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STUDIES ON COORDINATION COMPOUNDS

Part VII. Phthalhydrazide Complexes of Cobalt(II)

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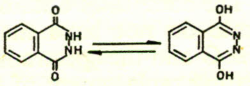
Abstract. Phthalhydrazide complexes of cobalt(II) have been prepared with metal–ligand ratio of 1:2 and 1:1. The spectra and solubility of the two compounds are different. The conditions of preparation and the spectra suggest that they are formed as inner complex salts through enolization of the carbonyl and have structure I and II.

The complex I is obtained as the diaquo compound and has been reacted with ethylenediamine, dipyridyl, acetylacetone, *o,m,* and *p*-phenylenediamine. While ethylenediamine and dipyridyl replace the two water molecules, there is a replacement of the ligand by acetylacetone and the phenylenediamines. Also on reacting the acetylacetonate and ethylenediamine complexes a replacement series phthalhydrazide $>$ Cl^- $>$ acac $>$ en $>$ bipy $>$ H_2O $>$ phenylenediamines is obtained.

Conductivity measurements suggest that the complexes are neutral. The IR bands at 565 and 425 cm^{-1} are assigned to asymmetric and symmetric M—O stretching frequencies. The IR and UV spectra are consistent with an inner complex salt formation. The magnetic moment corresponds with an octahedral complex for both I and II. The higher moment for II does not suggest any metal–metal interaction.

The reaction of phthalic anhydride and hydrazine is known to yield phthaldihydrazide.[1] This compound is, however, unstable and a variety of products are obtained under different reaction conditions.[2] One of the main products is phthalhydrazide or 2,3-dihydro-1,4-phthalazinedione (hereinafter designated as PH).



I

The coordination chemistry of this ligand does not appear to have been studied. Reports regarding the chemiluminescent determination of cobalt using aminohydro-1,4-phthalazinedione-(luminol),[3] the catalytic activity of cobalt in chemiluminescence[4] and the complex formation in the copper or cobalt luminol system[5] are the only ones so far available. We have been interested in the isolation of complexes of dihydrazides with metal salts.[6,7] The present study is an extension of the results on the adipyl dihydrazide complexes. We find that phthalhydrazide forms very stable complexes of cobalt and that the metal is quantitatively extracted by using a weakly alkaline solution of the ligand.

Experimental

The analyses were carried out by the Microanalytical Section of this Laboratory. The physical measurements were carried out by the methods and instruments mentioned earlier. The ligand was prepared by condensing phthalic anhydride with hydrazine hydrate. For this reaction phthalic anhydride (14.8 g, 100 mM) and hydrazine hydrate (6.0 g, 120 mM) in 50 ml ethanol were heated to refluxing temperature for 30 min and then the flask was cooled. The solids separated were filtered out and washed with water, followed by alcohol and ether. The dry amorphous solid, m.p. 333–35°C (lit. m.p. 335–38),[1] was soluble in ammoniacal or alkaline solutions.

For the preparation of the complexes, the cobalt salt was added to one equivalent of the ligand in dilute aqueous ammonia. It was observed that two types of coloured solids were obtained: one which deposited immediately was pink and granular and the other was purple and amorphous. When the ligand was added in excess of 2:1 the pink complex was the main product. With a control of the pH of the solution and using an excess of the ligand it was possible to obtain one form in preference to the other. When the pH was adjusted at 5.5–7.0 and one equivalent of cobalt chloride was reacted with two equivalents of phthalhydrazide, the pink product was immediately precipitated which was washed with water, ethanol and ether. When freshly precipitated the compound is highly aquated (III). When dried under vacuum (H_2SO_4) the analytical results indicated it to be bis-(phthalhydrazide)-diaquo cobalt. The reaction when carried out in a slightly alkaline medium at pH 7.0–8.0 the amorphous purple precipitate was obtained as II.

