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1,3-Bis(4-pyridyl)propane Complexes of Divalent Metal Halides and Pseudohalides

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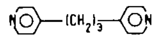
Summary

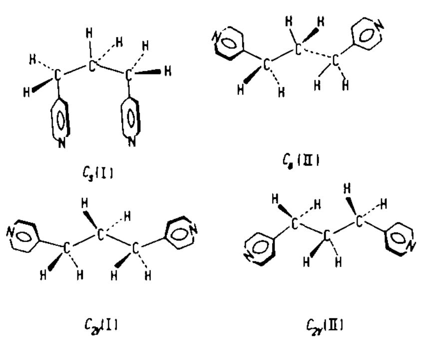
Coordination compounds formed by the interaction of 1,3-bis(4-pyridyl)propane (DPP) with some divalent metal halides and pseudohalides have been prepared and characterized by magnetic susceptibilities, electronic and i.r. spectral measurements down to 200 cm^{-1} in the solid state. The i.r. spectra indicate that DPP acts mostly as a bidentate bridging ligand in these complexes. Moreover, the two pyridyl rings which are nonplanar in uncoordinated DPP become coplanar upon coordination. Tentative stereochemistries of the complexes have been suggested in the solid state. The ligand field parameters Dq, B, β, λ and ν_2/ν_1 have been calculated for the cobalt(II) and nickel(II) complexes and are consistent with the proposed stereochemistries.

Introduction

Although coordination compounds of metal(II) salts with bidentate ligands like 1,10-phenanthroline, 2,2′-bipyridine and 4,4′-bipyridine have been studied extensively there is only one report$^{(1)}$ on the complexes of 1,3-bis(4-pyridyl) propane (DPP). DPP may act as a mono- or a bidentate ligand and molecular and scale models show considerable free rotation about its carbon-carbon bonds. In one of the possible configurations, the two pyridyl rings may be parallel to each other (C_s symmetry) and the two nitrogen atoms may coordinate to the same metal ion. The chelate ring thus formed would be large (twelve-membered). Another possible DPP geometry arises when the two pyridyl rings are remote from each other (C_{2v} symmetry with the pyridyl rings in one and the same plane, or C_s when the two rings are nonplanar). Such configurations would not permit chelation as the two nitrogen atoms, being far apart, would be unable to coordinate to the same metal ion. Coordination of the two pyridyl nitrogen atoms to different metal ions would thus be favoured, resulting in polymeric chain structures. It was, therefore, considered of interest to study the coordination behaviour of DPP towards some divalent metal halides and pseudohalides. Magnetic susceptibilities, electronic and i.r. spectral measurements down to 200 cm^{-1} have been carried out on the complexes in order to elucidate the mode of DPP bonding and of the anionic groups. Tentative stereochemistries of the complexes isolated in the solid state are discussed.



1,3-Bis(4-pyridyl)propane



Possible Symmetries

Experimental

Preparation of the complexes

DPP was obtained from the Reilly Tar and Chemical Corporation, U.S.A., and was used as such. All the metal(II) halides and pseudohalide complexes, with the exception of mercury(II) thiocyanate, were obtained by mixing hot EtOH solutions of the respective divalent metal salt and DPP. The preparation of the mercury thiocyanate complex involved boiling a suspension of the metal thiocyanate in EtOH with an excess of the ligand. The mixture was then filtered. The stoichiometries of the solid complexes isolated were checked gravimetrically by metal and halogen/pseudohalogen estimations.

Physical measurements

Electronic spectra of the divalent manganese, cobalt and nickel complexes were recorded as nujol mulls in the 300–1700 nm range on a Cary 14 recording spectrophotometer. The mulls were smeared on filter paper and run against a reference consisting of a similar piece of filter paper soaked in nujol. The i.r. spectra of DPP and of the complexes were recorded as nujol mulls on Perkin-Elmer 621 (rock salt region) and Beckmann IR-12 (700–200 cm^{-1}) spectrophotometers. Magnetic susceptibilities were measured at room temperature with a Cahn R. G. Electrobalance Model 7550 by the Faraday method using $HgCo(CNS)_4$ as the susceptibility standard. Diamagnetic corrections were

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Table 1. Analytical and partial i.r. psectral data[a)] of DPP and its metal complexes

