) R.J.H. Clark and C.S. Williams, *Spectrochim. Acta*, **22**, 1081 (1966).

- (12) C.W. Frank and L.B. Rogers, *Inorg. Chem.*, **5**, 615 (1966).
- (13) I.S. Ahuja and A. Garg, *J. Inorg. Nucl. Chem.*, (in Press).
- (14) A. Albert in « Physical Methods in Heterocyclic Chemistry » Vol. 1, edited by A.R. Katritzky, Academic Press, New York, 1963.
- (15) H. Luther, D. Mootz, and F. Radwitz, *J. prakt. Chem.*, **5**, 242 (1958); P. Chirboli and A. Bortoluzza, *Ann. Chim.*, (Rome) **49**, 245 (1959); K.K. Deb, *Ind. J. Phys.*, **35**, 535 (1961); **35**, 557 (1962); R. Ammini Amma, K.P.R. Nair, and S.N. Singh, *Ind. J. Pure & Appl. Phys.*, **7**, 567 (1969); R. Ammini Amma, S.N. Thakur, and K.P.R. Nair, *Appl. Spectrosc.*, **24**, 344 (1970).

Table I. Analytical Data: Zinc(II), Cadmium(II) and Mercury(II) Complexes with Quinoline.

Compound	Method of prepn.*	M.P. (°C)	Metal (%)		Anion (%)	
			Found	Calc.	Found	Calc.
ZnQ ₂ Cl ₂	A	230	16.5	16.6	17.9	18.0
ZnQ ₂ Br ₂	A	235	13.4	13.5	33.0	33.1
ZnQ ₂ I ₂	A	242	11.2	11.3	44.1	43.9
ZnQ(NCS) ₂	A	184	20.9	21.1	37.6	37.4
CdQCl ₂	A	>250	36.0	35.9	22.6	22.7
CdQBr ₂	A	>250	28.2	28.0	39.6	39.8
CdQI ₂	A	247	22.8	22.7	51.0	51.2
Cd ₂ Q ₃ (SCN) ₄	A	178	26.5	26.6	27.8	27.5
HgQCl ₂	A	186	50.2	50.0	17.8	17.7
HgC ₂ Cl ₂	B	183	38.0	37.8	13.5	13.4
HgQBr ₂	A	198	41.0	41.0	32.7	32.7
HgQ ₂ Br ₂	B	141	32.5	32.4	25.9	25.8
HgQ(CN) ₂	A	195	52.3	52.5		^a
Hg ₂ Q ₃ (SCN) ₄	C	132	39.5	39.3	22.5	22.7

Q = Quinoline; ^a Found: C = 35.0, H = 1.85, N = 11.2; Calc. C = 34.6, H = 1.83, N = 11.0. * Methods of preparation: (A) An excess of the appropriate ligand was added to a hot solution of the metal(II) salt in ethanol. The complex which crystallized out or precipitated was filtered off, washed with ethanol and dried. (B) The metal(II) salt was dissolved by heating in an excess of the appropriate ligand. The complex which crystallized out on cooling was filtered, washed with anhydrous ether and dried. (C) A suspension of the metal(II) salt in ethanol was boiled with an excess of the ligand. The mixture was filtered hot and the complex which crystallized out on cooling was suction-filtered, washed with ethanol and dried.

Table II. Analytical data: Zinc(II), Cadmium(II) and Mercury(II) Complexes with Isoquinoline.