Addition Reactions

Reaction of $Co(PH)_2.2H_2O$ *with Ethylenediamine.* One ml (16.3 mM) ethylenediamine and 100 mg (0.23 mM) $Co(PH)_2.2H_2O$ were mixed and heated on a water-bath. A dark brown solution was formed. Yellow solids settled down on concentrating the solution. They were purified by adding a small volume of ethanol followed by an excess of ether. The complex so obtained had the formulation: $[Coen(PH)_2]7H_2O$.

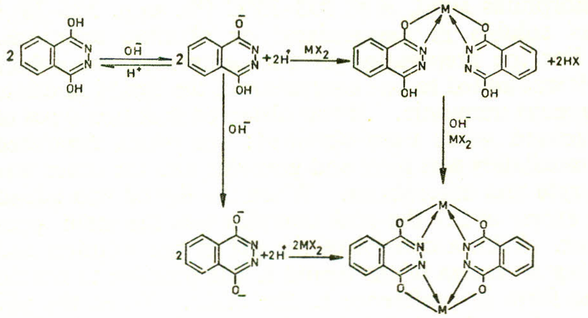
Reaction of Phthalhydrazide with en-$CoCl_2$ *Mixture.* One ml (16.3 mM) ethylenediamine in 2 ml distilled water was mixed with 0.238 g (1 mM) $CoCl_2.6H_2O$ and was added to 0.81 g (5 mM) phthalhydrazide solution in NaOH (pH 9.0). This gave a dark brown solution from which orange solids were deposited on concentrating the solution and adding a small volume of ethanol. They were purified by treatment with ethanol followed by ether. The product corresponds to the formula $[Co(PH)en_2Cl]7H_2O$.

Reaction of $Co(PH)_2.2H_2O$ *with Dipyridyl.* α,α-Dipyridyl, 156 mg (1mM) in 10 ml ethanol and 100 mg (0.23 mM) $Co(PH)_2.2H_2O$ were heated on a water-bath to give a brown solution. Grey solids were obtained on concentrating the solution and adding a small volume of ethanol and a slight excess of ether. The product corresponded with the formulation [Co dipy$(PH)_2]2H_2O$.

Replacement Reactions

Reaction of Phthalhydrazide with Co-Acetylacetonate. Cobalt acetate 498 mg (2 mM), and sodium acetate 328 mg (4 mM), were reacted by refluxing in 10 ml (98 mM) acetylacetone. Pink precipitates of cobalt acetylacetonate were obtained.

Cobalt actylacetonate, 259 mg (1 mM), was dissolved in distilled water and added to 162 mg (1 mM) phthalhydrazide solution in NaOH (pH 9.0). The purple precipitates which settled down had the same IR spectrum as that of II.



II

$Co(PH)_2.2H_2O$, 109 mg (0.25 mM), was reacted with 27 mg *o*, *m* or *p*-phenylenediamine in ethanol by heating on a water-bath. Some of the complex was dissolved and at the same time some white precipitates settled down. The IR of the white solid was identical with that of phthalhydrazide. The other product was the unchanged complex showing no reaction with the phenylenediamine.

Reaction of Phthalhydrazide with $(Ph_3P)_2CoCl_2$. $(Ph_3P)_2CoCl_2$, 129 mg (0.332 mM), was dissolved in hot ethanol and reacted with 162 mg (1 mM) phthalhydrazide in NaOH solution (pH 9.0). The pink precipitate which formed had an IR spectrum similar to that of I. When $Co(PH)_22H_2O$ was refluxed with triphenylphosphine in alcohol no reaction seemed to occur.

Results

The analytical data in Table 1 indicate that two series of complexes are obtained: (1) amorphous solid with a metal to ligand ratio of 1:1, and (2) crystalline solid with a ratio of 1:2. They are sparingly soluble in water and alcohol and practically insoluble in all organic solvents. The spectrum in the UV region is very much similar to that of the ligand but for the enhancement in the intensity of the corresponding bands. The magnetic susceptibility of the complexes had a value of 4.29 for $[(PH)_2Co]2H_2O$ and 4.5–4.8 for $(PH)_2Co(H_2O)_n$ and 5.1 for $(PH)_2Co_2.5H_2O$ which is the range for octahedral compplexes. The IR spectra are consistent with bonding through the carbonyl group with interactions clearly from nitrogen. The N—N stretching frequency is observed at 800 cm^{-1} which is the lower limit for this absorption. The complexes obtained from cobalt sulphate and nitrate do not have the strong bands for $\nu S{=}O$ and $\nu N{=}O$ and the spectra in the two cases are identical indicating replacement of these anions.