Compound	Found (Calcd.)% Metal	 Anion	ν(C$\overset{\cdots}{-}$C)	Ring vibrations	ν(M–X)	ν(CN)	ν(CS)	δ(NCS)	ν(M–NCS) or ν(M–SCN)
DPP			1650s	992ms					
			1600s	575s, 402ms					
			1550ms						
Mn(DPP)$_2$Cl$_2$	10.8	13.9	1608s	1010s					
	(10.5)	(13.6)	1556m	612m	235ms				
Co(DPP)Cl$_2$	18.3	21.9	1608s	1010mw	295m				
	(17.9)	(21.6)	1550ms	616m, 416ms					
Co(DPP)Br$_2$	14.3	38.4	1610s	1015ms	250ms				
	(14.1)	(38.4)	1551m	615m, 420ms					
Co(DPP)$_2$(NCS)$_2$	10.5	20.3	1610s	1012s		2070m	832m	487m	255ms
	(10.3)	(20.3)	1550m	615ms, 415m		2060vs		481m	
Ni(DPP)$_2$Cl$_2$	11.1	13.7	1611s	1012s	248m				
	(11.1)	(13.5)	1550ms	616ms, 416ms	235ms				
Ni(DPP)$_2$Br$_2$	9.9	26.3	1608s	1015s					
	(9.5)	(26.0)	1550m	612ms, 424ms					
Ni(DPP)$_2$(NCS)$_2$	10.7	20.6	1612ms	1005w		2083m	796m	485m	251m
	(10.3)	(20.3)	1556ms	613s, 415ms		2060vs		480m	
Zn(DPP)Cl$_2$	19.6	21.5	1612s	1010w	327m				
	(19.4)	(21.2)	1554ms	612ms, 416ms	291s				
Zn(DPP)Br$_2$	16.6	37.9	1610s	1005w	253m				
	(16.6)	(37.8)	1558m	620s, 418ms	223m				
Zn(DPP)I$_2$	12.7	49.4	1612s	1013m					
	(12.5)	(49.1)	1560ms	617s, 419ms					
Zn(DPP)(NCS)$_2$	17.4	30.9	1614s	1020sh		2088vs	839m	490sh	318ms
	(17.1)	(30.6)	1556s	621s, 424ms				479m	270m
Cd(DPP)Cl$_2$	29.7	18.7	1608s	1011ms	232m				
	(29.4)	(18.6)	1554ms	608m, 425ms					
Cd(DPP)Br$_2$	23.8	34.5	1607s	1008ms					
	(23.8)	(34.0)	1553m	613ms, 424m					
Cd(DPP)I$_2$	20.1	45.4	1608m	1015ms					
	(19.8)	(45.0)	1558ms	608ms, 420s					
Cd(DPP)(SCN)$_2$	26.5	27.6	1608s	1010ms		2106sh	738m	465m	280m
	(26.3)	(27.2)	1553ms	612ms, 422ms		2096vs		460m	
Hg(DPP)Cl$_2$	42.6	15.5	1600s	1013ms	274ms				
	(42.6)	(15.1)	1551ms	617m, 425m					
Hg(DPP)Br$_2$	35.8	28.9	1617ms	1018ms	215m				
	(35.8)	(28.6)	1558m	608ms					
Hg(DPP)(SCN)$_2$	39.3	22.7	1608s	1006ms		2120vs	705m	454m	287m
	(38.9)	(22.5)	1556m	615s				422m	
Hg(DPP)(CN)$_2$	44.7		1602s	1022ms					
	(44.4)		1560ms	615ms, 424s		2160ms		ν(Hg–C)	δ(HgCN)
								415s	308ms

[a)] cm^{-1}.

estimated from Pascal's constants and magnetic moments were calculated by use of the equation $\mu_{\mathrm{eff}} = 2.84\sqrt{\chi_M\,\mathrm{corr}_T}$.

Results and Discussion

The complexes and their analytical data, together the characteristic i.r. absorption bands of uncoordinated DPP and of the complexes are listed in Table 1. Assignment of the observed bands in DPP has been made from a comparison of the vibrational modes in closely related molecules such as propane, pyridine and 4,4′-bipyridine(2). The insolubility of these complexes in suitable organic solvents (except that of the mercury cyanide complex) precluded molecular weight and conductivity measurements. The electronic spectral data, ligand field parameters and magnetic moments of the manganese(II), cobalt(II) and nickel(II) complexes are given in Table 2.

The i.r. spectra of the DPP metal(II) complexes studied here indicate clearly the bidentate bridging nature of DPP (except in the 1 : 1 mercury cyanide: DPP complex). The location of the two nitrogen atoms in the ligand precludes chelation but favours coordination to different metal ions. Coordination through only one of the pyridyl rings (monodentate DPP) would have resulted in a rather complicated spectrum particularly in the regions which suffer splitting or shifting upon coordination. Furthermore, the i.r. spectra due to coordinated DPP in these complexes exhibit fewer absorption bands as compared with the uncoordinated ligand spectrum. This is attributed to the fact that the two pyridyl rings, which are nonplanar in the free ligand, become coplanar upon coordination and that the coordinated DPP achieves a higher symmetry.