Compound	Method of prepn.*	M.P. (°C)	Metal (%)		Anion (%)	
			Found	Calc.	Found	Calc.
Zn(IQ) ₂ Cl ₂	A	204	16.6	16.6	18.1	18.0
Zn(IQ) ₂ Br ₂	A	205	13.6	13.5	33.2	33.1
Zn(IQ) ₂ I ₂	A	193	11.2	11.3	44.0	43.9
Zn(IQ) ₂ (NCS) ₂	A	190	15.0	14.9	26.5	26.4
Zn(IQ) ₂ (OAc) ₂	B	104	14.7	14.8		^b
Cd(IQ)Cl ₂	A	>250	36.0	35.9	22.6	22.7
Cd(IQ) ₂ Br ₂	A	>250	21.3	21.2	30.0	30.1
Cd(IQ) ₂ I ₂	A	178	17.9	18.0	40.8	40.6
Cd(IQ) ₂ (SCN) ₂	A	220	23.0	23.1	24.5	24.4
Cd(IQ) ₂ (OAc) ₂	B	93	22.8	23.0		^c
Hg(IQ)Cl ₂	A	150	50.0	50.0	17.8	17.7
Hg(IQ) ₂ Cl ₂	B	129	38.0	37.8	13.5	13.4
Hg(IQ)Br ₂	A	188	41.1	41.0	32.9	32.7
Hg(IQ) ₂ Br ₂	B	140	32.5	32.4	26.0	25.8
Hg(IQ)(CN) ₂	A	206	52.6	52.5		^d

* Methods as given in Table I. IQ = Isoquinoline; ^b Found: C = 59.9, H = 4.58, N = 6.39; Calc. C = 59.7, H = 4.53, N = 6.34. (c) Found: C = 54.5, H = 4.11, N = 5.78; Calc. C = 54.0, H = 4.09, N = 5.73. (d) Found: C = 34.9, H = 1.81, N = 10.9; Calc. C = 34.6, H = 1.83, N = 11.0

been studied by several workers.¹⁵ Recently Wait and McNerney¹⁶ have made a complete assignment of the observed i.r. absorption bands in these amines and found a good agreement of the observed frequencies with the calculated assignments. There is also some report on the i.r. spectra of complexes in which the quinoline is coordinated to transition metal(II) ions.^{12,17,20}

I.R. spectra of zinc(II), cadmium(II), and mercury(II) complexes with quinoline and isoquinoline studied here show close resemblance to the spectra of the

corresponding free amines. This is in accord with the previous observations on pyridine¹⁸ and quinoline^{12,17} complexes in that with the exception of relatively minor shifts and splitting of some absorption bands the fundamental frequencies of the free amines are altered little on coordination to metal ions.

METAL(II) HALIDE COMPLEXES

Zinc(II) Halide Complexes. All the zinc(II) complexes studied are of the stoichiometry ZnL₂X₂, where L = quinoline or isoquinoline, and X = Cl, Br, or I. In the low frequency i.r. spectra of these complexes strong absorption bands were observed at ~300 cm⁻¹ in the chloro- and at ~245 cm⁻¹ in the bromo-derivatives. Since the frequency of these bands is halogen dependent and in fair agreement to Zn-Cl and Zn-Br stretching modes in many other zinc(II) halide complexes ZnL₂X₂ (L = monodentate ligand) known

(16) S.C. Wait, Jr., and J.C. McNerney, *J. Mol. Spectrosc.*, **34**, 56 (1970).

(17) C.S. Williams and F.F. Fouche, *Z. Naturforsch.*, **19A**, 363 (1964); M. Goldstein, E.F. Mooney, A. Anderson, and H.A. Gebbie, *Spectrochim. Acta*, **21**, 105 (1965); D. Forster and D.M.L. Goodgame, *J. Chem. Soc.*, 454 (1965); C.D. Burbridge and D.M.L. Goodgame, *J. Chem. Soc.*, A, 1074 (1968).

(18) N.S. Gill, R.H. Nuttall, D.E. Scaife, and D.W.A. Sharp, *J. Inorg. Nucl. Chem.*, **18**, 79 (1961).

(19) I.S. Ahuja, D.H. Brown, R.H. Nuttall, and D.W.A. Sharp, *J. Inorg. Nucl. Chem.*, **27**, 1105, 1625 (1965).

(20) J.R. Allan, D.H. Brown, R.H. Nuttall, and D.W.A. Sharp, *J. Inorg. Nucl. Chem.*, **27**, 1305 (1965).

Table III. Partial I.R. Spectral data (cm⁻¹): Quinoline Complexes.