The insolubility of the complexes does not permit a PMR spectrum but the spectrum of the ligand in an alkaline medium does not indicate an N—H proton. It is known that this ligand forms a disodium salt. This is because the acidity of the N—H group is enhanced by the presence of a carbonyl group adjacent to the nitrogen. The formation of the dianion in this manner will, therefore, not allow the observation of the N—H proton. The PMR spectra of the complexes is poorly resolved because of the limited solubility. However, the spectrum of the ethylenedia-

Table 1. Chracterization of Phthalhydrazide Complexes.

Complexes	M.p. (°C)	C(%)		H(%)		(N(%)		Co(%)		Cl(%)	
		Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
$[Co_2(PH)_2].5H_2O$	Above 360	36·22	36·70	3·77	4·84						
$[Co(PH)_2].2H_2O$	140	45·97	45·84	2·89	3·90						
$[Co(PH)_2].8H_2O$	145	36·53	36·7	4·60	4·84						
$[Co(PH)_2en].7H_2O$	240–45	38·1	38·42	5·62	7·10	21·7	22·00	10·9	10·4		
$[Co(PH)en_2Cl].7H_2O$	235–40					16·70	16·6	11·73	11·63	7·15	6·7
$[Co(PH)_2dipy].2H_2O$	185	54·5	54·21	3·84	4·56	14·3	13·45				

mine complex has a broad band in the en region indicating a fast ligand exchange.

Discussion

The reaction between phthalhydrazide and a cobalt salt requires slightly alkaline conditions with a pH range of 5.5–8.0. After the precipitation of the complex the solution becomes slightly acidic having a pH 5.0–5.5 and the anion is totally replaced. This shows that an inner complex salt of phthalhydrazide is formed.

The control of pH is important for obtaining the two compounds according to the above reaction scheme. The product I is obtained at a pH 5.5–7.0 while II is obtained at 7.0–8.0. The two compounds have different stoichiometry and different IR spectra. The complexes in each case are highly aquated and are usually amorphous. On heating at 110°C or on storage under vacuum (H_2SO_4) they retain at least two molecules of water. They are decomposed by acids to free the ligands and form the corresponding cobalt salt. These results indicate that the complexes are formed through the chelation of the enolic form, i.e. the enol group is salt forming as in the acetylacetonates and the chloranilates[9] while the tertiary nitrogen is coordinated to the metal atom. It may be seen that the chelating group fills in four coordination positions. This explains the stability of the diaquo complex which accounts for the remaining two coordination positions. The disposition of the chelating ligand and the water molecules is further supported by the formation of the ethylenediamine and dipyridyl complexes.

Ethylenediamine Complex. The reaction with ethylenediamine gives two different products according to the method of preparation: (1) when ethylenediamine is refluxed with the diaquo complex, a yellow amorphous solid of formula $[Co.en(PH)_2]\ 7H_2O$ is obtained; (2) the addition of an alkaline solution of PH to an aqueous solution of $(Co.en_3)\ Cl_2.6H_2O$ gave an amorphous solid with colour ranging from orange to reddish brown depending on the degree of aquation and having the formula $[Co(PH)en_2Cl]_nH_2O$. The sharp melting orange product has the formula $[Co(PH)en_2Cl]7H_2O$. Both of these complexes are soluble in water but the former is slightly soluble in alcohol and insoluble in all other solvents while the latter is insoluble in all organic solvents.