Manganese(II), cobalt(II) and nickel(II) halide complexes

The 1 : 2 manganese(II) chloride: DPP complex is white, has a room temperature magnetic moment of 5.9 B.M. and its far i.r. spectrum shows a band at 235 cm^{-1} due to ν(Mn-Cl) consistent with terminal chlorines in the DPP-bridged polymeric chain octahedral environments of four

Table 2. Selected electronic bands, spectral parameters[a)] and magnetic moment values for the DPP complexes

Compound	ν_1	ν_2	ν_3	μ_{eff} (B.M.)	10Dq	B_{35}	β_{35}	$\frac{10Dq}{B_{35}}$	ν_2/ν_1	$-\lambda$
$Co(DPP)Cl_2$	–	6600	16000	4.32	3122	882	0.908	3.53	–	93.6
$Co(DPP)Br_2$	–	6000	15380	4.50	3212	783	0.806	4.10	–	128
$Co(DPP)_2(NCS)_2$	8330	16130	20200	4.80	7800	756	0.778	10.31	1.94	..
$Ni(DPP)_2Cl_2$	8330	16390	25316	3.30	8330	1114	1.070	7.47	1.96	337
$Ni(DPP)_2Br_2$	10540	18180	25640	3.10	10540	813	0.780	12.93	1.73	237
$Ni(DPP)_2(NCS)_2$	9335	17390	..	3.00	9335	1174	1.125	8.00	1.86	130

a) cm^{-1}.

nitrogen atoms and two terminal chlorines around the metal ions.

The 1 : 1 cobalt(II) chloride and bromide complexes with DPP are blue and have room temperature magnetic moments of 4.32 and 4.50 B.M., respectively. Electronic spectra of both these compounds show bands at *ca.* 6000 and *ca.* 16000 cm^{-1} due to $^4A_2 \rightarrow {}^4T_1(F)$ and $^4A_2 \rightarrow {}^4T_1(P)$ transitions, respectively, consistent with high-spin slightly distorted[(4)] tetrahedral environments around the cobalt(II) ions. The ν(Co-Cl) and ν(Co-Br) frequencies (Table 1) are consistent with terminal cobalt halogen bonds in tetrahedral cobalt(II) complexes[(5)]. The 1 : 1 metal : ligand ratio, bidentate bridging nature of DPP, magnetic moments, electronic and far. i.r. spectral data suggest that both these complexes have polymeric, four-coordinated tetrahedral environments of the two nitrogen atoms (from bridging DPP molecules) and two terminally bonded halogens around the cobalt(II) ions:

The 1 : 2 nickel(II) chloride and bromide complexes with DPP are light green and have room temperature magnetic moments of 3.30 and 3.10 B.M., respectively. The observed electronic bands, ligand field parameters and magnetic moment values (Table 2) are consistent with distorted octahedral environments around nickel(II)[(4)]. Moreover, the low frequency i.r. spectrum of the nickel(II) chloride complex shows bands at 248 and 235 cm^{-1} due to terminal ν(Ni-Cl) modes in polymeric octahedral structures[(5, 6)]. Based on the magnetic moments, electronic spectral data, ligand field parameters, the bidentate bridging nature of DPP and the terminal Ni-halogen bonds the 1 : 1 nickel(II) chloride and bromide complexes with DPP are suggested tentatively to have polymeric, distorted octahedral environments of the four nitrogens (from bridging DPP molecules) and two terminally bonded halogens around the metal ions.

Zinc(II), cadmium(II) and mercury(II) halide complexes

The positions of the metal-halogen stretching modes[(7)] in the 1 : 1 zinc(II) chloride, bromide (and by inference also in the iodide), cadmium(II) chloride and mercury(II) chloride and bromide complexes with DPP strongly suggest polymeric tetrahedral environments of the two nitrogen atoms (from the bridging DPP molecules) and two terminally bonded halogens in these complexes. The ν(Cd-Br) and ν(Cd-I) modes are expected to absorb[(8)] below 200 cm^{-1}, the lower frequency limit of the spectrophotometer used in the present studies. Hence there is no positive evidence as to the coordination arrangements for the 1 : 1 cadmium(II) bromide and iodide complexes with DPP. In spite of the higher mass of mercury compared to cadmium, ν(M–X) in the mercury(II) halide complexes occurs at higher energies compared with the corresponding cadmium(II) complexes. This is probably because of the greater covalent character of the Hg–X relative to Cd–X bonds. The effect of mass on ν(M-Hal) in the cadmium(II) and mercury(II) complexes thus appears to be compensated by the reverse effect of the covalent character of the metal-halogen bond.