Compound	Metal-halogen Mode		Ligand Modes						
Quinoline ZnQ ₂ Cl ₂	315, 296		627	611	522	479	392	377	277
			634	620	520	489	398	374	277
ZnQ ₂ Br ₂	239		633	621	530	465	400	374	275
						490			
						488			
ZnQ ₂ I ₂			640	623	536	466	382	374	276
						484			
						476			
ZnQ(NCS) ₂	νCN 2065 2050 2015		635	620	531	465	400	374	274
						483			
						476			
CdQCl ₂	νCS 840,835,740,737; δNCS	461,440;	630	620	527	290	395	373	274
						480			
CdQBr ₂			633	620	530	468	394	374	273
						485			
CdQI ₂			628	625	529	480	394	374	280
						489			
						484			
Cd ₂ Q ₂ (SCN) ₄			630	623	527	470	397	375	274
						465			
						483			
HgQCl ₂	νCN 2113,2095; νCS 770; δSCN	460,453	655	625	530	467	390	374	275
						484			
HgQ ₂ Cl ₂	270		627	620	526	464	389	375	masked by Hg-Cl band
						480			
HgQBr ₂			634	620	529	464	397	375	274
						485			
HgQ ₂ Br ₂			627	622	526	464	393	376	276
						480			
HgQ(CN)			625	620	525	464	394	377	276
						482			
Hg ₂ Q ₂ (SCN) ₄	νCN 2180,2110,2090; νHg-C	422;	630	625	527	463	396	377	276
						δHg-C-N 316			
						483			
	νCN 2123,2112; 2 × δSCN	920,864;				465			
						388			
						456,430;			
						νCS 791; δSCN			
						456,430;			
						νHg-S 271			

to have tetrahedral environments about the metal atoms,^{5-8,12,19} they are thus identified as i.r. active Zn-Cl (~300 cm⁻¹) and Zn-Br (~245 cm⁻¹) stretching modes respectively. The Zn-I stretching modes would be expected to occur below 200 cm⁻¹. This similarity in Zn-Cl and Zn-Br stretching modes suggests that the chloro- and bromo- and by inference the iodo-complexes studied here have monomeric tetrahedral structures. Moreover, the frequency of metal-halogen modes in these complexes is consistent with similar modes in 1:2 cobalt(II) halide-quinoline complexes²⁰ which have been shown by ultraviolet and visible reflectance spectroscopy to have tetrahedral environment of the ligands about the metal atoms.²¹ The bridging metal-halogen stretching modes in polymeric octahedral compounds ZnQ₂/(IQ)₂X₂ would be expected to occur at much lower frequencies than terminal metal-halogen modes of the monomeric tetrahedral structures.²²

Cadmium(II) Halide Complexes. Cadmium(II) chloride, bromide and iodide gave 1:1 complexes with

(21) D.H. Brown, R.H. Nuttall, and D.W.A. Sharp, *J. Inorg. Nucl. Chem.*, **26**, 1151 (1964).

(22) R.J.H. Clark, *Spectrochim. Acta*, **21**, 955 (1965); *Rec. Chem. Prog.*, **25**, 269 (1965).

quinoline. Cadmium(II) chloride gave 1:1 complex with isoquinoline but the bromide and iodide formed 1:2 compounds. The 1:1 cadmium(II) halide complexes may have (i) halogen-bridged dimeric tetrahedral structures permitting two sets of cadmium-halogen modes — (a) terminal, and (b) bridging; or (ii) halogen-bridged polymeric octahedral structures in the solid state. The low frequency i.r. spectra of CdLCl₂ complexes (L = quinoline or isoquinoline) did not show any band in the range 250-200 cm⁻¹ which could be assigned to terminal Cd-Cl stretching mode in the chlorine-bridged dimeric structure.²³⁻²⁵ This rules out the possibility of halogen-bridged dimeric structures for the 1:1 chloro-complexes in the present study. The 1:2 cadmium(II) bromide and iodide complexes with isoquinoline may have the metal atoms in (i) monomeric tetrahedral, or (ii) halogen-bridged polymeric octahedral environments.⁵ The Cd-Cl, Cd-Br

(23) G.B. Deacon and J.H.S. Green, *Chem. Comm.*, 629 (1966); *Spectrochim. Acta*, **24A**, 845 (1968); **25A**, 355 (1969); G.B. Deacon, J.H.S. Green, and D.I. Harrison, *Spectrochim. Acta*, **24A**, 1921 (1968).