Dipyridyl Complex. The reaction of dipyridyl with an ethanolic suspension of the diaquo complex gives a grey amorphous solid with the formulation of $[Co(dipy)(PH)_2].2H_2O$. This product is soluble in water and alcohol and is insoluble in other organic solvents. It is possible to expel the two molecules of water by heating or storage under vacuum (H_2SO_4). The same are, therefore, not in the coordination sphere.

It is significant to note here that while ethylenediamine is able to displace the water molecules from the coordination position the phthalhydrazide moiety is undisturbed indicating a stronger Co–phthalhydrazide compared with the Co–en bonding. Carrying out the reaction in the reverse order replaces only one Cl by PH which shows that in the ideal average environment so obtained the stability of M–PH is placed near about the M–Cl bond. Dipyridyl does not displaces a phthalhydrazide group from the complex and hence the stability of the latter is greater than that of amines mentioned above.

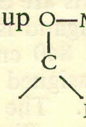
Reaction with other Diamines. *o,m*, or *p*-Phenylenediamine and triphenylphosphine and cobalt pthalhydrazide do not react to give a stable product. A violet solution is obtained in each case but it has not been possible to isolate any addition compound. The reaction with the preformed complexes of these ligands on the other hand produces cobalt phthalhydrazide (II).

Reaction with Acetylacetone. When an alkaline solution of phthalhydrazide was mixed with an aqueous solution of cobalt acetylacetonate, a purple amorphous solid complex corresponding to the polymeric cobalt phthalhydrazide (II) was obtained. In the reverse order the reaction of acetylacetone with the diaquo complex at a pH of 5.0–5.5 produced white solids of phthalhydrazide and a purple solution which deposited cobalt acetylacetonate on concentration. It has already been shown that under acidic conditions the phthalhydrazide complex is unstable, hence the replacement under acidic conditions does not really indicate that the acetylacetonate is more stable. The replacement in the basic medium, therefore, indicates the higher stability of the phthalhydrazide complex.

These reactions, therefore, conclusively suggest that the phthalhydrazide forms salt like complex and their stability can be placed in the following series above acetylacetone.

$$\text{Phthalhydrazide} \approx \text{Cl} > \text{acac} > \text{en} > \text{bipy} > H_2O > \text{diamines}$$

IR Spectra. The spectra of the two types of compounds, i.e. I and II are different from one another and from the ligand. There are five peaks occurring in the ligand at 1255, 1300, 1320, 1340 and 1370 cm^{-1}. In the complexes the absorptions are noted at 1250 and 1370 for I and at 1248 and 1380 for II, i.e. the bands at 1300, 1320 and 1340 are lost as a result of complex formation. It may be mentioned that in the sodium salt also the 1300–1340 bands do not appear which shows that these bands are due to NH-twisting. This evidence also suggests the formation of the complexes by enolization. The 1370 cm^{-1} band is assigned to νC—N while the one at 1250 cm^{-1} is an aromatic skeletal vibration. (Figs. 1-3)

There are two bands of high intensity occurring at 1480 and 1658 cm^{-1} besides the one at 1598 with moderate and at 1550, 1440 and 1430 cm^{-1} with weak intensity in the ligands. The 1658 and 1480 bands are both shifted to lower frequencies at 1640 and 1470 cm^{-1} while 1598 cm^{-1} band is shifted to 1570 and 1550 cm^{-1} band disappears. The four bands have almost the same intensity. The shifting of 1480 and 1658 cm^{-1} bands shows a symmetric coordination of the ketomine group  as has been observed in the cases of the carboxylates.[10]

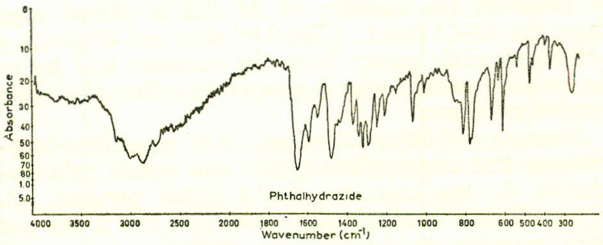


Fig. 1.