Metal(II) thiocyanate complexes

Cobalt(II) and nickel(II) thiocyanates formed 1 : 2 complexes, while zinc(II), cadmium(II) and mercury(II) thiocyanates gave 1 : 1 complexes with DPP. Magnetic moments, electronic spectral bands and the ligand field parameters (Table 2) in the cobalt(II) and nickel(II) thiocyanate-DPP complexes are consistent with distorted octahedral stereochemistries. Moreover, the absorption band frequencies associated with coordinated thiocyanato groups in the i.r. spectra (Table 1) are consistent with terminally N-bonded thiocyanato groups[(9)]. It is suggested therefore, that the metal atoms in both these complexes have six-coordinated, polymeric octahedral environments of the six nitrogen atoms, four from DPP molecules and two from NCS groups.

In addition to the ligand modes, modified, slightly on account of coordination, new absorption bands are observed at 2088, 839, 479, 318 and 270 cm^{-1} in the i.r. spectrum of the 1 : 1 zinc(II) thiocyanate-DPP complex. Such bands are not observed in the i.r. spectra of zinc(II) chloride, bromide or iodide complexes with DPP and are, therefore, identified as ν(CN) (2088 cm^{-1}), ν(CS) (839 cm^{-1}), δ(NCS) (479 cm^{-1}) and ν(Zn-NCS) (318, 270 cm^{-1}) modes due to coordinated terminally N-bonded NCS groups[(9, 10)]. It is suggested that the metal atoms in the 1 : 1 zinc(II) thiocyanate-DPP complex have a four-coordinated polymeric tetrahedral environment of the four nitrogen atoms – two from the bridging DPP molecules and two from N-bonded NCS groups – in the solid state.

The i.r. spectra of the 1 : 1 cadmium(II) and mercury(II) thiocyanate : DPP complexes show absorption bands at *ca.* 2100, 720, 430 and 270 cm^{-1}, which are identified as ν(CN), ν(CS), δ(SCN) and ν(M-SCN) modes, respectively, due to coordinated thiocyanato groups. These frequencies are consistent with terminally S-bonded thiocyanato groups[(9, 10)], and a four-coordinated polymeric tetrahedral environment for the two nitrogens (from bridging DPP molecules) and two sulphur atoms (of the terminally S-bonded

SCN groups) is suggested about the metal atoms in the 1 : 1 cadmium(II) and mercury(II) thiocyanate complexes with DPP. In spite of the higher mass of mercury than cadmium the frequency of ν(M-SCN) or ν(M-NCS) in the 1 : 1 zinc(II), cadmium(II) and mercury(II) thiocyanate: DPP complexes occurs in almost the same range as in M-NCS, where M = Co^{II} or Ni^{II}. It seems that the frequency of the metal-thiocyanate (N-bonded or S-bonded) bond is determined by the entire mass of thiocyanate group. The effect of mass on ν(M-NCS) in these complexes appears to the compensated (as in the halide complexes) by the reverse effect of the covalent character of the metal-ligand bond. Moreover, there seems to be a general increase in the frequency of the metal-ligand vibration as the coordination geometry changes from octahedral to tetrahedral ones(9). Consequently, the Metal-NCS or M-SCN vibration in the zinc(II), cadmium(II) and mercury(II) thiocyanate complexes would be expected to occur in almost the same frequency range.

Mercury(II) cyanide complex

Only mercury(II) cyanide gave a 1 : 1 complex with DPP. Absorption bands at 2160, 415 and 308 cm^{-1} in the i.r. spectrum of this complex are identified as ν(CN), ν(Hg-C) and δ(HgCN) modes respectively (due to coordinated cyano groups) and strongly suggest the presence of only terminal cyano groups(11, 12). Since the compound is monomeric as indicated by its molecular weight (determined by Rast's method in camphor: – Found. 470; calcd. 450) and that the DPP cannot chelate, the compound must contain three-coordinate mercury(12) and unidentate DPP (with a higher symmetry).

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Iron(III) Acetates

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Summary

The compound, $Fe_2Cl_2(OH)_2(MeCO_2)_2 \cdot 2MeCO_2H \cdot H_2O$, combines with lithium and silver acetates to form $Fe_2Cl(OH)_2(MeCO_2)_3 \cdot 2MeCO_2H$ and $Fe_2(OH)_2(MeCO_2)_4 \cdot H_2O$, respectively. Iron(III) chloride in tetrahydrofuran reacts with silver acetate to give a precipitate consisting of a mixture of $Fe(MeCO_2)_3$ and AgCl which, when extracted with boiling acetic acid, yields $Fe_2O_2(MeCO_2)_2 \cdot 3MeCO_2H$. With DMSO on the other hand an adduct $Fe(MeCO_2)_3 \cdot DMSO$ is formed which loses DMSO *in vacuo* to give ferric acetate, $Fe(MeCO_2)_3$. I.r. spectra, molar conductance, thermal decomposition, molecular weight and magnetic susceptibility measurements are reported.

Introduction

Iron(III) salts react with acetic acid or alkali metal acetates in aqueous systems to yield basic acetates which

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