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

(25) D.M. Adams, M. Goldstein, and E.F. Mooney, *Trans. Faraday Soc.*, **59**, 2228 (1963); T. Onishi and T. Shimanouchi, *Spectrochim. Acta*, **20**, 325 (1964); I.R. Beattie, T. Gilson, and P. Cocking, *J. Chem. Soc.*, **A**, 702 (1967).

Table IV. Partial I.R. Spectral Data (cm⁻¹): Isoquinoline Complexes

Compound	Metal-halogen Mode	Possible Metal - Isoquinoline Mode	Ligand Modes/L					
Isoquinoline			638	522	504	481	459	380
Zn(IQ) ₂ Cl ₂	325,300	233,223	640	538	513	482		394
			635	523				
Zn(IQ) ₂ Br ₂	254	237,221	639	540		485	463	387
			634	524		477		
Zn(IQ) ₂ I ₂		235	639	536		483	463	382
			636	522		475		
			633					
Zn(IQ) ₂ (NCS) ₂		233	637	542		481		387
				522		477		375
Zn(IQ) ₂ (OAc) ₂	νCN 2080; νCS 820; δNCS 477;	νZn-NCS	313,263					
			640	540	502	482	468	387
			632	523		476		
			618					
Cd(IQ)Cl ₂	ν _{asym} CO 1560; ν _{sym} CO 1430; δOCO 675;	νZn-O	300					
			640	528		482	464	386
			636	522		474		
Cd(IQ) ₂ Br ₂			642	525		486	460	380
			632	518		474		
			627					
Cd(IQ) ₂ I ₂			639	530		483	460	387
			636	516		474		
			628					
Cd(IQ) ₂ (SCN) ₂			640	524		481	461	386
			633	516		470	masked by δSCN	
	νCN 2080; νCS 770; δSCN 466,461							
Cd(IQ) ₂ (OAc) ₂			637	523		487	465	386
			624			482		
			617			476		
	ν _{asym} CO 1540; ν _{sym} CO 1404; δOCO 658;	νCd-O	318					
Hg(IQ)Cl ₂	320,208		637	529		482	463	382
			631	522		478		369
Hg(IQ) ₂ Cl ₂	298,278		639	526	513	485	463	380
			635	518		475		369
Hg(IQ)Br ₂	226		640	525	513	475	464	383
			632	515				
Hg(IQ) ₂ Br ₂	213		637	525	514	482	463	380
						474		
Hg(IQ)(CN) ₂			632		514	460		383
	νCN 2187; νHg-C 422; δHg-C-N 316							

and Cd-I stretching modes in halogen-bridged chloro-, bromo- and iodo- complexes and the terminal Cd-Br and Cd-I stretching modes in monomeric tetrahedral and halogen-bridged dimeric tetrahedral structures are expected to absorb²³ below 200 cm⁻¹. Hence there is no positive evidence as to the coordination arrangement in the complexes containing these halogens reported here.

Mercury(II) Halide Complexes. Mercury(II) chloride and bromide formed 1:1 and 1:2 complexes with both quinoline and isoquinoline. The 1:2 complexes may have (i) monomeric structures with pseudotetrahedral environments,^{5,23} or (ii) polymeric structures with distorted octahedral stereochemistry^{2,6,9} about the metal atoms. The low frequency i.r. spectrum of 1:2 mercury(II) chloride-pyridine complex has been studied for the first time by Coates and Ridley.⁵ Except for a single band at 418 cm⁻¹ due to coordinated pyridine these workers did not observe any band in the range 500-200 cm⁻¹ which could be assigned to a terminal νHg-Cl mode in tetrahedral Py₂HgCl₂. These workers concluded that all the chlorine atoms are