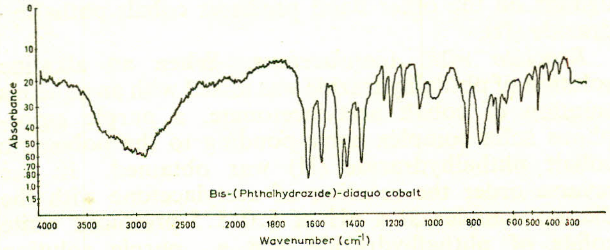


Fig. 2.

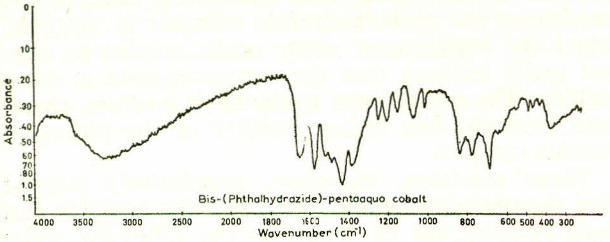


Fig. 3.

Table 2. IR Spectral Bands of Complexes.

PH (cm^{-1})	[Co(PH)$_2$] $\cdot$2H$_2$O (cm^{-1})	[Co(PH)$_2$] $\cdot$8H$_2$O (cm^{-1})	[Co$_2$(PH)$_2$] $\cdot$5H$_2$O (cm^{-1})	Assignments
3150s	3790w	3080s		
3000s				
	2920s			
2890s				
2750s				
2670s				
		2530s		
2400s		2320m		
1765w				
1710w				
1658vs	1645vs	1640vs	1640s	C=O enolized
1598s	1570s	1570s	1565s	C=N
1550s				
			1515s	
1480s	1470s	1478vs	1480s	O—M—N symmetric coordination
1450s	1450s	1445s	1425vs	C—O streching
1435				C—C aromatic
1370s	1370s	1370s	1380s	C—N
1340s				δN—H
1320s				δN—H
1255s	1250w	1250s	1248w	νC—C aromatic
1215s	1220w	1218s	1210w	βC—H aromatic
1155w	1160w	1155w	1150w	βC—H aromatic
1072s	1072	1072s	1072w	βC—H aromatic
1050w				
1015w	1010w	1010w	1010w	βC—H aromatic
990w				
965w				
910w				
860m	875w	875w	880w	N—N streching
	838s	835s	840m	δC=O
815s				
782s	775s	770s	775s	C—H out-of-plane bending
672s	680s	700s	685s	Aromatic C—H out-of-plane bending
640w	650w	675s	645w	Coordinated water
	635w	635s		
		625s		δC—O
618s				
550w		565w	565m	M—O assymmetric streching
	510w	510w	510w	
488w	482w	480m	485w	M—O symmetric streching
	425w	420w	450w	
388w	375w	365w		
350w	660w	610w		
275w				

s, strong; vs, very strong; m, medium; w, week.

The disappearance of 1550 cm^{-1} band is related to enolization while the gain in intensity and shifting to lower frequency of 1598 cm^{-1} band indicates co-ordination with the formation of the C=N group.

The 1480 and 1658 cm^{-1} bands are further shifted to 1425 and 1640 cm^{-1} in II. The 1425 cm^{-1} band has the highest intensity. The band may be related to the C=O stretching frequency, which, incidentally is also the highest intensity band in the sodium salt. This together with the loss of intensity of 1640 cm^{-1} band suggests that in II both the carbonyls are enolized.

The bands at 1370, 1250, 1215, 1155, 1072, 1020, 780 and 680 are little affected by complex or salt formation and are, therefore, assigned to the aromatic vibrations. The medium to weak intensity band at 680 cm^{-1} in the ligand is shifted to slightly higher frequencies of 872 and 880 cm^{1-} in I and II respectively. This shift is similar to the complexes of adipyl dihydrazide reported earlier. The region is appropriate for the N—N stretching frequency and the characteristic shift to higher frequency again indicates lack of resonance stabilization by the C = O obviously because of enolization. A higher shift in II perhaps indicates that both the carbonyls are enolized.

