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Studies on the Metal–Amide Bond.
Part IV*. Metal Complexes of N,N'-bis(2'-pyridinecarboxamide)-1,2-cyclohexane

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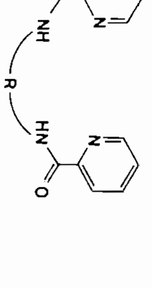
As part of our studies on the coordination of bis-(N-substituted) picolinamide ligands (I) we report here some complexes of N,N'-bis(2'-pyridinecarboxamide)-1,2-cyclohexane ($bpchH_2$) I, R = 1,2-C_6H_{10}. Both protonated and deprotonated complexes have been obtained and those isolated and characterised are listed in Table I. Table II gives the results of the thermogravimetric studies performed on the complexes.



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The paramagnetic complexes have moments and visible reflectance spectra consistent with the metal atoms having octahedral environments or tetrahedral in the case of the cobalt thiocyanate complex. The deprotonated nickel complex is diamagnetic indicating square-planar coordination. The visible spectra in the solid state and in solution for the protonated copper complexes, with the exception of the bromide complex, are similar and show no significant dependence on the anion. Although in solution the spectrum of the bromide complex is similar to that of the others, in the solid state it indicates possible coordination of the bromide ions.

The IR spectrum of the ligand shows a strong band of intensity at 3300 cm^{-1} due to ν_{N-H} which will be absent in the deprotonated complexes. For the protonated complexes this absorption is obscured by the board ν_{O-H} of the water molecules. On dehydration of the chloride and bromide copper complexes of the neutral ligand a sharp absorption band at *ca.* 3300 cm^{-1} is observed with the main features of the spectra remaining unchanged from those of the hydrate forms. On coordination via the amide group the amide I band [2] shifts to lower

TABLE I. Magnetic, Spectral and Analytical Data for some Complexes of N,N'-bis(2'-pyridinecarboxamide)-1,2-cyclohexane ($bpchH_2$).