present in bridging rather than in terminal positions and assigned a polymeric, halogen-bridged octahedral structure for the complex. X-ray structural determinations² have shown the complex Py₂HgCl₂ as a 6-coordinated structure in which the metal atom has a distorted octahedral environment with two chlorine atoms at 2.34 Å, two nitrogen atoms at 2.60 Å and two more chlorine atoms at 3.25 Å. In their extensive studies on the far i.r. spectra of metal halide complexes with pyridine and related ligands Clark and Williams⁶ observed absorption bands at 292 cm⁻¹ and 215 cm⁻¹ in Py₂HgCl₂ and Py₂HgBr₂ respectively and considered these bands in accordance with the presence of one pair of short Hg-X (X = Cl or Br) in these complexes. The weak longer metal-halogen bonds² would be expected to occur at much lower frequencies. The 1:2 mercury(II) chloride and bromide complexes with isoquinoline show new strong bands at ~290 cm⁻¹ and ~210 cm⁻¹ in the chloro- and bromo-complexes respectively. The 1:2 mercury(II) chloride-quinoline complex shows a strong band at 270 cm⁻¹ but not the corresponding bromo-derivative. In view of the relatively lower frequency of

$\nu\text{Hg-Cl}$ (270 cm^{-1}) in the 1:2 mercury(II) chloride-quinoline complex, the $\nu\text{Hg-Br}$ in the corresponding bromo-complex would be expected to occur below 200 cm^{-1} . The close similarity in the frequency of $\nu\text{Hg-Cl}$ and $\nu\text{Hg-Br}$ in $\text{HgQ}_2/(\text{IQ})_2\text{X}_2$ complexes with similar modes in $\text{Py}_2\text{HgX}_2^6$ and L_2HgX_2^9 ($\text{L} = \text{methyl or dimethyl pyridine}$) suggests that the complexes $\text{HgQ}_2/(\text{IQ})_2\text{X}_2$ have structures similar to $\text{Py}_2\text{HgX}_2^2$.

The low frequency i.r. spectra of 1:1 mercury(II) chloride and bromide complexes with isoquinoline show new bands at 320 cm^{-1} and 208 cm^{-1} in the chloro- and at 226 cm^{-1} in the bromo-derivatives. These complexes may be postulated as either (i) 4-coordinate halogen-bridged dimeric structures^{5,9,23,26} thus permitting two sets of metal-halogen stretching modes^{5,9,23} — (a) terminal, and (b) bridging, or (ii) polymeric, 6-coordinate structures with only bridging halogens in the solid state. HgCl_2 , Ph_3AsO is, however, oxygen-bridged dimeric structure with only terminal chlorines.² The observed frequency of metal-halogen stretching modes in 1:1 mercury(II) chloride and bromide complexes with isoquinoline is in good agreement with similar modes in the complexes $\text{Ph}_3\text{P HgX}_2$, $\text{Ph}_3\text{As HgX}_2$ and HgLX_2 ($\text{L} = \text{monodentate ligand; X} = \text{Cl or Br}$) which are considered to have halogen-bridged dimeric structures in the solid state.^{9,23} These absorption bands are, therefore, identified as i.r. active terminal $\nu\text{Hg-Cl}$ (320 cm^{-1}) and $\nu\text{Hg-Br}$ (226 cm^{-1}) modes. The low frequency band at 208 cm^{-1} is assigned to the bridging $\nu\text{Hg-Cl}$ mode.²³ The bridging Hg-Br mode would be expected to occur well below 200 cm^{-1} . Moreover, absence of absorption bands at $\sim 300\text{ cm}^{-1}$ and $\sim 220\text{ cm}^{-1}$ in the 1:1 mercury(II) chloride and bromide-quinoline complexes expected for terminal $\nu\text{Hg-Cl}$ and $\nu\text{Hg-Br}$ modes respectively in the halogen-bridged dimeric structures strongly suggest that these complexes are 6-coordinate polymeric structures with only bridging halogens.