The band 815 cm^{-1} in the ligand is also shifted to higher frequencies of 835 and 840 cm^{-1} in I and II respectively. This has been assigned in the previous cases to the δC—O frequency. The blue shift may again be due to enolization. Similarly the disappearance from I and II of a strong absorption in the ligand at 618 cm^{-1}, assigned previously to δC=O (out of plane vibration) also indicates the bonding through enolization. There are two weak bands at 635 and 645 cm^{-1} which may be assigned to co-ordinated water. The medium intensity bands at 565 and 435 cm^{-1} are both assigned to the M—O asymmetric and symmetric stretching by analogy with the metallic chloranilates.

Electronic Spectra. The evidence regarding the participation of the anionic form of the ligand is provided by the electronic spectra of the complexes. It is noted that the spectra of the complexes are quite similar to that of the ligand. There is a very slight red shift in the frequency of the absorption at 305 μ but the intensity enhancement is quite marked. The similarity of the spectra and small shifts 5–10 μ for all the bands viz. those at 220, 265, 305 and 818 μ shows that there is no deformation of the π system of the ligand. The gain in intensity is related to the $\pi \rightarrow \pi^*$ charge transfer involving metal and ligand orbitals. The similarity shows further that the ligand is present in an anionic form as in I since the spectra were recorded in a slightly alkaline medium with pH 7.5. The assembly of models also suggests an enolate since bonding through nitrogen and coordination, through the carbonyl group would appreciably deform the ligand—a case not supported by the spectra. These spectra have remarkable similarity to the complexes of pyrrole derivatives[11] where also there is only intensity variation and a very slight change in energy.

The unresolved broad band at 510 μ is assigned to a *d*—*d* transition. The position of this band suggests an octahedral configuration for the inner complex salts of phthalhydrazide as well as of its ethylenediamine and dipyridyl complexes.

Conductivity Measurements. The conductivity measurements suggest that the complexes are neutral. The aquo, the ethylenediamine and the dipyridyl complexes have nearly the same conductivity suggesting that they all have the same charge and could be formulated as $[Co^{II}(PH)_2\,2H_2O]$, $[Co^{II}(PH)_2\,en]$ and $[Co^{II}(PH)_2\,bipy]$ respectively. It may be pointed out here that the complex $[Co^{II}(PH)en_2Cl]7H_2O$ has also the same conductivity and hence the formulation.

Table 4 also lists the stability constant or the dissociation constant of these compounds. These values are of the same order as the 8-hydroxyquinolinates. This yields a value 6.5 for the change in free energy $\triangle G$. The small solubility of the aquo and bipyridyl complexes does not give reliable values of $\triangle H$ but it may be noted that for the ethylenediamine complexes they are quite small. This value may have to be verified by other methods since this method does not seem to take the solution of the ions into account.

Magnetic Measurements. Table 5 shows the magnetic properties of the phthalhydrazide complexes which indicate that the complexes are octahedrally coordinated. It would also be noted that the magnetic moment of the 1:1 complex is slightly higher than the average. A reduction in moment is related to spin interaction which is common among the carboxy-

TABLE 3. ELECTRONIC SPECTRAL BANDS OF COMPLEXES.