Compound	Colour	μ_{eff} B.M.	Visible Reflectance λ_{max} (nm)	I.R. Absorption (cm^{-1})[a]			Found (%)					Calculated (%)				
				Amide I	Amide II	Amide III	C	H	N	Other		C	H	N	Other	
$Cu(bpch)\cdot 2H_2O$	dark blue	2.05	560	1620(ss)	1400(s)		51.7	5.4	12.9	Cu: 14.8		51.2	5.2	13.3	Cu: 15.0	
$Ni(bpch)\cdot 2.5H_2O$	yellow	diam		1625(ss)	1405(ss)		50.5	5.2	13.2	Ni: 14.1		50.7	5.4	13.1	Ni: 13.8	
$Pd(bpch)\cdot 2.5H_2O$	yellow	diam		1620(ss)	1395(ss)		45.6	4.8	11.8	Pd: 22.4		45.6	4.9	11.8	Pd: 22.5	
$Pt(bpch)\cdot 2.5H_2O$	yellow	diam		1625(ss)	1380(ss)		38.4	3.8	9.9	Pt: 35.4		38.4	4.1	10.0	Pt: 34.8	
$Cu(bpchH_2)Cl_2\cdot 4.5H_2O$	blue	1.86	700	1620(s)	1565(s)	1355(m)	40.0	4.7	10.4	Cu: 11.6	Cl: 13.3	40.0	5.4	10.4	Cu: 11.8	Cu: 13.4
$Cu(bpchH_2)Br_2\cdot 4.5H_2O$	dark brown	1.98	670, 540	1620(s)	1560(s)	1350(m)	34.5	3.8	8.7	Cu: 10.4	Br: 25.1	34.3	4.6	8.9	Cu: 10.1	Br: 25.3
$Cu(bpchH_2)(SO_4)\cdot 6H_2O$	pale blue	1.77	660	1620(s)	1560(s)	1360(m)	36.5	4.4	9.2	Cu: 10.6	S: 6.3	36.5	5.4	9.5	Cu: 10.7	S: 5.4
$Cu(bpchH_2)(NO_3)_2\cdot 3H_2O$	blue	2.00	670	1620(s)	1560(s)	b	38.3	4.0	14.8	Cu: 11.4		38.2	4.6	14.8	Cu: 11.2	
$Cu(bpchH_2)(ClO_4)_2\cdot 3H_2O$	blue	2.15	640	1620(s)	1560(s)	1380(m)	33.7	3.7	8.5	Cu: 9.6	Cl: 11.7	33.7	4.1	8.7	Cu: 9.9	Cl: 11.1
$Zn(bpchH_2)I_2\cdot 0.5H_2O$	yellow	diam		1635(ss)	1560(s)	1360(m)	33.1	3.2	8.5	Zn: 9.9	I: 38.8	33.1	3.2	8.6	Zn: 10.0	I: 38.6
$Co(bpchH_2)(SCN)_2\cdot 2H_2O$	blue	4.86	620, 520(sh)	1630(ss)	1570(s)	1350(m)	44.8	4.2	16.0	Co: 11.1	S: 12.2	44.9	4.5	15.7	Co: 11.0	S: 12.0
$Pt(bpchH_2)Cl_2\cdot 2H_2O$	yellow	diam		1655(s)	1525(s)	1350(m)	34.4	3.5	9.0	Pt: 31.0		34.5	3.8	8.9	Pt: 31.1	
$Ag(bpchH_2)(ClO_4)\cdot 3H_2O$	white	diam		1670(s) 1650(s)	1515(s)	1325(m)	36.8	3.6	9.2	Cl: 7.2		36.9	3.8	9.6	Cl: 6.1	
$Ag(bpchH_2)(NO_3)\cdot 2H_2O$	white	diam		1645(ss)	1520(ss)	b	40.6	3.9	13.5			40.7	4.5	13.2		
$Ni_2(bpchH_2)_3(ClO_4)_4\cdot 10H_2O$	pale blue	3.40	610	1625(s)	1570(s)	1355(m)	38.9	4.0	9.9	Ni: 7.2	Cl: 8.3	38.9	4.8	10.1	Ni: 7.0	Cl: 8.5
$Co_2(bpchH_2)_3(ClO_4)_4\cdot 11H_2O$	pale pink	4.68	495(sh)	1625(ss)	1565(s)	1355(m)	38.3	3.8	10.0	Co: 7.2	Cl: 8.3	38.4	4.9	10.0	Co: 7.0	Cl: 8.4
$bpchH_2$				1650(ss)	1530(ss)	1335(m)	66.5	6.2	17.0			66.7	6.2	17.3		

[a] Amide 1 –($\nu_{C-O} + \nu_{C-N}$); Amide II –($\nu_{C-N} + \delta_{N-H}$); Amide III –($\delta_{N-H} + \nu_{C-N}$) see ref. 1; s = strong; ss = strong and sharp; m = medium; sh = shoulder. [b] Obscured by nitrate vibrations.

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*Part III, ref. [1].

TABLE II. Results of Thermogravimetric Studies.