ZINC(II), CADMIUM(II), AND MERCURY(II) THIOCYANATE COMPLEXES

Zinc(II) Thiocyanate Complexes. Zinc(II) thiocyanate-quinoline complex gave metal-ligand ratio 1:1 while 1:2 complex was obtained with isoquinoline. In addition to the ligand vibration modes modified slightly on account of coordination new absorption bands were observed at 2080, 820, 477 (ligand band masked), 313, 263, and 233 cm^{-1} in the i.r. spectrum of 1:2 zinc(II) thiocyanate-isoquinoline complex. Except for the band at 233 cm^{-1} (due to Zn-isoquinoline mode) the other bands were not observed in the i.r. spectra of 1:2 zinc(II) chloride, bromide and iodide complexes with isoquinoline. These bands are, therefore, identified as νCN (2080 cm^{-1}), νCS (820 cm^{-1}), δNCS (477 cm^{-1}), and $\nu\text{Zn-NCS}$ ($313, 263\text{ cm}^{-1}$) modes respectively due to the coordinated thiocyanate groups. The frequencies of the fundamental modes due to coordinated thiocyanate groups in the 1:2 zinc(II) thiocyanate-isoquinoline complex are in good

agreement with similar modes in 1:2 zinc(II) thiocyanate complexes with pyridines^{10,11,13} and considered to have terminal N-bonded thiocyanate groups. It is, therefore, suggested that the metal atoms in this complex have a 4-coordinate tetrahedral environment of two N-bonded thiocyanate groups and two isoquinoline molecules. The observed frequencies due to coordinate thiocyanate groups rule out the possibility of thiocyanato-bridged polymeric octahedral structure for the complex.

The 1:1 zinc(II) thiocyanate-quinoline complex may be postulated as (i) thiocyanato-bridged dimeric tetrahedral structure with terminal and bridging thiocyanate groups thus permitting two sets of νCN and νCS modes²⁷ — (a) terminal, and (b) bridging —, or (ii) 6-coordinate polymeric octahedral structure with only bridging thiocyanate groups. I.R. spectrum of the complex showed absorption bands at (2065, 2050, 2015 cm^{-1}) and (842, 835, 740, 737 cm^{-1}). These bands are, therefore, identified as νCN (2065, 2050, 2015 cm^{-1}) and νCS (840, 835, 740, 737 cm^{-1}) modes due to coordinated thiocyanate groups. The frequencies of these modes indicate the presence of both terminal and bridging thiocyanate groups. The frequency of νCN in complexes containing bridging thiocyanate groups is usually higher than that for terminally bonded thiocyanate.^{10,11} However, such factors as coordination number and stereochemistry of the complex may also affect the frequency of νCN and examples are known bridging νCN may appear at lower frequencies.^{27,28} The observed frequencies due to the coordinated thiocyanate groups in the 1:1 zinc(II) thiocyanate-quinoline complex are consistent with thiocyanato-bridged dimeric tetrahedral structure.

Cadmium(II) Thiocyanate Complexes. Cadmium(II) thiocyanate formed 1:2 complex with isoquinoline but 2:3 with quinoline. The observed frequencies due to coordinated thiocyanate groups in both these complexes are in good agreement with similar modes in $\text{ML}_2(\text{SCN})_2$ complexes which have been shown by X-ray crystallography²⁹ and/or magnetic and i.r. spectral measurements^{10,11,13} to have only bridging thiocyanate groups. The cadmium(II) thiocyanate-quinoline/isoquinoline complexes may thus be assigned polymeric octahedral structures with adjacent metal atoms linked by two $-\text{SCN}-$ bridges to form quasi-planar eight-membered ring — $\text{Cd}(\text{SCN})_2\text{Cd}$ —.

Mercury(II) Thiocyanate Complex. Mercury(II) thiocyanate formed 2:3 complex with quinoline but did not react with isoquinoline under similar conditions. The frequencies of νCN ($2123, 2112\text{ cm}^{-1}$) and νCS (791 cm^{-1}) in the i.r. spectrum of the complex suggest the presence of bridging thiocyanate groups;³⁰ the complex may thus be assigned thiocyanato-bridged polymeric octahedral structure.