Complexes	cm⁻¹	Log ε	Assignments
Phthalhydrazide(PH) in 10% NH_4OH	47170	4·341	CT
	45455	4·1694	CT
	39216	3·3734	$\pi \rightarrow \pi^*$
	37724	3·4033	$\pi \rightarrow \pi^*$
	32786	3·8070	CT
	12223	1·9012	CT
$[Co(PH)_2]\cdot 2H_2O$ in 10% NH_4OH	47393	4·8065	CT
	45455	4·6604	CT
	39216	3·9435	$\pi \rightarrow \pi^*$
	37880	3·9155	$\pi \rightarrow \pi^*$
	32363	4·1761	CT
	19666	1·8839	*d*—*d* transition
	12196	0·3415	CT
$[Co\ (PH)_2]\cdot 8H_2O$ in 10% NH_4OH	46950	4·8352	CT
	45046	4·7043	CT
	39526	4·0512	$\pi \rightarrow \pi^*$
	38023	3·9890	$\pi \rightarrow \pi^*$
	32256	4·2320	CT
	19665	2·0459	*d*—*d* transition
	12196	0·4821	CT
$[Co(PH)_2en]\cdot 7H_2O$ in water	48780	5·0927	CT
	45455	4·6685	CT
	38760	3·9339	$\pi \rightarrow \pi^*$
	37736	3·9483	$\pi \rightarrow \pi^*$
	31746	4·1800	CT
	21740	1·9243	*d*—*d* transition
	12530	0·7432	CT
$[Co(PH)_2en_2Cl]\cdot 7H_2O$ in water	48780	4·9049	CT
	44416	4·5345	CT
	39216	4·0973	$\pi \rightarrow \pi^*$
	32258	4·1407	CT
	31250	4·7916	CT
	21740	2·0336	*d*—*d* transition
	12656	0·7216	CT
$[Co(dipy)(PH)_2]\cdot 2H_2O$ in methanol	47846	4·6650	CT
	45455	4·4962	CT
	42016	4·3413	$\pi \rightarrow \pi^*$
	39683	4·1951	$\pi \rightarrow \pi^*$
	34483	4·3855	CT
	33896	4·3665	CT
	31446	4·9011	CT
	22303	2·1411	*d*—*d* transition
	12563	1·4962	$\pi \rightarrow \pi^*$

TABLE 5. MAGNETIC SUSCEPTIBILITY OF COMPLEXES.

Complexes	Temp (°C)	$X_g \times 10^{-6}$	$X_M \times 10^{-6}$	Corrected $X_M \times 10^{-6}$	μ_{eff} BM
$[Co(PH)_2]\cdot 2H_2O$	26	18·73	7845	7999·46	4·29
$[Co(PH)_2]\cdot 8H_2O$	26	18·1	9537	9754·48	4·74
$[Co_2(PH)_2]\cdot 5H_2O$	27	41·12	21780	22011	5·17

TABLE 4. CONDUCTIVITY OF COMPLEXES IN ETHANOL.

Complexes	Λo (°C)		Λm (°C)		α (°C)		*K* ion (°C)		K_5 (°C)	
	25	35	25	35	25	35	25	35	25	35
$[Co(PH)_2.2H_2O]$	206	180	28·02	26·43	0·1360	0·1469	$4{\cdot}922 \times 10^{-6}$	$7{\cdot}841 \times 10^{-6}$	$2{\cdot}032 \times 10^{-5}$	$1{\cdot}276 \times 10^{5}$
$[Co(PH)_2en].7H_2O$	102·2	131·4	21·92	27·43	0·2145	0·2087	$5{\cdot}26 \times 10^{-6}$	$5{\cdot}06 \times 10^{-6}$	$1{\cdot}857 \times 10^{-5}$	$1{\cdot}973 \times 10^{5}$
$[Co(PH)en_2Cl_2].7H_2O$	121·4	145·2	36·93	41·96	0·3045	0·2889	$2{\cdot}44 \times 10^{-5}$	$2{\cdot}15 \times 10^{-5}$	$4{\cdot}09 \times 10^{-4}$	$4{\cdot}6 \times 10^{5}$
$[Co(PH)_2(dipy)].2H_2O$	142·3	159·3	29·44	33·38	0·2068	0·2094	$3{\cdot}373 \times 10^{-6}$	$4{\cdot}01 \times 10^{-6}$	$2{\cdot}94 \times 10^{5}$	$2{\cdot}49 \times 10^{5}$

lates.[12] The absence of any lowering in the magnetic moment suggests that the two metallic atoms are outside the range of effective overlap of the metallic orbitals.

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