Complex	Temp. Range °C	Vol. products[a]	Wt. Loss (%)		Metal (%)	
			Found[b]	Calc.	Found[c]	Calc.
Cu(bpch)·$2H_2O$	35–125	$2H_2O$	8.3	8.5		
	175–800	bpch	78.1	76.4		
		Total loss	86.4	84.9	13.6	15.1
Ni(bpch)·$2.5H_2O$	35–145	$2H_2O$	8.0	8.4		
	235–635	$0.5H_2O$ + bpch	77.7	77.8		
		Total loss	85.7	86.2	14.3	13.8
Pd(bpch)·$2.5H_2O$	35–260	2.5 H_2O	10.0	9.5		
	290–800	bpch	67.6	68.0		
		Total loss	77.6	77.5	22.4	22.5
Pt(bpch)·$2.5H_2O$	50–120	$2H_2O$	6.5	6.4		
	170–610	$0.5H_2O$ + bpch	58.1	58.8		
		Total loss	64.6	65.2	35.4	34.8
Cu($bpchH_2$)Cl_2·$4.5H_2O$	35–225	$4.5H_2O$ sublimes	14.5	15.0		
Cu($bpchH_2$)Br_2·$4.5H_2O$	35–225	$4.5H_2O$ sublimes	12.0	12.8		
Cu($bpchH_2$)(SO_4)·$6H_2O$	35–80	$3H_2O$	9.0	9.1		
	105–180	$2H_2O$	6.0	6.0		
	225–260	H_2O	3.8	3.0		
	290–800	$bpchH_2$ + SO_4	68.7	71.1		
		Total loss	87.5	89.3	12.5	10.7
Cu($bpchH_2$)$(NO_3)_2$·$3H_2O$	50–145	$3H_2O$	9.3	9.5		
Cu($bpchH_2$)$(ClO_4)_2$·$3H_2O$	35–145	$2.5H_2O$	6.8	7.0		
Zn($bpchH_2$)I_2·$0.5H_2O$	35–260	$0.5H_2O$ sublimes	1.5	1.4		
Co($bpchH_2$)(SCN_2)·$2H_2O$	35–180	$1.5H_2O$	5.0	5.0		
	260–390	$0.5H_2O$ + $bpchH_2$	62.0	62.2		
	430–560	$2SO_2$	12.5	12.0		
	720–880	2HCN	8.9	9.7		
		Total loss	88.4	88.9	11.6	11.1
Pt($bpchH_2$)Cl_2·$2H_2O$	65–130	H_2O	3.0	2.9		
	170–650	H_2O + bpch + 2HCl	66.0	66.0		
			69.0	68.9	31.0	31.1

[a] $bpchH_2$ = N,N'-bis(2'-pyridinecarboxamide)-1,2-cyclohexane. [b] Final weight loss corrected for uptake of oxygen. [c] Assuming the following oxides to be the remaining solids for the respective metals: CuO, NiO, ZnO, Co_3O_4. For Pd and Pt remaining solids are the metallic elements.

frequencies and for the protonated complexes the amide II band shifts to higher frequencies. In the deprotonated complexes the amide II band is replaced by a medium intensity band at *ca.* 1400 cm^{-1} assigned to ν_{C-N} [2]. For the protonated complexes of silver and platinum there is no significant shift in the amide I band but the amide II band shifts to lower frequencies which suggests that in these complexes the amide groups remain uncoordinated.

In the deprotonated complexes coordination is *via* the four nitrogen atoms giving an essentially square-planar metal atom environment. Evidence for the coordination of both isomeric forms of the ligand is apparent in the deprotonated copper complex. On crystallisation a mixture of [Cu(*cis*-bpch)-H_2O]·H_2O and [Cu(*trans*-bpch)H_2O]·H_2O crystal forms is obtained and both have been characterised by X-ray structural studies [3]. In both structures the copper atom has a square-based pyramidal environment with the apical position occupied by a water molecule. For the protonated complexes polymeric or iminol structures as previously proposed for analogous complexes of N,N′-bis(2′-pyridinecarboxamide)-1,2-benzene [4] are suggested.

Proton NMR studies of the nickel, palladium and platinum complexes were undertaken. For the platinum complexes the ^{195}Pt–^{1}H coupling to the 6- and 6′-hydrogen atoms of the pyridyl rings is observed. However, detailed interpretation of the NMR spectra of the complexes and the ligand is the subject of further investigation which requires the separation of isomeric forms.

Experimental

The ligand, $bpchH_2$, was prepared as described previously [5] using a 70/30% misture of the *trans*- and *cis*-isomers of 1,2-diaminocyclohexane (Tokyo Kasei Kogyo Co. Ltd.). The deprotonated complexes of Cu, Ni, Pd were prepared by mixing a hot ethanolic solution of the ligand with a hot aqueous solution of the acetate for Cu and Ni and K_2PdCl_4 for Pd. The protonated complexes were prepared in a similar manner using the appropriate metal salt solution. For the Pt complexes K_2PtCl_4 was used, the protonated complex precipitated initially and was filtered off and then on further heating the deprotonated complex formed. Microanalyses, elemental analyses and physical measurements were carried out as described previously [4].

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