(27) A.R. Davis, C.J. Murphy, and R.A. Plane, *Inorg. Chem.*, **9**, 423 (1970); S.C. Jain and R. Rivest, *Inorg. Chim. Acta*, **4**, 291 (1970).

(28) P.C.H. Mitchell and R.J.P. Williams, *J. Chem. Soc.*, 1912 (1960).

(29) M.A. Porai-Koshits and G.N. Tishchenko, *Kristallografiya*, **4**, 239 (1959).

(30) J.L. Burmeister, *Coordin. Chem. Revs.*, **1**, 205 (1966); **3**, 225 (1968).

(31) D.A. Dows, A. Haim, and W.K. Wilmarth, *J. Inorg. Nucl. Chem.*, **21**, 33 (1961).

(26) R.C. Evans, F.G. Mann, H.S. Peiser, and D. Purdie, *J. Chem. Soc.*, 1209 (1940); L.S.D. Glasser, L. Ingram, M.C. King, and G.P. McQuillan, *J. Chem. Soc. A*, 2501 (1969).

Mercury(II) Cyanide Complexes. Mercury(II) cyanide gave 1:1 complexes with both quinoline and isoquinoline. I.R. spectrum of the quinoline complex shows absorption bands at 2180, 2110, and 2090 cm^{-1} in the νCN region indicating the presence of bridging and terminal cyanide groups.³¹ The high frequency band (2180 cm^{-1}) may be assigned to bridging νCN and the low energy doublet (2110, 2090 cm^{-1}) to terminal νCN . On the other hand, the isoquinoline complex shows νCN at 2187 cm^{-1} . The frequency of this band is in almost the same range as in mercury(II) cyanide (2193 cm^{-1}) in the solid state,³² which is known as a linear cyanide-bridged polymeric structure.³³ Even the high frequency band assigned as bridging νCN in the quinoline complex occurs at lower energies than in pure $\text{Hg}(\text{CN})_2$. No definite information can be derived from $\nu\text{Hg}-\text{C}$ and $\delta\text{Hg}-\text{C}-\text{N}$ modes which occur at 422 cm^{-1} and 316 cm^{-1} respectively in both these complexes.

Zinc(II) and Cadmium(II) Acetate Complexes. Zinc(II) and cadmium(II) acetates formed 1:2 complexes with isoquinoline only. I.R. spectra of these complexes indicate the presence of coordinated isoquinoline and acetate groups. The free acetate ion has a very low symmetry (C_{2v}) and has 15 fundamental vibrations all of which do show up i.r. and Raman spectra.³⁴ On coordination the selection rule does not differ since all the modes are already i.r. active. However, the effect and type of coordination are usually judged from the magnitude of separation of

the CO asymmetric and symmetric stretching frequency shifts caused by coordination.^{34,35} In addition to the ligand vibration modes modified slightly on account of coordination, strong absorption bands were observed in the regions ~ 1560 , ~ 1420 , and ~ 660 cm^{-1} in the rock salt region i.r. spectra of the acetate complexes. These bands are, therefore, identified as CO asymmetric (~ 1560 cm^{-1}), CO symmetric (~ 1420 cm^{-1}) stretching and OCO bending (~ 660 cm^{-1}) modes respectively due to coordinated acetate groups. The observed carboxy frequencies with a separation of ~ 130 cm^{-1} in these complexes are in good agreement with similar modes (1550 and 1430 cm^{-1} ; separation 120 cm^{-1}) in bisacetatobisazoquinone(II),³⁵ $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ which has been shown by X-ray crystallography to have a pseudo-octahedral structure with both the acetate groups acting as symmetrical chelates.³⁶ From a consideration of i.r. frequencies due to coordinated acetate groups it is suggested that the 1:2 zinc(II) and cadmium(II) acetate-isoquinoline complexes are pseudo-octahedral structures with bidentate symmetrically chelated acetate groups.^{35,36}

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

(33) J. Hvoslof, *Acta Chem. Scand.*, 12, 1568 (1958).

(34) K. Nakamoto, I. Fujita, S. Tanaka, and M. Kobayashi, *J. Am. Chem. Soc.*, 79, 4904 (1957).

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

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